Monday Morning, April 24, 2017

Plenary Lecture

Room Town & Country - Session PL

Plenary Lecture

8:00am **PL-1 Grain Boundary Segregation: A Key Tool for Stabilizing Nanostructure in Next-Generation Coatings*, Chris Schuh,*** Massachusetts Institute of Technology, USA **INVITED**

The performance of many coatings depends on the development of an internal nanostructure for optimal properties, but nanoscale structures are frequently thermodynamically unstable. The future of nanostructured coatings, therefore, lies in our ability to stabilize their structure. This talk will review the proliferating strategy of stabilizing nanostructure *via* grain boundary segregation, not only as a means of kinetically slowing structural evolution, but as a means of bringing a nanostructured state closer to thermodynamic equilibrium. After a review of the basic science, a general strategy for coating design will be established, illustrating how market and scientific considerations can combine to guide the development of nanostructured coatings. A series of coating design case studies will be presented for both electrodeposited and physical vapor deposited coatings, and the scientific issues underlying alloy configuration and structural stability will be examined. Commercial applications and adoption trajectories of several of these coating systems will be reviewed. Finally, future augmentations to the design strategy, such as the incorporation of meso-scale super-grain structure within the coating, will be speculated upon.

Coatings for Use at High Temperatures
Room San Diego - Session A1-1

Coatings to Resist High Temperature Oxidation, Corrosion and Fouling

Moderators: Vladislav Kolarik, Fraunhofer Institute for Chemical Technology ICT, Prabhakar Mohan, Solar Turbines, USA, Anton Chyrkin, Forschungszentrum Jülich GmbH

10:00am **A1-1-1 High-resolution Studies of Phase Transformations in Metal/oxide Composite Films for High-temperature Applications***, **Gordon Tatlock**, M Duffield, K Dawson,* University of Liverpool, UK*; D Hernandez-Maldonado,* SuperSTEM Laboratory, UK*; J Lewis,* 2DHeat Ltd, UK **INVITED**

A novel thick film technology has been developed for the manufacture of electric heating elements from partially oxidised Ni-Cr-Fe alloy powder. The sprayed films were a mixture of metallic alloys and Ni-based oxides and could be sprayed directly onto a substrate to give good thermal efficiency. Electron microscopy and analysis was used to monitor the transformations in the films during subsequent heat treatment. In particular, it was found that homogeneous grains of Cr and Fe doped Ni-based oxides were transformed into NiO grains containing numerous, ordered Ni, Cr and Fe rich spinel particles which grew topotactically within the matrix to give a uniform distribution of particles of about 40nm diameter. High resolution electron microscopy and analysis was used to study these transformations in detail; and the ionic site occupancy of the octahedral and tetrahedral sites in the spinel was determined by electron energy loss spectroscopy at the atomic scale.

10:40am **A1-1-3 High Temperature Corrosion Of Ni-Base Coatings For Boiler Applications - A Microstructural Study***, **Johan Eklund**, J Phother-Simon,* Chalmers University of Technology, Sweden*; E Sadeghimeresht,* University West, Sweden*; L Johansson, T Jonsson,* Chalmers University of Technology, Sweden*; S Joshi,* University West, Sweden*; J Liske,* Chalmers University of Technology, Sweden

The increasing demand for energy and the urgent need to curb CO_2 emissions are global drivers for introducing new"green"fuels, such as biomass and waste, which can be fired in boilers to generate electricity. However, the resulting boiler environment is much more corrosive compared to power boilers burning fossil fuels. Among the most important corrosive constituents in the boiler environment are alkali chlorides (e.g., KCl). The corrosion problems are especially severe in the steam superheaters due to the relatively high material temperature. To mitigate corrosion so as to avoid unplanned stoppages and reduce maintenance costs, the maximum steam temperature is kept relatively low in these boilers, resulting in poor power efficiency.

To make electricity generation from biomass- and waste-fired boilers more competitive, the power efficiency has to be increased and maintenance costs decreased. This requires solving the fireside corrosion problems, e.g., by using new, more corrosion-resistant materials. However, the new materials must be both affordable and fulfil the stringent mechanical requirements of the application. Both in-plant studies and laboratory experiments mimicking the fireside conditions in boilers show that certain Ni-base alloys tend to be more corrosion resistant than low-alloyed steels and stainless steels in these applications. However, Ni-base alloys are much more expensive than the other materials. The demand for high corrosion resistance at a reasonable price can in principle be fulfilled by applying corrosion resistant coatings on a cheaper substrate material which satisfies the mechanical requirements.

In this work, Ni-base alumina- and chromia- forming coatings are sprayed on a low alloy (16Mo3) substrate using High Velocity Air Fuel (HVAF) technology. The samples are exposed isothermally at 600ºC for up to four weeks under well-controlled conditions in the laboratory. The samples are subjected to environments containing alkali chloride + N_2 + O_2 + H_2O. Exposures in N_2 + 5%O_2 + 20%H_2O are used as reference. Coating performance is compared to 304L-type stainless steel and to the FeCrAl alloy Kanthal APMT. The oxidation kinetics are studied and the samples are investigated before and after the corrosion experiment using SEM/EDX of cross sections prepared by focused ion beam (FIB) and broad ion beam (BIB) milling.

11:00am **A1-1-4 Coatings for Oxidation and Hot Corrosion Protection of Disk Alloys***, **James Nesbitt**, T Gabb, S Draper,* NASA Glenn Research Center, USA*; R Miller,* Vantage Partners, LLC, USA*; I Locci,* University of Toledo, USA*; C Sudbrack,* NASA Glenn Research Center, USA

Increasing temperatures in aero gas turbines is resulting in oxidation and hot corrosion attack of turbine disks. Since disks are sensitive to low cycle fatigue (LCF), any environmental attack, and especially hot corrosion pitting, can potentially seriously degrade the life of the disk. Application of metallic coatings are one means of protecting disk alloys from this environmental attack. However, simply the presence of a metallic coating, even without environmental exposure, can degrade the LCF life of a disk alloy. Therefore, coatings must be designed which are not only resistant to oxidation and corrosion attack, but must not significantly degrade the LCF life of the alloy.

Three different Ni-Cr coating compositions (29, 35.5, 45wt.% Cr) were applied at two thicknesses by Plasma Enhanced Magnetron Sputtering (PEMS) to two similar Ni-based disk alloys. One coating also received a thin ZrO_2 overcoat. The coated samples were also given a short oxidation exposure in a low PO_2 environment to encourage chromia scale formation. Without further environmental exposure, the LCF life of the coated samples, evaluated at 760°C, was less than that of uncoated samples. Hence, application of the coating alone degraded the LCF life of the disk alloy. Since shot peening is commonly employed to improve LCF life, the effect of shot peening the coated and uncoated surface was also evaluated. For all cases, shot peening improved the LCF life of the coated samples. Coated and uncoated samples were shot peened and given environmental exposures consisting of 500 hrs of oxidation followed by 50 hrs of hot corrosion, both at 760°C. The high-Cr coating showed the best LCF life after the environmental exposures. Results of the LCF testing and post-test characterization of the various coatings will be presented and future research directions discussed.

11:20am **A1-1-5 High Temperature Oxidation Protection of γ-Titanium Aluminide using Amorphous (Cr,Al)ON Coatings Deposited by High Speed Physical Vapor Deposition***, K Bobzin, T Brögelmann, C Kalscheuer, **Tiancheng Liang**,* Engineering Institute - RWTH Aachen University, Germany

In recent years great efforts have been made in the development of γ-TiAl alloys for use in aerospace applications such as turbines, where low densities and high temperature strength are required. However, γ-TiAl alloys show poor oxidation resistance at temperatures T > 850 °C due to the formation of a non-protective oxide layer consisting of a mixture of TiO_2+Al_2O_3 in air, which is easily spalled off, resulting in a shortened lifetime of the components. One promising way to overcome this problem is the deposition of an oxidation protective coating with low oxygen permeability at high temperatures. However, the interdiffusion between coating and substrate is still challenging even for advanced coatings such as MCrAlY (M = Ni or Co) and Al_2O_3 ceramic coatings, which have made great progress in increasing the oxidation resistance of γ-TiAl. The present work focuses on the (Cr,Al)ON coating system, inspired from its outstanding diffusion barrier properties. Four (Cr,Al)ON coatings with different Cr:Al and N:O ratios were deposited onto γ-TiAl substrate by the innovative high speed physical vapor deposition (HS-PVD) technology, which enables the deposition of oxygen-rich coatings in a stable plasma process without target poisoning. Basing on hollow cathode discharge (HCD) and gas flow sputtering (GFS), the HS-PVD made it possible to deposit (Cr,Al)ON coatings at a deposition rate > 8 µm/h. The amorphous microstructure of the as-deposited coatings was proved by X-ray diffraction (XRD) and investigated by transmission electron microscopy (TEM). The thermal stability of the coatings was evaluated by means of in-situ high temperature X-ray diffraction (HT-XRD) in air. It was confirmed that the amorphous structure even remained up stable to a temperature T = 1,050 °C. Moreover, cross-sectional SEM images of the coated samples after the HT-XRD measurements showed neither the formation of oxides at the coating substrate interface nor the interdiffusion of Ti into the coating, indicating a promising performance of the diffusion barrier. Furthermore, cyclic oxidation tests were conducted at T = 950 °C in air and the results demonstrated that the oxidation resistance of γ-TiAl has been improved by the (Cr,Al)ON coating significantly. Finally, the mass change Δm of the coated samples in the temperature interval between T = 25 °C and T = 950 °C was evaluated using thermogravimetric analysis (TGA). The results of the conducted research reveal a high potential of the HS-PVD deposited (Cr,Al)ON coatings for the oxidation protection of γ-TiAl at T > 850 °C in turbine applications.

11:40am **A1-1-6 Cyclic Oxidation and Hot Corrosion Behaviour of Plasma Sprayed CoCrAlY/WC-Co Coating on Turbine Alloys**, *H Nithin, V Desai,* ***Ramesh Motagondanahalli Rangarasaiah,*** National Institute of Technology Karnataka, India

Components in energy-production systems suffer a variety of degradation processes as a consequence of complex multicomponent gas environment which include oxidation and molten-salt-induced attack. Coatings provide a composition that will grow the protective scale at high temperature having long term stability. Plasma thermal spraying has been used to deposit CoCrAlY/WC-Co composite coatings on turbine alloys of Hastelloy X and AISI 321(Midhani Grade). Thermo cyclic oxidation behavior of coated alloys was investigated in static air as well as in molten salt (Na_2SO_4-60%V_2O_5) environment at 700ºC for 50 cycles. The thermogravimetric technique was used to approximate the kinetics of oxidation. X-ray diffraction, SEM/EDAX and EPMA techniques were used to characterize the oxide scale formed. The CoCrAlY/WC-Co coatings showed lower oxidation rate in comparison to uncoated alloys. The coatings subjected to oxidation in air show slow scale growth kinetics and oxides of α-Al_2O_3 CoO and Cr_2O_3 were formed on the outermost surface where as accelerated oxidation induced by the molten salt exhibits metastable modification of Al_2O_3. The preferential oxidation of Al and Cr blocks the transport of oxygen into the coating through pores and voids, thereby making the oxidation rate to reach steady state.

Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B1-1
PVD Coatings and Technologies

Moderators: Joerg Vetter, Oerlikon Balzers Coating Germany GmbH, Jyh-Ming Ting, National Cheng Kung University

10:00am **B1-1-1 Tunable Low Energy Ion Bombardment and its Influence on AlN Thin Films Deposited in Confocal DC Magnetron Sputtering**, ***Mathis Trant,*** *M Fischer, K Thorwarth, J Patscheider, H Hug,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Many thin film properties are strongly influenced by ion bombardment during the deposition. Control of the ion flux and the understanding of its influence on the growth mechanism are crucial for tailoring thin film characteristics such as residual stress and growth morphology. In this work the effect of the magnetic configuration on plasma parameters are studied along with the impact on aluminum nitride thin film growth.

An electromagnetic coil is used to generate an additional tunable magnetic field in order to alter the plasma confinement. Electrical and calorimetric probes are used to measure the plasma parameters in the vicinity of the substrate. The setup allows varying the ion-to-neutral ratio by more than one order of magnitude. This holds for the closed field as well as the open field configurations. Because of its symmetric geometry the latter provides roughly double the ion current density when averaged over the entire sample holder.

The effect of varied ion bombardment and substrate temperature are compared for aluminum nitride thin films, taking into account plasma heating. The residual stress was found to depend only on the ion flux density and could be varied from tensile (+0.9GPa) to compressive (- 4 GPa) by increasing this parameter. This goes along with a change from columnar structure towards more dense films. The films showed a preferential (002) orientation for the entire range of parameters covered in this work.

10:20am **B1-1-2 Unprecedented Al Supersaturation in Single-phase Rock Salt Structure VAlN Films by Al^+ Subplantation**, ***Grzegorz Greczynski,*** Linköping University, (IFM), Sweden*; S Mraz, M Hans,* Aachen University, Germany*; D Primetzhofer,* Uppsala University, Angstrom Laboratory, Sweden*; J Lu, L Hultman,* Linköping University, (IFM), Sweden*; J Schneider,* Aachen University, Germany

Conventional design approaches for transition metal nitride coatings with improved thermal and chemical stability are based on alloying with Al. The solubility of Al in NaCl-structure transition metal nitrides is, however, limited which presents a great challenge to increase Al concentration substantially, while avoiding precipitation of thermodynamically-favored wurtzite-AlN phase (w-AlN), detrimental to mechanical properties.

Here, we use VAlN as a model system to demonstrate a new concept for the synthesis of a metastable single-phase NaCl-structure thin films with Al content far beyond solubility limits obtained with conventional plasma processes. This is achieved by separating the film-forming species in time and energy domains through synchronization of the pulsed substrate bias with intense periodic fluxes of energetic Al^+ metal ions during reactive hybrid high power impulse magnetron sputtering (HIPIMS) of Al target and direct current magnetron sputtering of V target in Ar/N_2 gas mixture. 70-µs-long bias pulses with an amplitude of -300 V are applied synchronously with the Al^+-rich portion of HIPIMS discharge, to increase implantation depth of ionized Al. At all other times the substrate is floating at -10 V, which suppresses ion mixing due to gas ion bombardment and leads to VN-rich surface even for the case where time-averaged Al flux significantly exceeds that of V. Thus, single-phase cubic VN crystallites dominate the surface and provide a template for subplanted Al^+ metal ions to crystallize in the metastable NaCl structure rather than to nucleate second phase w-AlN. We show that Al subplantation enables an unprecedented 42% increase in metastable Al solubility limit in $V_{1-x}Al_xN$, from x = 0.52 obtained with conventional method to 0.75. High Al-content cubic VAlN films grown by the Al^+-subplantation technique exhibit fully-dense nanostructure and excellent mechanical properties with hardness in the range of 28-30 GPa for Al fractions on the cation lattice as high as 84%. The elastic modulus is with 325±5 GPa in excellent agreement with density functional theory calculations, and approximately 50% larger than for VAlN films grown with dc magnetron sputtering. This substantial improvement with respect to the conventional techniques opens the way for synthesis of supersaturated single-phase alloy thin films combining excellent mechanical properties with high oxidation resistance. Extensions of the presented method to other materials systems are expected to be straightforward.

10:40am **B1-1-3 Ion Beam Designed Thin-film Metasurfaces**, ***Carsten Ronning,*** Friedrich-Schiller-Universität Jena, Institut für Festkörperphysik, Germany **INVITED**

Metamaterials and metasurfaces enable unprecedented flexibility in manipulating electro-magnetic waves. The optical response of most metamaterials is static, modified only by adjusting the geometric parameters of the constituent building blocks. Many functionalities of metamaterials and metasurfaces may be greatly enhanced by hybridizing these materials with functional matter, like phase-change materials, where the dielectric properties can be controlled in real-time by an external stimulus such as an applied electric field, light, mechanical stress or temperature.

We demonstrate a new type of temperature-tunable metasurfaces based on ultra-thin films of phase change materials [1]. One of the most widely studied phase change materials is vanadium dioxide (VO_2), which exhibits a reversible insulator to metal transition (IMT) as the temperature is increased above a critical temperature TC ~ 68°C. At high temperatures, VO_2 is in a metallic rutile phase, while the low-temperature insulating state is monoclinic. The transition temperature is very sensitive to structural defects and strain. In thin epitaxial VO_2 films the IMT occurs gradually because of the strain distribution imposed from lattice mismatch with the substrate. Therefore, in the vicinity of the IMT, nanoscale islands of the metallic phase start to nucleate surrounded by insulating VO_2, which then grow and connect in a percolation process. Because of this naturally occurring coexistence of sub-wavelength domains of metallic and insulating phase, VO_2 can already be thought of as a natural disordered metamaterial during its phase transition.

In this contribution, I will demonstrate that phase coexistence can also be artificially introduced in VO_2 by patterned local ion beam irradiation with spatial resolution much smaller than the wavelength of light. The presence of a small amount of structural defects caused by ion irradiation significantly decreases the transition temperature – even below room temperature – of the irradiated regions. Thus, the metal and insulating phase of VO_2 coexist in a regular pattern in the temperature range between the IMT of irradiated and intrinsic VO_2. This results in a metasurface with effective optical properties that can be predicted applying an appropriate effective medium theory. These thin film structures are promising for dynamic polarization control, reconfigurable absorbers and emitters, and the tuning of plasmonic and dielectric resonant nanostructures for adaptive optics applications.

[1] J. Rensberg, et al. “Active Optical Metasurfaces Based on Defect-Engineered Phase-Transition Materials” *Nano Letters* 16, 1050 (2016).

11:20am **B1-1-5 Mechanical and Thermal Behavior of Magnetron Sputtered Zr–Cu and Zr–Hf–Cu Metallic Glasses**, ***Michal Zitek,*** *P Zeman, S Zuzjakova, R Čerstvý, S Haviar, M Kotrlova,* University of West Bohemia, Czech Republic

Metallic alloys are commonly fabricated as crystalline materials by a relatively slow-cooling casting of a melt. Magnetron sputter deposition as a non-equilibrium process with high cooling rates (higher than 10^6 K/s) allows us to prepare metallic alloys also as thin-film materials in an amorphous

glassy state. A short-range atomic order, based mainly on icosahedral clusters, in these metastable materials gives rise to their exceptional physical and functional properties compared to their crystalline counterparts.

Recently, we have showed that Zr–Cu thin-film alloys can be prepared as metallic glasses in a very wide composition range (30–65 at.% Cu) by non-reactive magnetron co-sputtering. In the present study, we focus on characterization of their mechanical and thermal behavior in more detail. In addition, we investigate the effect of an incorporation of Hf into the Zr–Cu thin-film metallic glasses on a potential improvement of their behavior. The films were deposited using three unbalanced magnetrons equipped with Zr, Hf and Cu targets in pure argon. The magnetron with the Zr and Hf targets were operated in a dc regime while the Cu magnetron in a high-power impulse regime. The Zr, Hf and Cu contents in the films were controlled by adjusting the dc powers and the average target power in a period, respectively. The films were deposited without an external heating onto rotating substrates. The films were analyzed by X-ray diffraction, energy dispersive X-ray spectroscopy, differential scanning calorimetry, micro- and nanoindentation, scanning electron microscopy and atomic force microscopy.

Mechanical properties of the Zr–Cu thin-film metallic glasses are strongly dependent on the elemental composition. A gradual growth of hardness with increasing Cu content up to 70 at.% correlates well with an evolution of the glass transition temperature and the crystallization temperature. This behavior can be explained by an increasing concentration of icosahedral clusters having the highest atomic packing density. The Zr–Cu films prepared with the Cu content higher than 50 at.% or at a moderate substrate bias exhibit a tendency to be more resistant to the formation of shear bands during indentation. An incorporation of Hf into the Zr–Cu thin-film metallic glasses improves the mechanical properties of the films and the thermal stability of their glassy state. Further experiments are still in progress and will be presented as well.

11:40am **B1-1-6 The Development of Ultrathin Zr-Cu-Ni-Al-N Thin Film Metallic Glass as a Diffusion Barrier for Cu-Si Interconnect***, **Joseph Lee,*** National Tsing Hua University, Taiwan*; Y Chen,* Metal Industries R&D Centre (MIRDC), Taiwan*; J Duh,* National Tsing Hua University, Taiwan

In this study, a Zr-Cu-Ni-Al-N thin film metallic glass (TFMG) has been developed and applied for the diffusion barrier between copper and silicon. The Si/TFMG/Cu stacked structures with various TFMG thickness have been fabricated. Rapid thermal annealing was conducted at 500, 600, 700 and 800 ^{o}C. The X-ray diffraction analysis was applied to identify the formation of Cu_3Si intermetallic compound. The ESCA depth profile was executed to quantitatively evaluate the degree of Cu-Si inter-diffusion. With the aid of HR-TEM, the microstructure of the TFMG and the whole stack could be observed. Finally, the correlation between microstructure, thermal properties, thickness and barrier performance of the TFMG will be revealed and discussed.

Hard Coatings and Vapor Deposition Technologies
Room California - Session B5-1

Hard and Multifunctional Nanostructured Coatings

Moderators: Jiri Capek, University of West Bohemia, Robert Franz, Montanuniversität Leoben

10:00am **B5-1-1 Synthesis and Characterization of HfNbTiVZr High Entropy Alloy Thin Films***, **Stefan Fritze**, D Karlsson, P Berastegui, D Rehnlund, L Nyholm, M Sahlberg, E Lewin, U Jansson,* Uppsala University, Angstrom Laboratory, Sweden

High entropy alloys (HEAs) are multicomponent alloys with at least five elements in approximately equimolar concentrations. Due to the high entropy of mixing, solid solutions of e.g. a simple bcc or ccp phase are formed. Many HEAs exhibit unique properties such as extremely high strength, ductility, high thermal stability and corrosion resistance. Recently, we have also demonstrated that a HfNbTiVZr alloy with a bcc structure has exceptional hydrogen storage capability [1].

In this study we report the first successful deposition of highly textured HfNbTiVZr thin films by non-reactive unbalanced magnetron sputtering using five metal targets. The films were characterized with SEM, XPS, XRD and nanoindentation. Bragg-Brentano XRD analyses of these coatings show that the HfNbTiVZr films crystallize in a simple bcc structure with a strong (110) orientation. No additional phases were observed in the as-deposited films ensuring that the sample is a single phase HEA. The SEM cross-sections exhibit a dense microstructure and EDS mapping shows a random distribution of all five elements with no noticeable segregation.

The as-deposited films exhibited a hardness of 5.4 GPa. This is more two times higher than expected from rule of mixture. The high hardness can be explained by a significant lattice strain due to large differences in atomic radii. Upon annealing, XRD shows the formation of a second alloy phase which is unexpected for a true HEA. The precipitation of a second phase leads to a further hardness increase with at least 100%. The phase stability and the precipitation of secondary phases in the HfNbTiVZr films will be discussed based on lattice strain effects in the alloy. Finally, the electrochemical properties of the HfNbTiVZr films have been investigated. The films exhibited, compared to steel alloys, a very high corrosion resistance in chlorine-containing solutions.

[1] M. Sahlberg, D. Karlsson, C. Zlotea and U. Jansson, submitted

10:20am **B5-1-2 Structural Stability of ZrN/SiN$_x$ Multilayered Coatings under Harsh Environments***, **Gregory Abadias,*** Institut P', Université de Poitiers-UPR 3346 CNRS-ENSMA, France*; I Saladukhin, V Uglov, S Zlotski, V Shymasnki,* Belarusian State University, Belarus

Synthesis of nitride-based multilayered structures is prospective for enhancement of mechanical properties and wear resistance as well as for their resistance to harsh environments exposure, in particular, to high temperature oxidation and ion irradiation. Multilayered ZrN/SiN$_x$ films (with bilayer thickness ranging from 6 to 40 nm) with a total thickness of about 300 nm were deposited at 300°C by reactive magnetron sputtering by sequentially alternating ZrN and SiN$_x$ layers [1]. Annealing under air atmosphere was carried out for temperature intervals ranging from 400 to 950°C using *in situ* temperature XRD. Ion irradiation by Xe ions (180 keV, doses $5x10^{16}$ cm^{-2} $1x10^{17}$ cm^{-2}) was performed at room and high (800°C) temperatures.

According to TEM and XRD analysis the multilayered films consist of nanocrystalline ZrN and X-ray amorphous SiN$_x$ layers. While pure ZrN films are characterized by [111] preferred orientation, the presence of SiN$_x$ layers results in its change to [200]. Multilayered ZrN/SiN$_x$ films show the improved oxidation resistance compared to ZrN reference layer. For pure ZrN film, the oxidation starts at 550°C. Higher oxidation resistance is observed for ZrN/SiN$_x$ films and it strongly depends on ZrN fraction and number of layers. So, for ZrN/SiN$_x$ (5 nm/10 nm) film the onset of oxide phase formation is delayed up to 950°C and nitride ZrN phase still remains. The presence of SiN$_x$ layer favors the formation of tetragonal ZrO_2 phase during annealing.

There is no evident change of ZrN/SiN$_x$ film structural state after Xe ion irradiation as it was proved by XRD investigations. However, the lattice parameter increase occurs that is connected with Xe incorporation. It was revealed by RBS analysis that the maximum concentration of Xe in the film bulk is about 4 at.% after irradiation at room temperature and about 5 at.% after high temperature irradiation. The shape of Xe concentration profile also changes. TEM studying indicates amorphization of ZrN layers and Xe bubbles formation in the film. There is a tendency of Xe depth penetration decrease with the SiN$_x$ layer thickness increase. Thus multilayered ZrN/SiN$_x$ films are considered to be promising for oxidation and irradiation resistance enhancement.

1. G. Abadias, V.V. Uglov, I.A. Saladukhin et al., Surf. Coat. Technol., under press

10:40am **B5-1-3 Magnetron Sputtered High-Temperature Hf–B–Si–C–N Films with Controlled Electrical Conductivity and Optical Transparency***, **Veronika Simova,*** *J Vlcek, S Zuzjakova, R Čerstvý, J Houška,* University of West Bohemia, Czech Republic

The present work focuses on the effect of nitrogen addition into hard and electrically conductive Hf–B–Si–C films [1] in order to significantly improve their thermal stability in air at very high temperatures (above 1200°C). Our motivation has been to develop new hard thin-film materials with a very low electrical and thermal conductivity, and high optical transparency or with a sufficiently high electrical conductivity for high-temperature protective coatings of electronic and optical elements, and for harsh-environment sensors.

Hf–B–Si–C–N films were deposited onto Si(100) and SiC substrates using pulsed magnetron co-sputtering of a single B_4C–Hf–Si target (at a fixed 15% Hf fraction and a 20% Si fraction in the target erosion area) in Ar + N_2 gas mixtures at the N_2 fraction ranging from 0% to 50%. A planar unbalanced magnetron (127×254 mm^2 target) was driven by a pulsed dc power supply operating at a repetition frequency of 10 kHz with an average target power of 500 W in a period and voltage pulse durations of 50 µs and 85 µs (duty

cycles of 50% and 85%). The substrates were held at a floating potential and a temperature of 450 °C.

An increasing N content (from 0 to 52 at.%) in the films was compensated by decreasing contents of B (from 39 to 24 at.%), Si (from 24 to 15 at.%), Hf (from 25 to 4 at.%) and C (from 7 to 3 at.%). The structure of the Hf–B–Si–C film prepared in pure argon was nanocomposite, while the Hf–B–Si–C–N films were amorphous. An increase in the N_2 fraction in the gas mixture, resulting in an increasing N content in the films, led to a rapid rise in the optical transparency and the electrical resistivity of the films. All films exhibited a high hardness in the range of 17–21 GPa.

The as-deposited, optically non-transparent $Hf_7B_{23}Si_{22}C_6N_{40}$ film with 2 at.% of Ar possessing a hardness of 20 GPa and electrical resistivity of 4 Ωm, which was prepared with the 15% N_2 fraction in the gas mixture at the voltage pulse duration of 50 μs, and the as-deposited, highly optically transparent and electrically insulating $Hf_6B_{21}Si_{19}C_4N_{47}$ film with 3 at.% of Ar possessing a hardness of 20 GPa, which was prepared with the 25% N_2 fraction in the gas mixture and at the same voltage pulse duration, exhibited a very high oxidation resistance in air even up to 1600°C.

[1] J. Kohout, J. Vlcek, J. Houska, P. Mares, R. Cerstvy, P. Zeman, M. Zhang, J. Jiang, E.I. Meletis, S. Zuzjakova, Hard multifunctional Hf–B–Si–C films prepared by pulsed magnetron sputtering, Surf. Coat. Technol. 257 (2014) 301–307.

11:00am **B5-1-4 Reactively Sputtered Multicomponent (TiZrHfVNb)N Thin Films***, **Kristina Johansson**, E Lewin,* Uppsala University, Angstrom Laboratory, Sweden

(TiZrHfVNb)N thin films, synthesised by reactive DC magnetron sputtering, demonstrate a large homogeneity range for a solid solution phase with the NaCl-type structure. The films have been deposited using elemental targets of the respective element and a gas mixture consisting of Ar and N_2 (15 % of total gas flow). In earlier studies, (TiZrHfVNb)N films have been synthesised by cathodic arc vapour deposition using a high entropy alloy of Ti-Zr-Hf-V-Nb as cathode material. These films have showed very interesting mechanical properties, such as high hardness and high wear resistance.[1] However, there are no previous studies on sputter deposited (TiZrHfVNb)N films. By using this deposition technique it could allow for more design possibilities, which is explored in this study by varying composition of the material. The films were characterised by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM).

Large variations in metallic ratio were obtained for the (TiZrHfVNb)N coatings, about 10-50 % for Ti, 20-35 % for Zr,10-50 % for Hf,10-30 % for V and 5-15 % for Nb. XPS spectra for each transition metal showed that the films are fully nitrided. The coatings were found to be of single NaCl type phase for all studied compositions. The lattice parameter varied from 4.32 Å for Ti rich coatings to 4.44 Å for Hf rich coatings, which is within the range of the corresponding binary nitrides (4.13 Å for VN and up to 4.58 for ZrN) and thus indicating a solid solution phase of all constituent elements. Cross sections of the coatings studied by SEM showed a columnar growth which varied in density depending on deposition conditions such as substrate temperature and bias.

Reference:

[1] A.D. Pogrebnjak *et al*., *Mater. Chem. Phys.,* 147 (2014) 1079

11:20am **B5-1-5 Deposition of Fluor-doped WS_2-C Coatings on Nanostructured Anodized Aluminum Alloy Substrates for Wettability Control***, S Rodrigues,* SEG-CEMUC, Portugal*; **Sandra Carvalho**,* University of Minho and University of Porto, Portugal*; A Cavaleiro,* SEG-CEMUC, Portugal

Currently, lubrication procedures of mechanical components in automotive industry, such as ignition systems, are often stopped for tool cleaning or replacement due to high friction phenomena faced because of lubricant accumulation. Then, the development of a functional surface; addressing either longer lifetime due to an improvement of the wear resistance, or energy savings, by the decrease of the friction, is now welcome particularly when they can also avoid or reduce the excessive use of liquid lubricants which are harmful for the environment and the human health.

This work intends to create a new surface acting as solid lubricant, gathering the outstanding self-cleaning and *nearzero* friction properties of fluor-doped WS_2-C coatings. These coatings can be deposited onto different porous anodized aluminum alloy surfaces in order to be able to control the water and oil wettability.

W-S-C-F coatings were produced by magnetron sputtering in reactive mode using an Ar/CF_4 gas mixture. The fluorine insertion in the produced coatings was controlled by varying the CF_4 gas flow aperture (0-20%).

Top view and cross-sectional morphologies, chemical composition/bonding, structure and wettability characterization of the coatings were respectively performed through FIB/SEM-EDS, XRD techniques and water/oil contact angle measurements. Mechanical properties such as hardness, elastic modulus and adhesion were also conducted under nanoindentation procedures and *scratch* testing.

The results revealed that the fluorine insertion on the W-S-C coatings did not change significantly the structure and morphology in relation to pure W-S-C coatings. However, a decrease on the mechanical properties was observed. Furthermore, the changes in the contact angles values show a potential for the control of the wettability behaviour in relation to water and oils.

Fundamentals and Technology of Multifunctional Materials and Devices
Room Royal Palm 4-6 - Session C2-1

Thin Films for Active Devices

Moderators: Vanya DarakchievaMarco Cremona, Pontificia Universidade Católica do Rio de Janeiro, Junichi Nomoto, Kochi University of Technology, Japan,

10:00am **C2-1-1 Application of Gallium Oxide for High-Power Electronics***, **Masataka Higashiwaki**, M Wong, K Konishi,* National Institute of Information and Communications Technology, Japan*; K Sasaki, K Goto,* Tamura Corporation, Japan*; H Murakami, Y Kumagai,* Tokyo University of Agriculture and Technology, Japan*; A Kuramata, S Yamakoshi,* Tamura Corporation, Japan **INVITED**

Wide bandgap semiconductor material - gallium oxide (Ga_2O_3) - has emerged as a new competitor to SiC and GaN in the race toward next-generation power devices by virtue of the excellent material properties and the relative ease of mass wafer production. In this talk, following a short introduction of material properties and features of Ga_2O_3, an overview of our recent development progress in device processing and characterization of Ga_2O_3 field-effect transistors (FETs) and Schottky barrier diodes (FP-SBDs) will be reported.

State-of-the-art Ga_2O_3 metal-oxide-semiconductor FETs (MOSFETs) were fabricated with unintentionally-doped (UID) β-Ga_2O_3 (010) epitaxial layers grown on semi-insulating Fe-doped substrates by ozone molecular beam epitaxy [1]. Selective-area Si-ion implantation doping of the UID Ga_2O_3 epilayer formed the device channel and ohmic contacts, while the high resistivity of UID Ga_2O_3 was harnessed for planar device isolation without mesa etching. SiO_2-passivated depletion-mode MOSFETs with a gate-connected field plate (FP) demonstrated a high off-state breakdown voltage (V_{br}) of 755 V, a large drain current on/off ratio of over nine orders of magnitude, DC-RF dispersion-free output characteristics, and stable high temperature operation against thermal stress at 300°C.

We also fabricated and characterized Pt/Ga_2O_3 FP-SBDs on n^--Ga_2O_3 drift layers grown on n^+-Ga_2O_3 (001) substrates [2], owing to the success of halide vapor phase epitaxy (HVPE) for high-speed growth of high-quality Ga_2O_3 thin films [3, 4]. The illustrative device with a net donor concentration of 1.8×10^{16} cm^{-3} exhibited a specific on-resistance of 5.1 mΩ·cm^2 and an ideality factor of 1.05 at room temperature. Successful FP engineering resulted in a high V_{br} of 1076 V. Note that this was the first demonstration of V_{br} of over 1 kV in any Ga_2O_3 power device.

In summary, we succeeded in fabricating depletion-mode Ga_2O_3 FP-MOSFETs and vertical Ga_2O_3 FP-SBDs on single-crystal β-Ga_2O_3 substrates. Despite the simple structures, both the FP-MOSFETs and FP-SBDs revealed excellent device characteristics and demonstrated great potential of Ga_2O_3 electron devices for power electronics applications.

This work was partially supported by Council for Science, Technology and Innovation (CSTI), Cross-ministerial Strategic Innovation Promotion Program (SIP), “Next-generation power electronics” (funding agency: NEDO).

[1] M. H. Wong *et al.*, IEEE Electron Device Lett **37**, 212 (2016), [2] K. Konishi *et al., 74th Device Research Conference IV-A.5, 2016*, [3] K. Nomura *et al.*, J. Cryst. Growth **405**, 19 (2014), [4] H. Murakami *et al.*, Appl. Phys. Express **8**, 015503 (2015).

10:40am **C2-1-3 Phenomenon of Oxygen Ion Migration in In_2O_3-Based Resistive Random Access Memory**, ***Cheng-Hsien Wu,*** National Sun Yat-sen University, Taiwan*; T Chang, T Tsai,* National Sun Yat-Sen University, Taiwan

In this study, we demonstrate how using a positive bias or negative bias in the forming process can control whether the switching layer of a Pt/In_2O_3/TiN device is near the Pt electrode or the TiN electrode. This means that In_2O_3-based resistive random access memory (RRAM) not only can be switched at either the active or inert electrode, with resistive switching I–V curves for both electrodes exhibiting stable memory windows. Therefore, it is a bilaterally operating RRAM device. Since RRAM usually switches at the active electrode, we investigate the mechanism during operation at the inert electrode. After curve fitting, we found multi-set and multi-reset stages, both dominated by Schottky emission, as well as gradual changes in the value of the slope and the intercept. Finally, we use this result to propose a model with oxygen ions.

11:00am **C2-1-4 Vapor-Liquid-Solid Growth of SnO_2 Nanowires Utilizing Alternate Source Supply and Their Photoluminescence Properties**, ***Tomoaki Terasako,*** *K Kohno,* Ehime University, Japan*; M Yagi,* National Institute of Technology, Kagawa College, Japan

An important *n*-type wide band gap semiconductor, tin dioxide (SnO_2), has various high functionalities. Especially, we pay attention to the applications of SnO_2 to the gas-sensing devices. It is expected that the use of the nanowires (NWs), nanorods and nanobelts is effective for achieving the high gas-sensing performance. Among the various techniques, vapor-liquid-solid (VLS) growth based techniques are most widely studied because of their high forming position and diameter controllability. In general, the diameters of the NWs grown through the VLS growth can be controlled by the diameters of the catalyst particles or the thickness of the catalyst film. However, the film growth on the NW's side walls by vapor-solid (VS) growth contributes to the increase in average diameter and obstructs the growth of the NWs with the well-controlled diameters [1,2]. In this paper, we will examine the possibility of suppressing the influence of the VS growth on the shapes of the NWs utilizing alternate source supply (ASS). During the VLS growth process, the catalyst particle acts not only as a crystal growth front, but also as a "storage box" of the metal atoms by forming the alloy droplet. The ASS technique utilizes the latter.

The SnO_2 NWs were grown on the Au/α-Al_2O_3(001) substrates by atmospheric-pressure CVD using Sn powder and H_2O as source materials. Both the substrate and Sn powder were heated by the horizontal furnace, whereas H_2O was vaporized in its own vaporizer. Both the vapors of Sn and H_2O were timely separated and transported onto the substrate by nitrogen carrier gaseous.

X-ray diffraction measurements and SEM observations revealed the successful growths of the SnO_2 NWs by the ASS conditions. The average diameter of the SnO_2 NWs grown under the simultaneous source supply (SSS) condition increased exponentially with increasing growth temperature (T_g), reflecting the enhancement of the contribution of the VS growth. In contrast to this, the average diameter of the NWs grown under the ASS condition was almost independent of T_g, indicating that the contribution of the VS growth is effectively suppressed using the ASS condition. PL spectra showed the increase in the intensity of the orange band emission with increasing Tg, suggesting that the increase in the O vacancies and/or Sn interstitial atoms [3]. Moreover, the NWs average diameter was found to be independent of cycle number in the cycle number range of 300-700.

This work was supported by JSPS KAKENHI Grant Number JP26390029.

[1] T. Terasako *et al*., Thin Solid Films 528 (2013) 237.

[2] T. Terasako *et al*., Thin Solid Films (to be published).

[3] D. Calestani *et al*., Mater. Sci. Eng. C 25 (2005) 625.

11:20am **C2-1-5 Endurance Improvement and Resistance Stabilization of Transparent Multilayer ReRAM with Oxygen Deficient WO_x Layer and Heat Dissipating AlN Buffer Layer**, ***Yu-Hsuan Lin,*** National Chiao Tung University, Taiwan*; D Huang,* Peking University, China*; T Tseng,* National Chiao Tung University, Taiwan

This paper discusses the transparent resistive random access memory (ReRAM) from ITO/WO_3/ZnO/ITO structure to multilayer ITO/WO_x(x<3)/WO_3/ZnO/AlN/ITO structure with oxygen concentration distribution and heat dissipating layer. The X-ray photoelectron spectroscopy (XPS) is used to confirm the existence of WO_x/WO_3 double layers. The transmission electron microscopy (TEM) images show the AlN layer has limited effect on the grain structure and the interface roughness of ZnO. Moreover, the transmittance of the multilayer ReRAM achieves 85.49% that is suitable for optoelectronic applications.

The bipolar ReRAM mechanism is based on filament model with the movement of oxygen vacancies. Because the oxygen ions may recombine with the vacancies and break the conductive path near the top electrode during the SET operation, the WO_x between electrode and WO_3 provides sufficient vacancies for efficient resistive changes. In the meanwhile, the WO_3 can limit the rupture and formation region of filaments. This gradient tungsten oxide stabilizes the low resistance states, decreases the operating voltages, and increases the endurance from < 10^3 cycles to 10^4 cycles. Since the electrical field and heat drive the movements of ions and vacancies, the inserted AlN with high thermal conductivity can dissipate the uncontrollable heat and remain the directional electrical field. This AlN layer prevents the ReRAM from the heat-activated ion movement and further masters the high resistance state, so the resistance levels of the multilayer ReRAM are tight and stable. Conclusively, in the ITO/WO_x/WO_3/ZnO/AlN/ITO ReRAM, the operating voltages of SET and RESET operations are 1.9V and -1.1V, respectively, the retention stay more than 10^4s at 150°C, the endurance is 10^4 cycles with resistance ratio over 20x, and both of the low and high resistance states are extremely stable during cycling.

11:40am **C2-1-6 Mechanism of Selectivity Increased during Operation on Vanadium Oxide Based Selector**, *C Lin,* National Sun Yat-sen University, Taiwan*; T Chang, K Chang,* National Sun Yat-Sen University, Taiwan*; T Tsai, C Pan,* National Sun Yat-sen University, Taiwan*;* ***Jih-Chien Liao,*** National Tsing Hua University, Taiwan*; P Chen,* National Sun Yat-sen University, Taiwan*; C Chen,* National Sun Yat-Sen University, Taiwan*; S Sze,* National Chiao Tung University, Taiwan

Technological development for memory, logic IC, on-display devices and batteries is indispensable for advanced portable electronic products. Among all these devices, a reliable, fast-working, and energy-saving non-volatile memory is extremely important. There are several next generation memory under developed, RRAM, PCRAM, MRAM, MTJ, FeRAM. All these devices must use array to storage, but the sneak path current is still the problem that we can't integrate large amount of advanced RAM into a chip. One Selector connect to one Memory is one of the solution to sneak current, and it is the most efficient method to integrate memories into array chip.

Selector can be used in any resistance-changed memory. There are large amounts of selectors developed in recent year, one of they use transition metal oxide to achieve double side diode properties. Metal insulator transition (MIT) has been widely developed because of its volatile state switch. In this article, we use Vanadium Oxide to be our device to find two factors that influences the switch characteristic. Because MIT happens in the difference of temperature, we think the thermal and electric field will influences the devices meanwhile. By current fitting and Comsol simulation, we conclude the phenomena happens in transition layer.

Coatings for Biomedical and Healthcare Applications
Room Sunrise - Session D2

Bio-corrosion, Bio-tribology, and Bio-tribocorrosion

Moderator: Anna Igual Munoz, Ecole Polytechnique Federale de Lausanne

10:20am **D2-2 Evaluation of Tribocorrosion Kinetics and Biocompatibility of Electrochemically Induced Tribolayer for Hip Implants**, *M Lyvers, D Bijukumar,* University of Illinois College of Medicine at Rockford, IL, USA*; A Moore,* Winnebago High School, USA*; P Saborio,* Rush University Medical Center, USA*; D Royhman,* Rush University Medical Center and Northwestern University, USA*; M Wimmer,* Rush University Medical Center, USA*; K Shull,* Northweswtern University, USA*;* ***Mathew T. Mathew,*** University of Illinois College of Medicine at Rockford and Rush University Medical Center, USA

As the number of annual Total Hip Replacement (THR) surgeries continues to increase, the longevity of metal based hip implants is a major concern. Tribochemical Reactions cause the Cobalt-Chromium-Molybdenum (CoCrMo) hip implant to release wear debris that interacts with decomposed proteins to form a tribolayer. We conducted an electrochemical investigation in order to understand the role of molybdenum in the stability of the tribolayer under mechanical wear and electrochemical corrosion. Tribolayers made of a bovine calf serum (BCS) and bovine calf serum with sodium molybdates (BCS-Mo) were electrochemically deposited on high carbon CoCrMo discs and subjected to

corrosion and tribocorrosion experiments under potentiodynamic conditions in a hip-simulator . Cyclic-polarization, Electrochemical Impedance Spectroscopy (EIS) tests and surface characterization techniques were carried out. The results indicate an increased resistance to corrosion under mechanical wear by BCS-Mo coated surface which is more distinct when Mo is added into the electrolyte. In addition, biocompatibility evaluation using MG63 osteosarcoma cells on BCS and BCS-Mo coated samples did not show any statistically significant difference in cell growth compared to uncoated CoCrMo discs. These findings suggest a pre-formed electrochemical tribolayer with sodium molybdates may be a promising pre-implantation treatment of THRs to extend the longevity of implants *in vivo*.

10:40am **D2-3 Tribocorrosion from Nano to Macroscale – the Effect of Proteins on Friction of CoCrMo Biomedical Alloy***, **Nuria Espallargas**,* NTNU, Norway **INVITED**

The tribocorrosion performance of CoCrMo biomedical alloy has been widely studied in many different electrolytes (mainly simulated body fluids) and in the presence of proteins (mainly bovine serum albumin). In a recent review it was pointed out that the main outcome of the tribocorrosion of CoCrMo biomedical alloys exposed to simulated body fluids is the increase in wear as the electrode potential increases from cathodic to anodic. This is a very important conclusion that highlights the importance of the combination of electrochemistry with the mechanical action in biomedical bearing implants. However, it is still unclear what is the role played by proteins in this scenario. Indeed, it is very well stablished that proteins significantly affect the electrochemical performance of CoCrMo biomedical alloys, specially altering the cathodic kinetics and enhancing passive dissolution. However, the role played in friction and ultimately wear is still an open and interesting discussion. Therefore, in an attempt to investigate this phenomenon from a different perspective, I will present a nano-scale tribocorrosion set-up. These results will be compared with the classical macro-/micro-tribocorrosion results.

11:20am **D2-5 Fretting Corrosion of Biomaterials Dedicated to Dental Implants: Quantitative and Qualitative Insights***, P Corne, A Vaillant-Corroy, P De March, F Cleymand,* Institut Jean Lamour, France*; **Jean Geringer**,* Mines Saint Etienne, France

600,000 dental implants are implanted in France every year; it is a question of more than 1 million all over the world. The total implants lifetime is about 10 years nowadays. Unfortunately during these 10 years 15-20% of implants did not succeed. Some combinations of biomaterials are available in order to mimic the anchorage process of teeth. A study based on fretting corrosion investigations has been performed. In order to be so close as possible to the actual conditions, some biomaterials used for manufacturing dental implants have been tested in human saliva. The targeted combination is around the dental implant and the abutment. Ti-6Al-4V, pure Ti, zirconia stabilized with Yttria, PEEK (PolyEtherEtherketone) are the studied materials.

The device is a Fretting corrosion machine that has been developed by Mines Saint-Etienne and Bose Company. The sliding conditions were: a sinusoidal displacement of 80µm during 16 and 4 hours. The contact stress has been estimated from the actual junction between implant and abutment (Astra™ TX4.5, Dentsply™/Atlantis™ titanium abutment) from modeling investigations (Finite elements). The average contact stress was considered of 130 MPa.

After tests, the total average wear volume of titanium was the highest against zirconia material. At the opposite the lowest titanium wear volume has been reached thanks to PEEK counter material. Thus the Open Circuit Potential (OCP) evolution has been precisely checked. The lowest decrease at the beginning of the fretting test has been highlighted by Ti-6Al-4V against PEEK material. Additionally some investigations with SEM high resolution have been performed in order to show different wear mechanisms.

11:40am **D2-6 Mechanical and Anti-Corrosive Properties of Various Titania/Silica Hybrid Composite Film as the Interlayer of a Diamond-Like Carbon Deposited Ti6Al4V Substrate by Sol-Gel Technique***, N Wu, **Wen-Hsien Wu**, C Chou,* National Taiwan Ocean University, Taiwan*; R Wu,* National Institute for Materials Science, Japan*; J Lee,* Ming Chi University of Technology, Taiwan

Ti6Al4V alloy is one of the most popular implant material in the bio-medical application. In order to enhance the implant's wear resistance and anti-corrosion capability under the physiological environment, a diamond-like carbon (DLC) film with an amorphous silicon (a-Si) interlayer is the most popular coating system implemented on the Ti6Al4V substrate. However, many clinic failures of the implants caused by the crevice corrosion and delamination of the a-Si interlayer were reported after years of operation. In this study, titania/silica hybrid composite ($TiSi_xO_y$) films were built on Ti6Al4V alloy by sol-gel dip coating technique. The compositions of the films were changed by adjusting the Ti/Si ratios of the precursor solutions, and then, sintered at 650 °C under an argon atmosphere. A DLC outmost layer was deposited on these samples by radio frequency plasma enhanced chemical vapor deposition. An a-Si coated sample was also prepared as a benchmark. The surface and mechanical properties of $TiSi_xO_y$ films were evaluated by using scanning electron microscopy, atomic force microscopy, micro-scratch test, and nano-indentation. The composition and structure of $TiSi_xO_y$ films were investigated by using thermogravimetric analysis, X-ray diffraction spectroscopy, Fourier transform infrared spectroscopy, and X-ray photoelectron spectroscopy. The phase and structure of the DLC film was identified by a Raman spectroscopy. Corrosion resistance of Ti6Al4V substrates coated with only an interlayer or the whole DLC system was evaluated by electrochemical impedance spectroscopy. The results showed that an appropriate Ti/Si ratio of the $TiSi_xO_y$ interlayer can increase the hardness and, in the meantime, significantly promote the adhesion and anti-corrosion capability of the DLC-coated Ti medical alloy compared with the traditional a-Si coated one.

New Horizons in Coatings and Thin Films
Room Royal Palm 1-3 - Session F1-1

Nanomaterials and Nanofabrication

Moderators: R. Mohan Sankaran, Case Western Reserve University, Sumit Agarwal, Colorado School of Mines

10:00am **F1-1-1 Sculptured Thin Films by Ion Beam Sputtering***, **Bernd Rauschenbach**, C Grüner,* Leibniz Institute of Surface Modification, Germany

Nanostructures with a three dimensional tailored shapes are promising candidates for a variety of applications. The sputter induced glancing angle deposition technique is a sophisticated method to create nanostructures with custom-made structure geometries. This new technology is characterized, that the sputtered particle flow arrives the substrate under an extremely grazing angle. In the consequence highly porous thin films are produced, which consist of slanted needles. An additionally constant or periodically interrupted substrate rotation during sputter induced deposition is used to tailor structures like chevrons, posts, circular and quadratic spirals or zig-zags. The structure formation is based on geometric shadowing, where the arriving particle flux is supposed to be caught by the top of structure, and no growth occurs in the structure shadow.

In this presentation a report about the growth nanostructures on non-pattered and regularly arranged nanostructures and the growth conditions is given and some applications of such three-dimensional nanostructures are demonstrated. The growth of the nanostructures is studied in dependence on substrate temperature, substrate pre-patterning, substrate rotation speed, and deposition rate using scanning electron microscopy, X-ray diffraction and high-resolution transmission electron microscopy. The metal and semiconductor nanostructures were grown using ion beam sputter induced GLAD in an ultrahigh vacuum chamber [1-4].

Because this process provides precise nanoscale control over the structure and grain orientation characteristics, the mechanical, magnetic and optical properties of the sculptured films may be engineered for various applications. Finally, recent studies on first applications will be presented [5-6].

This work is supported by projects within German Excellence Initiative and an International Research group of the Deutschen Forschungsgemeinschaft (DFG).

[1] C. Patzig, T. Karabacak, B. Rauschenbach, Phys. Stat. Sol. B 247 (2010) 1310.

[2] C. Patzig, Ch. Khare, B. Rauschenbach, Phys. Stat. Sol. B 247 (2010) 1332.

[3] C. Patzig, B. Rauschenbach, B. Fuhrmann, J. Appl. Phys. 103 (2008) 024313.

[4] C. Patzig, H.S. Leipner, B. Rauschenbach, J. Nanosci. & Nanotechn. 8 (2008) 1.

[5] C. Grüner, B. Rauschenbach, Appl. Phys. Lett. 95 (2009) 103107

[6] S. K. Srivastava, A. Shalabney, I. Khalaila, C. Grüner, B. Rauschenbach, I. Abdulhalim,

Small 10 (2014) 3579

10:20am **F1-1-2 The Effect of Thermal Treatment on the Structure and Surface Plasmon Resonance of Ag-coated ZnO Nanoparticles by Sol-gel Method**, ***Chih-Chiang Wang***, National Chung Hsing University, Taiwan; *H Shih,* Chinese Culture University, Taiwan

Zinc oxide (ZnO) is an n-type II-VI semiconductor with a hexagonal wurtzite structure, a wide band gap (3.3 eV) and a higher exciton binding energy (60 meV), and has been applied in the field of ultraviolet or visible optoelectronic devices, photocatalyst, gas sensors, solar cells. On the other hand, silver (Ag) nanoparticles show the variable surface plasmon resonance (SPR) properties by controlling the particles shape, size, and density. In this study, the ZnO nanoparticles were fabricated by sol-gel method at the ambient environment. Subsequent baking was conducted at the 500°C in air. The Ag nanoparticles were coated on the ZnO surface by surface decoration process and baked in the lower pressure condition (~10^{-3} torr) at several temperatures (100, 300, and 500°C).

XRD patterns showed that peaks of (100), (002), (101), (102), (110), (103) planes belonged to the pure ZnO nanoparticles as the wurtzite structure. The peak of (111) plane at 38.1°appeared at the baking temperature of 300 and 500°C indicating that the Ag metal and its grain size increased with the increasing baking temperature. The TEM images and SAD patterns indicated that the Ag-coated ZnO nanoparticles kept the same crystal structure with a prominent facets (002) of the ZnO and (111) of the Ag nanoparticles.

The PL spectra displayed a tendency of blue shift in the UV light emission of 3.18 to 3.2eV and 3.08 to 3.1eV, respectively, while the Ag nanoparticles size increased. The former was the intrinsic emission, and the latter was caused by the V_O^+. Raman spectra revealed the peaks at 99cm^{-1} (E_2^{low}), 331cm^{-1} (multiphonon), 439cm^{-1} (E_2^{high}), and 580cm^{-1} (E_1 LO). The intensity of E_2^{low} mode showed the apparent increasing as the baking temperature increased. However, the intensity of multiphonon, E_2^{high}, and E_1 LO mode revealed the opposite tendency. The binding energy in XPS analysis of the $Zn2p_{3/2}$ and $Zn2p_{1/2}$ were observed at 1021.3 and 1044.8eV, respectively. In addition, the deconvolution of $Ag3d_{5/2}$ showed 368.5 (Ag^0) and 367.4(Ag^+)eV. The ratio (Ag^0/Ag^+) increased with the increasing baking temperature, meaning more Ag metals on the Ag-coated ZnO nanoparticles. The UV-Vis spectrum revealed the noticeable peak centered at λ=420nm due to the SPR effect of Ag nanoparticles, and showed the red shift toλ=460nm as the Ag nanoparticles size increased.

10:40am **F1-1-3 In-situ Electron Microscopy of Synthesis, Chemistry and Self-Assembly of Colloidal Nanostructures**, ***Eli Sutter***, University of Nebraska-Lincoln, USA **INVITED**

In-situ microscopy, particularly real-time imaging of dynamic processes has developed into an active field of research and is expected to be one of the key enabling techniques for understanding the formation of nanostructures, catalytic reactions, phase transformations, self-assembly, and other central issues in nanoscience and technology. *In-situ* transmission electron microscopy can be used to follow the behavior and measure the properties of nanostructures over a wide range of environmental conditions with resolution down to the atomic scale. Liquid-cell electron microscopy has developed into a powerful technique that allows the imaging of various processes in wet environments, such as liquids, solutions, or colloidal suspensions, and the investigation not only of a wide range of inorganic nanoscale objects but of biological systems as well.

I will illustrate the power of liquid-cell electron microscopy applied to imaging colloidal synthesis (nanoparticles, core-shell structure), electrochemistry (galvanic replacement reactions) and the self-assembly of nanocrystal superstructures in solution. Our results demonstrate that real-time electron microscopy can substantially advance our understanding of a wide range of processes involving nanoscale objects in bulk liquids.

11:20am **F1-1-5 Deposition of PTFE – TiO_2 Composite Coatings Combining Superhydrophobic and Photocatalytic Properties by Reactive pDC Magnetron Sputtering from a Blended Powder Target**, ***Marina Ratova***, *P Kelly, G West,* Manchester Metropolitan University, UK

Photocatalytic materials are used as a sustainable approach to air and water purification, water splitting and decontamination and disinfection of surfaces. Superhydrophilicity (water contact angles of 10° or lower) is one of the widely reported features of titania-based photocatalytic surfaces. However, superhydrophobic surfaces (water contact angles of 150° or higher) are often more desirable for environmental cleaning than superhydrophilic ones, as they prevent adhesion of contaminants and microorganisms to the surface and therefore have an anti-fouling effect that helps to prevent the deterioration of photocatalytic properties.

Typically, coatings combining photocatalytic and superhydrophobic properties are produced using chemical methods, such as hydrothermal, liquid phase deposition, etc. Pulsed DC magnetron sputtering is a well-known method for thin film deposition, and photocatalytic coatings in particular. In this work a reactive pulsed DC magnetron sputtering technique using a blended PTFE – titanium dioxide powder target was employed for the production of photocatalytic superhydrophobic coatings. The surface characteristics and photocatalytic properties of the deposited composite coatings were studied with Raman spectroscopy, optical profilometry and scanning electron microscopy. Hydrophobicity was assessed through measurements of water contact angles, and photocatalytic properties were studied via methylene blue dye degradation under UV irradiation. It was found that variations of gas flow and, hence, process pressures allowed deposition of samples combining superhydrophobicity with stable photocatalytic efficiency under a UV light source. Reversible wettability behaviour was observed with alternating light-dark cycles.

11:40am **F1-1-6 The Mechanisms of Growth of Zr-Fe-O Whiskers**, ***Jingjing Gu***, University of North Texas, USA; *P Petry,* University of Rouen, France; *I Hammood, M Carl, R Reidy, S Aouadi,* University of North Texas, USA

Ceramic whiskers are materials with high melting point, low density, good thermal and electric conductivity, and excellent corrosion-resistant materials. Whiskers are usually selected chosen as a reinforcing material in structural composites. In this presentation, whiskers were created by mixing and pressing nanopowders of ZrC, SiC, Y_2O_3, and Fe_2O_3 carbides. The nano-sized powders were then sintered at 1100°C for 6 hours, which resulted in the formation of Zr-Fe-O whiskers that were a few micometers in diameter and millimeters long. A model is proposed that accounts for the formation of these whiskers and for the thermodynamic processes that control whisker diameter.

Coatings for Use at High Temperatures
Room San Diego - Session A1-2

Coatings to Resist High Temperature Oxidation, Corrosion and Fouling

Moderators: Vladislav Kolarik, Fraunhofer Institute for Chemical Technology ICT, Prabhakar Mohan, Solar Turbines, USA, Anton Chyrkin, Forschungszentrum Jülich GmbH

1:30pm **A1-2-1 Pt Effect on Oxidation Resistance and Durability of β-NiAl Coatings : A Coupled *ab initio* and Physics-based Modeling***, **Prakash Patnaik,*** Gas Turbine Laboratory, Aerospace Portfolio, National Research Council, Canada*; K Chen,* Structures, Materials and Manufacturing Laboratory, Aerospace Portfolio, National Research Council, Canada

Possible new mechanisms of the beneficial effect of Pt on oxidation resistance and durability of β-NiAlcoatings were proposed using a coupled *ab initio* calculations and physics-based models combining thermal physical formulae and atomic diffusion theory. First, the beneficial effect of Pt on reducing the β-NiAl/Al_2O_3 interfacial tensile stress was assessed. The coefficients of thermal expansion (CTE) of Pt, β-NiAl and β-NiAl+Pt were calculated using *ab initio* method and thermal physical formulae. The calculated CTE of the β-NiAl, along with the experimentally measured CTE of Al_2O_3, were then incorporated into the interface stress model to evaluate thermal tensile stress at the undulated β-NiAl/Al_2O_3 interface. The results showed that addition of Pt to b-NiAl coating significantly reduced the interfacial tensile stress, thus contributing to the improvement of thermal cyclic durability of the coating. Second, the beneficial effect of Pt on lowering the diffusivity of sulfur in b-NiAl was evaluated. The apparent activation energy and the pre-exponential factor of diffusivity via the next nearest neighbour atom transportation were analyzed, and the bonding characteristics of sulfur with its surrounding atoms were calculated and compared with experimental results to elucidate the diffusion process of sulfur. Addition of Pt in b-NiAl was found to significantly reduce the diffusivity of sulfur, thus supressing the detrimental segregation of sulfur to the β-NiAl coating/a-Al_2O_3 scale interface.

1:50pm **A1-2-2 Synthesis and Characterization of Superalloy Coatings by Cathodic Arc Evaporation***, J Ast,* Laboratory for Mechanics of Materials and Nanostructures, Empa, Switzerland*; M Döbeli,* Ion Beam Physics, ETH Zurich, Switzerland*; A Dommann,* Center for X-ray Analytics, Empa, Switzerland*; M Gindrat,* Oerlikon Metco AG, Switzerland*; X Maeder,* Laboratory for Mechanics of Materials and Nanostructures, Switzerland*; A Neels,* Center for X-ray Analytics, Empa, Switzerland*; P Polcik,* Plansee Composite Materials GmbH, Germany*;* ***Jürgen Ramm****, H Rudigier,* Oerlikon Surface Solutions AG, Liechtenstein*; K von Allmen,* Center for X-ray Analytics, Empa, Switzerland*; B Widrig,* Oerlikon Surface Solutions AG, Liechtenstein

Superalloy targets were produced from Ni-(Al-C-Co-Cr-Mo-Ta-Ti-W) and Ni-(Al-B-C-Co-Cr-Hf-Mo-Ta-Ti-W-Zr) powders. The crystalline structure of the as produced targets was investigated by XRD analysis and compared with the development of phases resulting from the operation of the cathodic arc at the target (cathode) surface. The targets were utilized to synthesize coatings at different substrate materials from the pure metallic vapour. Deviations in the compositions of the superalloy targets and the synthesized coatings are discussed. The interfaces between coating and different substrate types are investigated by TEM for the as deposited state and after high temperature cycling at 1200°C. In addition to the non-reactive cathodic arc evaporation, the superalloy targets were evaporated in pure oxygen environment and the influence of the oxygen reactive gas is investigated for the processes at the cathode surface and for the synthesized oxygen containing coatings. This has been done for the synthesis of partially as well as fully oxidized coatings. Also for these coatings, high temperature cycling was performed. The diffusion processes in the interface to the different substrates and to the coating surface are investigated by cross-section TEM analysis and a combination of RBS and ERDA analysis. XRD analysis was utilized to demonstrate the differences in the phase formation after high temperature cycling depending on the oxygen content of the coating.

2:10pm **A1-2-3 High Temperature Binary or Doped Nickel Aluminide Coatings on Superalloys: An Industrial Approach***, **Vasileios Papageorgiou,*** *S Vogiatzis, H Strakov, A Zainal, M Auger,* IHI Ionbond AG, Switzerland

The ongoing demand for remarkably efficient turbine engines for aircraft propulsion and power generation has always been paced by the results of development of higher strength-at-temperature superalloys. However, the compositional requirements for improved high temperature strength and optimum high temperature oxidation and hot corrosion resistance are in general not compatible. A way to solve this problem is to apply coatings which provide adequate protection against oxidation and corrosion, while the composition and microstructure of the substrate are fully optimized for high temperature strength. A modern technique which allows not only the single deposition of such a coating but even the controlled alloying of it with additional elements, by means of various metal halides, is the so-called Chemical Vapor Aluminizing (CVA). Into this work, the industrial CVA technology is used to demonstrate its advantages using tight process deposition control of any binary NiAl coating and to promote various advanced co-deposition processes with addition of different metal elements such as Cr, Si, Co, Zr and Hf to the aluminide coatings. As the major challenge for the development of compatible high temperature coating systems is the coating resistance against spallation induced by thermal cycling, elevated temperature cycling oxidation tests been also performed and presented respectively.

2:30pm **A1-2-4 Corrosion Behavior of Iron Based Alloys Coated with Aluminum Oxide by RF Magnetron Sputtering***, D Melo-Maximo, L Melo-Máximo, A Murillo, O Salas,* ***Brenda García,*** ITESM-CEM, Mexico*; E Uribe,* ITESM-QRO, Mexico*; J Oseguera,* ITESM-CEM, Mexico

Metal dusting is a common problem in Fe, Ni and Co based alloys exposed to a corrosive environment. Several studies show that the presence of aluminum oxide coatings is a viable alternative to offer protection against this type of corrosion. Based on these studies, the main objective of this work was to evaluate the potential of thin film aluminum oxide coatings as a protective coating for iron based alloys. The coatings were produced by reactive magnetron sputtering with an RF power supply on 304L steel. Coated and uncoated samples were exposed to an atmosphere of CH_4+H_2+residual oxygen at 800°C in a thermobalance. The results indicate that the Al oxide thin films are promising coatings for the protection of ferrous materials in C-rich corrosive atmospheres at high temperature.

2:50pm **A1-2-5 Effect of the Microstructure on Corrosion and Deformation Behavior of Zn-Mg Coatings on Steel Substrate***, **JoungHyun La,*** *K Bae, S Kim, S Lee, Y Hong,* Korea Aerospace University, Republic of Korea

Zn-Mg alloy is a strong candidate for the protective coating material of steel sheets due to the excellent corrosion resistance of Zn-Mg alloy compared with pure Zn. However, during the PVD process Zn-Mg coatings show the various structures such as amorphous and crystalline depending on the deposition conditions. In this study, the Zn-Mg coatings with various structures were synthesized on the steel substrate using sputtering process and the effect of structure on corrosion and deformation behavior of Zn-Mg coated steel were investigated. The microstructure and the crystal phase of the Zn-Mg coatings were evaluated using the field emission scanning electron microscopy (FE-SEM) and X-ray diffraction (XRD). The corrosion and deformation behavior of Zn-Mg coated steel were investigated using the salt spray test (SST) and the punch stretching test (PST). The Zn-Mg coatings synthesized below 50°C showed the amorphous and featureless structure while the porous crystalline Zn-Mg coatings were synthesized above 100°C. The Zn-Mg coated steel with amorphous coating showed the enhanced corrosion resistance compared to that with crystalline Zn-Mg coating. By contrast, during plastic deformation of Zn-Mg coated steel the cracks and the detachments on the amorphous coatings were generated. The featureless microstructure of the amorphous Zn-Mg coatings improved its corrosion resistance by obstructing the direct pathway between a corrosive environment and the substrate, but the intrinsic brittleness of amorphous structure degraded the ductility and formability of coating.

Acknowledgement

This study is financially supported by the Smart Coating Steel Development Center, WPM(World Premier Materials) Program of the Korea Ministry of Knowledge Economy.

3:10pm **A1-2-6 A Comparative Analysis of Ternary Element Addition on Corrosion Behavior of Aluminide Coatings in Harsh Environmental Conditions***, **Umutcan Erturk,*** *B Imer,* Middle East Technical University, Turkey

Ni-based super alloys are widely used in industrial gas turbines due to their excellent mechanical strength and creep resistance at high service temperatures. Diffusion coatings including aluminide coatings are widely preferred to improve high temperature oxidation and corrosion resistance of turbine blades. Aluminide coatings form stable oxides that prevent oxygen diffusion to substrate materials. Increasing durability of aluminide coating is an important design criterion to extend life time of turbine

blades. It is well-known that addition of reactive and alloying elements have beneficial effect on oxidation behavior of aluminide coatings. Many studies show that addition of hafnium, yttrium, zirconium, chromium, platinum and cobalt improves performance of aluminide coating by increasing oxide adherence and selective oxide formation rate. However, addition of these elements may have adverse effect such as surface rumpling, martensitic transformation and formation of unstable oxides. In this research, effect of ternary elements (Hf, Y, Zr, Y/Zr, Y/Hf) addition on aluminide coating corrosion behavior were investigated. Ternary element addition to aluminide coatings was done by chemical vapor deposition for five different sample set. Accelerated isothermal corrosion tests were conducted under natural gas exhaust. To simulate harsh environmental conditions, Na_2SO_4 and V_2O_5 containing solutions were applied to substrate surface prior to corrosion test. Sampling and weighing was performed in varying periods for each sample set. Mass change data plotted against time to observe oxide formation and spallation behavior of coatings. Microstructural changes and oxide layer thicknesses was analyzed by scanning electron microscopy (SEM). Compositional changes in aluminide coating after corrosion tests was examined by energy dispersive spectroscopy (EDS) and wavelength dispersive spectroscopy (WDS). Formation of metastable oxide phases and undesirable coating phases was analyzed by X-ray crystallography (XRD). Subsequently, effect of ternary element additions on aluminide coating corrosion behavior were analyzed to extend life time of turbine blades.

3:30pm **A1-2-7 Cyclic and Isothermal Corrosion Testing of Aluminide Slurry Coatings in Molten Nitrates for Heat Storage in Concentrated Solar Power Plants**, ***Alina Agüero***, *S Rodríguez, P Audigié,* Instituto Nacional de Técnica Aeroespacial (INTA), Spain

In concentrated solar power plants, thermal energy storage is possible by means of heat transfer fluids (HTF) such as molten nitrate mixtures, which are currently in use in several plants world-wide. Molten nitrates have a high working temperature (» 570 ºC), good thermal and physical properties as well as an excellent capability for thermal energy storage overnight. The molten salt mixture is circulated through steel or Ni based alloy piping in the CSP receiver during the day and held in storage tanks to be used when needed to create superheated steam. This technology is still very expensive as compared with traditional fossil fuels and other renewable sources to produce energy, in particular with photovoltaics which have experienced an important price reduction quite recently. By increasing thermal efficiency, cost reduction can be achieved in concentrated solar plants with molten salt heat storage. Obtaining supercritical steam by increasing pressure and temperature constitute a strategy to achieve this goal. This requires new salt mixtures with higher thermal stability properties as well as understanding the materials corrosion behavior, and finding methods to prevent it or at least mitigate it when using low cost steels instead of expensive Ni based alloys. Coated ferritic or carbon steels are an alternative for the tubing and the storage tanks respectively in solar concentration tower plants. In particular, slurry aluminide coatings are a low cost alternative that allow uniform coating of internal surfaces. Some published work is available regarding the behavior of steels and Ni base alloys under exposure to molten nitrates but little is known of the performance of slurry aluminide. Moreover, the type of oxides formed on steels as well as the mechanisms of formation has not been studied in depth. In this work the comparison of the behavior of coated and uncoated carbon steel A516, and P91 a 9 wt. % Cr ferritic steel, exposed to the molten so called "Solar Salt" (eutectic mixture of 60 % $NaNO_3$ – 40 % KNO_3) at 580º C under both isothermal and cyclic conditions. The coating provides very high resistance to molten nitrate corrosion up to 2000 h both under cyclic and isothermal conditions exhibiting only a very slight weight loss under cyclic corrosion, conditions attributed to losses of the protective oxide. On the other hand the uncoated materials develop thick oxides with a stratified, loosely coherent and little adherent morphology, with oscillating Cr concentration on P91 and under cycling conditions a high degree of spallation was observed.

3:50pm **A1-2-8 Sol-gel ZrO_2-Y_2O_3 Coatings Validated in Molten Salt Environment for CSP Applications**, *V Encinas Sánchez, M Lasanta, M de Miguel, G García Martín,* ***Francisco Javier Pérez Trujillo***, Complutense University of Madrid, Spain

Material degradation owing to corrosion has been an important subject of study related to molten salts and CSP plants. Ferritic-martensitic steels have been widely used for industrial applications mainly because of their cost, despite of their properties, which are worse in comparison with other materials, such us stainless steel, since they are prone to localize corrosion from severe effects. To prevent this phenomenon occurrence numerous methods can be used, one of them being the use of protective coatings. Numerous methods exist for the preparation and deposition of coatings, sol–gel coatings and dip-coating technique presenting many advantages. On the one hand, frequently, sol-gel protective coatings are formed by oxides. Within them, yttrium-stabilized zirconia seems to be a great option because of its properties. On the other hand, sol-gel solutions can be deposited through various methods (spin-coating, spraying, electro-deposition, dip-coating, etc.) Dip-coating technique is an easy deposition solution that allows the preparation of uniform coatings through an easy control of the withdrawal rate at low cost.

Thus, the aim of this work was to obtain ZrO_2-Y_2O_3 coatings deposited on P92 substrates under various conditions and evaluate their protective behavior against corrosion through static immersions tests in molten salts.

Previously superficially modified coupons of P92 were dip-coated with the prepared sol-gel solution of ZrO_2-Y_2O_3 at the withdrawal rate of 25 mm·min^{-1} and thermally treated at 500ºC. The yttria-doped zirconia solution was synthesized by a previously reported procedure. After characterizating, the samples were tested through isothermal immersion tests in a nitrate molten salt mixture (60 wt.% $NaNO_3$/40 wt.% KNO_3) at 500ºC for 1000 h and evaluated via gravimetric at various times. The study was developed by static tests. The samples were characterized after 500 and 1000 h of testing by SEM and XRD.

The gravimetric results show the good behaviour of the coated substrates in comparison with the uncoated ones. One of the reasons of this behaviour would be probably the high uniformity and compaction obtained at this withdrawal rate, which was selected on the basis of a previous work.

The good behaviour of these coatings is also observed by SEM-EDX and XRD. In SEM-EDX cross-section is observed the compact appearance of the coatings coated at 25 mm·min^{-1}. SEM and XRD also show the good behaviour of the coatings after 1000 hours of testing.

From results it is concluded that ZrO_2-Y_2O_3 coatings could be suitable for solar applications. However, it would be interesting to study this system at longer times and using more coating layers.

Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B1-2

PVD Coatings and Technologies

Moderators: Joerg Vetter, Oerlikon Balzers Coating Germany GmbH, Jyh-Ming Ting, National Cheng Kung University

1:30pm **B1-2-1 Air-based Deposition of Oxynitride Thin Films**, ***Fu-Hsing Lu***, National Chung Hsing University, Taiwan **INVITED**

Many oxynitride thin films exhibit superior mechanical, optical, and electrical properties. Conventionally, pure oxygen and nitrogen with different ratios are employed as reactive gases during sputtering to make oxynitride thin films. Here, air instead of O_2/N_2 mixing gases was used as the reactive to make the films. Hence, high vacuum is not required for the deposition, which could save a large amount of processing time and cost. Titanium oxynitride (TiN_xO_y) has been selected as a model system. Increasing the air/Ar ratios, the color would change and the films transformed from crystalline to amorphous phases. A large range of O/N contents for the oxynitride films could be tailored by simply varying the air/Ar ratios. Kinetically controlled formation of the films would be discussed. Hardness of the films was determined by nanoindentation. The films could also exhibit a wide range of electrical resistivities, from conductive, semiconductive, to insulating behavior. The carrier concentration and mobilities of the oxynitride films were also investigated by Hall-measurements. This much simpler technique could achieve similar quality of the films as reported from the literature. The air-based sputtering technique can also be applied to many other oxynitride film systems, which may bring in much more technical applications.

2:10pm **B1-2-3 Effect of Oxygen Contamination on PVD AlN Growth**, ***Katherine Knisely***, *B Griffin, R Timon, M Olewine, T Young, M Monochie, H Dallo,* Sandia National Laboratories, USA

Sputtered aluminum nitride (AlN) is a widely used piezoelectric material used in sensor and resonator designs because it is CMOS compatible, supports high acoustic velocity waves, and has relatively low levels of electrical loss. The piezoelectric coupling of PVD AlN, a polycrystalline thin film, is highly dependent on the quality and uniformity of the grains. Here we report the effects of substrate surface preparation on AlN grain structure. Oxygen contamination is found to degrade grain structure for

AlN grown on Si and metallic surfaces, causing large triangular grain growths in the film that initiate on the substrate surface.

2:30pm **B1-2-4 Optical and Mechanical Properties of Al-doped Zinc Oxide Thin Film Fabricated by a High Power Impulse Magnetron Sputtering**, ***YuCi Hong***, *J Lee,* Ming Chi University of Technology, Taiwan*; B Lou,* Chang Gung University, Taiwan

Transparent conducting zinc oxide (ZnO) films have been extensively studied recently due to its unique electrical conductivity, transmittance properties and lower cost. The higher conductivity of ZnO film can be obtained by doping with Al to form AZO film. High power impulse magnetron sputtering (HIPIMS) is the latest coating technology, which can make the film denser and improve its mechanical properties. In this study, aluminum doped zinc oxide thin films were deposited without intentional heating by high power impulse magnetron sputtering under different duty cycles. Effects of duty cycle of HIPIMS power on the optical and mechanical properties of AZO coatings were discussed. The films were characterized using X-ray diffractometer, Field-emission scanning electron microscopy, Atomic force microscope, Nanoindentation, Scratch tester, Tribometer and UV-visible spectrometer. According to the experimental results, it was found that the average transmittance in the visible range was generally above 82% for all the films. For mechanical properties evaluation, all AZO films showed good adhesion and high hardness.

2:50pm **B1-2-5 Non-reactive and Reactive dc Magnetron Sputter Deposition of Molybdenum Oxide Thin Films**, *J Pachlhofer,* ***Robert Franz,*** Montanuniversität Leoben, Austria*; E Franzke,* Plansee SE, Austria*; A Tarazaga Martín-Luengo,* Johannes Kepler University, Austria*; H Köstenbauer, J Winkler,* Plansee SE, Austria*; A Bonanni,* Johannes Kepler University, Austria*; C Mitterer,* Montanuniversität Leoben, Austria

Due to their unique optical, electrical and chemical properties oxide-based thin film materials are widely used in industrial applications ranging from hard coatings, diffusion barriers to thin films in optical and electronic applications. Molybdenum oxide thin films synthesised by dc magnetron sputter deposition from a Mo target in an industrial-scale system revealed a change in structure and properties as a function of their oxygen content which was controlled by adjusting the O_2 partial pressure during deposition. At medium O_2 partial pressures, MoO_2-structured films were obtained with electrical conductivities similar to metallic Mo and high optical absorbance of up to 70%. Exceeding a critical O_2 partial pressure results in the formation of highly transparent, but insulating MoO_3-structured films. However, such reactive deposition processes are typically disadvantageous for the large-scale synthesis of oxide thin films due to process instabilities that originate from target poisoning effects at elevated O_2 partial pressures. As an alternative, the synthesis of molybdenum oxide films via non-reactive dc magnetron sputter deposition using ceramic MoO_x targets was explored within this work. The films deposited in non-reactive mode exhibited a MoO_2 dominated structure with properties similar to the ones from the reactive process. Adding O_2 to the process gas caused the same transition in structure and properties of the films observed in the reactive mode but at a significantly lower O_2 partial pressure. In general, the use of oxide targets in dc magnetron sputter deposition of molybdenum oxide thin films offers an efficient and reliable alternative to the use of metal targets and, hence, enables the usage of such films for a wide range of optical and electrical applications.

3:10pm **B1-2-6 Piezoelectric Coefficient Enhancement in Low Mg Content Wurtzite $Mg_xZn_{1-x}O$ Films**, ***YiJu Chen***, *S Brahma, C Liu, J Huang,* National Cheng Kung University, Taiwan

Environmentally friendly piezoelectric nanogenerators are the subject of the intense research in recent years, where waste mechanical energy is converted into electricity through piezoelectric materials. Wurtzite structure materials such as ZnO exhibits piezoelectric and semiconducting properties with piezoelectric coefficient as a dominant physical characteristic. In this paper, we investigated the dependence of piezoelectric coefficient on Mg content in MgZnO thin films onto Si (111), prepared by using radio frequency magnetron sputtering with ZnO and MgO as two independent targets. The Mg content was varied by varying applied power to MgO target, while maintaining a constant power of 50W to ZnO target. The deposition temperature is fixed at 250℃ and all the films were deposited to reach the same thickness around 380 nm. X-ray diffraction analysis confirms that all MgZnO films show high crystallization with strong preferential orientation along [0001] growth direction. Besides, whereas most MgZnO films are Wurtzite phase, the $Mg_xZn_{1-x}O$ films deposited at higher MgO power present a mixed phase of hexagonal Wurtzite phase and tetragonal cubic phase. Moreover, the diffraction peaks shift toward higher angles confirm to the smaller ionic radius of magnesium substituting for larger zinc. The morphology and composition of films are examined by scanning electron microscopy and energy dispersive X-ray spectroscopy. Finally, the piezoelectric coefficient of MgZnO films were measured by piezoelectric force microscopy, exhibiting the maximum occurring at an intermediate Mg concentration, which is largely improved by compared to ZnO. The MgZnO films hold great promise to be applied in piezoelectric nanogenerators.

3:30pm **B1-2-7 Ternary and Quaternary Hard Transparent Thin Films Made from Al, Si, O and N**, ***Maria Fischer***, *M Trant, K Thorwarth, H Hug, J Patscheider,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Al-O-N and Al-Si-N are two ternary material systems providing attractive properties for transparent hard coatings. Thin films of these materials were deposited by reactive unbalanced closed field direct current magnetron sputtering (R-UCFDCMS). Metallic Al targets and the two reactive gases O_2 and N_2 are required for Al-O-N, while Al-Si-N films are made by co-sputtering from an Al and a Si target and N_2 gas only.

O_2 addition induces a gradual transformation of crystalline wurtzite AlN via Al-O-N nanocomposite towards amorphous Al_2O_3. Incorporation of O into wurtzite is feasible up to a solubility limit of 8 at% and induces a replacement of N, which acts as electron acceptor in Al-N bonds. By contrast, Si integration causes substitution of Al, the electron donor. Despite the different nature of these exchanges, the Al-Si-N system transforms equivalently to Al-O-N. For example, the unit cell dimensions and the residual stress states evolve the same way in both ternary systems. The reason for this analogy is an excess of electrons that both O and Si bring along in comparison to N and Al they replace. In each of the two systems, these additional electrons are compensated by the generation of Al vacancies, which exert a major influence on the material system evolution in either case. Ab initio calculations are in good agreement with the experimentally determined lattice spacing changes and result in energy optimization for vacancy generation, confirming the hypothesis.

Combining Al-O-N and Al-Si-N in a quasi-binary way leads to Al-Si-O-N. Thin films of this quaternary material were also deposited by R-UCFDCMS and characterized analogously to the two ternary systems. Understanding the material evolution in Al-Si-O-N allows for the fabrication of transparent coatings with a wide range of finely adjustable properties.

3:50pm **B1-2-8 Characteristics of TiAlSiN Having a Hexagonal Structure**, ***Shingo Inagaki***, *A Kawana,* Japan Coating Center Co., Ltd., Japan

TiAlN has been developed as for a cutting tool because of its excellent oxidation resistance. The oxidation resistance is proportional to the amount of aluminum, therefore, TiAlN including high concentrated aluminum has been studied. However, when the Aluminum content is more than 60at%, it can be seen that the film hardness decreases drastically, and it has cause a decrease in tool life. That's because hexagonal AlN phase which has low hardness is precipitated in the film. Cubic structure is necessary for film using for a cutting tool to keep that wear resistance and mechanical strength.

The purpose of this study is to improve the cutting performance of TiAlN including Aluminum as high content without losing its excellent oxidation resistance. We have examined a multi-layered TiAlN with the addition of Silicon which has a hexagonal structure and keeps excellent oxidation resistance. We report a new features that cause of improvement of cutting performance by this film. We have prepared some of the target of changing the Aluminum concentration. In this study, these film were deposited by cathodic arc in PVD. It was formed using bias voltage as a parameter.

TiAlSiN whose Aluminum concentration is more than 70at% is confirmed with the hexagonal structure by X-ray diffraction (XRD). When changing the bias voltage in the same composition ratio, whose samples were also confirmed hexagonal structure. However, the crystalline orientation of the hexagonal phase was changed with increase of bias voltage. The hexagonal structure wasn't confirmed in Aluminum concentration 64at% TiAlN by XRD as it is known that Aluminum concentration 60at% TiAlN has cubic structure.

However hexagonal structure was confirmed in films which included 8at% of silicon to the Aluminum concentration 61at%. In general, stable phase for AlN is hexagonal structure. However, when the amount of Titanium increases, AlN takes cubic structure the same as TiN. Since TiAlN is replaced to Al from Titanium in the crystal structure, film hardness is increased by change in the lattice constant. TiAlSiN whose Aluminum concentration is less than 53at% was exhibit a strong peak of cubic structure.

Cutting performance was evaluated about composite film using TiAlSiN. TiAlSiN having a high Aluminum concentrations above 60at%. As a result, cutting performance was improved using TiAlSiN. The tool temperature during cutting was measured by thermography. The tool temperature of TiAlSiN was lower than the tool temperature of TiAlN. They had a difference of 150 degree C.

4:10pm **B1-2-9 A study of Preferred Orientation of VN Thin Film on Si Substrate Deposited by Unbalanced Magnetron Sputtering**, ***Cheng-Han Lin***, *J Huang, G Yu,* National Tsing Hua University, Taiwan

The purpose of this study was to investigate the texture evolution of VN thin film on Si (100) substrate by unbalanced magnetron sputtering (UBMS) method. Based on previous studies of TiN and ZrN thin films, the preferred orientations of the transition metal nitride thin films can be controlled as (111), random and (200) by adjusting nitrogen flow rates or introducing minor oxygen gas. The mechanism of formation (200) texture in TiN and ZrN is mainly by using ion or oxygen to retard the adatom migration on the (200) plane. However, in our previous study of VN film, the (111) preferred orientation of VN thin film become prominent by introducing higher nitrogen flow rate. The result was inconsistent with the studies of TiN and ZrN thin films. However, there was little information on the mechanism of changing preferred orientation in VN thin films. In this study, different nitrogen flow rates and different DC gun powers were adopted to study the evolution of preferred orientation of VN thin film and the accompanying effects on the film properties. After deposition, the composition of specimen was determined by X-ray photoelectron spectroscopy (XPS). X-ray diffraction (XRD) was used to characterize the structure and preferred orientation, and field emission gun scanning electron microscopy (FEG-SEM) was used to measure the thickness and observe the microstructure. The hardness and electrical resistivity were measured by nanoindentation and four-point probe, respectively. Based on the experimental results, a reasonable mechanism of the texture evolution of VN can be proposed.

4:30pm **B1-2-10 Structure and Mechanical Property of AIP Deposited (AlxCr100-x)N Coatings with X > 70at%**, ***Kenji Yamamoto***, *H Nii, M Abe,* Kobe Steel Ltd., Japan*; S Takada, Y Iwai,* University of Fukui, Japan

AlCrN has been used for various metal working tools including cutting tools and molds / dies for increasing wear resistance. AlCrN is a solid solution of metastable cubic AlN into CrN NaCl type unit cell. Makino et al. calculated maximum solubility of metastable cubic AlN in NaCl type transition metal nitride by band-parameter method and reported it is 65.3 at% for Al-Ti-N system and 77. 2 at% for Al-Cr-N system [1]. Mechanical as well a chemical property of AlCrN is influenced by the Al composition and crystal structure as well as deposition parameters. In this study, AlCrN coatings with different Al compositions, particularity Al composition is close to the maximum solubility, were synthesized by cathodic arc under different deposition conditions and mechanical and structural property of the resulting coating was investigated.

AlCr targets with 65, 70, 75 and 80 at% Al were used. AlCrN coatings were deposited by laboratory type AIP equipment from Kobe Steel Ltd. (AIP-S20). Coatings were deposited under N2 atmosphere at 4 Pa with arc current of 150A. Substrate bias during the deposition was varied from 40 up to 200V. Chemical composition was determined by EDX and crystal structure was analyzed by XRD. Mechanical property of the coating was investigated by nano-indentation for hardness and Young's modulus. Wear resistance was evaluated by Micro-Slurry Jet Erosion Method [2].

All AlCrN coatings deposited with Al 65 and 70 at % targets were all in cubic single phase independent of substrate bias. Although, the hardness and Young's modulus was monotonously increased as the substrate bias was increased. In case of 75 at% Al sample, hexagonal was observed at 40V and became cubic single phase 70 V and more. In case of Al 80 at %, trace of hexagonal phase was observed up to 100V, but became cubic dominant structure at 125V. The hardness showed increasing trend as the substrate bias became higher which is corresponding to transition from hexagonal to cubic structure. Wear resistance of the coating with different Al composition deposited under fixed substrate bias of 70 V was evaluated by MSE. Erosion rate became small as the Al composition increased up to 75 at% at where showed a minimum value. Further increase in Al composition to 80 at% resulted in a slight increase of the erosion rate.

Micro-structure as investigated by TEM and discussion relationship between erosion rate and hardness or Young's modulus will be presented.

[1] Y. Makino: ISIJ International, 38 (1998) 925

[2] Y. Iwai et al. Wear 251 (2001) 861

4:50pm **B1-2-11 Control of Elastic-Plastic Deformability and Hardness in Nitride Hard Coatings on Cubic Boron Nitride Sintered Compact Cutting Tool**, ***Masakuni Takahashi***, *S Sato, T Maekawa,* Mitsubishi Materials Corporation, Japan

Recently, with more expansion of automotive production, characteristic to be required to cubic boron nitride sintered compact (CBN) cutting tools for hardened steel parts have changed into not only high efficiency but also a more stable performance and extension of life. One of the keys for stable cutting performance is to make the coating do normal wear without fracture of the coating in intermittent cutting.

On the other hand, generally in case of using high hardness coating for high wear resistance the coatings lose its deformability to external force and break itself, and in case of using high deformability coating to external force for better fracture resistance the coatings lose its hardness and wear resistance. For pursuit of both fracture resistance and wear resistance concerning the cutting performance in turning processing of high hardness steel by using CBN cutting tools, with changing the composition and the composition ratio of the hard coatings which were deposited by arc type physical vapor deposition method on CBN cutting tool we investigated the relationship between the deformability to external force, the hardness and the cutting performance of the tool.

The deformability to external force and the hardness were evaluated by using nanoindentation method. We used elastic-plastic deformation work rate in the indentation tests as a barometer of the deformability. With respect to $Al_xTi_{1-x}N$ and $Al_xCr_{1-x}N$, the elastic deformation work rate and the hardness increase monotonically in the range of $x \leq 0.6$. In this range the increase ratio of the elastic deformation work rate and the hardness of $Al_xCr_{1-x}N$ are larger than $Al_xTi_{1-x}N$, and it shows $Al_xCr_{1-x}N$ has controllable potential for both elastic deformation work rate and the hardness.

In addition, by introduction of the 3rd element such as Si in $Al_{0.3}Cr_{0.7-x}Si_xN$, the rate of change of the elastic deformation work rate and the hardness change with the content rate of the Si. Evaluating the cutting performance of the CBN cutting tools which were coated with the coatings of several compositions and composition ratios described above, the hard coatings were able to show the wear resistance and also the fracture resistance to external force. This result shows the importance of coating design optimizing materials properties, especially elastic-plastic deformability and hardness, in order to bring out cutting performance of coated CBN cutting tools.

5:10pm **B1-2-12 Effect of Preferred Orientation on the Fracture Toughness of VN Hard Coatings**, ***Liang-Ru Wei***, *J Huang, G Yu,* National Tsing Hua University, Taiwan

The purpose of this study was to measure the fracture toughness of VN hard coatings using internal energy induced cracking (IEIC) method, and find out the effect of pure (200) and mixed (200) with (111) textures on the fracture toughness of VN coatings. VN coatings were deposited on Si (100) substrates by unbalanced magnetron sputtering (UBMs) with different nitrogen flow rates. By changing the nitrogen flow rates, we could control the ratio of (111) and (200) texture coefficient in VN coatings. The fracture toughness of one set of strong (200) textured VN and two sets of mixed (111), (200) textured VN coatings were compared with the mechanism of TiN and ZrN. So far there were relatively few studies about VN coatings, especially on the fracture toughness. On the basis of Griffith's criterion and the modified delamination model proposed by Freund and Suresh [1,2], the total stored elastic energy (G_s) existing in the film can be given by,

$$G_s=[(1-\nu_f^2)/2E_f]\sigma_m^2 h_f$$

where ν_f and E_f are the Poisson's ratio and Young's modulus of the thin film, respectively, h_f is the thickness of the thin film, and σ_m is the residual stress. As the film thickness increases, G_s will reach a critical value G_c that leads to the occurring of fracture in the film. Therefore, G_c can be considered as the fracture toughness of VN. For the measurement of G_c, the Young's modulus was determined by nanoindentation (E_{NI}), film thickness was measured from the cross-sectional image of scanning electron microscopy (FEG-SEM), and residual stress was obtained from two methods: the laser curvature method (LCM) and the average X-ray strain (AXS). The LCM method was utilized to obtain the overall residual stress in the film. The average X-ray strain (AXS) [3,4] was measured by $\cos^2\alpha\sin^2\psi$ XRD method at several rotational angles. By using AXS plus E_{NI} technique the accuracy of the stress measurement can be increased and comparable to LCM.

[1] A.A. Griffith, Philos. Trans. R. Soc. S-A, 221 (1921) 163.

[2] L.B. Freund, S. Suresh, Thin film materials: stress, defect formation and surface evolution, Cambridge University Press, 2004.

[3] J.-H. Huang, Y.-H. Chen, A.-N. Wang, G.-P. Yu, H. Chen, Surf. Coat. Techol., 258 (2014) 211.

[4] A.-N. Wang, C.-P. Chuang, G.-P. Yu, J.-H. Huang, Surf. Coat. Techol., 262 (2015) 40.

Hard Coatings and Vapor Deposition Technologies
Room California - Session B5-2

Hard and Multifunctional Nanostructured Coatings

Moderators: Jiri Capek, University of West Bohemia, Robert Franz, Montanuniversität Leoben

1:30pm **B5-2-1 B_4C and Mo Coatings Characterization regarding Stamping Dies Application**, *F Silva,* ***Liliana Fernandes****, M Andrade,* ISEP - School of Engineering, Polytechnic of Porto, Portugal*; R Alexandre,* TeandM - Technology, Engineering and Materials, S.A., Portugal*; A Baptista,* INEGI - – Instituto de Ciência e Inovação em Eng. Mecânica e Eng. Industrial, Portugal*; C Rodrigues,* Colep Portugal, S.A., Portugal

Prestigious brands of cookies usually use metallic tins as package to distribute and sell their products, trying to impress the customer through the look and avoiding cookies' break and/or damage during logistics operations. These packages are made commonly in tin coated (2.8 g/m^2) thin steel sheet (electrolytic Tin plate), which originates severe wear problems on both die and punch tool components during the stamping process. The border of the package represents a non-considerable deformation, despite their almost perpendicular orientation to the top surface, but this top is usually patterned, also implying the flow of the sheet between the top and bottom die surfaces. Due to the softness of the Tin coating, it easily adheres to the die generating premature wear and several concerns in maintaining the required final shape of the tin lid. Lubrication would be an easy way to solve the problems above referred but lubrication operations should be avoided regarding that these kind of packages are for food purposes.

This study has been developed in order to find the best coatings which avoid Tin adhesion and wear on the stamping surfaces when deforming Tin coated steel plate. Two advanced PVD coatings (B_4C and Mo) were characterized and tested leading to improve the wear behavior of the punch and die under these work conditions. The transfer of Tin material from the metallic sheet to the punch and die was also studied, as well as the friction coefficient of this sheet against some selected coatings, also trying to minimize the Tin adherence to the tool surfaces. Tribological tests under medium loads were carried out in order to realize what kind of coating presents better wear behavior in those work conditions. Worn surfaces were studied by Scanning Electron Microscopy (SEM) and material transfer was analyzed by Energy Dispersive Spectroscopy (EDS).

Results obtained with some of the tested coatings allow to confirm that it is possible to minimize the Tin transfer from the covered steel sheet to the die and punch, ensuring a longer life of these parts, decreasing the tool maintenance operations and improving the Overall Equipment Efficiency (OEE) of that stamping process.

1:50pm **B5-2-2 Effect of Energy on Structure, Microstructure and Enhanced Resistance to Cracking of Hard Sputter Deposited Ti(Ni)N_x and Ti(Al,V)N_x Films**, ***Martin Jaroš,*** *J Musil, R Čerstvý, S Haviar,* University of West Bohemia, Czech Republic

The paper reports on the preferred orientation, structure and mechanical properties of magnetron sputtered Ti(Ni)N_x and Ti(Al,V)N_x films and their resistance to cracking in bending. The films were reactively sputtered on Si(111) plate and Mo strips in a mixture of Ar+N_2 gases using a DC magnetron equipped with a TiAlV alloy target (6 at.% Al, 4 at. % V), or a TiNi alloy target (5 at. % Ni) respectively. The preferred orientation, structure, macrostress, mechanical properties (the hardness H, effective Young's modulus E^*, elastic recovery W_e), of Ti(Ni)N_x and Ti(Al,V)N_x films and theirs resistance to cracking in bending were characterized by (i) the X-ray diffraction (XRD), (ii) Scanning Electron Microscope (SEM), (iii) the bending of Si(111) plate using the Stoney`s formula, (iv) the diamond indentation test and (v) the bending of coated Mo strip around a fixed cylinder of small radius (down to 5 mm), respectively. It was found that: (1) the preferred orientation of sputtered Ti(Ni)N_x and Ti(Al,V)N_x nitride films depends on energy $E_{bi} \approx U_s \times i_s / a_D$ delivered to the film during its growth, here is U_s the substrate bias, i_s the substrate current density and a_D the deposition rate. The texture continuously changes from (i) TiN(220) -> TiN(111)+TiN(200) -> TiN(220) for Ti(Ni)N_x films and (ii) TiN(200) -> TiN(220) -> TiN(111)+TiN(220) for Ti(Al,V)N_x nitride films with increasing E_{bi}. (2) The Ti(Al,V)N_x and Ti(Ni)N_x nitride films with low resistance to cracking are prepared at lower value of E_{bi} < 1.5 MJ/cm^3 exhibit (i) low ratio $H/E^* \leq 0.1$, low elastic recovery $W_e \leq 65$ %, compressive macrostress (σ < 0 GPa) and (ii) are composed of grains contain TiN(200) and show a columnar structure. (3) The Ti(Al,V)N_x and Ti(Ni)N_x nitride films with enhanced resistance to cracking are prepared at higher value of E_{bi} > 3.7 MJ/cm^3 exhibit (i) high ratio $H/E^* > 0.1$, high elastic recovery W_e > 65 %, compressive macrostress (σ < 0 GPa) and (ii) are composed of grains witch do not contain TiN(200) and show a dense structure.

2:10pm **B5-2-3 Ultra-thick, Superhard Nanocomposite Coatings Deposited using Plasma Enhanced Magnetron Sputtering (PEMS) and their Practical Applications**, ***Ronghua Wei,*** Southwest Research Institute, USA **INVITED**

In this presentation, the research on thick TiSiCN-based nanocomposite coatings (up to 560 µm) conducted at Southwest Research Institute (SwRI®) will be reviewed. These coatings have been developed using a plasma enhanced magnetron sputtering (PEMS) process via sputtering of Ti from all targets in a gas mixture of Ar, N_2 and TMS (trimethylsilane). In the PEMS process, in addition to the magnetron plasma, a global plasma is generated by W filament thermionic emission for the enhanced ion bombardment. The coatings thus produced have a dense structure, good adhesion to the substrate, low internal stress and superior mechanical properties compared to those obtained with the conventional magnetron sputtering. The coatings formed have a microstructure composed of nanocrystalline TiC_xN_{1-x} (x=0, 0.3 or 0.7) with the grain size of 4-10 nm in a matrix of amorphous SiC_yN_z, or nc-TiC_xN_{1-x}/a-SiC_yN_z. The microstructure of the coatings results in the super-hardness (up to 4600HV). However, the internal stress was found to be less than 1 GPa, thereby allowing the deposition of ultra-thick coatings of over 500 µm. The coatings also have high toughness characterized by high values of H^3/E^{*2} and H/E^*. The nanocomposite coatings have been developed specifically for severe environments including sand erosion, sand abrasion, water droplet erosion, and heavy load sliding wear on various alloy substrates including Ti-6Al-4V, Inconel 718, Al alloys, synthetic diamond inserts, WC-Co and various steels. These coatings have a few specific industrial applications including compressor blades or vanes for aero engines; piston rings, cylinder liners and stamping dies for automotive; and ball valves, valve stems, valve seats and plungers the for oil and gas industry. In this paper we review the method for preparing these coatings, discuss their microstructural, mechanical and tribological properties, and present examples for practical applications.

2:50pm **B5-2-5 Role of Interfaces in Determining the Fracture Resistance of Nanocomposite/Metal Nitride Multilayers**, ***Naureen Ghafoor,*** Linköping University, IFM, Thin Film Physics Division, Sweden

Role of interfaces in determining the fracture resistance of nanocomposite/metal nitride multilayers

Naureen Ghafoor[a], Jeni Barrirero[b], Claire Davis[c], F. Mücklich[b], W.J. Clegg[c],

[a]Thin Film Physics Division, Department of Physics, Chemistry, and Biology (IFM), Linköping University, Linköping, Sweden

[b]Functional Materials, Department of Materials Science, Saarland University, Saarbrucken, Germany

[c] Gordon Laboratoty, Department of Materials Science and Metallurgy, University of Cambridge, Pembroke St, Cambridge CB2 3QZ, UK

We present mechanical response of TiN/ZrAlN multilayers and monolithic ZrAlN nano-composite coatings investigated through nano indentation and micropillar compression tests. The study highlights effect of interface structure on pre yield and post yield behavior of nano scale multilayer deformation in compression.

To understand stress-strain response in a uniaxial micropillar compression tests the pillars of height of 1 mm and diameter of 300 nm were compressed using in situ SEM nanoindenter equipped with a flat punch (diameter 5mm)[Ref 2]. The pillars were milled using focused ion beam. The interface structure of the multilayers is tuned by varying growth parameters during magnetron sputter deposition on MgO (001) substrates. The growth temperatures above 700 °C facilitated in situ segregation of ZrN-and AlN- rich domains within ZrAlN layer during growth [Ref 1]. The growth conditions and multilayer design are varied to tailor crystal structure of AlN rich domains from cubic to wurtzite and consequently to obtain coherent, semicoherent, and incoherent interfaces.

The degree of plastic deformation and work hardening is found to be dependent on the bilayer periodicity as well as on the nature of internal interfaces inside ZrAlN nano-composite layers. Micropillar compression tests revealed higher yield stresses and larger post yield displacements in 2 and 5 nm thin ZrAlN layers consisting of cubic phases of ZrN and AlN- rich domains forming coherent interfaces. For 15 and 30 nm thick ZrAlN layers, involving incoherent interfaces, the dominant crack propagation occur through layer interfaces. Nanoindentation measurements of the multilayers display a systematic variation of hardness with a value between 34 ± 1 to 22 ± 0.8 GPa as a function of layer thickness and interface structure. The dominant deformation mechanisms in connection with interface coherency and multilayer periodicity will be presented.

1: K. Yalamanchili,….N. Ghafoor, et al., Acta Materialia 89 (0) -2015, K. Yalamanchili,….N. Ghafoor, et al., Acta Materialia, [http://dx.doi.org/10.1016/j.actamat.2016.07.006]

2: S. Korte, W.J. Clegg, Scr. Mater. 60 (2009) 807–810.

xd

3:10pm **B5-2-6 Novel CrVN/TIN Nanoscale Multilayer Coatings Deposited by DC Magnetron Sputtering**, ***Elbert Contreras***, *Y Galindez, G Bejarano, M Rodas, M Gómez,* Universidad de Antioquia, Colombia

The constant search by development coatings with higher properties opened the doors to the research and development of nanoscale multilayer coatings, hardness higher than 40 GPa, friction coefficients lower 0.3, improved adhesion and increased heat and corrosion resistance are some of the most interesting properties of these multilayer coatings compared to monolayers. In this research novel CrVN/TiN nanoscale multilayer coatings were deposited onto H13 steel substrates by DC unbalanced magnetron sputtering. Prior to the coatings deposition an ionic cleaning was carried out to clean the surface of the substrates with a 40 sccm flow of Ar and a pressure of 2-3x10^{-2} mbar during 30 minutes. The deposition of multilayer coatings was using two targets opposite each other, Cr-V (70-30 %wt) and Ti, with a power density of 2.4 W/cm^2 at both, a nitrogen gas flow of 20% in the gas mixture (N_2/(Ar+N_2)) obtaining a working pressure of 6-7x10^{-3} mbar, deposition temperature was 250°C and a BIAS voltage of -70V. In order to varying the bilayer period a microcontroller was used to control the rotation and residence time of the substrates against each target in 15, 30 and 40 seconds, looking for some different bilayer periods, CrVN and TiN monolayer coatings were also deposited. Microstructural analysis by X-ray diffraction (XRD) showed a FCC crystal structure to the monolayer coatings CrVN and TiN with preferential orientation (111); multilayer coatings showed a preferred orientation (200); the roughness and grain size was characterized using an AFM technique, CrVN monolayer coating showed less roughness and the multilayer coatings showed a decrease of the grain size while decreasing the bilayer period. SEM images revealed columnar structure for CrVN and globular structure for TiN, similar structure was found in the multilayer coatings. Tribological properties of the coatings were investigated using Pin-on-disk, all the multilayer coatings showed lower friction coefficients and wear rates compared with the monolayer coatings.

3:30pm **B5-2-7 Carbon Supersaturated Fe-Cr-Ni-C Thin Films with a Unique Nanocolumnar Structure - a Tough, Low Friction and Corrosion Resistant Coating**, ***Tomasz Suszko***, *W Gulbinski, E Dobruchowska,* Koszalin University of Technology, Poland*; J Morgiel,* Institute of Metallurgy and Materials Science of Polish Academy of Sciences, Poland

Carbon supersaturated, amorphous FeCrNi:C coatings showing a unique nano-columnar structure have been deposited by pulsed magnetron sputtering of the 316L steel target in argon/acetylene atmosphere. HRTEM, EELS and XPS studies have shown that metallic cores of nano-columns oriented along the film growth direction are surrounded by amorphous carbon shells. The mechanism of growth of such a self-organized structure is discussed in terms of thermodynamically beneficial release of carbon from metastable metal carbides and from ternary phases formed during sputter deposition. The coatings are tough, have very good tribological behaviour in dry friction vs alumina and demonstrated excellent resistance to the formation and growth of pits in the corrosion environment containing chloride ions.

3:50pm **B5-2-8 Study of Wear Mechanism of Carbide and Ceramic Cutting Tools with Nano-structured Multi-layered Composite Functional Coatings**, ***Alexey Vereschaka***, *A Vereschaka,* MSTU Stankin, Russian Federation*; A Batako,* Liverpool John Moores University, UK*; N Sitnikov,* Federal State Unitary Enterprise "Keldysh Research Center", Russian Federation

The purpose of this study was to research wear mechanisms of carbide cutting tools with nano-structured multi-layered composite functional coatings under stationary cutting conditions. The study presents the results of extensive research of wear and failure mechanisms of carbide cutting tools with developed coatings on the basis of multi-component systems (for example, on the basis of systems Ti-TiN-(TiCrAl)N, Zr-ZrN-(ZrNbCrAl)N, and Ti-TiN-(NbZrTiAl)N) in longitudinal turning of steel of various compositions. The particular attention was paid to research of the kinetics and wear mechanisms of wear centres on contact areas of rake and flank faces of the tool with the use of a SEM equipped with microprobe analysis system. Chemical and phase compositions of developed coatings were studied by X-ray diffraction analysis. The objects of comparative analysis were represented by samples of carbides with wear-resistant coatings of traditional types (TiN, (TiAl)N). The particular attention was paid to the study of specifics of cracking mechanisms in coatings, as well as to interdiffusion processes taking place in the areas of contact between tool material and material being machined.

The following results were obtained:

- Tools with developed coatings provided the increase in tool life by 2-3.5 times as compared with uncoated tool and by 1.5-2 times - as compared with tool with tradition coatings .

- In the developed coatings deposited to carbide substrates, the mechanism of cracking is substantially different from the mechanism of cracking in the coatings of traditional type. In particular, the multi-layered architecture of developed coatings and the presence of sublayers of nano-meter thickness contribute to inhibition of initiation and development of cracks; nano-structured multi-layered composite coatings can be subjected to formation of rare longitudinal cracks less hazardous in context of failure of the coating in general with virtually no hazardous cross cracks, which are the major cause of premature complete failure of the coatings.

- The tests have detected active formation of oxides in areas adjacent to cracks and in the area of coating failure. Oxides of such metals as titanium and zirconium are formed very actively.

- Application of developed nano-structured multi-layered composite coatings contributes to the transformation of wear mechanisms of cutting tool. In particular, it almost completely excludes formation of cracks, microchipping and chipping of tool substrate (which is especially important for ceramic tools) and reduces the intensity of adhesion-fatigue wear; abrasive wear is mainly observed, and that results in increased tool life.

Fundamentals and Technology of Multifunctional Materials and Devices
Room Royal Palm 4-6 - Session C2-2

Thin Films for Active Devices

Moderators: Vanya DarakchievaMarco Cremona, Pontificia Universidade Católica do Rio de Janeiro, Junichi Nomoto, Kochi University of Technology, Japan,

1:30pm **C2-2-1 Ga-doped ZnO Films by Magnetron Sputtered at Ultralow Discharge Voltages: Effects of Defect Annihilation**, ***Yuyun Chen***, *M Fanping, F Ge, H Feng,* Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, China

Preparation of high quality transparent conductive oxide (TCO) films by sputter deposition involves an intricate balance of defect generation by the highly energetic negative oxygen ions (depending on the discharge voltage) and the concomitant annihilation of these defects during film growth. Ga-doped ZnO films with a low Ga content (1.7 at%) were deposited to investigate the effects of defect annihilation on the microstructure evolution as well as the optical and electrical properties. To achieve this aim, we prepared the GZO films by magnetron sputtering at ultralow discharge voltages (<80 V) to minimize the defect generation, and varied the substrate temperature (from room temperature to 673 K) to adjust the annihilation rates. The microstructure was systematically characterized by X-ray Diffraction (XRD), X-ray Reflectivity (XRR), Raman Spectroscopy, and Extended X-ray Absorption Fine Structure (EXAFS). The electrical and optical properties were obtained by a Hall-effect measurement system and Spectroscopic Ellipsometry (SE), respectively. It was found that (i) even

under the condition of highly controlled defect generation, a sufficient annihilation of the defects cannot be realized without externally heating the substrate; (ii) both the structural quality and the electrical properties were improved with the increased temperature; and (iii) there existed a critical temperature, above which the generated defects were sufficiently annihilated, resulting in significantly higher Hall mobility and carrier concentration. These results reveal that the growth temperature during the GZO film deposition has played an important role in effective annihilation of the irradiation-induced structural defects.

1:50pm **C2-2-2 Reactive Sputter Deposition and Annealing of Nanometer Scale NiO Thin Films for Metal-Insulator-Metal Tunnel Junction Diodes**, ***Frank Urban***, *S Bhansali,* Florida International University, USA; *A Singh,* Intel, USA; *D Barton,* Retired, USA

The increased switching speed of metal-insulator-metal (MIM) tunnel diodes over existing diodes has the potential to open new applications including high frequency detectors for example. This work here analyzes the effect of the insulator layer (NiOx) properties on performance of such Ni-NiOx-Cr based junctions. The films were deposited by reactive magnetron sputtering of a Ni target in an atmosphere containing oxygen. Films ranged from 10 to 30 nm in thicknesses and were smooth as determined by atomic force microscopy. Initial ellipsometry examination showed that the as-deposited films were inhomogeneous in the growth direction and exhibited high optical absorption across the visible wavelength range (midrange k = 0.8 and up). While this is not unexpected considering what is known about nucleation and initial growth, it is undesirable for the intended use. Consequently treatment of the films was carried out by annealing in an oxygen atmosphere at 400°C for 3, 6, and 12 minutes. This resulted in both a significant decrease in the optical absorption and a dramatic improvement in film homogeneity. Examination using Secondary Ion Mass Spectroscopy did not show significant increases in film oxygen suggesting that atomic rearrangement rather than oxidation occurred during annealing. Performance of MIM junctions with the annealed films was investigated using current-voltage measurements. The results were correlated with capacitance-voltage measurements.

2:10pm **C2-2-3 HVPE GaN and AlGaN Thin vs Thick Freestanding Films for Electronic and Optoelectronic Devices**, ***Tania Paskova***, North Carolina State University, USA **INVITED**

The current nitride electronic and optoelectronic technology employs two generally different groups of approaches. The first group is focused on development of bulk GaN and AlN substrates and the intensive research efforts during the last years have led to a demonstration of high-quality material with huge application potential, including for devices with nonpolar and semipolar alignment of the active regions. HVPE technique has led the effort in quasi-substrate development and is the only one offering GaN freestanding films of all surface orientations of interest. The cost of this method, however, remains still high and several challenges have to be resolved to allow the cost to go down. The second group of research efforts is focused on thin film template development of GaN, AlGaN and AlN on sapphire, SiC and Si substrates. Most of these efforts, using lateral overgrowth approaches, have showed devices with good performance and have been commercially implemented. Each of the approaches employs different buffer layers or nucleation schemas, as well different growth recipes, and results in as-grown substrates and templates with different thickness limitations. The doping alternatives, using either silicon or oxygen for achieving n-type conductivity and iron for achieving resistivity in wide ranges, respectively, were found to successfully alter the electrical properties of the materials, while the optical quality was largely maintained until reaching the saturation level. In addition, besides the reduced dislocation density achieved, the HVPE technique was proven capable of producing material of high purity, regarding residual impurities and point defects. This in turn leads to improved thermal conductivity, allowing better thermal management and device performance.

Recent advances in the research and development of a variety of optoelectronic and electronic devices produced on HVPE templates and freestanding quasi-substrates has resulted in a significant improvement of device performance for a number of applications. This motivates the increased demand for HVPE nitrides, which should boost the material availability and will drive down the production cost. In this talk, we will present a comparative summary of the most promising approaches for HVPE growth of GaN and AlGaN materials. The focus will be on the different doping approaches and their effect on the thermal transport in low-defect-density materials. High thermal conductivity values in wide temperature region will be presented and scattering mechanisms including at elevated temperatures, highly relevant for high power electronic and optoelectronic devices, will be discussed.

2:50pm **C2-2-5 Characteristics of Non-polar ZnO Films Grown by Catalytic Reaction Assisted Chemical Vapor Deposition**, *A Kato, M Ikeda, Y Adachi, R Tajima,* ***Kanji Yasui***, Nagaoka University of Technology, Japan

ZnO films are usually grown on c-plane sapphire substrates, which results in the films having a <0001> orientation. These films are often used in optoelectronic devices, such as light-emitting diodes and laser diodes, operating in the ultraviolet region. However, in such <0001>-oriented ZnO films, a macroscopic electrostatic field is generated along the growth direction, and this results in spontaneous piezoelectric polarization. This induced electric field can negatively affect the device properties by, for example, causing a decrease in the overlap between the electron and hole wave functions in quantum wells, which leads to a reduction in the internal quantum efficiency. In order to eliminate such polarization effects, growth of non-polar ZnO films is required.

In the present study, non-polar ZnO films were grown on r-plane sapphire substrates through a reaction between dimethylzinc and high-temperature H_2O produced by a Pt-catalyzed reaction between H_2 and O_2 [1]. The ZnO films were evaluated using atomic force microscopy, X-ray diffraction, and photoluminescence spectroscopy. The surface morphology of the films was found to be anisotropic, consisting of arrays of nanostripes. In the X-ray diffraction profile, an intense peak was present at 2θ=56.64°, which was associated with the ZnO (11-20) planes. The photoluminescence results indicated anisotropy in the polarization between the directions parallel and perpendicular to the c-axis. The angular dependence of the linear polarization of the band-edge emission was found to be large in ZnO films grown at low temperatures. The ratio between the maximum (the electric field vector *E*: perpendicular to the c-axis) and minimum (*E*: parallel to the c-axis) emission intensity was 4 for a ZnO film grown at 500°C, while it was 2 for a ZnO film grown at 700°C. The width of the nanostripes along the a-axis for the ZnO film grown at 500°C was less than 0.1 μm, while for the ZnO film grown at 700°C it was approximately 0.5 μm. The small domain width in the film grown at the lower temperature may enhance the anisotropy of the band-edge emission. This unique polarized light emission may be exploitable in various types of polarization-sensitive optoelectronic devices in the ultraviolet wavelength region.

Acknowledgements: This work was supported in part by a Grant-in-Aid for Scientific Research (No. 16H03869) from the Japan Society for the Promotion of Science.

Reference: [1] K. Yasui et al., MRS Symp. Proc., **1315** (2011) 21.

3:10pm **C2-2-6 Mechanism of a Number of Operation Resulted in Degradation on Multilayer Resistance Random Access Memory**, ***Yi-Ting Tseng***, National Sun Yat-sen University, Taiwan; *T Chang, K Chang, T Tsai,* National Sun Yat-Sen University, Taiwan; *C Wu,* National Sun Yat-sen University, Taiwan; *P Chen, C Lin,* National Sun Yat-Sen University, Taiwan; *S Sze,* National Chiao Tung University, Taiwan

Resistance random access memory (RRAM) is most potential to serve as the new generation nonvolatile memory (NVM). Because RRAM device has low power consumption, simple structure, fast operation and high density. Sneak path current issue is very important when RRAM is fabricated stand-alone memory array. To solve sneak path current problem, complementary resistive switching (CRS) RRAM was researched.

The Pt/ZnO/SiO_2/ZnO/TiN structure device has two electric characteristics bipolar RS and CRS behavior in previous experiment result. The reason the SiO_2 layer generated oxygen vacancies and became oxygen ion storage during the forming process. The endurance of bipolar RRAM device is over 10^7 times with pulse. But, the RRAM device was degradation that high resistive state (HRS) of value increased until its fail after operating over 10^7 times. The HRS fitting curve is Schottky emission every operated time. From Schottky emission of intercept and slope, the barrier height became large and dielectric constant became small. The SiO_2 layer of oxygen ions were been activation by joule heat generated by every a million times of operation. Therefore, a lots oxygen ions could switch resistance of RRAM and the SiO_2 layer generated a number of oxygen space resulted in degradation of RRAM device.

3:30pm **C2-2-7 An Ion Mass and Ion Energy Selected Hyperthermal Ion-Beam Assisted Deposition Setup for Nitride Nanofilm Synthesis**, ***JürgenW. Gerlach***, *P Schumacher, M Mensing,* Leibniz Institute of Surface Modification (IOM), Germany*; S Rauschenbach,* Max Planck Institute for Solid State Research, Germany*; B Rauschenbach,* Leibniz Institute of Surface Modification (IOM), Germany

Ion-beam assisted deposition (IBAD) is an effective physical thin film deposition technique which on the one hand offers the opportunity to investigate fundamental processes involved in ion-assisted film growth and on the other hand provides manifold possibilities to intentionally modify the properties of the prepared thin films. The technique is characterized by simultaneous irradiation of the growing thin film with energetic ions during deposition. IBAD or - at a higher level of sophistication - ion-beam assisted molecular-beam epitaxy (IBA-MBE) is mainly defined by the separability of the material fluxes, that are directed towards the sample, as well as by the accurately adjustable parameters vapor flux and ion flux, the latter generated in form of a broad ion beam. As for nitrogen ion beams however, nitrogen plasma based ion-beam sources counteract the demand to chose the ion-beam parameters as freely as possible, because the resulting ion beam consists of a blend of both molecular and atomic nitrogen ions. Particularly in the case of hyperthermal ion energies ranging from several 10 eV to a few 100 eV this creates great difficulties in assessing the dissemination of the ion energy to the growing film surface.

In the first part of this contribution, a custom setup is presented which allows to create a hyperthermal nitrogen ion beam with selectable ion mass and variable ion energy. This was realized by the unique combination of a constricted glow-discharge plasma beam source [1] with a quadrupole mass filter, equipped with entry and exit ion optics, ion-beam deflection, as well as ion-beam current monitoring. The key features of this setup are demonstrated. For the second part, as a model system for hyperthermal ion-beam assisted growth with energy and mass selected ions, thin films of gallium nitride (GaN) were deposited epitaxially on single-crystalline substrates at elevated temperatures. GaN is well known as base material for optoelectronic devices. In the present study, hyperthermal ion-beam assisted GaN film growth with either molecular or atomic nitrogen ions of well-defined energy was monitored *in situ* by reflection high energy elec-tron diffraction. The orientation relationships between substrates and films formed on them were obtained by x-ray diffraction. Scanning probe microscopy was applied to examine the topography of the obtained films. Influences of ion mass and ion energy on growth mode, topography, crystalline quality, defect structure and luminescence properties of the films are presented and the results are discussed.

[1] A. Anders and M. Kühn, *Rev. Sci. Instrum.***69**, 1340 (1998).

3:50pm **C2-2-8 Improve Switching Characteristic of Resistive Random Access Memory with Chemical Plasma Treatment on TiN electrode**, ***Chih-Hung Pan***, *T Chang, T Tsai,* National Sun Yat-sen University, Taiwan

In this letter, the TiN electrode was treated with CF_4 plasma to improve the switching characteristics of its random resistive access memory (RRAM). After CF_4 plasma treatment, not only did the stability of HRS increase but the distribution of SET voltages was more concentrated. Furthermore, the device can be operated without current compliance. In addition, the surface of the TiN electrode became rougher after CF_4 plasma treatment, leading to oxygen entering the TiN electrode to form a $TiNO_X$ layer on the electrode. The electrical characteristics of RRAM with $TiNO_X$ are different from that with a TiN electrode. Finally, we propose a model to explain the mechanism causing the improvement in RRAM after the CF_4 plasma treatment. This is due to the difference in TiN electrode surfaces after CF_4 plasma treatment, and was verified by electrical and material analyses.

4:10pm **C2-2-9 Critical Layer to Improve the Orientation Distribution and Carrier Transport of Direct-current Magnetron Sputtered Al-doped ZnO Polycrystalline Films using Various Al_2O_3 Contents Composite Targets**, ***Junichi Nomoto***, *H Makino, T Yamamoto,* Kochi University of Technology, Japan

We demonstrate a nanoscale materials design using a very-thin critical layer to achieve a high-Hall-mobility Al-doped ZnO (AZO) polycrystalline film showing a texture with a well-defined (0001) orientation. 500-nm-thick AZO films were deposited on glass substrates at a substrate temperature of 200 ºC by direct current (DC) magnetron sputtering with a DC power of 200 W using Al_2O_3 contents ranging from 0.5 to 3.0 wt.% in the composite targets. In this study, a 10-nm-thick Ga-doped ZnO films on a glass substrate deposited by ion plating with DC arc discharge having a texture with a preferential *c*-axis orientation was used a critical layer. First, we investigated the influence of various Al contents on the crystallographic orientations of critical-layer-free AZO films. The crystallographic orientations were characterized by X-ray diffraction (XRD) pole figures measurements of 0002 reflections. The peaks at *a* values of 0º (1st) attributed to the (0001) orientation and of about 66º (2nd) originated in a mixture of multiple orientations, such as (10-11), (20-21) and (30-32), were clearly observed. Note that with increasing Al_2O_3 contents (C_{Al2O3}) up to 3.0 wt.%, the intensity of the 2nd peak corresponding to the complex orientation decreased, whereas the 1st peak intensity increased. To characterize the degree of the (0001) orientation, we estimated the volume fraction of grains with the (0001) orientation, $V_{(0001)}$; the larger the value of $V_{(0001)}$, the higher the degree of the (0001) orientation. The values of $V_{(0001)}$ of AZO films with C_{Al2O3} of 0.5, 1.0, 2.0 and 3.0 wt.% were 84.6 %, 92.9 %, 96.3 % and 98.4 %, respectively. This clearly showed that an increase in C_{Al2O3} improves the orientation distribution of the AZO films. Then, we have developed a technology using the critical layer to tailor the degree of the crystallographic orientation of AZO films.

We deposited DC-magnetron-sputtered AZO films on glass substrates with critical layers. The resulting films had a 500-nm thickness. Note that the use of the critical layers improved theevolution of the orientation distribution of the AZO films, regardless of C_{Al2O3}.: all of the values of $V_{(0001)}$ of the AZO films with the critical layers turned to become of more than 99 %. We will demonstrate a relationship between the orientation distribution and carrier transport of AZO films without and with the critical layers.

4:30pm **C2-2-10 Next-Generation Electronic Materials Processing Tools Newly Developed at AFRL**, ***Brandon Howe***, Air Force Research Laboratory, USA

Next-generation warfighter electronics rely on the development of truly disruptive and robust electronic and optical materials in order to enable game-changing advancements in RF/microwave performance and frequency-agility. The community is extremely materials limited and the major scientific challenge lies in the creation of novel materials and heterostructures with exceptionally high crystalline quality in order to unlock and explore unique and interesting properties. In order to accomplish this, one must create novel processing schemes in order to access never-before-achieved synthesis space, thus unlocking the ability to grow materials with properties far beyond conventional materials. Recently, at the Materials and Manufacturing Directorate at AFRL, we have built up a state-of-the-art PVD epitaxy suite capable of quickly scanning through an enlarged processing space in order to rapidly assess and identify novel materials with enhanced physical properties towards AF application. This talk will focus on the buildup and characterization of both a fully automated UHV pulsed laser epitaxy tool for the growth of high quality ferromagnetic oxides and oxide heterostructures as well as a truly one-of-a-kind and fully automated multifunctional epitaxial growth system (MEGS) capable of applying magnetic fields during both magnetron sputter epitaxy as well as pulsed laser deposition and creating complex metal/metal nitride/oxide heterostructures never before achieve. I will show how these systems are already creating exceptionally high quality transition metal nitride for resilient plasmonics (as TiN and ZrN mirror the properties of gold and silver) and novel magnetic oxides with record magnetic and microwave performance. The nitrides grown by sputtering demonstrate properties among the best reported as well as reveal incredibly low roughness values and evidence of step-flow growth, while our novel AlNiZnFerrite material demonstrates record high magnetostriction while mitigating prohibitively large losses (microwave damping).

4:50pm **C2-2-11 The Role of Oxidized TiN Bottom Electrode in Resistive Random Access Memory with Supercritical CO_2 Fluid Treatment**, ***Yu-Ting Su***, *C Pan, T Chang,* National Sun Yat-sen University, Taiwan

This letter investigates an improvement of electrical characteristics attributed to oxidized TiN bottom electrode in resistive random access memory (RRAM) devices after supercritical CO_2 ($SCCO_2$) treatment. Compared to untreated devices, more oxygen ions exist in the bottom electrode, resulting in a layer of TiON. Due to this resistive layer, self-compliance behavior during the set process appears at a small current compliance and the current conduction of low resistance state (LRS) transfers to Schottky emission. Moreover, an analysis of Schottky currents at different compliances further verifies this proposed TiON mechanism.

5:10pm **C2-2-12 Excellent Bipolar Resistive Switching Behavior in WN Thin Film for Non-volatile ReRAM Device Application**, ***Ravi Prakash***, *D Kaur,* Indian Institute Of Technology Roorkee, India

Resistive memory using sputtered deposited insulating WN thin film as switching layer has been developed with Cu/WN/Pt stack configuration.

Excellent bipolar resistive switching (RS) properties have been observed at a low voltage of +0.9 and -1 V respectively, which favors device to reduce the power consumption. Formation/disruption of the conducting filament is verified as the main cause for exhibiting the RS properties. Ohmic behavior and trap-controlled space charge limited current (SCLC) conduction mechanisms are confirmed as dominant conduction mechanism at low resistance state (LRS) and high resistance state (HRS). High resistance ratio between HRS and LRS (10^6), good write/erase endurance (10^5) and non-volatile long retention (10^5s) are also observed. This study demonstrated that the sputtered WN thin films have a great potential for the future non-volatile resistive random access memory (ReRAM) device application.

Coatings for Biomedical and Healthcare Applications
Room Sunrise - Session D1

Surface Coatings and Surface Modifications in Biological Environments

Moderators: Kerstin Thorwarth, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland, Mathew T. Mathew, University of Illinois College of Medicine at Rockford and Rush University Medical Center, USA, Argelia Almaguer-Flores, Universidad Nacional Autonoma de Mexico, Mexico

1:30pm **D1-1 Reactively Sputtered Iridium Oxide Films for Biomedical Electrode Coatings: Microstructural Dependence of the In-Vitro Electrochemical Performance**, *N Page, J Lucchi, J Buchan, T Scabarozi,* Rowan University, USA*; S Amini,* Johnson Matthey Inc., USA*;* ***Jeffrey Hettinger,*** Rowan University, USA

Iridium oxide films have been synthesized by reactive magnetron sputtering in an oxygen rich environment. The films have been deposited onto various substrate materials at temperatures of 20, 200, and 400°C. The partial pressure of oxygen required to synthesize iridium oxide is approximately 20% at an overall pressure of 10mTorr and is reduced as the substrate temperature is increased.

The synthesized films have been characterized using x-ray diffraction, electron microscopy, cyclic voltammetry and electrochemical impedance spectroscopy. The microstructure of the coatings depends on temperature, oxygen partial pressure and the substrate material. For room temperature depositions, the grains are generally less than 100nm in size. As the temperature is increased, the grain size increases. An interesting surface microstructure is observed at elevated oxygen partial pressures and are most notable in coatings deposited with a substrate temperature of 200°C. Images of cross-sections indicate that the microstructure is a surface microstructure and does not extend to the coating-substrate interface.

The electrochemical measurements were performed in phosphate buffered saline solution between 0.80V and -0.60V. The measured results indicate that the most complex microstructures improve the coating charge storage capacity by an order of magnitude. Similar features to those that grow at 200°C grow at room temperature with elevated oxygen partial pressures. These features lead to more modest increases in charge storage capacity. The additional microstructure increases the coating surface area and is associated with the emergence of the (011) diffraction peak.

1:50pm **D1-2 Nanostructured Surfaces based on Tantalum Oxide for Osseointegrated Metallic Implants**, ***CristianaFilipa Almeida Alves,*** *J Oliveira, S Pires, L Marques,* University of Minho, Portugal*; D Schneider,* Fraunhofer Instituit für Werkstoffphysik und Schichttecnhologie, Germany*; A Cavaleiro,* University of Coimbra, Portugal*; S Carvalho,* University of Minho, Portugal

Tantalum (Ta) and tantalum oxide coatings have been proven as bioactive materials, so there are promising materials for promoting osseointegration and the performance of medical devices such as dental implants. A new approach has been used on this work. We propose the development of antibacterial and osseointegrated bioactive surfaces based on the synergetic effect of nanostructured and oxide surfaces of Ta-based materials.

In this work Ta-based coatings were deposited by DC magnetron sputtering onto Ti CP substrates in an Ar+O_2 atmosphere. Nanostructured anodic tantalum oxide was successfully prepared by electrochemical deposition.

Structural results show that the small increase of O content leads to a change of Ta phase from stable phase (α-Ta: bcc) to mixture with metastable phase (β-Ta: tetragonal) achieving the oxide phases with a large amount of O. Combined structural and mechanical results with DFT calculations shows that the increased addition of oxygen to the Ta phase, a decrease in the density of the crystal structures and increase in the elastic properties is observed, explained by the smaller atomic substitution of Ta and formation of stable TaO_x amorphous phases at grain boundaries.

Also, Ta surface were anodized and results show that the electrolyte, composed by H_2SO_4 and HF, in a 15-25V potential range allow us to control the Ta interconversion from nanopores to nanotubes array. Despite the capacity needed of HF to dissolve and create anodic oxide nanostructures (dissolution assisted by electric field), there is a clear dependence on H_2SO_4 concentration to obtain highly ordered nanostructures.

2:10pm **D1-3 Development of a Biocompatible Titanium Niobium Alloy Coating as a Buffer for Rigid Coatings on Polyetheretherketon**, ***Markus König,*** *K Bergner, H Scheerer, G Andersohn, M Oechsner,* TU Darmstadt, Germany

For the treatment of spinal disk diseases more and more polyetheretherketon (PEEK) implants are used instead of titanium implants. This is due to the excellent cytotoxicity, radiological transparency and low elastic modulus (E_{PEEK} = 3,5 GPa). Nevertheless using PEEK is going along with some disadvantages like the low tendency for a fast and reliable osseointegration. To overcome this drawback a thin osteoconductive coating is needed. Therefore Physical Vapour Deposition (PDV) offers a frequently applied technique to create good adhering coatings on polymers. Most of these coatings are based on ceramics or metals like *hydroxyapatite* or titanium. These materials have a much higher modulus of elasticity (approx. 100 GPa) and a lower elongation. This is the reason why such composites fail through the "eggshell effect".

To overcome this problem a more elastic and biocompatible layer in between is needed. As a casted alloy titanium and niobium (60 wt% Ti - 40 wt% Nb) has an elastic modulus of 60 GPa and excellent biocompatible properties. Till this day it has been unknown if this characteristics could be produced with thin film techniques. It was possible to generate such coatings by physical PVD magnetron sputtering. This was realized by the investigation of target configuration, power and gas settings. The generated coatings were investigated by nanoindentation, micro-scratch tests as well as modified scratch tests to characterise their mechanical abilities. X-ray diffraction, glow discharge optical emission spectroscopy and energy dispersive X-ray spectroscopy were used to characterise the chemical composition and to prove that an alloy is achieved. The realized alloy coating has a composition of 60 wt% titanium and 40 wt% niobium with an elastic modulus of 63 ± 5,7 GPa. Hence, the mechanical strength of biocompatible coatings on PEEK could be enhanced.

2:30pm **D1-4 Development of Novel Long-Lasting S-Phase based Anti-Bacterial Coatings**, *D Formosa,* ***Xiaoying Li,*** *H Dong,* The University of Birmingham, UK

It is well-known that biologically active Ag/Cu ions are strong bactericides and silver or copper nanoparticles have been used in polymer-based antibacterial coatings. However, their poor durability has limited their use in tribological applications. This problem has been largely addressed recently by developing novel plasma co-alloying of austenitic stainless steel surfaces with both nitrogen and Ag/Cu to form Ag/Cu doped hard and wear resistant S-phase. However, this technology is only applicable to austenitic stainless steel as the S-phase cannot be formed in other materials.

In this study, S-phase based anti-bacterial coatings have been, for the first time, developed using magnetron sputtering through co-deposition of austenitic stainless steel with Ag/Cu to form hard S-phase doped with Ag, Cu or both in monolayer and multilayer structures. These coatings where tested and optimised using multiple techniques such as – transmission electron microscopy, X-Ray diffraction, corrosion and wear testing, scratch and fretting techniques and anti-bacterial tests amongst others.

It has been found that it is possible to produce dense corrosion resistant S-phase microstructure with high adhesion to different substrates. Co-depositing S-phase with Ag and Cu dopants brings about significant anti-bacterial efficacy to the traditionally inactive S-phase surface. This was achieved while preserving the advantageous properties of the S-phase microstructure. As opposed to the popular diffusion based S-phase production such as plasma nitriding, this technology can also be applied on all kinds of surfaces, including low-cost steel surfaces, polymers and ceramics.

2:50pm **D1-5 Single-step, Environmentally-Friendly, Biological Functionalisation through Radicals generated by Plasma Surface Modification of Biomedical Devices**, ***Marcela Bilek***, *E Kosobrodova, A Kondyurin, B Akhavan, M Santos, E Wakelin, G Yeo, C Tran, D McKenzie, A Weiss,* University of Sydney, Australia*; M Ng, S Wise,* Heart Research Institute, Australia **INVITED**

Plasma Immersion Ion Implantation (PIII) is a process in which a bias voltage is applied to an object immersed in plasma, accelerating ions towards it. These ions are implanted into the surface creating highly reactive radicals in the sub surface region. For polymeric materials, the radicals are mobile within the subsurface so that they may be utilized to covalently immobilize bioactive molecules on the surface upon contact [1]. Where the surface to be functionalized is non-polymeric a carbon containing precursor gas is added so that a plasma polymer is deposited under ion bombardment. Both of these approaches as well as a new variation of these processes that enables the energetic ion implantation of complex interconnected 3D polymeric networks, such as tissue engineering scaffolds.

Short-lived radicals (with lifetimes of less than a day) as well as long-lived radicals with lifetimes of over a year are created [2]. Their diffusion is temperature activated [3] and kinetic theory shows that the depth of the treatment determines the lifetime of the long-lived radicals [1]. Covalent immobilization of functional (including biologically functional) molecules is then achieved by simple immersion or incubation of the surface in a solution containing the functional molecules to be immobilized. This eliminates the need for multiple stage linker chemistry and the associated solvent disposal and variable yield problems. The use of this approach to surface immobilize bioactive peptides, antibodies, enzymes, single stranded DNA and extra-cellular matrix proteins [4] onto the external surfaces of materials, including three-dimensional structures of biomedical devices, such as cardiovascular stents, scaffolds for tissue restoration and implantable prostheses, will be described. The benefits for and recent progress towards commercial applications in implantable biomedical and diagnostic devices will be reviewed.

References:

[1] Bilek MMM, et al, *PNAS* (2011) **108**:14405-14410

[2] Kosobrodova EA, et al, *NIMB* (2012) **280**:26-35

[3] Wakelin EA, et al, *ACS Appl. Mater & Interfaces* (2015) **7**:26340-26345

[4] M.M. Bilek, *Applied Surface Science* (2014) **310**:3-10

Key words: plasma immersion ion implantation (PIII), plasma immersion ion implantation and deposition (PIII&D), biological surface functionalisation, radicals, biomedical diagnostics, implantable biomedical devices, cardiovascular stents, tissue engineering scaffolds.

3:30pm **D1-7 Deposition and Characterisation of Silver Nanocomposite Coatings on Orthopaedic Grade Cobalt Chromium Alloys and the Related Antimicrobial Effects**, ***Liuquan Yang***, Wallwork Cambridge Ltd, UK*; L Richards,* MatOrtho Limited, UK*; A Misha, J Shelton,* Queen Mary University of London, UK*; S Collins,* MatOrtho Limited, UK*; S Banfield, L Espitalier,* Wallwork Cambridge Ltd, UK*; H Hothi, A Hart,* Royal National Orthopaedic Hospital, UK*; J Housden,* Wallwork Cambridge Ltd, UK

Silver containing materials have shown novel antimicrobial properties in various applications historically. Hard wearing PVD silver nanocomposite coatings have the ability to self-lubricate at high temperature and benefit from antimicrobial effect. This study focuses on the deposition of three different contents of silver nanocomposite coatings deposited on cobalt chromium (CoCr) alloy by electron beam physical vapour deposition (EBPVD) and the related characterisations. The coating structures are studied in terms of scratch test, nano-indentation, scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDS), X-ray photoelectron spectroscopy (XPS) and optical surface profilometry (OSP). The specific surface area, surface roughness and morphology of the silver particles are analysed and the coatings tested in vitro for antimicrobial effectiveness and wear characteristics against ultra-high molecular weight polyethylene (UHMWPE). The results have shown the silver nanocomposite hard wearing coatings are promising candidates in orthopaedic applications and may lower the risk of infection. Further investigations will optimise the silver coatings and will be subject to simulator tests and clinical trials.

3:50pm **D1-8 Oral Bacteria Adhesion on Saliva Coated and Uncoated Stainless Steel Surfaces: Experimental Characterisation and Modelling**, ***Jinju Chen***, *S Chinnaraj, Y Ammar, J Pahala Gedara, N Jakubovics,* Newcastle University, UK

Biofilms refer to bacteria growing within a matrix of extracellular polymeric substances attached to surfaces, which have significant impact to a wide range of industries and environment. The initial bacteria attachment is important for biofilm formation, which can be affected by various materials surface characteristics such as surface roughness, surface hydrophobicity, and surface chemistry. The total interaction energy required for bacteria to adhere to surfaces can be determined by extended DLVO theory (XDLVO) which considers Lifshitz van der Waals interactions, electrostatic interactions and acid-base interactions. The extended DLVO model can further be improved by considering the surface roughness of the materials. However, there is lack of experimental work and modelling of bacteria adhesion on patterned surfaces which are relevant to many medical implants.

In this study, streptococcus gordonii DL-1, a typical cocci shaped bacteria found in oral cavity, was cultured on the patterned stainless steel. The surface coverage of attached cells was calculated using MATLAB code. An in-house C++ code was developed to compute the bacteria deposition by implementing the surface roughness enhanced XDLVO. The simulated results qualitatively agree with the experimental measurement and both have shown that patterned surfaces would promote bacteria adhesion. In addition, it has demonstrated that the saliva coating does not have much effect on the initial attachment of streptococcus gordonii.

4:10pm **D1-9 Towards Antibacterial yet Biocompatible and Bioactive Surfaces**, ***Dmitry Shtansky***, *I Sukhorukova, A Sheveyko, E Levashov,* National University of Science and Technology "MISiS", Russian Federation

The fabrication of antibacterial yet biocompatible and bioactive surfaces is a challenge that biological and biomedical community has faced for many years, while no "dream material" has been developed so far. Various strategies for development of bioactive and bactericidal films with various antibacterial components (Ag, B, antibiotic, bacteriophages) providing long-lasting antibacterial effect are considered [1-4]. The substrates with different topography were produced via selective laser sintering, pulsed electro-erosion treatment, chemical etching, sandblasting, and laser treatment. Multicomponent biocompatable nanostructured films with different content of antibacterial components were deposited on substrates with different topography and roughness using PVD methods (magnetron and ion sputtering, ion implantation). Different functional treatments to provide antibacterial functionality including saturation with antibiotics or bacteriophages were fulfilled. In addition, thick (up to 30 μm) multicomponent biocompatible yet antibacterial coatings with high surface roughness (R_a > 6 μm) were obtained by pulsed electrospark deposition [5,6]. The obtained results show that under optimal surface chemistry and topography conditions the material can be biocompatible, bioactive and bactericidal.

[1] I.V. Sukhorukova, et al., J. Biomed. Mater. Res. B 2016, DOI: 10.1002/jbm.b.33534

[2] I.V. Sukhorukova, et al., Colloid Surface B 135 (2015) 158-165.

[3] I.V. Sukhorukova, et al., Applied Surface Science 330 (2015) 339-350.

[4] D.V. Shtansky, et al., Surf. Coat. Technol. 208 (2012) 14-23.

[6] A.N. Sheveyko, et al., Surf. Coat. Technol. 302 (2016) 327-335.

[5] N.V. Litovchenko, et al., Surf. Coat. Technol. (in press).

4:30pm **D1-10 Characteristics of Plasma Polymerization Films using HMDSO Precursor on 316L Stainless Steel**, ***Si-Bu Wang***, *J Lee, Y Lee,* Ming Chi University of Technology, Taiwan*; B Lou,* Chang Gung University, Taiwan

This study focused on the characterization of the organic film deposited on 316L stainless steel substrate using a plasma polymerization process with hexamethyldisiloxane (HMDSO) precursor. The organic films were fabricated under different HMDSO-O_2 gas ratios and the heating temperature of the monomer. The plasma characteristics during the plasma polymerization process were studied by an optical emission spectrometer. The structure and bonding of the deposited films were analyzed by a Fourier Transform Infrared Spectroscopy (FTIR). The scratch test was employed to evaluate the adhesion properties of coatings. Preliminary biocompatibility studies were carried out using MG-63 cell line (human osteosarcoma) to investigate cell-material interaction. The results of cell viability and toxicity are presented.

It can be found that the plasma polymerization grown films were free of pinholes and showed an excellent adhesion quality to the substrate. Good biocompatibility was also observed for the organic coating. Effects of HMDSO-O_2 gas ratio and the heating temperature of the monomer on the plasma status, structure, film thickness, mechanical property and biocompatibility of the films deposited on 316L stainless steel substrate were further discussed in this work.

4:50pm **D1-11 Structure and Biocompatibility of Fluorine-containing TaCN Thin Films***, **JangHsing Hsieh**, H Lin,* Ming Chi University of Technology, Taiwan*; S Liu,* National Taipei University of Technology, Taiwan

TaN thin film coatings are known to have good mechanical properties, impact toughness, as well as good biocompactibility. However, the friction coefficient of these films is sometimes too high, or the hemocompatibility is poor. The purpose of this study is to reduce the friction coefficient and lower the surface energy of TaN coating by introducing CFx into/onto the nitride coatings. CFx–doped TaN films, with and without CFx top layer, were deposited on silicon and tool steel substrates by magnetron sputtering. During the deposition process, C2F6 gas with various flow rates was added. During the deposition of 30 nm CFx top layer on some samples, the power to Ta target was shut off. After deposition, these films were then characterized using XRD, XPS, FTIR, FESEM, as well as a tribometer. The tribo-tests were carried out with and without argon flow. Surface energies of the films were also analyzed with contact angle measurement system. According to structural analysis, TaN phase would transform to Ta(FCN) with the increase of the fluoride gas flow rate, which would cause the decrease of friction coefficient and surface energy. According to the results obtained from tribotesting, it is found the increase of CFx would reduce the effects of moisture and oxygen on friction coefficient. The prepared films may have good hemocompatibility and wear-resistance.

New Horizons in Coatings and Thin Films
Room Royal Palm 1-3 - Session F1-2

Nanomaterials and Nanofabrication

Moderators: R. Mohan Sankaran, Case Western Reserve University, Sumit Agarwal, Colorado School of Mines

1:30pm **F1-2-1 Accelerated Development of CuSb(S, Se)$_2$ Thin Film Photovoltaic Device Prototypes***, **Colin Wolden**,* Colorado School of Mines, USA **INVITED**

Development of alternative thin film photovoltaic technologies is an important research topic due to the potential of low-cost, high-efficiency solar cells to produce terawatt levels of clean power. The development of unexplored yet promising absorbers can be hindered by complications that arise during solar cell fabrication. Here, a high-throughput, combinatorial sputtering method is applied to accelerate development of photovoltaic devices based on the novel CuSb(S, Se)$_2$ absorbers. These chalcogenide semiconductors have the appropriate band gap (1.1 -1.3 eV), absorption coefficient (10^5 cm^{-1}), and a hole concentration (~10^{17} cm^{-3}) for use in thin film solar cells. However, there are significant challenges to be overcome for these materials to fulfill their potential, particularly with respect controlling the properties of these ternary compounds and integrating them into solar cell architectures. Here, a high-throughput combinatorial method is applied to accelerate development of both the CuSb(S)$_2$ absorber materials as well as their integration into device structures. This approach revealed a three-stage, self-regulated growth process to control absorber purity and orientation. Device integration employed the $CuIn_xGa_{(1-x)}Se_2$ (CIGS) device architecture, and device development is also explored in a combinatorial as a function of absorber quality and thickness using a variety of back contacts. This study yielded initial CuSb(S, Se)$_2$ device prototypes with ~1% conversion efficiency, which was rapidly elevated to ~5% using the approaches described within. Analysis of device performance provides pathways for future improvements.

New Horizons in Coatings and Thin Films
Room Royal Palm 1-3 - Session F3

2D Materials: Synthesis, Characterization, and Applications

Moderators: Haitao Liu, University of Pittsburgh, USA, Jiaxing Huang, Northwestern University, Liping Wang, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences

2:10pm **F3-3 Tunable MoS_2 and MoS_2-based Electrocatalysts by Hot-injection Method for Hydrogen Evolution Reaction***, **Chia-Ling Wu**, P Huang, S Brahma, J Huang,* National Cheng Kung University, Taiwan*; S Wang,* Southern Taiwan University of Science and Technology, Taiwan

Hydrogen has been considered as one of the most promising renewable energy for production and storage to replace petroleum-based energy. The 2D structure and the presence of several effective active sites make MoS_2 an excellent electrocatalyst for hydrogen evolution reaction (HER). However, the most common syntheses nowadays are not only expensive but also time-consuming. Here, we report an efficient, fast and tunable hot-injection method to prepare MoS_2 and MoS_2-MoO_2 composite with/without tributyl phosphate (TBP). MoO_3 with oleic acid (OA) and S powder with oleylamine (OLA) are used as Mo- and S- precursor, respectively. With increasing reaction temperature and time, OA reorganize the octahedral units of MoO_3 and gradually turn into low valence of Mo. Fourier transform infrared spectroscopy (FT-IR) clearly shows the increase/decrease of the intensity of M=O and 2Mo-O bond vibrations. After injecting S-precursor, OLA first reduces Mo-precursor to MoO_2, and then S atoms replace O atoms to form MoS_2. The addition of a drop of tributyl phosphate (TBP) as surfactant in Mo-precursor significantly accelerate the production of MoS_2 via MoO_2 as the intermediate phase (MoO_3→MoO_2→MoS_2). The X-ray diffraction (XRD) (Fig.1) shows that the peaks of MoS_2 dominate by adding TBP, and the peaks of MoS_2 and MoO_2 are equal without adding TBP. Scanning electron microscope (SEM) shows the uniform layer like morphology of nanoscale MoS_2. Transmission electron microscopy (TEM) confirms the existence of few-layer MoS_2 with abundant edge sites (Fig.2) and the core-shell MoS_2-MoO_2 structure (Fig.3), respectively. HR-TEM image shows the MoS_2 (002) plane and d-spacing is measured as 0.62 nm. This simple, flexible and tunable synthesis has large potential for the production of MoS_2 and MoS_2-MoO_2 composite. High purity of MoS_2 and MoS_2-MoO_2 composite can combine with other materials for energy conversion and storage. The detailed electrochemical properties on HER will be reported in future.

2:30pm **F3-4 High-throughput Combinatorial Synthesis and Multimodal X-ray Analysis of Co-based Ternary Alloys***, **Janak Thapa**, C Gross, V Hegde, L Ward, S Naghavi, C Wolverton, Y Chung, M Bedzyk,* Northwestern University, USA

Cobalt-based superalloys have excellent high temperature properties such as creep resistance and chemical inertness during applications at elevated temperatures. Potential applications include high performance jet engine turbine blades and ultra-supercritical steam driven power plants. In this work, we undertook efforts to begin filling in the database gap of Co-based ternary systems. Such a database will facilitate the design and development of Co-based superalloys. We have observed new phases in previously empty regions. We use the naturally scalable techniques of photolithography, DC magnetron sputtering, and high-flux X-ray analysis for high-throughput studies. Gamma and gamma-prime phases, which are essential for high-temperature applications of conventional superalloys, are also being identified. High-throughput DFT is being employed to efficiently determine crystal structures based on X-ray data. These phase diagrams will provide a foundation of understanding to accelerate the creation and implementation of novel Co-based superalloys, and potentially other alloy systems.

2:50pm **F3-5 Development and Characterisation of Cost-Effective Graphene Oxide-Nickel Nanocomposite Coatings***, S Qi, X Li, **Hanshan Dong**,* The University of Birmingham, UK

Graphene is a very attractive new carbon-based coating material due to its extraordinary mechanical, thermal, chemical and optical properties. Notwithstanding the fact that some nano/micro scale studies have shown the potential of graphene as tribological and anti-corrosion coatings on Cu and Ni, its application for coatings on other metallic materials has yet to be fully explored. This is mainly due to the high cost and low yield of pristine graphene produced by exfoliation and the difficulties in transferring CVD-grown graphene films onto 3D real engineering surfaces with necessary bonding. Hence, how to cost-effectively deposit large-area graphene

coatings on metallic materials for corrosion and wear protection is a scientifically interesting and technologically important research area.

One possible solution is to use relatively low-cost graphene oxide (GO) in metallic matrix composite. In this work, a nickel/GO composite coating was deposited on steel using a purposely developed electrochemical deposition method to ensure homogenous distribution of GO in the matrix. The deposited Ni/GO coatings were fully characterised using XRD, FIB/SEM, Raman and TEM; their mechanical and tribological properties were evaluated using nano-indentation and friction/wear testing. The thermal stability of the Ni/GO coatings was investigated by thermal annealing at 100, 200, 40 and 600ºC for 30min.

The experimental results reveal that transparent and silk-like graphene oxide sheets are randomly distributed in the Ni matrix. As a result, the hardness and Young's module of Ni coating can be increased by 56% and 29% respectively due to the reinforcement and refinement of the matrix by GO sheets; the coefficient of friction is reduced from 0.6 for Ni to 0.4 for the Ni/GO nanocomposites and the wear rate is reduced by about 90%. Most importantly, the thermal stability of Ni coating can be significantly improved by adding GO. For example, when annealed at 400ºC for 30min, while the hardness of Ni coating was reduced by 36% no appreciable reduction in hardness was observed for the Ni/GO nanocomposite coatings.

3:10pm **F3-6 Fabrication of Functional Graphene Reinforced Polyurethane Nanocomposite Coatings with Regular Textures for Corrosion Inhibition***, **Wenjie Zhao,*** Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, China

In order to further enhance its anti-corrosion properties as a surface coating for protecting various materials from corrosion, polyurethane (PU) needs to be modified by adjusting the chemical composition and interface structure. In this work, a series of functionalized graphene (FG) reinforced PU nanocomposite coatings with regular texture were fabricated using a replication method. The structural and morphological properties of the as-prepared PU composite coatings were characterized by Fourier transform infrared spectroscopy, Raman spectroscopy, X-ray photoelectron spectrometer, transmission electron microscopy, scanning electron microscopy and atomic force microscopy. Results showed that FG was dispersed homogeneously in the PU matrix after chemical modification. Moreover, the morphology of the obtained coatings showed a circular cone with a diameter of 8 μm spaced 8, 6 and 4 μm apart, respectively. Most importantly, the presence of surface texture and well-dispersed FG effectively enhanced the anti-corrosion properties of the textured FG/PU composite coating. It is attributed to the hydrophobicity and barrier effect of the obtained coatings, which not only reduce the contact and interaction between water and the surfaces, but also increase the tortuosity of the corrosive medium diffusion pathway.

3:30pm **F3-7 Structure and Tribological Properties of TiSiCN Coatings Incorporated with Layered Structure of MAX Phase in Artificial Seawater***, **Jinlong Li**, Y Wang, C Dang, L Wang, Q Xue,* Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, China

The TiSiCN coatings were fabricated on Ti6Al4V alloy by arc ion plating at 500 º C. In order to obtain a MAX phase with like graphic layered structure, the different bias voltages were employed during the deposition of the TiSiCN coating. The structure of the TiSiCN coating were characterized using Scanning electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy and Transmission electron microscopy. The hardness and tribological properties of the TiSiCN coating were evaluated by nanoindentation, potentiostat and ball-on-plate wear tests. All TiSiCN coating shows a coupled structure of a TiN nanocystallite / Si_3N_4 amorphous. When the negative bias voltage increases to 100 V, some Ti_3SiC_2 MAX phase with a like graphic layered structure also is found in the TiSiCN coating. The TiSiCN coating has a higher hardness of 40 GPa. The MAX phase with a layered structure contributes to significantly decrease of the friction coefficient and wear rate of the TiSiCN coating. The imposed protection potential has a positive effect on protecting the coating from electrochemical corrosion. However, the cracks inside the coating will accelerate the coating failure.

3:50pm **F3-8 Graphene: Improving Material Performance by Keeping the Surface Cleaning***, **Haitao Liu,*** University of Pittsburgh, USA

Recent studies showed that graphitic materials can be easily contaminated by airborne and waterborne hydrocarbons. In this talk, I will discuss ways to protect a graphitic surface from airborne contamination. It was shown that a monolayer thick of water film significantly slows down the adsorption of airborne hydrocarbon. The water-protected graphitic surface showed extreme high electrochemical activity; the measured heterogeneous electron transfer rate is even higher than that of a Pt electrode.These results highlight the potential to achieve intrinsic material properties of graphitic materials under ambient environments.

Coatings for Use at High Temperatures
Room San Diego - Session A1-3

Coatings to Resist High Temperature Oxidation, Corrosion and Fouling

Moderators: Vladislav Kolarik, Fraunhofer Institute for Chemical Technology ICT, Prabhakar Mohan, Solar Turbines, USA, Anton Chyrkin, Forschungszentrum Jülich GmbH

8:00am **A1-3-1 Thin Co and Ce/Co Coatings on Ferritic Stainless Steel Interconnects for Solid Oxide Fuel Cells**, ***Hannes Falk-Windisch***, *M Sattari, L Johansson, J Svensson, J Froitzheim,* Chalmers University of Technology, Sweden

The use of Cr_2O_3-forming alloys for Solid Oxide Fuel Cell (SOFC) interconnects is challenged by the volatilization of Cr (VI) species that causes cathode poisoning and by rapid oxide scale growth causing increased electrical resistance. This work investigates the use of Cobalt (Co) and Cerium (Ce) nano coatings to mitigate both degradation mechanisms. The work involves coating the ferritic stainless steel Sanergy HT, which is designed for use as SOFC interconnects, with 640 nm Co and with 10 nm Ce + 640 nm Co using Physical Vapor Deposition (PVD). The materials were exposed in air at 650-850 ˚C for up to 3000 h and chromium volatilization, oxide scale growth and electrical resistance were studied. Mass gain was recorded to follow oxidation kinetics, chromium evaporation was measured using a denuder technique, and Area Specific Resistance (ASR) measurements were carried out on exposed samples. The oxide scale microstructure was characterized using Scanning Electron Microscopy (SEM), Scanning Transmission Electron Microscopy (STEM), and Energy Dispersive X-Ray Analysis (EDX). The results show that thin Co coatings effectively mitigated Cr volatilization. Sandwiching a 10 nm Ce layer between the Co coating and the steel greatly improved oxidation resistance, especially at higher temperatures. Also, ASR measurements revealed that the Ce + Co coated material had lower electrical resistance after exposure than the same material coated with only Co. The effect was attributed to the thinner scale formed on the steel coated with Ce + Co. The results imply that the duplex, Co + Ce thin film coating is suitable for ferritic stainless steel interconnects in Solid Oxide Fuel Cells.

8:20am **A1-3-2 Long-term Oxidation of MCrAlY Coatings at 1000 ^{o} C and an Al-activity Based Coating Life Criterion**, ***Pimin Zhang***, *Y Kang, R Lin Peng,* Linköping University, Sweden; *X Li,* Siemens Industrial Turbomachinery AB, Sweden; *S Johansson,* Linköping University, Sweden

MCrAlY type (M=Ni and/or Co) coatings are widely used for the protection of components in the hot sections of gas turbines at high service temperatures by forming a continuous α-alumina. A reliable criterion to estimate the capability to form α-alumina is of great importance to accurately evaluate coating lifetime. However, the traditional Al-concentration based criterion failed to properly predict the formation of a continuous α-alumina. Thus, a new life criterion, namely the critical Al-activity criterion, is proposed.

In this work, critical Al-activity to form a continuous α-alumina is calculated using Thermo-Calc software, based on literature survey of research results of critical Al-concentration to form α-alumina on binary Ni-Al and ternary Ni-Cr-Al system. Long-term oxidation test were performed to support the criterion: IN-792 superalloys coated with five different MCrAlY coatings were oxidized at 1000 ^{o}C for various periods of time up to 10000 hours. The microstructural evolution of MCrAlY coatings were analyzed using Scanning Electron Microscope. The near-surface Al concentration and interdiffusion behavior between substrate and coating were measured using Energy Dispersive X-ray Spectroscopy. The new critical Al-activity criterion has been successfully adopted in α-alumina formation prediction, showing a good agreement with experiment results. Therefore, it can be concluded that the extrapolation of new criterion from binary and ternary systems to multi-alloyed MCrAlY system is reasonable. Furthermore, the partial pressure of oxygen (P_{O2}) in atmosphere has been taken into consideration by combination with Al-activity to calculate the Gibbs energy of formation of α-alumina. The potential applicability of the methodology to predict MCrAlY life is also discussed .

8:40am **A1-3-3 The Preparation of Ti_2AlN MAX Phase Coatings and its Oxidation Mechanism under Different Atmosphere**, ***Zhenyu Wang***, University of Chinese Academy of Sciences, China; *P Ke, A Wang,* Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, China

Ti_2AlN belongs to a family of ternary nano-laminate alloys known as the MAX phases, which exhibit a unique combination of metallic and ceramic properties. In the present work, the dense and high-stability Ti_2AlN coating has been successfully prepared on Ti6Al4V (TC4) substrates through combined cathodic arc/sputter deposition method, followed by heat post-treatment. The oxidation of Ti_2AlN coating and the TC4 substrates were investigated in air and in water vapor at 750 °C for 200h. The results indicated that the oxidation processes of both TC4 substrates and the coated samples were accelerated for the presence of steam, resulting in slightly higher mass gains. The oxidation behavior of the bare substrates under different atmosphere exhibited linear kinetics, which indicates a continuous oxidation during its exposure at high temperatures. In contrast, the mass gain was significantly reduced for the coated samples, suggesting that the Ti_2AlN coating can provide an effective protection for the substrates. Moreover, the Ti_2AlN phase can still be found after oxidation in air atmospheres for 200h and the oxide scale showed local Al_2O_3 and rutile TiO_2 growth, namely the oxide did not cover the entire surface of the coating. However, the Ti_2AlN phase disappeared after oxidation in steam condition and double layer scales formed in the water vapor atmospheres, consisting of an outer rich-Al_2O_3 layer and an inner rich-TiO_2 layer. The enhanced oxidation resistance achieved under different condition by the Ti_2AlN MAX phase coatings may satisfy the optimal requirements for many applications in the field of nuclear power plants and aerospace components.

9:00am **A1-3-4 Effect of Coating Architecture on the Corrosion Behavior of Ti-N/Cr-N Multilayer Coatings**, ***Yu-Sen Yang***, National Kaohsiung First University of Science and Technology, Taiwan

Two coating architectures with distinct period number (PN) of Ti-N/Cr-N multilayer coatings were prepared by reactive magnetron sputtering process. Two coating architectures were designed as the multilayers TiN/CrN/…CrN/TiN/Ti/substrate (architecture T) and the CrN/TiN…TiN/CrN/Cr/substrate (architecture C). Four PNs with 1,5,10 and 15 were prepared in architecture T and C, respectively. This study investigates the effect of the coating architectures and PNs on the corrosion behaviors of the coatings. The corrosion rate were tested by immersion the coatings in the 3% HCl solution for 20 hours to measure the weight loss. The results show that the corrosion rate of the coatings were strongly related to the coating architecture and PN. In coating architecture T, the corrosion weight loss is decreased with PN increased. On the contrary, in architecture C, the corrosion weight loss is increased with increasing PN.

9:20am **A1-3-5 Effects of Encapsulating Material and Healing Agent Ratio on Crack Propagation Behavior for Thermal Barrier Coatings**, ***Soo-Hyeok Jeon***, *S Lee, S Jung, H Park, Y Jung,* Changwon National University, Republic of Korea; *J Zhang,* Purdue University, USA

Thermal barrier coatings (TBCs) are important parts to protect metallic substrate in gas turbine engines because turbine inlet temperature is continuously increased to improve fuel efficiency. Recently self-healing TBCs have been proposed to prevent delamination and spalling of TBCs during gas turbine operation. In this study, $MoSi_2$ as the healing agent was coated by three kinds of materials such as tetraethyl orthosilicate (TEOS), sodium methoxide (NaOMe), and their mixture (TEOS + NaOMe) for stabilizing $MoSi_2$ at high temperatures. YSZ and capsulated $MoSi_2$ were mixed with 90:10, 80:20, and 70:30 wt% ratios, respectively. Samples were fabricated by uniaxial compaction at 100 MPa and then sintered at 1300 ^{o}C and 1500 ^{o}C, respectively. Crack propagation behavior was investigated as functions of $MoSi_2$ stabilizing agent, stabilized $MoSi_2$ content, and sintering temperature. Furnace cyclic test (FCT) was performed at 1100 ^{o}C for a dwell time of 40 min, followed by natural air cooling for 20 min at room temperature, after generating artificial cracks in TBC samples by using Vickers indentation. The TBC sample with the $MoSi_2$ of 20 wt% capsulated with the mixture of TEOS and NaOMe and sintered at 1500 ^{o}C showed the best healing effect in FCT test. This study allows us to design reliable TBC systems in operating conditions.

9:40am **A1-3-6 Comparative Study of Monolayer and Multilayer CrAlSiN PVD Coatings Behavior at High Temperature in Steam Atmosphere**, *A Illana, S Mato,* Complutense University of Madrid, Spain*; E Almandoz, G Garcías Fuentes,* Navarra Industry Association, Spain*; F Pérez Trujillo,* ***Maríalsabel Lasanta****,* Complutense University of Madrid, Spain

Technological developments around electric generation power plants aim to increase thermal efficiency of conversion processes in steam turbines, developing materials able to resist ultra-supercritical (USC) vapor conditions at 600-650°C and 35 MPa. Ferritic-martensitic steels, commonly used so far, show very low oxidation resistance at these conditions. The solution is to modify their surface, by means of protective coatings that retard interdiffusion mechanisms which take place at that temperature range and to prolong their service life.

Hard coatings based on nitrides and deposited by PVD have been commonly applied in cutting tools, since possess tribological features that increase their wear and oxidation resistance in aqueous media, mainly alkaline and neutral. CrN coatings have been broadly employed for last decades for this application. The incorporation of Al and/or Si in these films produces an improvement in the mechanical properties, due to hardening for grain refining (Hall-Petch effect), and an increase of thermal resistance against oxidation in comparison to the pure CrN , due to the formation of protective oxides that avoid the migration of oxygen towards the substrate.

In order to contribute to the knowledge on this topic, a monolayer and two multilayers with different periodic thickness of magnetron-sputtered CrAlSiN coatings with similar Cr/Al ratio and Si content were deposited on P92 ferritic-martensitic steel and tested to assess their protection capability under the working conditions of USC steam turbines operation (at 650ºC in 100% steam atmosphere) during 2000 h. Common characterization techniques have been used to achieve this objective, such as: gravimetry analysis in order to study the kinetics of oxidation, x-ray diffraction (XRD) to explored the phases formed during the oxidation process and scanning electron microscopy with energy dispersive detector (SEM-EDX) to evaluate the morphology and semi-quantitative composition of the films.

CrAlSiN coatings have showed a significant improvement to the oxidation resistance of the bare substrate (P92 steel), due to the formation surface oxide layers. Cr_2O_3, SiO_2 and Al_2O_3 resulted more effective against the ionic interdiffusion and with greater compactness, which lead to a reduction of the oxidation rate at isothermal USC vapor conditions. After 2000 h of test, coated samples have shown no diffusion of species from the substrate into the coating and they have presented oxidation kinetics that follow a parabolic trend, typical of the material which has developed a protective oxide on the surface at high temperature.

10:00am **A1-3-7 Material Validation in Molten Salt Environment under Dynamic Conditions Using a Novel Pilot Plant Facility**, *M Lasanta, G García Martín,* ***Víctor Encinas Sánchez****, M de Miguel, F Pérez Trujillo,* Complutense University of Madrid, Spain

Solar thermal plants which concentrate the Sun's energy to produce steam and electricity often use molten salt mixtures as a heat transfer fluid (HTF) and/or as thermal energy storage (TES) medium. The most industrial compound used is an alkali-nitrate mixture composed by 60 wt.% $NaNO_3$/40 wt.% KNO_3 (Solar Salt®). On the other hand, corrosion behavior of materials is a very important issue as regards the molten salts and CSP plants. Up to now, all studies have been carried out through static immersion tests, parameters such as dynamic flow in contact with the substrate, oxidizing gas atmosphere and thermal cycling being dismissed. Thus, the aim of this work was to introduce a novel pilot plant facility and evaluate the corrosion resistance of A516 and 304 steels in Solar Salt in dynamic condition test at 500 ºC using it. The equipment used allows degradation tests of materials in contact with molten mediums simulating thermo-cycling process and keeping the stable conditions during whole studies. These results were compared with the static ones in order to evaluate the effect of the fluid-dynamics.

The isothermal dynamic and static immersion test results were analyzed via gravimetric measurements. Both tests were carried out at 500 ºC. The tested specimens were analyzed after 100 hours of testing and were characterized by SEM-EDX and XRD.

The average weight gain measured in the samples tested by dynamic test was higher than that measured by the static test. Dynamic test approach reproduce the conditions of CSP plants in a better way. Thus, results obtained by dynamic test are considered more reliable for the corrosion prediction behavior of the CSP plants. Furthermore, useful information was extracted from the tested samples after characterizing. The surface appearance of the two samples was quite different, the sample subjected to dynamic test showing more detachments. As expected, the greater thickness of the oxide layer on the sample subjected to the dynamic test was observed in the cross-section micrographs. XRD measurements confirm the observed species in SEM-EDX.

Experiments demonstrated how dynamics tests provokes an increase in corrosion rates, since mass gained is quite greater in samples subjected to dynamic tests than the ones gained through static tests. These results are also confirmed by SEM. This work is a new step forward in the future experimentation for materials and engineering processes for future CSP plants with molten salts.

Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B1-3

PVD Coatings and Technologies

Moderators: Joerg Vetter, Oerlikon Balzers Coating Germany GmbH, Jyh-Ming Ting, National Cheng Kung University

8:00am **B1-3-1 Synthesis and Applications of High-precision Thin Film Multilayers**, ***Andreas Leson****, S Braun, P Gawlitza, C Gruhne, A Kubec, M Menzel,* Fraunhofer Institute for Material and Beam Technology, Germany **INVITED**

Nowadays thin film coating technologies like magnetron or ion beam sputter deposition are successfully used for the fabrication of extremely precise and smooth nanometer thin films, which are needed for optical coatings especially in the short wavelength range. In most of the applications coatings with thickness gradients on curved substrates are needed. Using optimized coating parameters thickness deviations of only a few picometers from the target profile can be obtained. Another important parameter for the performance of the coatings is roughness. Recent improvements of the deposition process resulted in HSFR values of < 0.1 nm rms (HSRF = high spatial frequency roughness, usually measured with atomic force microscopy).

One of the current main drivers for the development of nanometer multilayers is extreme ultraviolet lithography. For this application Mo/Si multilayers are needed that have to have highest possible reflectances, precise thickness distributions, low film stress as well as high long-term and thermal stability. With dedicated improvements of our coating processes and by applying diffusion barrier layers we have succeeded to increase the EUV reflectance to world record values of > 70.5 % (photon wavelength l = 13.5 nm, incidence angle a = 5 degree). Additionally, the amount of diffuse scattered EUV light could be reduced by decreasing the roughness of the coatings down to Rq < 0.1 nm rms. In addition to Mo/Si multilayers numerous other material combinations of absorber (Ni, Cr, Mo, La, W) and spacer (B4C, C, Si, Sc) layers have been developed during the last years and applied for mirrors and monochromators.

Nanometer multilayers are not only used as reflectors for X-rays. It is also possible to use depth-graded multilayers as diffractive elements. In this case multilayer lamellas have to be fabricated and the individual layer thicknesses have to be chosen according to the zone plate law of Fresnel zone plates. Such kind of diffractive optics is called multilayer Laue lens (MLL). MLLs are promising complementary optics to zone plates particularly in the hard X-ray range where the small aspect ratios of zone plates limit the efficiency. One of the main challenges with the coating of MLL is that several thousand of nanometer layers are necessary in order to obtain lenses with apertures in the range of 20…100 µm. Only if all these layers have the right thickness, the diffraction at the artificial grating results in efficient X-ray focusing. With the latest developments MLLs with apertures of 50 µm x 50 µm have been developed that show X-ray spot sizes in the range of 30 nm x 30 nm at a photon energy of E = 10.5 keV.

8:40am **B1-3-3 Influences of Frequency and Duty Cycle on the Mechanical Properties of TiCrBN Thin Films Grown by a Hybrid Superimposed High Power Impulse Magnetron Sputtering and Radio Frequency sputtering technique**, ***ChiYu Lu****, J Lee, W Diyatmika,* Ming Chi University of Technology, Taiwan

The high power impulse magnetron sputtering (HIPIMS) technique has been studied intensively due to its extremely high peak power density to grow thin films with dense microstructure and excellent mechanical properties. Lots of efforts have been made to improve the low deposition rate of HIPIMS technique. In this study, a hybrid coating system consisting of a radio frequency power supply and a superimposed HIPIMS system was used to deposit the TiCrBN coatings with higher deposition rate. The phase

of each coating was studied by means of the X-ray diffractometer. The microstructures of thin films were examined by the field-emission scanning electron microscopy. Atomic force microscopy was used to characterize the surface morphology. The nanoindentation and scratch tests were used to evaluate the hardness and adhesion properties of thin films, respectively. It can be found that the deposition rate increased greatly due to the superimposed module and also the addition of RF sputtering. Influences of the frequency and the duty cycle of HIPIMS on the microstructure, chemical composition and mechanical properties were studied in this work.

9:00am **B1-3-4 Controllably Manipulating Adatom Mobility during PVD Deposition through Surface Acoustic Waves**, ***Piyush Shah***, *A Reed, A Waite, B Howe, M McConney,* Air Force Research Laboratory, USA

In this work we explore the ability to controllably manipulate adatom mobility in a spatially defined anisotropic way using standard physical vapor deposition (PVD) technique. Here we investigate the nucleation, growth, and microstructural evolution of PVD-based thin film growth under the influence of electrically induced surface acoustic waves (E-SAWs). Thin films made from classical and next generation resilient plasmonic materials are deposited on SAW grade lithium niobate substrate with inter-digitated electrode pattern to generate SAWs. Increase in adatom mobility and surface diffusion is primarily attributed to SAW-adatom coupling during the early stage nucleation process. As a result, we demonstrate improved crystallinity in thin films deposited under the influence of E-SAWs. Films are characterized using XRD, SEM and AFM techniques. We believe this technique of growing films is complementary to elevating the substrate temperature during deposition in a conventional PVD deposition system. These results are very promising for future work in the area of thin films deposition onto substrates coupled with SAWs.

9:20am **B1-3-5 Effects of Processing Parameters on the Fabrication of TiCrSiN Thin Films Deposited by a Hybrid HiPIMS and RF Sputtering System**, ***Yi-Xiang Qiu***, *Y Yang,* National Taipei University of Technology, Taiwan; *J Lee,* Ming Chi University of Technology, Taiwan

High power impulse magnetron sputtering (HiPIMS) is a relatively new physical vapor deposition technology, which is characterized for its ultra-high peak current, peak power density and high-density plasma to achieve unique thin film mechanical properties, such as high hardness, good adhesion and good wear resistance. In this work, a radio frequency (RF) and HiPIMS hybrid coating system was used to deposit TiCrSiN coatings with higher deposition rate. The TiCr and Si targets were connected to the HiPIMS and RF power supplies, respectively. The phase of each coating was studied by means of the X-ray diffractometer. The microstructures of thin films were examined by the field-emission scanning electron microscopy. Atomic force microscopy was used to characterize the surface morphology. The nanoindentation and scratch tests were used to evaluate the hardness and adhesion properties of thin films, respectively. The pin-on-disk wear test was employed to study the tribological property of coating. Effects of processing parameters, including duty cycle and pulse frequency of HiPIMS power on the microstructure, mechanical and tribological properties of TiCrSiN coatings were further discussed in this work.

9:40am **B1-3-6 Exploring the High-temperature Hardness of Nanocrystalline W-Ti Coatings**, ***Yip-Wah Chung***, *C Gross, X He,* Northwestern University, USA

Nanocrystalline coatings are harder than their bulk or microcrystalline counterparts because of the Hall-Petch effect. Their hardness tends to degrade with increasing temperature due to grain coarsening. Previous studies by Weissmüller, Kirchheim, and Schuh suggest that introduction of proper alloying elements can provide thermodynamic stabilization of the grain size, even at elevated temperatures. In this work, we have synthesized a series of W-Ti coatings by magnetron co-sputter-deposition of W and Ti. The coatings range in thickness from 450 to 525 nm and in composition from 85W-15Ti to 67W-33Ti. These coatings show high hardness at room temperature, with peak hardness values near 28 GPa. The hardness values are almost unchanged after 1h exposure at 600°C, remaining near 27 GPa. These results suggest the validity of a general strategy for designing thermally stable hard coatings that can maintain high hardness even after extended exposure to elevated temperatures.

10:00am **B1-3-7 Growth Mechanism of Sputter Deposited Self-assembled Alternating Layered Metal Containing Hydrogenated Amorphous Carbon Film**, *J Ting,* National Cheng Kung University, Taiwan; ***Wan-Yu Wu***, Da-Yeh University, Taiwan

The growth and characteristics of metal containing amorphous hydrogenated carbon thin films (a-C:H/Me) were studied in this research. a-C:H/Me thin films were synthesized using one single target, a rotating but not revolving substrate, and constant feed gas compositions in a conventional reactive sputter deposition chamber. The metals used include Al, Si, Cu, Pt, Fe and Ni. Various mixtures of methane and argon having fixed total flow rates were used as the feeds tocks. A number of growth parameters, including methane concentration, working pressure, electrode distance, dc power, substrate bias, and substrate temperature were used. Among the three distinct structures formed, self-assembled, alternating nano-layered structure is of particular interest. In order to understand the formation of these three distinct structures, correlations were first made among the deposition rate, the composition, the crystallinity, the surface chemistry, and the microstructure of a-C:H/Me thin films. It was found that the self-assembled, alternating nano-layered structures can be obtained under controlled growth parameters for selected metals. A growth mechanism based on the considerations of clustering of carbon and metal, segregation of carbon, catalytic effects of metal, formation of carbide, energy of adatoms, and surface diffusion of metal and carbon, has been developed. Further data analysis was also performed to verify the validity of the mechanism.

10:20am **B1-3-8 Phase Formation in Sputter Deposited Tantalum Coatings**, ***Glen West***, *M Ratova, P Kelly,* Manchester Metropolitan University, UK

Tantalum is a refractory metal with many applications. In bulk form, Ta generally has a bcc crystal structure, referred to as the α -phase. However, in thin film form, the metastable β -phase commonly forms. The β -phase is harder, but also more brittle than the α -phase and has other less desirable physical properties.

Control of phase formation in Ta films has been the subject of a number of recent studies. Several process/operating parameters have been put forward as influencing the final structure of the films, including choice of substrate material, use of a metallic interlayer between the substrate and film, substrate bias voltage, operating pressure, substrate temperature, mass of bombarding species and type of power delivery mode. These parameters can essentially be divided into those which influence the nucleation and growth of the film (e.g. substrate parameters) and those which control the energy delivered to the growing film (e.g. pressure, power delivery mode, temperature, etc.).

Of the thin film deposition processes available, magnetron sputtering is the process of choice for many commercial applications. It is a highly versatile, scalable technique capable of depositing high quality coatings of a very wide range of materials. The design of the magnetron(s) and the choice of power delivery mode allow a very wide process window to be readily explored to enable the determination of optimised deposition conditions for specific film/substrate combinations. A range of deposition parameters, magnetic field designs, power delivery modes, and biasing regimes, combined with a suite of surface analysis techniques has been utilized in a detailed study of the phase formation in tantalum films. This has enabled the conditions necessary for the deposition of α-tantalum to be identified.

Hard Coatings and Vapor Deposition Technologies
Room California - Session B4-1

Properties and Characterization of Hard Coatings and Surfaces

Moderators: Ulrich May, Robert Bosch GmbH, Diesel Systems, Chau-Chang Chou, National Taiwan Ocean University, Taiwan, Farwah Nahif, eifeler-Vacotec GmbH

8:00am **B4-1-1 Thermal Stability and Mechanical Properties of Sub-stoichiometric TiAlN Thin Films**, ***Katherine Calamba***, Linköping University, Sweden; *I Schramm,* Saarland University, Sweden; *M Johansson-Jõesaar,* SECO Tools, Sweden; *J Pierson,* University of Lorraine, France; *M Odén,* Linköping University, Sweden

Aspects on thermal stability of $(Ti_{1-x}Al_x)N_y$ alloys (y<1) were investigated because recent findings show that small amounts of nitrogen vacancies cause significant stability improvement by suppressing detrimental phase transformations, i.e. phase transformation of *c*-AlN to *w*-AlN is delayed to higher temperatures compared to stoichiometric films. The substoichiometric TiAlN alloys were deposited via cathodic arc evaporation technique and the degree of ionization of the arc plasmas was tuned by varying the bias voltage from -30V to -80V. The microstructural evolution and thermal stability of the coatings were examined using transmission electron microscopy, x-ray diffractometry, differential scanning

calorimetry, and atom probe tomography. In the as-deposited state, the highly biased films show higher hardness, i.e. the enhanced ion bombardment caused beneficial changes in morphology, microstructure, compressive stresses, and densification. However, at elevated temperature low biased films retain their hardness to higher temperatures compared to high biased films. This behavior is discussed in terms of an enhanced driving force for phase separation in the high biased films caused by self-interstitials, generated by the ion-bombardment during growth, diffusing into the excess vacancies to relive the stress. Such annihilation of defects causes the enthalpy of the system to increase, which promotes phase separation. On the other hand, low biased films with less self-interstitials show the highest phase stability and the age hardening effect was retained to the highest reported temperature to date for the Ti-Al-N material system. Our study shows that varying the nitrogen vacancy concentration of transition metal nitride thin films offers a mean to tune of thermal stability and mechanical properties for hard coating applications.

8:20am **B4-1-2 Microstructure and Hardness of Ti-B-N-C Nanocomposites Deposited from Ti and B_4C Targets**, ***Christina Wüstefeld,*** Institute of Materials Science, TU Bergakademie, Germany*; M Motylenko,* Institute of Materials Science, TU Bergakademie Freiberg, Germany*; M Síma, M Jílek,* SHM Ltd., Czech Republic*; D Rafaja,* Institute of Materials Science, TU Bergakademie Freiberg, Germany

The addition of boron to titanium nitride during the deposition of the Ti-B-N based coatings is known to facilitate the formation of nanocomposites with excellent thermal stability and very high hardness that are required for special machining applications. The Ti-B-N-based nanocomposites investigated in this study were deposited by using a combination of cathodic arc evaporation (operating with a Ti cathode) and magnetron sputtering (operating with a B_4C cathode). The amount of boron in the coatings was controlled by the magnetron power and the [B]/[N] ratio by the nitrogen flow in the working atmosphere. An additional parameter of the deposition process was the bias voltage, which influences mainly the kinetic energy of titanium ions.

The indentation experiments have shown that all deposition parameters, i.e., the magnetron power, the nitrogen flow and the bias voltage, strongly influence the hardness of the Ti-B-N-C nanocomposites. In order to be able to explain the observed correlation between the deposition parameters and the hardness of the coatings, the phase composition, the distribution and morphology of individual phases, the size and preferred orientation of crystallites and the residual stress were investigated by using a combination of glancing-angle X-ray diffraction (GAXRD), transmission electron microscopy with high resolution (HRTEM) and electron energy loss spectroscopy (EELS). The correlations between individual microstructure parameters like distribution of individual phases, morphology of crystallites or grains, preferred orientation of crystallites and residual stresses are discussed. The residual stress was measured via sample bending and by modified $\sin^2\psi$ method (GAXRD). The residual stresses obtained from the complementary methods will be compared.

8:40am **B4-1-3 Strategies for Fracture Toughness Enhancement of Nanostructured Films by Microstructural and Grain-boundary Design: The Role of Microstructure, Stress and Property Heterogeneity**, ***Rostislav Daniel,*** *C Mitterer, J Keckes,* Montanuniversität Leoben, Austria **INVITED**

In nature, extraordinary material properties are achieved by combining hard and soft or stiff and elastic constituents, which form very tough, hard and damage resistant architectures. The key for these outstanding properties is the variation in material microstructure and mechanical property distributions over large scales. In this paper, the inherent advantages of these principles will be demonstrated for nanostructured brittle thin films with the aim to establish a universal concept for improvement of fracture behavior of materials where a lack of plasticity compromises their application for surface protection despite their high strength and thermal stability. Besides strategies to enhance fracture toughness by transformation toughening, coherency strain or intrinsic compressive stress, the main focus will be on microstructural design of thin films to control crack formation and propagation. The microstructure- and property-dependent mechanisms controlling crack propagation (e.g. deflection by weak interfaces or crack path tortuosity) with subsequent toughness enhancement will be discussed in detail for various material combinations. Microstructurally and mechanically heterogeneous films including representative hard/soft crystalline/amorphous and crystalline/crystalline materials such as CrN/Cr, TiN/SiO_x and AlCrN, characterized with respect to their stiffness, fracture stress and toughness by micromechanical testing of microcantilever beams, will be some of the examples. In addition,special attention will be paid to a new strategy for fracture toughness enhancement by grain-boundary orientation and interface engineering, where crack propagation is inhibited by deflection of cracks at interfaces of columnar grains designed with chevron-like architecture and combined with elastic interlayers. In this way, even common nanocrystalline brittle materials may exhibit considerably enhanced plasticity.

9:20am **B4-1-5 Epitaxial Growth of HfN Films using Synchronized Pulsed Substrate Bias during HiPIMS Discharge**, *M Villamayor,* Linköping University, (IFM), Sweden*; T Shimizu,* Tokyo Metropolitan Univeristy, Japan*;* ***Julien Keraudy,*** *R Boyd,* Linköping University, (IFM), Sweden*; D Lundin,* LPGP, France*; U Helmersson,* Linköping University, (IFM), Sweden

Low-temperature epitaxial growth of high quality transition metal nitride materials is considered so far as one of the great challenges in advanced thin film technology. In this study, we demonstrate that low-energy-ion irradiation at the growth surface during high power impulse magnetron sputtering discharge (HiPIMS) is one of the most promising and widely applicable concepts to deposit stoichiometric, single-crystal HfN films on MgO(001) in the absence of applied substrate heating. The key point of this process is the appropriate selection of the chemical nature of the incident ions, *i.e*, inert gas vs. metal. To control the nature of the ion irradiation, two approaches have been chosen and have consisted to change the nature of the sputtering gas, Ar and Kr, and the time domain to apply substrate bias either continuously (DC) or synchronous in the last moment of the HiPIMS pulse (60 µs after the initiation of the pulse). The substrate bias was set at -60 or -100 V with a pulse width of 100 µs. *In situ* mass spectrometer measurements reveal that, by changing the gas atmosphere from Ar/N_2 to Kr/N_2, the last moment of the HiPIMS pulse evolved from a N^+-dominated phase to Hf^+-dominated phase. High-resolution x-ray diffraction, ω-2θ, azimuthal ϕ scans and reciprocal lattice maps combined with high-resolution cross-sectional transmission electron microscopy analysis established that switching from N^+ to Hf^+ bombardment, as well as switching from DC to pulse synchronized bias, help to promote the growth of fully-relaxed epitaxial HfN layers with an enhancement of the crystallinity by reducing the density of residual point defect.

9:40am **B4-1-6 HiPIMS and Ni Doping Induced Structure Reinforcement and Phase Change in nc-TiC/a-C:H Coatings**, ***Pavel Soucek,*** *J Daniel, J Hnilica, K Bernatova, L Zabransky,* Masaryk University, Czech Republic*; V Bursikova,* Masaryk Univerisity, Czech Republic*; M Stupavska, P Vašina,* Masaryk University, Czech Republic

Nanocomposite coatings consisting of nanocrystallites embedded in an amorphous matrix such as nc-TiC/a-C:H can be tailored to exhibit an unusual combination of properties such as high hardness and modulus combined with low friction and wear. These coatings are usually deposited utilizing direct current magnetron sputtering (DCMS) leading to low ionization of the sputtered titanium. High Power Impulse Magnetron Sputtering (HiPIMS) depositions usually lead to much higher ionization of the sputtered titanium which can alter the deposition process and in turn the properties of the deposited nc-TiC/a-C:H coatings. Using HiPIMS it was possible to make arc-free deposition of coatings with much higher carbon content (> 90 at.%) which was impossible for DCMS. When DCMS was employed black carbon layers were created on the target including the racetrack, whereas HiPIMS employment led to a much cleaner target. This was due to significant ionization of sputtered titanium and its back attraction to the target in HiPIMS. This proved to be highly advantageous for deposition of coatings with high carbon content with regards to arc occurrence and moreover the deposition rate of carbon rich coatings was higher for HIPIMS compared to DCMS. Lower fraction of the a-C matrix phase was found to be created in HiPIMS deposited nanocomposite coatings with < 55 at.% of carbon as compared to DCMS deposited coatings. HiPIMS deposited coatings also exhibited better stoichiometry of the TiC grains. This shows that HiPIMS ensured carbon incorporation into TiC grains rather than forming of a-C matrix. Lower amount of a-C matrix corresponded with smaller mean grain separation distance of the TiC grains by the a-C matrix. This enhanced the nanocomposite grain boundary strengthening leading to overall higher hardness of HiPIMS deposited coatings compared to those deposited by DCMS. HiPIMS deposited coatings also exhibited lower lattice parameter. The crucial parameters for obtaining hardest coatings were found out to be the TiC grain stoichiometry and small mean grain separation by the a-C matrix corresponding to only a few monolayers of the matrix between the grains. HiPIMS utilization favored this structure enhancement making it a promising method of nc-TiC/a-C:H coating preparation. Ni doping led to Ni incorporation into the grains. The grain size as well as the mean grain

separation was smaller and the surface features were refined. Thus doping by weak carbide forming Ni can also be used as tool for fine tuning of structure of nc-TiC/a-C:H coatings.

This research has been supported by project LO1411 (NPU I) funded by Ministry of Education, Youth and Sports of the Czech Republic.

10:00am **B4-1-7 Correlation of Plasma Parameters and Thin Film Properties of HiPIMS Al-Cr-N films using a Combinatorial Approach***, **Lars Banko**, D Grochla, S Ries, P Awakowicz, A Ludwig,* Ruhr-Universität Bochum, Germany

HiPIMS power supplies provide a variety of settings to tune the plasma in PVD processes. In this work, the direct influence of plasma properties like ion energy, ion flux and electron density on coating features like microstructure and mechanical properties was investigated.

Single phase fcc - Al-Cr-N films were deposited at 500°C by reactive co-deposition of Al und Cr in N_2/Ar – plasma. Continuous composition materials libraries ((Al_{100-x} -Cr_x)-N (0.4 < x < 0.9)) were synthesized by confocal alignment of two 4 inch cathodes. Both cathodes were powered by HiPIMS with an average power of 200 W. The pulse length was kept constant at 40 µs. Three depositions with frequencies of 100, 200 and 400 Hz were carried out resulting in a variation of peak power (0.3 – 2.5 kW/cm^2) and peak current density (0.5 – 3.8 A/cm^2).

Time- and space-resolved plasma diagnostics were applied to characterize ion energy, ion flux and electron density at five positions corresponding to different compositions. The electron density was investigated using Langmuir probe and the ion energy distribution function was determined by retarding field energy analyzer. Without additional bias, maximum ion energies of 70 eV were measured. The mean ion energy was found to vary between 4.5 and 9 eV, depending on the applied frequency.

The materials libraries were characterized regarding microstructure, morphology, composition, hardness, Young's modulus and residual stress. The residual stress was measured on 120 µm thick micro-cantilever stress sensors. By thermal cycling of the sensors after the deposition, intrinsic and extrinsic stress components could be determined separately.

The results of this investigation clearly show the influence of ion energy and ion flux on composition, microstructure and morphology and thereby on mechanical properties like residual stress and hardness. The effect of ion flux and ion energy on the materials properties are amplified by increasing Al-concentration.

Acknowledgment: SFB-TR 87

Fundamentals and Technology of Multifunctional Materials and Devices
Room Royal Palm 4-6 - Session C1

Optical Metrology in Design, Optimization, and Production of Multifunctional Materials

Moderators: Ludvik Martinu, Polytechnique Montreal, Nikolas Podraza, University of Toledo

8:00am **C1-1 Metamaterials: from Design and Modeling to the Experimental Confirmation of their Optical Performance***, **Michel Lequime**,* Institut Fresnel, France **INVITED**

Control of the microstructure of the matter at the sub-wavelength scale offers a great flexibility for designing artificial materials with an exotic electromagnetic response at optical frequencies, like for instance, the near-zero or negative index of refraction. The optical properties of such new, artificial materials (usually called meta-materials) are derived both from the inherent properties of their constitutive elements as well as the geometrical arrangement of these elements. Their development paves the way for controlling and manipulating light through entirely new schemes (slow light, perfect lens ...).

Numerous examples of such metamaterials including fishnet structures and metasurfaces will be provided. Manufacturing techniques, such as electron-beam lithography, focused ion-beam milling or interference lithography will be described, as well as the characterization methods including refraction measurements, spectral transmittance and reflectance measurements, interferometric measurements.

Possible applications to thin-films and multilayer stacks will be analyzed in a preliminary way.

8:40am **C1-3 Use of FDTD Method for Data Analysis of Spectroscopic Ellipsometry Data of Non-periodic sub-wavelength Structures***, **Juan Antonio Zapien**,* City University of Hong Kong, Hong Kong*; Y Foo,* City University of Hong Kong, Hong Kong Special Administrative Region of China

The optical response of complex, non-planar samples have the capability to determine superb sub-wavelength imaging information based on spectroscopic ellipsometry (SE), non-imaging, measurement and full vectorial data analysis. This has played a vital role in optical critical dimension (OCD) characterisation for the semiconductor industry. Rigorous coupled-wave analysis (RCWA) sets the standard in the determination of the fine structure of 1D gratings based on polarimetric and scattering techniques [1]. The ability to reproduce that level of detail in the characterization of complex nanostructured samples, particularly 2D or plasmonic nanostructures, is yet to be demonstrated using RCWA and is also much needed for sensing, active metamaterials research, and others [2,3]. To date, the use of RCWA analysis for such complex structures is largely limited to quantitative modeling of reflectance ratios whereas phase information, crucial for enhanced sensing capabilities [3], is largely disregarded. It seems necessary to secure additional analysis tools to provide complimentary fully-vectorial SE data analysis of nano-structured 2d and plasmonic materials. The finite difference time domain (FDTD) method presents attractive advantages as generality, ability to retrieve wide frequency range from single simulations as well as non-linear effects or non-periodic morphologies [4]. Previously, we have shown that the SE response of thin films can be obtained from FDTD using far-field projections of near-field simulation based on the FDTD method [5]. In this contribution we provide new results discussing the difficulties and strategies to needed to accurately model the SE response of non-periodic samples at large AoI. We will discuss the optimization of the modeling strategies and expected applications.

The authors acknowledge the generous support of the Research Grants Council of the Hong Kong, SAR China (Project No. CityU 122812).

References

[1] E. Liu, F.L. Terry, *Immersion scatterometry for improved nano-scale topography measurements*, Phys. Status Solidi **205**, 784 (2008).

[2]Losurdo M, Hingerl K. Ellipsometry at the nanoscale. Springer-Verlag: Berlin Heidelberg, 2013.

[3] Johann Toudert *Spectroscopic ellipsometry for active nano- and meta-materials* Nanotechnol Rev **3**, 223 (2014).

[4] A. Taflove, S.C. Hagness, Computational *Electrodynamics: the Finite-Difference Time-Domain Method*, 3rd ed. Artech House, MA, 2005.

[5] K.T. Cheung, Y. Foo, C.H. To, J.A. Zapien, *Towards FDTD modeling of spectroscopic ellipsometry data at large angles of incidence*, Appl. Surf. Sci. **281**, 2 (2013).

9:00am **C1-4 Analysis Procedures for Multiple Sets of Ellipsometric Spectra***, **Nikolas Podraza**, K Ghimire, P Uprety, M Junda,* University of Toledo, USA

Ellipsometric parameters are collected as a function of photon energy, spatial position on a sample, and time during a process. Analysis provides spectroscopic complex dielectric functions, $\varepsilon = \varepsilon_1 + i\varepsilon_2$, and structural information (layer thicknesses, surface roughness, interfaces). The particular photon energies measured can yield information pertaining to component layer intrinsic properties, with some regions of the spectrum more closely linked to particular material and electrical properties. Also, depending on material ε and the arrangement of materials in a sample, different spectral ranges are more or less sensitive to layer structure. To more fully understand the nature of materials comprising a sample, ellipsometric spectra are often measured over wide spectral ranges, using more than one instrument, and analyzed jointly. In other scenarios, multiple sets of ellipsometric spectra are collected either as functions of spatial position on a sample or time during a process to identify subtle material variations. Here we will discuss details of data analysis pertaining to four scenarios: (1) applying realistic parametric models of ε over the appropriate spectral ranges to deduce structural information, (2) simultaneous analysis of measurements collected from the millimeter (THz) to the ultraviolet spectral range using $\geq$2 ellipsometers, (3) utilizing spatially resolved mapping measurements to deduce material property variations, and (4) analysis of in situ time real time spectroscopic ellipsometry (RTSE) collected during thin film growth or post deposition modification. For (1) and (2) metal oxides will be considered, specifically aluminum doped zinc oxide (ZnO:Al) with particular attention to the analyzed spectral range dependence on resultant electrical properties. For (3), disordered nano-

/polycrystalline semiconductors (Si:H, CdTe, $CuIn_{1-x}Ga_xSe_2$) for use in thin film solar cells will yield maps of thicknesses and degree of crystallinity. (4) Methylammonium lead iodide ($CH_3NH_3PbI_3$) perovskites will be monitored using RTSE during vapor deposition and post-deposition atmospheric exposure to track phase segregation into component CH_3NH_3I and PbI_2 as well as changes in the perovskite itself. The respective strengths and weaknesses of these methods are discussed.

9:20am **C1-5 High Precision Absorption Measurements in Optical Films using the TRACK Method: Comparison with the Laser-induced Deflection**, *R Vernhes,* Polytechnique Montreal, Canada*; C Muhlig,* Leibniz-Institute of Photonic Technology (IPHT), Germany*;* ***Ludvik Martinu,*** Polytechnique Montreal, Canada

The accurate determination of optical constants of thin films is both challenging and critical for many optical applications. In this study, we focus on the methodology for the precise evaluation of the extinction coefficient (k) assessed by multi-angle spectrophotometry using the recently developed TRACK method [1]. More specifically, we present how absorption can be directly derived from transmission and reflection spectra in p polarization for complex samples showing non-idealities such as inhomogeneities, interfaces and thickness non-uniformity. As an example, we apply this method to a non-uniform inhomogeneous silicon nitride film deposited on glass and we demonstrate that the complete optical modeling of the non-idealities is not necessary to obtain k values. Finally, we compare the results determined by this method to those obtained by the highly sensitive laser induced deflection (LID) technique over a broad spectral range (400 to 1000 nm) and for various materials of interest for optical applications, such as TiO2, ZnO, silicon, etc.

1. R. Vernhes and L. Martinu, "TRACK – A new method for the evaluation of low-level extinction coefficient in optical films," Optics Express 23 (2015) 28501.

9:40am **C1-6 Durability and Wear Mechanisms of Easy-to-clean Coatings on Glass and Displays Assessed by *in situ* Tribometry**, *J Qian, T Schmitt, B Baloukas,* ***Jolanta Ewa Klemberg-Sapieha,*** *L Martinu,* Polytechnique Montreal, Canada*; C Kosik-Williams, J Price, E Null,* Corning Incorporated, USA

Fluorine-based easy-to-clean (ETC) coatings, with contact angles higher than 110º and friction coefficients of ~0.1, are widely applied on touch-screen displays to reduce staining and to enhance abrasion resistance.

In the present work, we evaluate the durability and study the wear mechanisms of ETC coatings on glass substrates using an *in situ* tribometer (TribTik) equipped with a camera system; this allows one to image, in real time, the contact area between the glass substrate and the abrading counterpart. Through this unique combination, the instantaneous friction coefficient and the contact area's status can be monitored and correlated *in situ,* thus offering the opportunity to abort the test at critical stages of the wear process and study its progression.

The morphology and composition of the wear tracks are further examined at different stages to understand the wear mechanisms of the ETC. We demonstrate, with the support of optical, SEM and EDX analyses that the instantaneous friction coefficient and the obtained *insitu* images correlate very well with the wear process. The progression of the wear mechanism is then defined as follows: 1) generation of unconsolidated debris, 2) formation of a layered tribofilm, 3) cracking of the tribofilm, and 4) damage to the underlying glass substrate.

10:00am **C1-7 Insitu Metrology for Surface Topography and Stress Characterization**, ***Wojtek Walecki,*** Frontier Semiconductor, USA

Novel metrology tool for in-situ characterization of surfaces of coatings during deposition process. The tool measures the total integrated scatterer for smooth wafers when measuring forward, or back-reflection at very large angles of incidence. The tool is insensitive to vibrations and stray light. We discuss polarization resolved data and characterize our technique using NIST traceable standards. We discuss it's applications to semiconductor manufacturing.

The grazing angle reflection measurements were subject of radar [1], semiconductor [2], machine vision [3], space [4], traffic materials [5], and theoretical research [6]. The grazing angle forward reflection metrology was reported by us earlier [7], however, we are not aware of the fully polarization resolved grazing angle back-reflection metrology of roughness of functional coatings.

In addition we discuss recently developed polarization sensitive Raman scattering tool, and submicroradian and nanoradian beam deflection techniques for characterization of stress tensor in coatings on global and microscopic scale.

[1] Billingsley, J. Barrie. *Low-angle radar land clutter: measurements and empirical models*. IET, 2002.

[2] Stover, John C. *Optical scattering: measurement and analysis*. Vol. 2. Bellingham: SPIE optical engineering press, 1995.

[3] Ngan, Addy et al. "Experimental Analysis of BRDF Models." *Rendering Techniques* 2005.16th (2005): 2.

[4] Speicher, Andy. *Identification of geostationary satellites using polarization data from unresolved images*. Diss. UNIVERSITY OF DENVER, 2015.

[5] Belcour, Laurent, et al. "Bidirectional reflectance distribution function measurements and analysis of retroreflective materials." *JOSA A* 31.12 (2014): 2561-2572.

[6] Elfouhaily, Tanos Mikhael, et al. "A critical survey of approximate scattering wave theories from random rough surfaces." *Waves in Random Media* 14.4 (2004): R1-R40.

[7] Walecki, Wojciech, et al. "Robust diffuser and roughness metrology tool for LED manufacturing." *SPIE OPTO*. International Society for Optics and Photonics, 2015.

10:20am **C1-8 Scratch Failure vs Residual Stress: a Relationship Applied to Optical Coatings**, *T Poirié,* ***Thomas Schmitt,*** Polytechnique Montreal, Canada*; E Bousser,* University of Manchester, UK*; L Martinu, J Klemberg-Sapieha,* Polytechnique Montreal, Canada

The display industry became an engineering-driven sector which has shifted from mainly industrial uses to consumer products such as flat-panel displays, touch screens, multimedia devices, transportation, ophthalmic lenses and many others. The use of these devices implies various mechanical solicitations that become very critical in situations when sensitive substrates, such as polymers, are applied. Specifically, optical coatings in use today involve transparent ceramic-based materials which show a strong mechanical mismatch with the substrate. In addition, their typical thickness, which ranges from several tens to several hundreds of nanometers, makes their mechanical durability very challenging. It is therefore crucial to understand the failure mechanisms occurring during mechanical loading of these coated systems, and their relationships with the intrinsic properties such as internal stress.

In this work, we systematically study the scratch resistance and the delamination behavior of thin e-beam evaporated TiO_2 films deposited on plastic substrates. The use of Ion Beam Assisted Evaporation has been used to tailor the residual stress and to produce coatings which exhibit stress levels ranging from tensile to compressive. By combining an *in situ* scratch testing technique and a new approach based on reverse scratching sequence starting from high to low load, we were able to assess specific failure mechanisms in dependence on the stress level. Moreover, this method establishing the relationship between the scratch failure and the internal stress allows one to extract the yield strength, in the present context applied to model thin TiO_2 coatings. Finally, this study and the related methodology significantly enhances the understanding of the failure mechanisms occurring during scratch testing, and it can be applied to any optical and other films.

10:40am **C1-9 Fast Characterization of nm Thin to Thick Coatings using Pulsed-Rf Glow Discharge Optical Emission Spectrometry**, ***Philippe Hunault,*** *M Chausseau, K Savadkouei,* HORIBA Scientific, USA*; P Chapon, S Gaiaschi,* HORIBA Scientific, France

Glow Discharge Optical Emission Spectrometry (GD-OES) provides direct measurement of the chemical composition of materials as a function of depth and can be used to characterize various coatings, made of both thin and thick layers, conductive or non-conductive materials

It consists in a pulsed radiofrequency glow discharge plasma source that is sputtering a large area of the material of interest and real time detection by a high resolution optical spectrometer of the sputtered species excited by the same plasma. All elements from H to U can be measured using this technique.

With its capability to perform depth profiling with a nanometric resolution and to go up to 150 µm deep into the sample within few minutes, GD-OES is an ideal tool to evaluate depth profiles on materials and to study interfaces between layers, diffusion processes or to optimize coatings processes. Many elements can be analyzed simultaneously, including Oxygen, Hydrogen, Deuterium, Carbon, Fluorine, Sulfur, Lithium… GD-OES

is a versatile tool to study materials that complements other techniques such as XPS and SIMS.

Results obtained on various nm thin and thick oxide coatings, nitriding, carburizing, galvanization and energy storage will be shown. Examples of GD-OES as a tool for layer thickness determination will also be presented.

Coatings for Biomedical and Healthcare Applications
Room Sunrise - Session D3

Medical Devices, Biosensors, and Biodegradation

Moderators: Jessica Jennings, University of Memphis, USA, Robin Pourzal, Rush University Medical Center, USA

8:00am **D3-1 Challenges for Polymeric Orthopedic Implants - Enhanced Surface Functionalities using coatings deposited by HiPIMS**, ***Kerstin Thorwarth,*** Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; G Thorwarth,* IMT AG Greifensee, Switzerland*; J Patscheider,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

For treatment of the human spine and its degenerative diseases, a large variety of materials and treatment techniques are available, to which a short overview is given. One task frequently encountered for new solutions is the need for strongly adherent metallization of polymeric surfaces. Such materials are favored due to their low stiffness, comparable to cortical bone material and radiolucency, but generally they present surface properties unfavorable for successful tissue integration. This is especially true for an unmodified PEEK surface designated for bone integration. To address this issue, the common approach is a metallic coating by plasma spray (APS or VPS). The disadvantages inferred by this process comprise remelting of the surface and incomplete coverage of non-line-of-sight features.

As an alternative, a highly adherent HiPIMS based coating process was developed and is discussed in this presentation. Along with characterization of the general process, it is shown that a proper selection of pre-treatment and coating parameters like surface activation and micro-pulsed HiPIMS operation can improve the adhesion strength to >30 MPa, whilst delivering a surgical grade (ISO 5832-2) conformal titanium coating. Based on FEM simulations, the problem of adhesion measurement on deforming substrates is addressed, and subsequent treatments to further enhance the osseointegration and biocompatibility are elucidated.

8:20am **D3-2 Alginate Coatings on Silver-decorated Calcium Phosphate nanospheres as an Antimicrobial coating component**, ***Jessica Jennings,*** *C Nelson, S Mishra, M Ghimire, J Bumgardner,* University of Memphis, USA

Silver-decorated calcium phosphate nanospheres have been previously studied and shown to inhibit bacterial growth and adhesion when incorporated into chitosan coatings on metal. While effective against bacterial strains common in oral and orthopaedic infections, preliminary cell culture and elution evaluations have demonstrated that substantial and potentially toxic amounts of ionic silver are released during the acidic fabrication process of the chitosan coating. We hypothesized that creating a degradable shell coating around these nanoparticles will prevent initial leaching of silver into the coatings so that a biocompatible antimicrobial surface is maintained over an extended period.

Coatings of alginate were applied to non-loaded and silver-decorated calcium phosphate nanospheres by immersion in sodium alginate at weight% ranges of 1 to 8%. Particles were sonicated for one hour and then centrifuged and rinsed to remove residual alginate. SEM images were acquired of coated and non-coated nanospheres.

Zeta potential of particles decreased from -4.62 to -17.19 after alginate coatings, indicating that alginate shells were formed around calcium phosphtate nanospheres. When incorporated into chitosan coatings, these alginate shells may prevent leaching of silver into coatings for slow release and/or containment within the coatings for surface antimicrobial activity. Ongoing and future studies will determine silver release, incorporation into chitosan coatings, antimicrobial activity, and cytocompatibility.

8:40am **D3-3 Manufacturing, Testing, and Regulatory Aspects of Implant Coatings**, ***Dirk Scholvin,*** *J Moseley,* Wright Medical, USA **INVITED**

Medical implants must meet a number of criteria to serve their intended purpose safely. They must possess basic properties such as an adquate minimum tensile or fatigue strength, wear and corrosion resistance, or elastic modulus. Depending on their use, they may also require an enhanced ability to integrate with the biologic environment. For example, allowing bone ingrowth to achieve improved fixation for an orthopedic implant. They may need to be resistant to bacteria or cell attachment in order to improve sterility of a surgical implant or to prevent biofouling of a sensor surface. It is not uncommon to find applications requiring surface properties that cannot be met by a bulk implant material.

In this presentation, an overview of different types of implant coatings is given, with a focus on the orthopedic implant industry. The history of coatings in the orthopedics industry is used as a case study to show opportunities for device coatings while highlighting testing, manufacturing and regulatory challenges.

9:20am **D3-5 Implant Alloy Microstructure can Enable Cell Induced Corrosion in Total Hip Replacements**, ***Robin Pourzal,*** *D Hall, R Urban, S McCarthy,* Rush University Medical Center, USA*; J Ehrich, A Fischer,* University of Duisburg-Essen, Germany*; J Jacobs,* Rush University Medical Center, USA

Corrosion within modular taper junctions is a major concern for the longevity of total hip replacements (THR). It has been shown that cells within the joint environment can alter the local chemical composition of the joint fluid [1]. We have shown that the presence of cells on the surface of the taper surface of femoral heads is associated with a column-like damage pattern of proximal to distal running troughs [2]. It was the purpose of this study to determine corrosion pathways leading to column damage in THRs.

Thus, a retrieval study was conducted on 165 retrieved femoral heads that had either moderate corrosion (n=57) or severe corrosion (n=108). Samples were screened for the occurrence of column damage. Replicas of the head taper surfaces were made and measured with a non-contact 3D profiler (Ortholux, Redlux).

In selected cases, heads were sectioned to visualize damage patterns in a SEM.The implant alloy microstructure was evaluated by metallographic methods.

Colum damage was observed in 28% of the retrieved heads. The troughs of the column damage pattern exhibited no material pile-up on the sides, had an etched surface appearance, and exhibited a depth of 20-40μm. On 3 of the 15 head tapers analyzed by SEM, there was clear evidence of preserved cells adherent to areas with column damage, but there was no evidence of cells adhering to corresponding stem tapers. Based on morphology and size, the cells appeared similar to macrophages or osteoblasts. It was evident that cells generated an etching trail which exposed crystallographic features. The metallographic analysis revealed that implants with column damage exhibited longitudinal segregations within the implant alloy.

In conclusion, column damage is a common occurrence in femoral heads with corrosion damage. It appears to be the result of a chemical process such as etching. Interestingly, the width an orientation of the troughs appeared similar to segregations within the implant alloy. Such segregations must have been already present in the CoCrMo bar stock material that heads were made form. The result is an alloy microstructure with longitudinal stripes with varying corrosion properties thus enabling local galvanic interactions. It appears that once cells are able to enter the taper interface, they generate a more corrosive environment by the release of reactive oxygen species as earlier suggested [1]. The combination between the segregated alloy and a corrosive environment enabled by cells provides conditions that lead to column damage, increasing material loss and higher risk of implant failure.

[1] Gilbert JL et al Semin Arthoplasty 24(4):246, 2015, [2] Hall DJ Trans ORS 41:400, 2016

9:40am **D3-6 Characterization of Solid-supported Thin Films and Molecular Interactions using Multi-Parametric Surface Plasmon Resonance**, ***Annika Jokinen,*** *N Granqvist, J Kuncova-Kallio, J Sadowski,* BioNavis Ltd., Finland

Surface Plasmon Resonance (SPR) is commonly used method to measure molecular binding kinetics and affinities, however, the physical phenomenon is also applicable to characterization of thin films [1]. Multi-parametric surface plasmon resonance (MP-SPR) utilizes full SPR angular spectral measurement at multiple wavelengths characterizing thin films in terms of thickness and optical properties.

The method effectiveness has been extensively demonstrated using different ultrathin films systems [2-4]. Chemical-vapour-deposition (CVD)-grown graphene films thickness was determined using MP-SPR and after first initial layer thickness was found to be 0.37nm / monolayer on a solid support [3]. Atomic Layer Deposition (ALD) (PICOSUN™ R-150) was used to deposit Platinum (Pt) and nanolaminate (Al_2O_3 and Pt) layers on a glass

substrate. Target thickness of the layers were 11 nm for Pt, and altering 5nm each for nanolaminate. Thickness was found to be in good agreement with the target thicknesses. Stearic acid (SA) Langmuir Blodgett films showed approximately 2.5±0.2 nm thickness, and linear increment with increasing layer number [2]. The SPR curves (angular spectra) were analyzed using BioNavis LayerSolver software to determine layer thickness and refractive indexes. Additionally to layer properties MP-SPR measures in real-time interactions on a thin films. Protein and cell samples binding on a Plasma Sprayed hydroxyapatite coating was measured label free [4].

The non-invasive MP-SPR is proved to be an effective tool for the nanoscale metal, nanolaminate, oxide, polymer, and ceramic layers characterization in air and in liquid. High sensitivity enables characterization of even subnanometer thick layers and within the same measurement also material interactions can be measured.

References

[1] Albers, Vikholm-Lundin, Chapter4 in Nano-Bio-Sensing, Springer 2010

[2] Granqvist et al., Langmuir,29(27),2013,8561-8571, 2013

[3] Jussila et al. Optica, Vol.3, No.2, 2016

[4] Vilardell et al. J. Funct. Biomater. 7, 23, 2016

10:00am **D3-7 Effect of Processing on the Structure and Biofuncionalization of AlN Thin Films Produced by r.f. Reactive Magnetron Sputtering**, *A Murillo,* ***Olimpia Salas****, L Melo-Máximo, B García, D Melo-Maximo,* Tecnológico de Monterrey-CEM, Mexico*; K García,* Tecnológico de Monterrey-CCM, Mexico*; J Oseguera,* Tecnológico de Monterrey-CEM, Mexico

Al/AlN/Al thin films were evaluated in terms of their structure and easiness of biofunctionalization as prospective materials for biosensors. First, Al/AlN layers were deposited by r.f. reactive magnetron sputtering at various levels of applied power and Ar/N_2 mixtures on stainless steel substrates. The films were characterized by x-ray diffraction, glancing angle x-ray diffraction, scanning electron microscopy + energy dispersive microanalysis, and transmission electron microscopy. The results indicate that the applied power had a stronger influence than the atmosphere composition on the structure obtained and that the orientation of the films can be controlled through the processing parameters. However further work is needed as some residual non-nitrided Al was found within the layers. The films that showed the most promising structural characteristics for biosensing, were then coated with an additional Al layer on the surface and subjected to biofunctionalization experiments.

10:20am **D3-8 Effect of Zn on the Improvement of Corrosion Performance of MAO Coated Biodegradable Mg-Sr-Zn Alloys**, ***Mehmet Yazici****,* Ondokuz Mayis University, Turkey*; Y Azakli, S Cengiz, Y Gencer, M Tarakci,* Gebze Technical University, Turkey

Recenty, magnesium alloys are commonly studied as biomaterials due to their promising biodegradability in ortohopedic applications. Degradability is an important property of a biomaterial tough high corrosion rate is a handicap for orthopedic applications. One of the solutions can be followed is to keep the corrosion rate of the material under limits by modifying its surface. Coating techniques such as microarc oxidation (MAO), sol-gel, electrophoretic deposition etc. might be used to increase the corrosion resistance. In this study, ternary Mg-Sr-Zn alloys with Zn content ranging with 0.35, 1.5 and 3 weight percent were prepared via stainless steel mold casting following induction melting. The MAO coating was deposited on these samples by pulsed direct current. Corrosion experiments of the coated samples were tested in SBF and degradations rates were compared. The surface roughness, microstructure, phase content and chemical composition of the coatings were characterized by using scanning electron microscopy, profilometry and X-ray diffractometry.

10:40am **D3-9 Antimicrobial Silver Oxide Films with Rapid Bacteria Contact Killing**, *A Ogwu,* ***Nathaniel Tsendzughul****, G Mackay, C Williams,* University of the West of Scotland, UK

We report on the antimicrobial properties of silver oxide thin films prepared by reactive magnetron sputtering. The films were characterised with x-ray diffraction combined with radial distribution function analysis to evaluate nano-crystalline particle sizes formed during deposition. The growth mode of the prepared films was monitored with the scanning electron microscope. The chemical composition and stoichiometry of the films was monitored with Raman spectroscopy, FTIR and X-ray photoelectron spectroscopy (XPS) using the binding energy peaks, all confirming the presence of antimicrobial phases in our deposited films. Spectrophotometry was used to confirm up to 80% optical transmission in the visible range. Atomic absorption spectroscopy was used to monitor ion release in the silver oxide films both in water and saline solution. We were able to confirm 100% microbial cell deaths of E.coli and S. Aureus within 20 minutes on exposure to silver oxide films using killing curve measurements. The mechanism of bacterial attack can be associated with nano-crystalline particles in the deposited films, ion release, the ease of ligand replacement in the silver oxide stoichiometries in the films and their exchange and interference with biological ligands in the microbes. Our current finding opens the door to furthering the development of non-ultraviolet (UV), but visible light activated antimicrobial surfaces.

New Horizons in Coatings and Thin Films
Room Royal Palm 1-3 - Session F2-1

HiPIMS, Pulsed Plasmas and Energetic Deposition

Moderators: Tiberiu Minea, Université Paris-Sud, Tomas Kubart, Uppsala University, Angstrom Laboratory, Sweden

8:00am **F2-1-1 An Ionization Region Model of the Reactive Ar/O_2 High Power Impulse Magnetron Sputtering Discharge**, ***Jon Gudmundsson****,* University of Iceland, Iceland*; D Lundin,* CNRS, Université Paris-Sud, France*; N Brenning, M Raadu, C Huo,* KTH - Royal Institute of Technology, Sweden*; T Minea,* CNRS, Université Paris-Sud, France

In the reactive high power impulse magnetron sputtering discharge experimental findings indicate that there is a significant increase in the discharge current and this current increase appears to follow one of two paths as the discharge enters the poisoned mode. On one hand the current waveform becomes distinctly triangular in shape and on the other hand the current maintains the shape of the non-reactive waveform [1,2]. A reactive ionization region model (R-IRM) is developed to describe the reactive Ar/O_2 high power impulse magnetron sputtering (HiPIMS) discharge with titanium target [3]. It is then applied to study the temporal behaviour of the discharge plasma parameters such as electron density, the neutral and ion composition, the ionization fraction of the sputtered vapour and the oxygen dissociation fraction. We study and compare the discharge properties when the discharge is operated in two well established operating modes, the metal mode and the poisoned mode. Using the R-IRM we find that when the discharge is operated in the metal mode Ar^+ and Ti^+ -ions contribute most significantly (roughly equal amounts) to the discharge current while in the poisoned mode the Ar^+-ions contribute most significantly to the discharge current while the contribution of O^+ -ions and secondary electron emission is much smaller. Furthermore, we find that recycling of atoms coming from the target, and subsequently ionized, are required for the current generation in both modes of operation. In the metal mode self-sputter recycling dominates and in the poisoned mode working gas recycling dominates, and it is concluded that the dominating type of recycling determines the discharge current waveform.

[1] J. T. Gudmundsson, Plasma Phys. Contr. Fusion, 58(1) (2016) 014002

[2] F. Magnus, T. K. Tryggvason, S. Olafsson and J. T. Gudmundsson, J. Vac. Sci. Technol. A, 30(5) (2012) 050601

[3] J. T. Gudmundsson, D. Lundin, N. Brenning, M. A. Raadu, Chunqing Huo and T. M. Minea, Plasma Sources Sci. Technol. accepted for publication 2016

8:20am **F2-1-2 Residual Stress Control of Al-rich (Ti,Al)N Hard Coatings by Pulse Duration in High Power Impulse Magnetron Sputtering**, ***Tetsuhide Shimizu****, S Takahashi, H Komiya,* Tokyo Metropolitan Univeristy, Japan*; Y Teranishi, K Morikawa,* Tokyo Metropolitan Industrial Technology Research Institute, Japan*; M Yang,* Tokyo Metropolitan Univeristy, Japan*; U Helmersson,* Linköping University, IFM, Sweden

A present study demonstrates the controllability of residual stress of deposited ternary nitride films by regulating pulse duration in high power impulse magnetron sputtering (HiPIMS). Optical emission spectrum (OES) measurements were firstly performed in the plasma of Al-rich $Ti_{0.33}Al_{0.67}$ alloy sputtered in an Ar/ N_2 gas mixture to analyze ion and excited neutral densities at different peak current intensities and plasma compositions. Based on the OES spectra, specific pulse conditions of 100, 200 and 1000 µs with a same pulse off time of 3000 µs were chosen to deposit (Ti, Al)N films on Si (100) wafer. Residual stress of the deposited films was estimated by a deflection of 50 µm-thick thin glass sheets. Chemical composition, surface morphology and phase composition of the films were analyzed by an energy dispersive spectroscopy, an atomic force microscopy and X-ray diffraction, respectively. Mechanical properties were characterized by using nanoindentation. As results, clear gradual variation from tensile to

compressive stress was demonstrated by varying pulse duration from 1000 to 100 µs. A compressive stress was found in the film grown using the shortest pulse duration of 100 µs, which also had the highest Ti ion-to-neutral ratio, while the pulse duration of 200 µs and 1000 µs showed the tensile stress. In particular, the pulse duration of 200 µs showed almost no residual stress but the highest hardness with highest crystallinity of mixed cubic and hexagonal phase. The cause of these tendencies in residual stress between different pulse duration was discussed based on the effect of ionization degree of sputtered species and compositions of the gas and metallic ions in the discharge plasma.

8:40am **F2-1-3 Energetic Deposition of Electronic Materials**, ***Jim Partridge***, *B Murdoch, N McDougall, D McCulloch,* RMIT University, Australia*; R Ganesan, M Bilek, D McKenzie,* The University of Sydney, Australia*; M Tucker, N Marks,* Curtin University, Australia **INVITED**

Energetic deposition provides increased control over the micro-structural, electrical and optical properties of thin films. In our work, high power impulse magnetron sputtering (HiPIMS) and filtered cathodic vacuum arc deposition systems have been employed to form high quality metal oxide and carbonaceous materials. Electronic and optical applications for these materials including transparent thin film transistors, photo-detection and resistive memory storage devices have been explored. Process and film characteristics will be discussed for materials including ZnO, HfO_2, HfO_xN_y, BN and C. In particular, the plasma and target conditions during HiPIMS growth of metal oxides and carbonaceous materials will be related to microstructural, electronic and optical measurements performed on the films produced. In addition, work will be presented in which ab initio calculations and X-ray absorption spectroscopy have been employed to characterise defects in energetically grown hBN.

9:20am **F2-1-5 Controlled Reactive HiPIMS of Thermochromic VO_2 Films at a Low Deposition Temperature (300 °C)**, ***David Kolenaty***, *J Vlcek, T Kozak, J Houška, R Čerstvý,* University of West Bohemia, Czech Republic

Vanadium dioxide (VO_2) is the most interesting thermochromic material due to its reversible phase transition from semiconducting IR transparent state (monoclinic structure) to metallic IR reflective state (tetragonal structure) at around 68 °C. A high IR transmittance modulation makes the VO_2–based films a suitable candidate for optical switching applications, such as self-tunable infrared filters, temperature sensing devices and "smart" windows regulating the solar transmission. Current drawbacks limiting the application potential of the VO_2 films include high deposition temperatures (> 400 °C) of the films and the necessity to use a substrate bias potential in the case of their magnetron sputter deposition.

Reactive HiPIMS with a feed-back pulsed reactive gas (oxygen) flow control and an optimized location of the oxygen gas inlets in front of the target and their orientation toward the substrate made it possible to form crystalline thermochromic VO_2 films at very high values of the maximum target power density of up to 5 $kWcm^{-2}$ in a pulse. The thermochromic VO_2 films (80 nm thick) were deposited onto floating glass substrates without any nucleation–promoting "seed" layer at the temperature of 300 °C. The depositions were performed using a strongly unbalanced magnetron with an indirectly water-cooled planar vanadium target (50.8 mm in diameter) in argon-oxygen gas mixtures at the argon pressure of 1 Pa. The duty cycle was set to a constant value of 1%, the voltage pulse durations were 50 µs and 80 µs, and the corresponding repetition frequencies were 200 Hz and 125 Hz, respectively. The deposition-averaged target power density was approximately 13 Wcm^{-2}. The target-to-substrate distance was 150 mm.

The phase composition of the VO_2 films was determined by X-ray diffraction. The thermochromic behavior of the films was investigated using a spectrophotometer and spectroscopic ellipsometer equipped with custom designed heat cells to control the measurement temperature of the samples from 25 °C to 100 °C. The temperature-dependent electrical resistivity of the films was measured by a four-point probe. The time-averaged energy distributions of positive ions were measured with an energy-resolved mass spectrometer placed at the substrate position.

The VO_2 films prepared at the voltage pulse duration of 50 µs exhibited a high IR modulation (ΔT_{2500nm} ~ 45% between 25 °C and 90 °C), an optical transmittance of about 40 % in the visible region, a large drop in the electrical resistivity (from 5.5×10^{-3} Ωm to 1.5×10^{-5} Ωm) after the semiconductor-to-metal transition, and a lower transition temperature of 58 ˚C than the bulk VO_2 (68 ˚C).

9:40am **F2-1-6 High Power Impulse Plasma Magnetron Sputtering – Dawn of Industrialization**, *W Gajewski, P Rozanski, P Lesiuk, P Ozimek,* ***Rafal Bugyi***, TRUMPF Huettinger Sp. z o.o., Poland

Since the first presentation of the High Power Impulse Magnetron Sputtering (HiPIMS) idea by *Kouznetsov and co-workers* in 1999 the basic architecture of a DC-charged capacitor bank dissipating periodically its energy into the plasma in pulses evolved to a sophisticated electronic device commercially available for industry. In order to meet rigorous requirements of industrial application, engineers have proposed different modifications of HiPIMS power delivery units to make the pulse shape and duration independent on the size of the capacitor bank and time-dependent plasma impedance. Since typically pulses longer than 100 µs are required to reach metal self-sputtering regime, a precise control of voltage and current pulse shape is required during the whole pulse length. Furthermore, for tuning ionization of the plasma species and deposition rate flexibility in power delivery regulation is of a key importance.

This contribution provides a series of case-study examples where HIPIMS was tested and qualified for industrial applications. First, the examples from the hard and decorative coating applications will be discussed. Using the basic facts about the HIPIMS plasma parameters the influence of the modified rectangular-like current peak on the plasma composition and dynamics will analyzed. As next, a novel approach of a flexible and application selectable HiPIMS power delivery control will be presented: *(i)* peak current regulation, *(ii)* pulse frequency, and *(iii)* pulse length. The in-field experiments data will be used to discuss the influence of peak current regulation on the ionization degree of the sputtered species as well as the influence of frequency regulation on the deposition rate.

Finally, tests performed in reactive processes both on metallic and ceramic target materials will complete the discussion on HIPIMS industrialization demonstrating the importance of fast arc detection and suppression algorithms required for a long term stability of industrial processes.

10:00am **F2-1-7 Comparison of CrN from Planar and Rotating Target using Highly Ionized Processes**, ***Holger Gerdes***, *A Themelis, R Bandorf, M Vergöhl, G Braeuer,* Fraunhofer Institute for Surface Engineering and Thin Films IST, Germany

CrN is used in many industrial applications. It provides good electrical conductivity, high hardness, corrosion resistance and high temperature stability. As known from many other investigations high power impulse magnetron sputtering (HIPIMS) lead to significant improved properties.

This presentation will discuss the influence of different HIPIMS techniques on the adhesion, hardness and composition of the thin film. Therefore, the gas composition (ratio between Ar and N2), the working pressure were changed. Additionally, the influence of the sputtering plant and target geometry was investigated. Two sputtering plants were used. The first one, a lab scale one, was equipped with a planar target (132 mm x 224 mm) and the second one with a planar (130 mm x 470 mm) and a rotating (Length of 500 mm) target.

While conventional processes require temperatures in the range of 250 °C and additional biasing the presented films all showed hardness values up to 2900 HV without substrate bias or additional heating.

10:20am **F2-1-8 Molybdenum Thin Films Deposited by High Power Impulse Magnetron Sputtering**, ***Arutiun P. Ehiasarian***, *D Loch,* Sheffield Hallam University, UK

Molybdenum thin films used in chalcopyrite solar cells can influence the Na diffusion rates and the texture of the $Cu(InGa)Se_2$ absorber according to the microstructure and morphology. The lowest resistivity films are achieved at low working pressure and are accompanied by high residual stress and poor adhesion due to the resulting high energy of the deposited flux. High Power Impulse Magnetron Sputtering was employed to ionise the sputtered flux, achieve high adatom mobility at low energy and influence the growth of Mo back contacts. Pulse durations in the range 60 to 1000 µs, sputtering voltages between 800 and 1500 V and deposition pressures of 2×10^{-3} mbar and 4×10^{-3} mbar resulted in ten-fold variations in the flux ratios of Mo^{1+}/Mo^0 Mo^{2+}/Mo^{1+}, Ar^{2+}/Ar^{1+} and Mo^{1+}/Ar^{1+} as determined by optical emission spectroscopy and time-resolved plasma-sampling energy-resolved mass spectroscopy. The energy of metal and gas double- and single-charged ions reduced with pulse duration and increased with voltage. The microstructure of the films varied from open columnar with faceted tops to fully dense as observed by secondary electron microscopy. The reflectivity of the films improved by 20% compared to industry-standard materials. The lowest resistivity was in the range of 12 µΩ-cm as observed by four-point probe measurements of 570 nm thick

films. The correlation between resistivity, microstructure, crystallographic texture and deposition flux characteristics is discussed.

10:40am **F2-1-9 Epitaxial Growth of Copper Thin Films on Si(001) by HiPIMS***, **Felipe Cemin**,* Université Paris Sud, France*; G Abadias,* Université de Poitiers, France*; D Lundin, T Minea,* Université Paris-Sud, France

The heteroepitaxial growth of metallic thin films on semiconductor substrates is usually required to provide a special growth direction for subsequent deposition of magnetic ultrathin layers or to reduce the dislocation density of lattice mismatched heterostructures. However, epitaxial relationship may be only obtained if the substrate surface is free of native oxides and contaminants, i.e., an atomic cleaning process is required. Conventional pre-treatment methods include the heating of the substrate at relatively high temperatures (800 °C) and the creation of a hydrogen-termination layer on the substrate surface through chemical etching with hydrofluoric acid. In this contribution we report a new route to grow epitaxial copper thin films at room temperature on silicon(001) wafers covered with native oxide without any prior substrate cleaning process. This method consists in a single-step deposition using high power impulse magnetron sputtering (HiPIMS) and substrate biasing. The studied Cu thin films were deposited onto Si(001) wafers by HiPIMS and conventional direct current magnetron sputtering (DCMS) at different substrate bias voltages. The stress evolution during deposition was monitored *in situ* using the real-time wafer curvature method. The as-deposited Cu films were characterized *ex situ* by X-ray diffraction, focused ion beam scanning electron microscopy, electron backscattering diffraction and atomic force microscopy. It was found that for higher bias voltages, a Cu/Si epitaxial growth is achieved following the Cu(001) [100] // Si(001) [110] orientation relationship in HiPIMS films, while polycrystalline Cu films with [111] preferred orientation are obtained using a DCMS discharge under the same deposition conditions. Detailed investigation of the film structure correlated with the intrinsic stress measurements shows that the substrate bias voltage affects the early growth stages of HiPIMS Cu films on Si, and thus their final microstructures.

Exhibitors Keynote Lecture

Room Town & Country - Session EX

Exhibition Keynote Lecture

11:00am **EX-1 Success and Failure in the Commercialization of CVD Diamond***, **Chris Engdahl**,* Crystallume, USA **INVITED**

The reality of diamond thin films caught the interest of many researchers when the rest of the world learned from the Soviet Union how to grow diamond from the gas phase in the early 1980s. Besides the allure of being highly sought after gem-quality crystals, diamond has some impressive physical attributes: highest hardness, best electrical insulator, best thermal conductor, broadband optical transparency, high acoustic velocity, and extreme chemical inertness. Funding for basic research and creation of private companies poured in. However, due to inadequate understanding of the scientific challenges during the early stages of research and difficulties in scaling up production-level deposition sytems, this resulted in a long cycle of public and private investors spending large sums of money for products that proved to be not viable. As a result, most large commercial efforts ceased to exist, and investors turned their attention away from CVD diamond. The primary commercial success for CVD diamond for the next 15-20 years was as an abrasive material used on polishing pads, cutting tools, and low-volume niche markets.

This presentation will cover the early promise and evolution of the field of CVD diamond, illustrating some of the problems and advantages in developing a novel and compelling coating into useful products. Several commercial applications of CVD diamond in use today will be discussed, along with a few of the most interesting applications being positioned for the market in the near future. Interest in CVD diamond thin films has continued to thrive in academia, and commercial interest is undergoing a rebirth. Practical applications and useful deposition systems are now combining to support realistic commercial growth in the field.

Coatings for Use at High Temperatures
Room Sunrise - Session A2-1

Thermal and Environmental Barrier Coatings

Moderators: Lars-Gunnar Johansson, Chalmers University of Technology, Sweden, Kang Lee, NASA Glenn Research Center, USA

2:10pm **A2-1-3 Property Comparisons of Air Plasma Sprayed and Dense Homogeneous Yttrium Disilicate**, ***Cory Parker***, *R Golden, E Opila,* University of Virginia, USA

Modeling efforts for Rare Earth (RE) silicate Environmental Barrier Coatings (EBCs) typically utilize properties of dense homogeneous materials, yet EBCs are often processed using an Air Plasma Spray (APS) process which results in heterogeneous phase distribution, porosity, and splat microstructures. In this paper, properties of dense homogeneous yttrium disilicate processed by Spark Plasma Sintering (SPS) are compared to those of APS yttrium disilicate. Specifically, phase stability during thermal cycling, thermal expansion, and stability in high temperature steam are compared. Phase changes during repeated temperature cycling were characterized with X-ray diffraction. APS phase mixtures evolved during cycling whereas SPS yttrium disilicates were more phase stable. Thermal expansion of both materials was characterized up to 1400°C using dilatometry. Coefficients of Thermal Expansion (CTE) for APS yttrium disilicate varied significantly without a prior annealing treatment. Once annealed, the CTEs for the SPS material were significantly more consistent than those of the APS material. The silica depletion depth for yttrium disilicate samples was measured after steam-jet exposures at 1200°C for times of 60 to 250 hours and steam velocities between 150-180 m/s. The silica depletion rate was lower in dense homogeneous SPS yttrium disilicate compared to the more porous and heterogeneous APS materials. Cross sectional analysis of APS specimens showed both silica depletion to greater depths at splat boundaries and localized yttria-rich areas with minimal silica depletion. The implications of the heterogeneity of APS RE silicate phases and microstructures for EBC applications will be discussed.

2:30pm **A2-1-4 Performance of Vacuum Plasma Spray Bond Coatings**, ***Michael Lance***, *A Haynes, B Pint,* Oak Ridge National Laboratory, USA

The effects of composition, temperature and environment on the performance of vacuum plasma sprayed (VPS) NiCoCrAlYHfSi bond coatings (BC) on directionally-solidified (DS) 247 substrates with air plasma sprayed Y_2O_3-stabilized ZrO_2 has been investigated. Four compositions were investigated including the base composition and additions of Ti, B and Ti+B. The addition of B did not improve the average coating lifetime in 1-h cycles at 1100 °C in air with 10% H_2O in either case, however, the addition of Ti caused a decrease in lifetime. Photo-stimulated luminescence spectroscopy was used to map residual stresses in the thermally-grown Al_2O_3 scale. To study performance near the operating temperature of BCs in land-based turbines, the effect of water vapor was studied at 900 °C in laboratory air and air with 10% H_2O for 10-500 h cycles. Water vapor had little effect on the measured parabolic rate constants at 900 °C and a comparison of the oxide microstructures will be reported.

Research sponsored by the U. S. Department of Energy, Office of Fossil Energy's Turbine Program.

2:50pm **A2-1-5 Predicting Microstructural Evolution in Aluminide Coatings during Manufacturing and Degradation in Service**, ***Rishi Pillai***, *A Chyrkin, T Galiullin, W Leng, D Grüner, D Naumenko, W Quadakkers,* Forschungszentrum Jülich GmbH, Germany **INVITED**

Protective metallic nickel aluminide (NiAl) diffusion coatings enhance the oxidation and corrosion resistance of the underlying high temperature materials. Aluminising provides a cost effective alternative and allows coating of complex shaped components. However, the composition of the substrate and the specimen geometry influence the final coating microstructure during the aluminising process and govern the high temperature behaviour of the coating system during subsequent exposure.

The formation of a protective alumina scale and the diffusion from the coating into the substrate result in the loss of Al and thereby the dissolution of the ß-NiAl phase in the coating. The extent of interdiffusion depends on the coating and substrate composition. The compatibility of a given type of a coating with its base material substantially influences the performance of a coated material during service. Potentially detrimental precipitate phases may form especially in the interdiffusion zone (IDZ) during the aluminising process and during subsequent service depending on the composition of the base material. Evaluation of the material's high temperature behaviour requires extensive experimental testing. Computational methods can substantially reduce the extensive experimental efforts required for coating evaluation and qualification.

In the current work, an in-house developed coupled thermodynamic and kinetic computational model was employed to predict the microstructural evolution in nickel aluminide (NiAl) diffusion coatings on Ni-base wrought and cast alloys during the coating (aluminising) process as well as during the subsequent high temperature service. Three Ni-base alloys (602 CA, IN718 and Rene80) were chosen to evaluate the influence of specimen thickness and alloy composition on the performance of nickel aluminide (NiAl) coatings. Specimens of different thicknesses (0.1-2 mm) were coated with nickel aluminide via chemical vapour deposition (CVD) on 602 CA and IN718 and via a slurry coating process on Rene80. The specimens were discontinuously exposed for 1000 h at 1100 °C in laboratory air. Specimens were removed from the furnace at 100, 300 and 1000 h.

Element concentrations and phase distribution were obtained by scanning electron microscopy (SEM). Phases were identified by energy/wavelength dispersive X-ray spectroscopy (EDX/WDX) and electron backscatter diffraction (EBSD). The modelling results were validated with experimental data. The computational approach assists in estimating the lifetime of the coating and provides a tool to predict microstructural changes in coating systems as a function of alloy/coating composition, time and temperature.

3:30pm **A2-1-7 Engineered Architectures of Gadolinium Zirconate/YSZ based TBCs Subjected to Hot Corrosion Test**, ***Satyapal Mahade***, University West, Sweden; *K Jonnalagadda,* Linköping University, Sweden; *N Curry,* Treibacher Industrie AG, Austria; *N Markocsan, P Nylén,* University West, Sweden; *R Peng,* Linköping University, Sweden; *X Li,* Siemens Industrial Turbomachinery AB, Sweden

Gadolinium zirconate (GZ) is considered as a promising top coat candidate for high temperature TBC applications. Suspension plasma spray has shown the capability to generate a wide range of microstructures including the desirable columnar microstructure. In this study, a triple layered TBC comprising a thin YSZ base layer beneath a relatively porous GZ intermediate layer and a denser GZ top layer was deposited by axial SPS process. Additionally, a blend TBC double layered architecture of GZ and YSZ comprising a thin YSZ base layer and GZ+YSZ mixed ceramic top layer was deposited by SPS. SEM analysis of the cross section in both layered and blend architectures revealed a columnar microstructure. The porosity content of the deposited TBCs was measured using image analysis and water intrusion method. The as sprayed TBCs were exposed to corrosive salt environment which comprised of a mixture of vanadium pentoxide and sodium sulphate at 900°C for 8 hours. The top surface and cross section of the TBCs after the hot corrosion test were analyzed by SEM/EDS. The phase content in the as sprayed and corroded TBCs were also analyzed by XRD.

3:50pm **A2-1-8 Thermal Barrier Coatings: The Next Generation**, ***Maurice Gell***, *E Jordan, R Kumar,* University of Connecticut, USA; *C Jiang, J Wang, B Nair,* HiFunda LLC, USA

Thermal barrier coatings (TBCs) must exhibit a multitude of properties to be successful. Critical properties include: high temperature phase stability, low thermal conductivity, sinter resistance (retention of low thermal conductivity) and thermal cycle durability. It has recently been shown that yttrium aluminum garnet (YAG) TBCs made by the Solution Precursor Plasma Spray (SPPS) process can potentially be used at temperature 200oC higher than state-of-the-art YSZ TBCs. To further improve the properties of SPPS YAG TBCs, emphasis has been given to greater reductions in thermal conductivity by introducing linear arrays of porosity, called inter-pass boundaries (IPBs), and by demonstrating that thicker coatings with adequate durability can be fabricated. This presentation will present the results of these efforts and the associated thermal cycling durability.

4:10pm **A2-1-9 Microstructure of Gas Flow Sputtered Thermal Barrier Coatings**, ***Nils Rösemann***, Institute for Materials, TU Braunschweig, Germany; *K Ortner,* Fraunhofer Institute for Surface Engineering and Thin Films IST, Germany; *M Bäker,* Institute for Materials, TU Braunschweig, Germany; *J Petersen,* Fraunhofer Institute for Surface Engineering and Thin Films IST, Germany; *G Bräuer,* Institute of Surface Technology, TU Braunschweig, Germany; *J Rösler,* Institute for Materials, TU Braunschweig, Germany

Thermal barrier coatings (TBC) reduce the thermal load of gas turbine components. State-of-the-art TBCs consist of partially yttria stabilized zirconia (PSZ) and are deposited by thermal spray techniques (e. g. atmospheric plasma spraying) or electron beam physical vapor deposition (EB-PVD). The resulting microstructure is dependent on the process and

strongly influences the coating´s properties and time to failure. Columnar structures exhibit a higher lifetime and are thus favored.

This talk investigates an alternative deposition technique (gas flow sputtering - GFS), which also gives rise to columnar microstructures. The aim of this work is to gain a fundamental understanding of the influence of crucial process parameters such as substrate temperature and bias voltage on the microstructure, and the suitability of GFS coatings for the use as TBCs.

PSZ coatings were deposited on polished FeCrAlY-Alloy substrates and described utilizing WDX, SEM, FIB and XRD.

The substrate temperature has been identified to be a crucial parameter. Between 500 and 800 °C, four different types of columnar microstructures are defined based on XRD pattern and morphology. The growth direction of the columns changes from <111> to <100> accompanied by a change in column shape from triangular to four-sided. The principal shape of the columns is furthermore explained using a growth model.

Applying bias voltage at a given substrate temperature does not give rise to a new type of microstructure but alters the microstructure defined by the substrate temperature. While low bias values lead to more regular columns, high bias voltages lead to further densification and compressive stresses, rendering these conditions unsuitable for TBC manufacturing.

Concluding, promising microstructures are presented accompanied by general guidelines for the suitable process parameters.

4:30pm **A2-1-10 Current Environmental Barrier Coatings Research at NASA**, ***Kang Lee***, *D Waters,* NASA Glenn Research Center, USA

SiC/SiC Ceramic Matrix Composites (CMCs) are a game changer for advanced power generation equipment because of their high temperature capability, oxidation resistance, and light weight that translate to significant reduction in fuel consumption and pollution. Limitations of SiC/SiC CMCs include surface recession and component cracking and associated chemical and physical degradation in the CMC. The solution pursued to mitigate surface recession of SiC/SiC CMCs is the incorporation of coating systems that provide surface protection, which has become known as an Environmental Barrier Coating (EBC). Other key life-limiting EBC degradation modes include oxidation in steam environments, CMAS-EBC reactions, and thermal fatigue. The first and second generation EBCs developed in mid 1990s-early 2000s laid the foundation for current EBCs. Many engine tests have been conducted since late 1990s and a first CMC component entered into service in 2016 in a commercial engine. The introduction of CMCs represents significant challenges as failure of the EBC means rapid reduction in component life. A reliable life model and testing methods relevant to engine conditions to validate life model need to be developed. This paper will discuss the current research activities on EBC development and testing at NASA.

4:50pm **A2-1-11 CMAS Infiltration Prediction for 7YSZ TBCs Deposited by EB-PVD**, ***Juan Gomez,*** The University of Texas at El Paso, USA*; R Naraparaju, U Schulz,* German Aerospace Center (DLR), Germany*; R Chintalapalle,* University of Texas at El Paso, USA

The current demand for higher gas turbine engine operating temperatures has brought into attention the hot corrosion attack to thermal barrier coatings (TBCs) due to siliceous debris infiltration into gas turbines. The debris are commonly composed of calcium-magnesium-alumino-silicates (CMAS) which are carried in environmental pollution in the form of sand, fly ash, volcanic ash, among others. Previous studies in standard 7YSZ coatings deposited by EB-PVD techniques have shown a significant relation of coating micro-structure and CMAS infiltration depth. In the previous study a physical model was proposed to estimate CMAS infiltration into EB-PVD coatings by simplifying the micro-structure as a concentric pipe (kernel pipe) with open channels (feather arms) which distribute the CMAS reducing the infiltration time into the TBC. Therefore, it is of highly importance to understand the kinetics of CMAS infiltration since by refining the deposition parameters (deposition pressure, rotation, etc.) CMAS infiltration can be reduced. The current work correlates experimental results obtained for short term CMAS infiltration performed at 5 min. using a synthesized CMAS source with theoretical results using the proposed “concentric pipe model”. The calculated results are in good agreement by closely predicting the infiltration time for a given depth when compared with short term infiltration experiments. Additionally, the results were compared with the “open pipe” infiltration model which has been previously used in literature for CMAS infiltration estimation. The results also show a significant error in infiltration prediction for the open pipe model which proved a more realistic approach for CMAS infiltration using the proposed concentric pipe model.

5:10pm **A2-1-12 Oxidation Behavior of CrN, AlCrN, and AlTiN Cathodic Arc PVD Coatings**, ***Zuhair Gasem***, *A Adesina,* King Fahd University of Petroleum and Minerals, Saudi Arabia

The oxidation behaviors of CrN, AlCrN, and AlTiN *PVD-cathodic-arc* coatings were evaluated isothermally at 800°C, 900°C and 1000°C for a duration of 5hr in ambient atmosphere using 304 stainless steel substrates. A novel substrate design was employed where all substrate edges were chamfered at both faces to coat both surfaces and edges. The oxidation rate measurement of all-surface-coated samples were conducted using *in-situ* thermogravimetric apparatus. The coating composition, morphology, and hardness were analyzed before and after the oxidation test using X-ray diffraction (XRD), energy dispersive spectroscopy (EDS), and scanning electron microscope (SEM).

XRD results for CrN revealed the evolution of various temperature-dependent oxides forming within and beneath the coating including Cr_2O_3, Fe_2O_3, and Cr_2O after the oxidation tests. The diffraction peaks for CrN coating (1.8 um in thickness) disappeared entirely after the oxidation test at 1000°C suggesting complete transformation of the CrN layer into mixed oxide layer. The specific weight gain curves showed continuous increase with exposure time at all temperatures examined. The oxidation resistance of AlCrN coating exhibited significant improvement as compared to CrN coating as can be evident by comparing the oxidation kinetic curves of the two coatings owing to the formation of the more protective Al_2O_3 in addition to Cr_2O_3. The coating provided effective protection at 800°C and 900°C as can be inferred from the oxidation rate curves. The thickening of AlCrN layer, the absence of oxidation product at the interface between the coating and the underlying substrate, and the asymptotic oxidation rate behavior suggest persistence of protection of AlCrN coating up to 1000°C.

The major oxidation products of AlTiN coating over 900-1000°C comprised of TiO_2 and Al_2O_3. The oxidation kinetics showed initial rapid growth stage and a delayed linear behavior. The initial stage may be attributed to the formation of porous TiO_2 with non-continuous Al_2O_3. The delayed linear oxidation rate is similar to the oxidation rate of AlCrN coating at 1000°C. This has been explained in terms of the dominance of the growth of continuous Al_2O_3 layer in both coatings at high temperature.

Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B1-4

PVD Coatings and Technologies

Moderators: Joerg Vetter, Oerlikon Balzers Coating Germany GmbH, Jyh-Ming Ting, National Cheng Kung University

1:50pm **B1-4-2 Combinatorial Exploration of the High Entropy Alloy System Fe-Mn-Ni-Co-Cr**, ***Alexander Kauffmann,*** Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM-WK), Germany*; M Stüber, H Leiste, S Ulrich,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM-AWP), Germany*; S Schlabach, D Szabó,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM-WK)*; B Gorr,* University of Siegen, Germany*; H Chen,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM-WK), Germany*; H Seifert,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM-AWP), Germany*; M Heilmaier,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM-WK), Germany

The concept of high entropy alloys (HEA) differs from conventional alloy design strategies by increasing the number of base elements as well as their concentrations. Rather than being composed of a single principal element and minor additions for obtaining desired microstructures and materials properties, HEAs are chemically complex composed of multiple principal elements in almost equiatomic ratios. Here, the basic intention is to maximize the configurational part of entropy and stabilizing disordered, single-phase materials with simple crystal structures. Nevertheless, configurational entropy is not the sole decisive factor for the thermodynamic stability of particular phases. Accordingly, efficient theoretical as well as experimental methods have to be conducted in order to screen the vicinity of the center of five or more component systems.

The FeMnNiCoCr HEA crystallizes face-centered cubic and is one of the few examples of HEAs which can be tailored by means of classical metallurgical processes. Thus, FeMnNiCoCr has attracted most interest by the scientific community among the class of HEAs so far. Its outstanding mechanical properties are resulting from a complex interplay of the impact of lattice

distortion and an interplay of deformation twinning and dislocation slip. In order to experimentally separate fundamental parameters like stacking fault energy which are strongly depending of Fe, Mn and Ni content and lattice distortion which are influenced by Cr and Mn content, deviations from the almost equimolar composition are necessary.

For exploring the phase field of the solid solution within the Fe-Mn-Ni-Co-Cr system, we use a combinatorial thin film method in the present contribution. The films are prepared by magnetron sputtering from a Fe-Mn-Ni-Co-Cr multi-element target with circular sectors onto Si substrates. The compositions of the prepared films with a thickness of about 5 µm were obtained by EDX. In the as-deposited state, the disordered solid solution is found in the near equimolar region of the films. The lattice parameter of bulk material obtained from conventional metallurgy could be verified. The microstructure of the obtained thin film in the center of the quinary system is examined by using TEM (FIB lift out) and 3D-APT. In addition, the results on the center of the phase diagram are complemented by analyses towards the binary border systems which are in our case Mn-Fe, Fe-Co, Co-Ni, Ni-Cr as well as Cr-Mn. Here, disordered solid solutions with fcc, bcc, hcp and alpha-Mn structure type crystal structure were found. The appearance of all phases is discussed based on CALPHAD calculations.

2:10pm **B1-4-3 The Effect of Mo-Cu Cathode Composition on Thin Film Synthesis and DC Vacuum Arc Characteristics**, ***Igor Zhirkov***, Linköping University, IFM, Sweden; *P Polcik, S Kolozsvári,* Plansee Composite Materials GmbH, Germany; *J Rosen,* Linköping University, IFM, Sweden

Mo-Cu alloys demonstrate high electrical and thermal conductivity, low coefficient of thermal expansion, and good high-temperature performance. The material properties are dependent on how well Mo and Cu can be mixed. Classical methods such as powder metallurgy and/or infiltration are limited due to the Mo/Cu grain size. An alternative synthesis method is vacuum arc, which allows generation of metallic flux even from refractory materials, and which also provide an increased Mo-Cu intermixing. In this work, we have studied the influence of $Mo_{1-x}Cu_x$ cathode composition (x = 0, 0.05, 0.1, 0.15, 0.3, 0.63, 0.95, 1 (wt%)) on plasma generation and materials synthesis in a DC vacuum arc discharge. It is found that the stability of the arc process is strongly correlated to the cathode composition. Highest stability, together with the lowest cathode potential (~ 19 V), is detected for the $Mo_{0.37}Cu_{0.63}$ (wt%) cathode, while the $Mo_{0.95}Cu_{0.05}$ (wt%) cathode shows the most unstable arc process with the highest cathode potential (~ 28 V). Moreover, plasma properties such as total intensity of ion flux, ion kinetic energy and ion charge state are all found to be strongly dependent on the relative Mo/Cu ratio. The intensity of macroparticle generation as well as the size of the droplets also correlate with the relative fraction of Cu within the cathode. However, there is an inverse correlation between the visually observed intensity of the macroparticle flux and the number of droplets on the resulting films. In particular, for the cathodes with low Cu content, there is an increased abundance of visually observed macroparticles while the films are (close to) free of droplets. The thickness and elemental composition of the deposited films also demonstrate a dependence on the elemental composition of the cathode. The obtained results are discussed in the light of a very limited solubility between Mo and Cu, surface and material properties of new and used Mo-Cu cathodes, and features resulting from high temperatures of the cathode surface during the arc process.

2:30pm **B1-4-4 Towards High-Rate Magnetron Sputter Deposition: Influence of Discharge Power on Deposition Process and Coating Properties**, ***Christian Saringer***, *R Franz,* Montanuniversität Leoben, Austria; *K Zorn,* MIBA High Tech Coatings, Austria; *C Mitterer,* Montanuniversität Leoben, Austria

Magnetron sputtering offers the possibility of depositing a vast variety of functional coatings and is nowadays widely established in research and industry. Its main advantage is the great versatility, which is owing to the possibility of freely adjusting the conditions during film growth, like the degree of thermalization, the substrate temperature and the ion bombardment. Thus, the mechanical, optical and structural properties of the coatings can be tailored on laboratory and industrial scale. However, the applicability is often limited due to the large amount of energy that is inherently dissipated into heat, resulting in a low deposition rate. Therefore, the increase of deposition rate is of great interest in order to improve productivity and cost-efficiency. Raising the overall power introduced to the process can be perceived as an approach for elevating the deposition rate which is, however, also affecting the properties of the resulting coatings. Within this work, we therefore studied the influence of the target power on the sputter deposition process and resulting coating properties during reactive and non-reactive sputtering. Chromium, titanium, TiN, TiO_2 and carbon coatings were deposited at different average power densities of up to 34 W/cm² in DC and pulsed DC mode. The coatings were examined by X-ray diffraction, scanning electron microscopy and nanoindentation experiments, which revealed that their mechanical and structural properties are significantly affected by the power density. It was also found that by controlling the discharge power it is possible to effectively influence the transition between metallic and poisoned mode during the reactive sputtering of titanium in N_2 as well as O_2 containing atmospheres. Additionally, conducted plasma investigations employing Langmuir probe analysis and optical emission spectroscopy revealed further details about the relations between discharge and coating properties contributing to establish a comprehensive understanding of high-rate magnetron sputter deposition.

2:50pm **B1-4-5 High Temperature Solid PVD Lubricants Based on Vanadium**, ***Vjaceslav Sochora***, *M Jilek, Jr., O Zindulka,* SHM, s.r.o., Czech Republic

The increase of the production in the industry demands higher cutting speeds of the tools. A higher speed means higher forces which increase the working temperature and decrease the tool life. One of the solutions is to use PVD coatings with a very good thermal stability or we can use a film with a low friction coefficient in high temperatures. In our work, we focus on the high temperature lubricant PVD coatings based on vanadium that are very promising for cutting and forming applications.

The studied systems were CrVN, VAlN, AlCrVN and VAlSiN prepared by the low voltage arc. The disadvantage of these systems is a narrow functional temperature interval that determines the specific application for the film.

We investigated the dependence of the hardness on the amount of vanadium in the film and then annealed the deposited coatings in the air at the temperatures of 500 – 700 °C and researched the change in hardness and oxidation rate. We also examined the structure by using SEM.

In the next step, we used face-turning test to simulate the real conditions to assess the friction properties of the coatings. The parameters of the cutting tests were set to achieve the thermal load from 550 °C to 700 °C.

The presence of vanadium in the system has a significant influence on the friction and enables to optimize the process application like hobbing or aluminum die casting.

3:10pm **B1-4-6 Grain Size-Dependent Metastable Phase Formation**, ***Marcus Hans***, *D Music,* RWTH Aachen University, Germany; *D Kurapov, J Ramm, M Arndt,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein; *H Rudigier,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Switzerland, Liechtenstein; *J Schneider,* RWTH Aachen University, Germany

Physical vapor deposited (PVD) TiAlN is the benchmark hard coating system utilized in metal cutting and forming applications today. However, phase formation prediction efforts by density functional theory (DFT) calculations for TiAlN are often inconsistent with experimental data. It is well known that the phase stability is affected by chemical composition, temperature as well as pressure. Recently, the impact of point defects on the phase stability [1] and the consequences of processing conditions in an industrial deposition system for the phase stability [2] were evaluated.

Here we consider for the first time the impact of grain size on the stability of metastable TiAlN coatings by relating calculated surface and volume energy contributions to the total energy. Typical grain sizes determined for PVD TiAlN are < 50 nm and, hence, these coatings contain domains with large surface-to-volume ratios. Our starting hypothesis is that the energetic "penalty" associated with the formation of these grain surfaces (= interfaces) will affect the experimentally determined stability. Therefore, we investigated the grain size-dependent phase stability of cubic and wurtzite $Ti_{1-x}Al_xN$ theoretically by considering a surface energy term in addition to the volume energy term. With this approach critical grain sizes for metastable phase formation are identified as a function of the Al concentration x.

$Ti_{1-x}Al_xN$ coatings were synthesized combinatorially by cathodic arc deposition and the here proposed, grain size dependent phase stability calculation is found to be consistent with experimental phase formation data. The results provide evidence that the extent of phase stability regions of TiAlN critically depends on the grain size. While these thoughts have been overlooked in the past we will demonstrate that the grain size-dependent phase formation is equally relevant for other material systems with large surface-to-volume ratios.

References:

[1] M. Hans, M. to Baben, D. Music, J. Ebenhöch, D. Primetzhofer, D. Kurapov, M. Arndt, H. Rudigier, J. M. Schneider, *Effect of oxygen incorporation on the structure and elasticity of Ti-Al-O-N coatings, synthesized by cathodic arc and high power pulsed magnetron sputtering*, J. Appl. Phys. 116 (2014) p. 093515.

[2] M. Hans, M. to Baben, Y.-T. Chen, K. G. Pradeep, D. M. Holzapfel, D. Primetzhofer, D. Kurapov, J. Ramm, M. Arndt, H. Rudigier, J. M. Schneider, *Substrate rotation-induced chemical modulation in Ti-Al-O-N coatings synthesized by cathodic arc in an industrial deposition plant*, Surf. Coat. Technol. 305 (2016) 249-253.

3:30pm **B1-4-7 Nanoengineering Periodically Structured SiCu Thin Film Anodes for Rechargeable LIBs**, ***Billur Deniz Polat Karahan***, *B Bilici,* Istanbul Technical University, Turkey*; O Eryilmaz,* Argonne National Laboratory, USA*; K Amine,* Argonne National Laboratory, USA, United States of America*; O Keles,* Istanbul Technical University, Turkey

In the quest for a radically better lithium-ion battery, a promising direction is suggested so-called “silicon (Si) composite” anodes, in which the negative electrode contains a higher proportion of Si with another material. In the current technology, while the Si composite electrodes have the potential to have far higher energy density, long cycle life and high reversibility are still not satisfactorily provided due to intrinsic properties of Si such as low electrical conductivity and high volumetric changes upon cycling.

Therefore, in this work, to create electron conduction pathway in the electrode and to increase the ductility of the film 10%at. Cu atoms are co-deposited with Si. Then to induce homogeneously distributed interspaces in the electrode structured composite thin film has been engineered by glancing angle electron beam deposition (GLAD) method. This process enables to deposit coatings of any materials without a need of binders or any conductive additives. Plus, various structures from nanocolumns to helices might be deposited by optimizing the evaporation rate of source materials, the incident angle and the azimuthal rotation rate of the substrate.

An innovative approach involving adaptation of ion assistance to GLAD has been also proposed in this study. The well adherent composite nanostructures are expected to provide large reaction area with Li, facile stress relaxation (to prevent electrode pulverization or delamination), effective electrical contacts with the substrate and short Li diffusion distances.

To evaluate the electrochemical performances of the structured composite films, two samples have been deposited on Cu collector with different evaporation rates: quartz crystal microbalances of Cu and Si show 0.4-4 Å/s and 0.9-10 Å/s for Samples 1 and 2, respectively. The morphological analyses show that depending on the evaporation rates of sources the structure of the film changes which affects their performances in cycling.

3:50pm **B1-4-8 Thin Film Metallic Glass: Novel Coating Providing High Toughness and Low Friction**, ***Chia-Chi Yu***, *J Chu,* National Taiwan University of Science and Technology, Taiwan*; Y Shen,* University of New Mexico, USA

The amorphous nature of thin film metallic glasses (TFMGs) provides outstanding mechanical properties, including high strength, large elastic limits, and excellent corrosion and wear resistance. The grain boundary-free structure of TFMGs produces an exceptionally smooth surface and low surface free energy, resulting in high hydrophobicity and a low coefficient of friction.

In this study, magnetron sputtering was used in the deposition of Zr-based TFMG coatings with the aim of enhancing the bending and fatigue properties of bulk metallic glasses (BMGs). A TFMG coating was shown to increase the plastic strain of BMG by 9.2%, without sacrificing its extraordinary strength. This was also shown to increase the fatigue endurance-limit of BMG by ~33%, from 300 MPa for bare BMG to 400 MPa for TFMG-coated BMG. The results of transmission electron microscopy and nanoindentation testing revealed that TFMGs are able to withstand enormous shear strain without fracturing. Used as a coating on syringe needles, the low coefficient of friction of TFMG (~0.05) reduced the insertion forces by ~66% and retraction forces by ~72%, when tested on polyurethane rubber blocks.

Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B2-1
CVD Coatings and Technologies

Moderators: Michel Pons, University Grenoble Alpes, SIMAP, CNRS, Makoto Kambara, The University of Tokyo

4:10pm **B2-1-9 Combined Effects of Supersaturation and Stress for the Control of AlN Film Quality**, ***Raphael Boichot***, *D Chen,* Grenoble-INP, France*; F Mercier,* CNRS, France*; M Chubarov,* Grenoble-INP, France*; G Giusti,* Sil'Tronix, France*; M Pons,* CNRS, France **INVITED**

The aim of this talk is to show the degrees of freedom offered to CVD experimenter to tune the properties of crystal during hetero-epitaxial growth. We will develop here the example of the AlN epitaxial growth by HT-CVD with $AlCl_3$ and NH_3 as precursors in H_2 as carrier gas.

We showed in previous studies that the epitaxial growth of AlN on various substrates can be obtained by carefully aiming a particular temperature-supersaturation-growth rate process parameters window, but we also found that the AlN crystal quality, into this "epitaxial window", does not depend so strongly on the growth parameters other than growth rate. N/Al ratio surprisingly does not play a crucial role in obtaining epitaxial growth or desirable crystal quality.

Clearly to increase further the crystal quality once epitaxial growth is reached, we must cover a wider range of growth parameters to achieve a good control of crystal properties. In one hand, we will explain how mechanical characteristics of layers at room temperature can give valuable information on the first steps of growth that are critical for crystal quality and properties. In the other hand, we will show how certain growth parameters, even considered as secondary or counter intuitive, could be key to explain crystal quality and properties due to their influence on the early steps of growth.

Due to the high variability in experimental results in CVD and the need to exhaustively cover growth parameters, we will present the interest of using DOE (design of experiments) method to fasten the research in crystal growth rather that the classical one-variable-at-a-time (OVAT) studies.

Our conclusions, summarized from a huge collection of statistically robust experimental results, are that the crystal quality is the harder parameter to control compared to other properties of the grown AlN layer. In particular, the final stress state and roughness is relatively easy to tune with process parameters. We found that good crystal quality are related to high tensile stresses in the grown layers but also to certain parameters not embedded into our previous studies. We propose some explanations to the process parameters/layer properties relationship that can be generalized to other materials grown by CVD.

4:50pm **B2-1-11 Fabrication of Boron-doped Diamond Films on Cemented Tungsten Carbide**, ***Kunio Saito***, Japan Coating Center Co., Ltd.,Chiba Institute of Technology, Japan*; A Kawana,* Japan Coating Center Co., Ltd., Japan*; A Suzuki, Y Sakamoto,* Chiba Institute of Technology, Japan

To deposit diamond coating on cemented tungsten carbide is quite difficult. Generally, to reduce reactivity of cobalt which is the binder of cemented tungsten carbide that pretreatment using the acid is carried out. On the other hand, study to improve the adhesion of nanostructured diamond coating is reported, which is to formed borides by plasma enhanced chemical vapor deposition using diborane for reducing reactivity of cobalt. Diborane (B_2H_6) and trimethyl boron {$B(CH_3)_3$} is often used as a boron source. However, it is necessary to control with special equipment because of having poisonous, flammability and explosiveness of these sources.

This study is an attempt to deposit boron-doped diamond directly on cemented tungsten carbide substrates by microwave chemical vapor deposition using trimethyl borate {$B(OCH_3)_3$} as a boron source. Trimethyl borate is liquid which dissolved boric acid(H_3BO_3) in methanol(CH_3OH), and introduce to vacuum chamber as a boron source with bubbling using hydrogen(H_2) as a carrier gas. Cemented tungsten carbide substrate was scratched with diamond powders and cleaned with ultrasonic cleaner before loaded into the vacuum chamber.

Boride was formed on the substrate surface to reduce reactivity of cobalt which is the binder of cemented tungsten carbide with introducing boron source into the vacuum chamber. At this stage, confirming a combination state of the surface product by X-ray photoelectron spectroscopy(XPS), existence of boride was confirmed. Diamond was formed continuously with using reactive gases of methan and hydrogen, after forming borides on the substrate surface. In the Raman spectrum, the peak of diamond due to SP_3

was observed and the presence of diamond was confirmed. As a result of observation the surface with scanning electron microscope(SEM), it was confirmed that diamond which grew up onto substrate surface. And, boron-doped diamond with low electrical resistance approximately 10^{-2}[Ω] was obtained.

It is possible to deposit boron-doped diamond with good adhesion by introducing the bonds with boron and cobalt without pretreatment.

Hard Coatings and Vapor Deposition Technologies
Room California - Session B4-2

Properties and Characterization of Hard Coatings and Surfaces

Moderators: Ulrich May, Robert Bosch GmbH, Diesel Systems, Chau-Chang Chou, National Taiwan Ocean University, Taiwan, Farwah Nahif, eifeler-Vacotec GmbH

2:10pm **B4-2-3 Measurement of Residual Stress on Transition Metal Nitride Hard Coatings by Combining Average X-ray Strain Method and Nanoindentation**, ***Jia-Hong Huang***, *A Wang, G Yu,* National Tsing Hua University, Taiwan **INVITED**

Among the nondestructive techniques for measuring residual stress in thin films, X-ray diffraction (XRD) is one of the well-established techniques, by which the strain tensors and crystal structure can be simultaneously determined. However, using conventional XRD $\sin^2\psi$ and the like methods to measure residual stresses in textured thin films are usually problematic. We previously developed an XRD technique named $\cos^2\alpha\sin^2\psi$ method to solve the problem by using grazing incidence asymmetrical diffraction configuration that effectively increased the irradiation volume from a thin-film specimen, thereby generating higher intensity for high-angle Bragg peaks compared with the conventional Bragg-Brentano geometry. The $\cos^2\alpha\sin^2\psi$ method has been successfully applied on single layer thin films, thin film with interlayer and multiphase oxynitride thin films. Nevertheless, the X-ray residual stress (XRS) is usually deviated from the stress measured by optical curvature method, even up to 30%, which is normally attributed to the use of incorrect elastic constants determined by mechanical methods such as nanoindentation. On the other hand, if X-ray elastic constants (XECs) are adopted, the uncertainty of the measured stress can be within 10%; however, the XECs are not readily available for most hard coatings. In this study, we proposed a method where the average X-ray strain (AXS) was determined using $\cos^2\alpha\sin^2\psi$ XRD technique at several rotational (f) angles, combining with elastic constant measured by nanoindentation (E_{NI}), to improve the accuracy of the measurement of XRS. The major concept was to increase sampling volume by measuring X-ray strain at multiple rotational angles. TiN hard coating on Si (100) substrate was selected as the model system, where the residual stress was determined by laser curvature technique and the accompanying AXS was measured by $\cos^2\alpha\sin^2\psi$ method at several rotational angles. By using AXS and elastic constant measured by nanoindentation (E_{NI}) to calculate X-ray stress, the stress deviation from that by laser curvature method could be substantially reduced even down to 3 % with sufficient sampling points. The results also indicated that AXS could be accurately measured down to a thickness of 350 nm by using lab X-ray source; however, the resolution of AXS was not sufficient to differentiate the strain for a specimen with a thickness less than 160 nm, which was mainly due to insufficient sampling volume. Therefore, AXS may serve as a convenient parameter, when combining with E_{NI},in X-ray stress measurement, by which residual stress of hard coatings comparable to that by laser curvature method can be obtained without using XECs.

2:50pm **B4-2-5 Investigation of the Tribocatalysis Mechanisms involved in the Extraction of Amorphous Carbon Boundary Films from Base Oils**, ***Giovanni Ramirez***, *O Eryilmaz, B Narayanan, Y Liao, G Kamath, S Sankaranarayanan, A Erdemir,* Argonne National Laboratory, USA

Aimed at solving some of the durability and efficiency problems existing in current mechanical systems, we have been studying the interactions between lubricants and solid surfaces and how one can possibly mitigate friction and wear in components with the use of novel environment friendly technologies. As an innovative approach, here we present the mechanisms involved in the extraction of carbon-based tribofilms directly from the hydrocarbon molecules of the base oils with the use of catalytically active nanocomposite coatings, and without the need of antiwear additives [1].

In this work, we present the tribocatalysis phenomena that allow the extraction of carbon-based tribofilms when surfaces are made of nanocomposite thin films/coatings that include a metal catalyst and called catalytically active nanocomposite coatings. Such metal catalysts (i.e., Cu, Ni, Co, etc.) seems to be responsible for lowering the activation energy that is required for first dehydrogenation and then cracking of the hydrocarbon molecules into dimers and trimers that in the end recombine under pressure to form a carbon-based deposit resembling a hydrogenated diamond like carbon film. To study these processes and show the presence of protective carbon tribofilms, not only several tribometers, but also advance surface characterization techniques such like Raman microscopy, TOF-SIMS and transmission electron microscopy were employed to elucidate the fundamental mechanisms involved. Further, detailed MD simulations were performed using classical and ab-initio molecular dynamics to explain the specific steps in the creation of a protective tribofilm that outperforms the more traditional boundary films resulting from ZDDP and other types antiwear additives. We will discuss the effects of having less catalyst on the coating on the formation of the carbon-based tribofilms.

Work supported by the US Department of Energy (DOE), Office of Energy Efficiency and Renewable Energy, Vehicle Technologies and Advanced Manufacturing Offices under contract DE-AC02-6CH11357. Use of the Center for Nanoscale Materials was supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, under contract DE-AC02-06CH11357.

[1] Ali Erdemir, Giovanni Ramirez, Osman L. Eryilmaz, Yifeng Liao, Badri Narayanan, Subramanian Sankaranarayanan. Carbon-based Tribofilms from Lubricating Oils. Nature (536) 67-71 (2016).

3:10pm **B4-2-6 Phase Stability and Strain Evolution in TiZrAlN Coatings During Annealing**, ***Lina Rogström***, *R Pilemalm, N Ghafoor,* Nanostructured Materials, IFM, Linköping University, Sweden*; L Johnson,* Sandvik Coromant, Sweden*; N Schell,* Helmholtz-Zentrum Geesthacht, Germany*; M Odén,* Nanostructured Materials, IFM, Linköping University, Sweden

TiAlN-based coatings are widely studied, and quaternary alloys within this system can further improve the mechanical properties as well as the thermal stability of hard and wear resistant coatings. TiZrAlN is still a relatively unexplored material system, while there are studies showing that addition of Zr to TiAlN can delay the formation of wurtzite AlN in the coating [1]. Theoretical results show that the decomposition route in TiZrAlN coatings is expected to vary depending on chemical composition [2] while the effect of chemical composition on the thermal stability of TiZrAlN coatings remains to be clarified.

Here, we study the phase stability and the strain evolution in TiZrAlN coatings during annealing. TiZrAlN coatings with Zr-contents on the metal sublattice between 24 and 69 at.% were grown by cathodic arc evaporation on polished WC-Co substrates. The coatings have a columnar structure and consist of a solid solution cubic (c) NaCl structure TiZrAlN phase which grows with a strong preferred 200 orientation. In situ wide angle scattering during annealing reveal that the thermal stability of the c-TiZrAlN phase depends on chemical composition. The coating containing 69 at.% Zr on the metal sublattice displays high stability. After 3 h at 1100 °C there is only a very small change in the lattice parameter of the c-TiZrAlN phase indicating that a small change in composition takes place, corresponding to formation of small amounts of other phases, or that point defects are annihilated. The strain in this coating relaxes during annealing above 800 °C. For the coatings containing less Zr, domains enriched in ZrN and TiAlN form during annealing above 600 °C. In the low Zr-content sample the microstructure is anisotropic with Al-rich domains elongated in the in-plane direction while the domains are more equiaxed in the case of higher Zr-content. The decomposition is associated with a large increase in compressive in-plane strain of the c-TiZrAlN phase. For a Zr-content of 48 at.%, the strain relaxes above 950 °C while for the lowest Zr-content the strain remains high throughout the 3 h anneal. The strain in the formed ZrN-rich domains depends on the composition of the coating and is largest for the low Zr-content (24 at.%) sample. The strain evolution is discussed in terms of microstructure and elastic properties.

[1] L. Chen et al., Thin Solid Films 519 (2011) 5503.

[2] H. Lind et al., AIP Advances 4 (12) (2014) 127147.

3:30pm **B4-2-7 Gas Inlet and Input Power Modulated Sputtering Molybdenum Nitride Thin Films**, ***JianYing Xiang***, National United University, Taiwan

The molybdenum nitride films were produced by RF magnetron sputtering with various structural features by the input power and gas flow ratio control. With Ar/N gas flow ratio s from 10/10 to 18/2 and RF input powers from 150 to 300W, the molybdenum nitride films evolved from significant columnar to amorphous structure. The coating deposited at an Ar/N_2 ratio of 16/4 and an input power of 300W showed an intensified Mo_2N microstructure with preferred (111) orientation. In comparison, the crystalline phase of the coating fabricated at an Ar/N_2 ratio of 10/10 and an input power of 150W was suppressed. The thickness, deposition rate and crystallinity of the molybdenum nitride increased with Ar/N_2 ratio and power input. To enhance the protective behavior of the molybdenum nitride coating, the crystalline and amorphous nitride layers were alternately stacked to form a nanolayered film. Hardness, Young's modulus, and tribological characteristics of the molybdenum nitride multilayer films were investigated. The correlation between structural evolution and mechanical behavior was discussed.

3:50pm **B4-2-8 Transition Metal Nitrides Deposition by HiPIMS in DOMS Mode**, ***João Oliveira***, *F Ferreira, R Serra, F Fernandes, A Cavaleiro,* University of Coimbra, Portugal

Transition metal nitrides (TMD) coatings are well known for their unique combination of outstanding mechanical properties (hardness and Young's modulus), high thermal and chemical stability and excellent resistance to wear and corrosion. TMD are commonly used in industry to improve the performance and enhance lifetime of tools and components in a wide range of applications, including automotive, energy, electronic, and machining applications. During the past decade huge investments have been made aiming at further improving their properties and thus reduce the costs due to wear and corrosion. High-power Impulse Magnetron Sputtering (HiPIMS) is a recently developed deposition process that already demonstrated a huge potential for coatings properties improvement. HiPIMS relies on the application of very high target power densities to ionize the sputtered material and thus allows a more effective control of the bombarding species during film growth than in D.C. Magnetron Sputtering (DCMS). In this work the properties of TMD thin films deposited by Deep Oscillations Magnetron Sputtering (DOMS), a variant of HiPIMS, are summarized and compared to their DC MS counterparts. Results obtained in four different coatings systems (CrN, TiN, TaN and TiSiN) are presented and discussed in light of the Ion Energy Distributions of metal and gaseous species impinging on the growing films.

The TMD coatings were deposited using a wide range of deposition conditions leading to very different bombardments regimes. The effect of the peak target power on the films properties was systematically studied. The structure, morphology, surface topography and mechanical properties of the films were characterized and related to the bombarding conditions. It was concluded that HIPIMS-DOMS allows using different sets of energy and incidence angle of the bombarding species as compared to DCMS and, therefore, enables the deposition of thin films with improved properties.

4:10pm **B4-2-9 Advanced HIPIMS Solution for R&D and Process Development**, ***Jason Hrebik***, Kurt J. Lesker Company, USA; *R Bandorf,* Fraunhofer IST, Germany

When HIPIMS was first introduced to the thin film coating industry, it was considered an advanced technique for production applications, which would provide optimal film properties and wear resistance. The HIPIMS supply options were very large scale directly suited to the production industry. However, it was found to have significant limitations in rate, which minimized its acceptance in production applications.

Recently, the introduction of smaller scale supplies triggered an emergence of the technology into the R&D community. This enabled a high rate of enhancements and helped innovate a more efficient capability and process optimization that could be utilized by HIPIMS supplies. This ultimately re-energized the interest and potential of HIPIMS in the thin film coating industry.

One of the solutions to emerge from the crowd was the IMPULSE supply, which brings a unique range of features to the HIPIMS community. The IMPULSE is a 2kW supply that is offered in a single and dual configuration. It features touch panel controllability, the fastest pulse frequency, 200A peak current, and the most competitive pricing in the industry. The supply is slave capable and can be scaled from its 2kW standard configuration by adding additional units. This makes it an excellent option for process development. Test results will be shared that show its unique performance capabilities and compatibility with higher scale power requirements.

4:30pm **B4-2-10 Determining of the Critical Loads of Transition Metal Nitrides on Steels**, ***Aysenur Keles***, Ataturk University Faculty of Engineering, Turkey; *H Cicek,* Erzurum Technical University, Turkey; *O Baran,* Erzincan University, Turkey; *Y Totik, I Efeoglu,* Ataturk University, Turkey

Transition metal nitride coatings are very attractive materials due to their hardness and toughness. On the other hand, adhesion properties of these coatings are generally low because of their brittleness. To overcome this disadvantage, this type of coatings are produced with different coating techniques. In this work, V and Nb doped ternary TiN-based coatings were deposited on M2 and H13 substrates with pulsed-dc closed field unbalanced magnetron sputtering (CFUBMS) system. The films microstructure were examined by SEM. The thicknesses of the films changed from 400 nm to 360 nm. The maximum nano hardnesses were meausred 35 GPa and 26 GPa for M2 and H13 steels, respectively. The critical load values of the coatings were pointed out using scratch tester. For M2 steel; the highest Lc value was obtained 63 N and for H13; the highest Lc value was obtained 47 N. It was cleary seen that pulsed-dc created very dense microstructure and utilized to improve the adhesion of transition metal nitride coatings on the steels.

4:50pm **B4-2-11 Tribocorrosion Behaviour of Nanocomposite TiSiCN Coatings Tested in PBS Solution**, ***Andre Hatem***, Pontifícia Universidade Católica do Paraná, Brazil; *J Lin, R Wei,* Southwest Research Institute, USA; *R Torres, C Laurindo, P Soares,* Pontifícia Universidade Católica do Paraná, Brazil

Recent articles have investigated the tribological performance of nanocomposite TiSiCN coatings mainly because of their high hardness, low friction coefficient and good adhesion to many substrates, especially, when compared to other ternary system coatings (TiSiN, TiCN). These properties are mainly attributed to the microstructure of the nanocomposite TiSiCN coatings which generally consists of TiC_xN_y nanocrystals embedded in an amorphous Si_3N_4 matrix. The proportional between these phases is much related to the silicon content presented in the coating. Higher silicon contents increase the amorphous matrix and hence decrease the nanocrystals size, which to some extent, provide nanocomposite TiSiCN coatings with higher hardness. Despite the nanocomposite TiSiCN coating appears as interesting candidate for severe wear applications, there are few wear studies under corrosive environments. Therefore, the main purpose of this study is evaluate the tribocorrosion performance under phosphate-buffered saline (PBS) solution of nanocomposite TiSiCN coatings with different silicon contents applied on Ti-6Al-4V samples. Plasma enhanced magnetron sputtering (PEMS) of Ti in a gas mixture of Ar, N_2 and silicon precursors, trimethylsilyl (TMS) and hexamethyldisilazane (HMDSN), were utilized to obtain the nanocomposite TiSiCN coatings in this study. The coatings silicon content could be varied by controlling the inlet flow of silicon precursors in the deposition chamber. Reciprocal sliding tribocorrosion tests were conducted under PBS solution on the nanocomposite TiSiCN coatings and compared to a Ti-6Al-4V bare alloy sample. Moreover, microstructure and composition of the coatings were evaluated using scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDS), X-ray diffraction (XRD) and Raman spectroscopy while mechanical properties were studied by scratch and nanoindentation tests. The results of tribocorrosion tests revealed that exists an optimal silicon content range where occur much lower wear rates. The same behaviour was observed to the mechanical properties of the samples in this same silicon content range. In conclusion, the TiSiCN nanocomposite deposited by PEMS emerge as a new generation of quaternary system coatings that promise high wear performance in corrosive environment since their deposition parameters are optimized for a desirable proportion between the nanocrystalline and amorphous phases.

Fundamentals and Technology of Multifunctional Materials and Devices
Room Royal Palm 4-6 - Session C2-3

Thin Films for Active Devices

Moderators: Vanya DarakchievaMarco Cremona, Pontificia Universidade Católica do Rio de Janeiro, Junichi Nomoto, Kochi University of Technology, Japan,

2:30pm **C2-3-4 High Dielectric Constant of Polymer-inorganic Nanocomposites as Gate Dielectrics for Organic Thin Film Transistor Applications**, ***Cheng-Huai Yang***, *Y Yu, C Chiu,* Ming Chi University of Technology, Taiwan

Organic thin film transistors (OTFTs) based on pentacene and hydroxyl-containing polyimide-zirconium dioxide (PI-ZrO_2) hybrid films were fabricated on silicon substrate in which the PI and ZrO_2 were as the semiconductor and the gate dielectrics, respectively. Zirconium butoxide ($Zr(OBu)_4$) was used as the precursor to synthesize nano-sized ZrO_2 colloid through the hydrolysis and condensation reaction in a sol-gel process. Then, PI-ZrO_2 hybrid solution was synthesized from a condensation reaction between hydroxyl-containing ZrO_2 and polyimide, followed by a spin coating to form the PI-ZrO_2 dielectric composites. Cyclic olefin copolymer (COC) was used as a modify layer to enhance the interface property between the semiconductor and the dielectric layer. In addition, PffBT4T-2OD was replaced by pentacene as semiconductor to expect a good performance on device. The thermal, optical, surface, dielectric, and electrical properties of the PI-ZrO_2 dielectric composites were investigated and correlated to ZrO_2 content due to the dispersion and aggregation behaviors of the nanoparticles. The PI-ZrO_2 hybrid dielectrics showed the tunable insulating properties, including high dielectric constants, high capacitances, and low leakage current densities. Besides, the bottom-gate top-contact OTFTs based on the PI-ZrO_2 hybrid dielectrics PZ30% and PZ30%-COC showed the best performance with the near zero threshold voltage and the field-effect mobility (μ) about 1.12 $cm^2V^{-1}s^{-1}$ and 3.25 $cm^2V^{-1}s^{-1}$ and the current on/off ratio (I_{on}/I_{off}) about $1.2x10^4$ and $1.2x10^6$, respectively. Based on the above results, PI-ZrO_2 hybrid dielectrics were synthesized and the OTFTs based on the PI-ZrO2 hybrid dielectrics and pentacene were fabricated successfully. The best performance for OTFTs was obtained when the ZrO2 content in hybrid films was 30%.

2:50pm **C2-3-5 Different Nitridation Condition Influence NBTI in FinFETs**, ***Hsi-Wen Liu***, *T Chang,* National Sun Yat-Sen University, Taiwan

This research uses different Nitridation condition to investigate negative bias instability (NBTI) in p-channel fin field effect transistors (p-FinFETs). We find that low Nitridation temperature device suppress NBTI compare to high Nitridation temperature device. It is because that nitrogen located at Si/SiON interface more at higher temperature. Beside, we compare spike and soak post-Nitridation anneal. We find soak one can suppress NBTI effectively.

3:10pm **C2-3-6 Analysis of Abnormal Transconductance in Body-tied PD SOI n-MOSFETs**, ***Chien-Yu Lin***, *T Chang,* National Sun Yat-sen University, Taiwan

This letter investigates the mechanism of abnormal transconductance (Gm) and abnormal charge pumping current (ICP) in body-tied partially-depleted silicon-on-insulator n-channel metal-oxide-semiconductor field effect transistors. The ICP second hump region increases with channel length, yet is not affected by channel width. The cross-sectional view of the L-gate structure along the width direction demonstrates that a part of the poly gate area near the body contact is covered by a P^+ implant, inducing a parasitic channel under the P^+ poly gate. This parasitic channel leads to the abnormal Gm and ICP hump, and such mechanism is further verified by body floating devices.

3:30pm **C2-3-7 Influence of the Ammonia Hardening on the Properties of Sol-Gel Thin Film Coatings**, ***Christophe Boscher***, *J Avice, H Piombini, X Dieudonné, P Belleville, K Vallé,* CEA, France

Introduction

The Laser Megajoule is one of the most important parts of simulation program of CEA. Its purpose is to create the thermodynamic conditions of a nuclear fusion at the laboratory scale. The LMJ is made of different large aperture components (typically 40X40 cm^2) in order to amplify and transport light and then to concentrate it on a millimetric microtarget.

To minimize the parasit reflexions and to maximize the energy on the target, all the components must be treated with an antireflective thin film coating. This surface treatment is realized thanks to a sol-gel process associated with a liquid phase coating.

2. Colloïdal silica antireflective coating

The sol-gel solution used for the antireflective treatment is a colloidal suspension synthetized by sol-gel route inspired of Stöber method [1]. The synthesis results of the hydrolyze-condensation of tetraethyl orthosilicate in an alcoholic solution. Then, it is deposited on optical components by spin/dip-coating or laminar induction method.

The cohesion between particles and the adherence on the substrate are relatively weak, that ' s why the coating is little adherent mechanically.

To increase the cohesion of these colloïdal thin films, a chemical modification of the nanoparticles is achieved thanks to a post-processing using ammonia vapors, called "ammonia hardening process" [2].

This process permits a modification of the nanocontact chemical bonds from Van Der Walls to Hydrogen & Covalent bonds.

The purpose of this study is to follow these modifications during the ammonia hardening process. We use different characterization techniques as IR spectroscopy or surface tension measurements (chemical changes inside the layer or in the surface), UV/VIS spectroscopy (refractive index or thickness modifications) and an acoustic pico-second method (mechanical changes).

3. Conclusion

The precise knowledge of the ammonia hardening mechanisms has permitted to reduce the duration of the ammonia hardening step. This point is crucial in order to increase the production rate in an industrial process.

4. Bibliography

[1] ***Werner Stöber*, *Arthur Fink*, *Ernst Bohn "controlled growth* of *monodisperse silica spheres***in the***micron size range" journal***of ***colloid***and***interface science*, *volume 26*, *issue 1*, *January 1968*, *pages 62-69* **Growth of Monodisperse Silica Spheres**

[2] Philippe F. Belleville and Herve G. Floc h, "Ammonia hardening of porous silica antireflective coatings", Proc. SPIE 2288, pp25-3, (1994).

3:50pm **C2-3-8 Miniaturized Shape Memory (SMA) Bimorph Actuators with Polymer Layers**, ***Cory Knick***, *G Smith, N Jankowski, C Morris,* US Army Research Laboratory, USA

Shape-memory alloy (SMA) actuators based on nickel-titanium (NiTi, or NITINOL) are promising candidates for miniaturized sensors and actuators in MEMS applications [1]. Thermal processing constraints currently limit monolithic SMA actuator integration for example in soft body micro robotics or onto soft polymer substrates. Other electronic materials can also degrade when exposed to typical NiTi crystallization temperatures in excess of 450 °C. Historically, NiTi crystallization requires sputter or anneal temperatures of 450 °C or more so there is a desire to obtain shape memory effects at lower processing temperatures.

To motivate the mating of polymer and crystallized NiTi SMA layers, we developed and carried out the microfabrication of a simple, yet novel, shape memory (SMA) bimorph actuator, outlined in Figure 1, and based on previous deposition and micromachining processes of NiTi on platinum [2, 3]. By following crystallized 270 nm NiTi SMA with a 1 micron photosensitive polymer layer, we created a bimorph with a large coefficient of thermal expansion (CTE) mismatch (>40 ppm/°C) allowing significant yet predictable curvature upon release. An analytical strain/curvature model [4] predicted the radius of curvature to within 10% as shown in Figure 2, and resulted in a measured radius of curvature down to 50 μm for an actuator that folded flat upon actuation.

The full benefits of combining SMA materials with polymers can only be realized without the constraint of high temperature crystallization coming before polymer deposition. To this end, we carried out experiments to investigate the crystallization of amorphous NiTi using a Novacentrix pulse forge additive manufacturing tool. This tool is used to sinter metal powders on standard polymer substrates, and our goal was to assess whether the as-deposited amorphous NiTi could be crystallized using intense (>10,000 W/cm^2) microsecond bursts of light. We tested experimental stacks of sputtered, amorphous submicron thick films of NiTi on Si and on 1.2 micron films of polyimide. We developed thermal models used to predict transient temperature profiles in the NiTi film/substrate stacks, using differential scanning calorimetry (DSC) scans on substrate-released NiTi films to determine specific heat values. Using these values, models and preliminary experiments using x-ray diffraction analysis indicate that the pulse forge method may be a novel technique to crystallize shape memory materials

while limiting thermal exposure of adjacent polymer layers or other electronic materials.

4:10pm **C2-3-9 Investigating Degradation Behaviors Induced by Hot Carriers in the ESL in Amorphous InGaZnO TFTs with Different Electrode Materials and Structure**, ***Chung-I Yang***, National Chiao Tung University, Taiwan; *T Chang,* National Sun Yat-Sen University, Taiwan

We discuss the indium gallium zinc oxide (InGaZnO) thin film transistor

hot carrier effect, the etching terminating layer contact window type element because

of source pole and drain pole excess electrode leads to electron injection in drain pole

excess electricity and lower channel etch stop layer, and the injected electron will be

confined to the excess electrode position, such electronic injection state gate source

capacitance curves is due to the phenomenon of two-stage uplift. The relationship

between the thermal field emission activation energy and the work function of the

metal materials can be found by the amount of different electrode materials.

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces
Room San Diego - Session E2-1

Mechanical Properties and Adhesion

Moderators: Gerhard Dehm, Max-Planck Institut für Eisenforschung, Etienne Bousser, The University of Manchester, Fan-Bean Wu, National United University, Taiwan

1:50pm **E2-1-2 Cross-sectional Investigation of Microstructure and Mechanical Properties of Graded Ti(N,B) Coatings**, ***Michael Tkadletz***, *N Schalk, C Mitterer, C Hofer, J Keckes,* Montanuniversität Leoben, Austria; *M Deluca,* Materials Center Leoben Forschung GmbH, Austria; *M Pohler, C Czettl,* CERATIZIT Austria GmbH, Austria

Chemical vapor deposited (CVD) TiB_2 coatings are typically grown on a thin TiN base-layer to prevent diffusion of B into the substrate. While CVD TiN coatings exhibit a rather large grain size in the µm range, tensile residual stress and a relatively low hardness, the TiB_2 coatings are characterized by a nanocrystalline microstructure, high compressive residual stress and high hardness. In order to alleviate the resulting sharp transition at the interface of these two layers, an additional Ti(N,B) layer with B content gradually increasing from pure TiN to pure TiB_2 was introduced. Subsequently, the coating was investigated using scanning- as well as transmission electron microscopy, cross–sectional synchrotron X-ray nanodiffraction and cross–sectional dynamic nanoindentation and modulus mapping techniques. A grain size gradually decreasing from the µm to nm range, a significant change of residual stress from 0.5 to -2 GPa and an increase in hardness from ~18 to ~45 GPa with increasing B content could be observed across the coating thickness. With increasing B content, a transition from the face centered cubic to the hexagonal structure was also found. The formed compounds and their three dimensional arrangement was investigated by combinatorial use of Raman and X-ray photoelectron spectroscopy as well as atom probe tomography. The obtained results provide the basis for an evolutionary design of TiN/TiB_2 and Ti(B,N) coatings with optimized B content.

2:10pm **E2-1-3 Nanocrystalline Pt-Au MEMS Electrical Switches**, ***Nicolas Argibay***, *M Dugger, D Adams, C Nordquist, A Grine, M Henry, P Lu,* Sandia National Laboratories, USA

Microelectromechanical systems (MEMS) relays have orders of magnitude higher figure of merit compared to semiconductor devices, along with lower power consumption and insertion loss. Unfortunately, MEMS switches have not penetrated high volume applications partly due to contact adhesion, contamination, high cycle switch life and microstructural evolution leading to performance drift.

Recent work has shown that it is possible to achieve extraordinarily stable nanocrystallinity in some binary metal alloys via solute segregation in the as-deposited state, even at high temperatures. One of these alloys, Pt-Au, may provide solutions to several challenges preventing greater adoption of MEMS switches. As-deposited nanocrystalline Pt grains are stabilized by the presence of Au at grain boundaries, presenting the possibility of reduced creep and relaxation in the electrical contacts and structural elements of a MEMS switch. Sputtered Pt-Au was used to construct MEMS switches, and initial results suggest performance improvements relative to baseline switches made from Au. MEMS switch performance and associated material evolution mechanisms will be discussed.

2:30pm **E2-1-4 Thin Film Metallic Glass: Novel Coating Providing High Toughness and Low Friction**, ***Chia-Chi Yu***, *J Chu,* National Taiwan University of Science and Technology, Taiwan; *Y Shen,* University of New Mexico, USA

The amorphous nature of thin film metallic glasses (TFMGs) provides outstanding mechanical properties, including high strength, large elastic limits, and excellent corrosion and wear resistance. The grain boundary-free structure of TFMGs produces an exceptionally smooth surface and low surface free energy, resulting in high hydrophobicity and a low coefficient of friction.

In this study, magnetron sputtering was used in the deposition of Zr-based TFMG coatings with the aim of enhancing the bending and fatigue properties of bulk metallic glasses (BMGs). A TFMG coating was shown to increase the plastic strain of BMG by 9.2%, without sacrificing its extraordinary strength. This was also shown to increase the fatigue endurance-limit of BMG by ~33%, from 300 MPa for bare BMG to 400 MPa for TFMG-coated BMG. The results of transmission electron microscopy and nanoindentation testing revealed that TFMGs are able to withstand enormous shear strain without fracturing. Used as a coating on syringe needles, the low coefficient of friction of TFMG (~0.05) reduced the insertion forces by ~66% and retraction forces by ~72%, when tested on polyurethane rubber blocks.

2:50pm **E2-1-5 Driving Force for the Texture Transformation of Thin Metal Films**, *E Ellis,* Cornell University, USA; *M Chmielus,* University of Pittsburgh, USA; *S Baker,* Cornell University, USA; *Y Cheng, P Liu,* ***Ming-Tzer Lin***, National Chung Hsing University, Taiwan **INVITED**

The texture transformation has been attributed to a competition between strain energy and interface energy. In FCC materials, the (111) orientation has the lowest interface energy, while the (100) orientation has the lowest biaxial modulus. Thus, at a given strain, the interface energy per unit volume decreases as the inverse of the film thickness, while the strain energy per unit volume is constant with film thickness. However, recent studies have questioned the role of both stresses and interface energies in this texture transformation. Where stresses are known with certainty, they have been shown to be insufficient to produce the texture transition, and the transitions seem to occur in films of similar thickness regardless of the interface conditions. We simulated the driving forces using a first principle density functional theory for the orientation selection mechanisms and investigated the transformation by using a bulge test apparatus to induce different stresses in thin Ag films under identical annealing conditions. *In situ* synchrotron XRD measurements show the change in texture during annealing, and reveal that applied stresses have no effect on the transformation. Stress analysis shows that differences in driving forces for texture transformation due to applied bulge pressure were significant (≈200 kJ/m^3), suggesting that a different, much larger driving force must be responsible. Reduction in defect energy has been proposed as an alternative. However, vacancy and dislocation densities must be exceptionally high to significantly exceed the strain energy and do not provide obvious orientation selection mechanisms. Nanotwins in reported densities are shown to provide greater driving force (≈ 1000 kJ/m^3) and may account for orientation selection. The large difference between the calculated strain and defect energies and the driving force for grain growth (21,100 kJ/m^3) casts doubt on the applicability of a thermodynamic model of texture transformation.

3:30pm **E2-1-7 Strength and Strain Hardening Behavior of Particle Strengthened Coherent Cu/Ni Multilayer Films**, ***Rachel Schoeppner***, *M Polyakov, G Mohanty, J Michler,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

There are many techniques used to increase the strength of a material depending on the application and desired results. Two such techniques include deposition of nanolaminate structures and the addition of hard particles to act as dislocation barriers. Particles have been known to act as barriers to dislocation motion as well as Frank-Read dislocation sources, which both increases the strength and strain-hardening ability of the material. This type of strengthening has traditionally only been applied to bulk alloys and oxide dispersion strengthened materials with no investigations focusing on the combined affect of particles distributed at

the interface of nanoscale multilayer films. Some molecular dynamic simulations focusing on steps and imperfections specifically at the interface of Cu/Nb multilayer films have shown additional strengthening can occur as the step size of the kink increases; however, the presence of these interfacial defects can also result in an initial decrease of the yield strength as they act as dislocation sources, initiating plasticity sooner than in films with pristine interfaces, which is similar to the concept of Frank-Read sources in traditional particle strengthened films. The extent of the interaction of hard W nanoparticles deposited at the usually coherent interface of Cu/Ni multilayer films has been investigated through both nanoindentation and micropillar compression to determine both the strengthening and strain-hardening affect of these particle enforced interfaces. Initial investigations have shown an overall increase in the nanoindentation hardness of these films by a maximum of 1 GPa when compared to CuNi multilayers without particles at the interface. However, as the particle density increases the amount of strengthening is actually shown to decrease in the range of volume fractions investigated here. Further microstructural and mechanical characterizations have also been conducted to more fully explain this phenomenon.

3:50pm **E2-1-8 Indentation Induced Deformation and Damage in Metal-Ceramic Multilayer Coatings***, **Yu-Lin Shen**, R Jamison,* University of New Mexico, USA

Metal-ceramic multilayer composite coatings are an exciting subset of materials with many promising attributes. This presentation highlights our recent studies on mechanical characterization of such coatings using the nanoindentation technique. We focus on aluminum (Al)/silicon carbide (SiC) nanolayers, which serves as a model system for investigating the constraining effect due to the highly mismatched mechanical properties of the constituents. How this structural heterogeneity can affect the indentation behavior is a current a subject of active research. The development of complex deformation patterns underneath the indentation, dictated by the structural heterogeneity, can lead to various forms of local damage. Our studies focus on the employment of numerical finite element modeling to corroborate with experimental observations as well as to extract meaningful constitutive properties. Special attention is given to the analyses of (i) plastic deformation in the metal layers, (ii) cyclic indentation response and composite modulus measurement and (iii) indentation-induced delamination.

4:10pm **E2-1-9 Influence of Various Interlayers on Mechanical Properties of CrAlN Coatings on Tungsten Carbide Substrate***, **HoeKun Kim**, J La, M Song, S Lee, Y Hong,* Korea Aerospace University, Republic of Korea

Among many ternary nitride protective coatings, the CrAlN coatings have been paid much attention to the cutting tool's coating applications due to their excellent properties such as high hardness, low surface roughness, and excellent thermal stability. It was reported that the interlayer with the median hardness to elastic modulus ratio (H/E ratio) between the value of the coating and the substrate improved the wear resistance of the coating. In this work, various interlayers such as CrN, CrZrN, CrN/CrZrSiN were synthesized between the CrAlN coating and the tungsten carbide substrate to improve mechanical properties of the coatings. All the coatings were produced by an unbalanced magnetron sputtering system on the WC-6 wt.% Co substrate, and total thickness was controlled to be 3 μm. The microstructure, hardness and elastic modulus, and friction coefficient were evaluated by field-emission scanning electron microscopy (FE-SEM), nano-indentation, and ball-on-disc type wear tester, respectively. All the coatings were annealed at temperatures from 600 to 1000˚C in furnace for 30 min, and the hardness values were investigated using nano-indentation.

The hardness and elastic modulus of all the CrAlN coatings were not affected significantly by type of the interlayer, and they were measured to be in the ranges of 35.5 to 36.2 GPa and 424.3 to 429.2 GPa, respectively. However, wear test showed that the CrAlN coatings with the CrN and CrN/CrZrN interlayer exhibited improved friction coefficient of 0.34 compared to the CrAlN coating with the CrZrN interlayer (COF 0.41), and the wear rate and width of those coatings showed lower values. These improved wear properties could be attributed to the H/E ratio of the interlayer between the CrAlN coating and the WC substrate. In view of the coating structure, there exists a gradual decrease in the H/E ratio from the CrAlN coating (H/E, 0.089), to the CrZrSiN interlayer (H/E, 0.083) and CrN interlayer (H/E, 0.076), and the WC substrate (H/E, 0.040). The CrZrSiN and CrN interlayers induced a smooth transition of the stress effectively under loading conditions during the wear test, and this led improved wear resistance of the CrAlN coating. During the thermal stability tests, the hardness of the CrAlN coating with the CrN/CrZrSiN coating was maintained up to 1000˚C due to excellent oxidation resistance of the CrZrSiN layer consist of the amorphous SiN phase .

4:30pm **E2-1-10 Numerical Investigation of Damage and Fracture in Hard Nano-coating Layers using Cohesive Zone Modeling***, **Shahed Rezaei**, S Wulfinghoff, S Reese,* RWTH Aachen University, Germany

Coating layers are usually applied on different manufacturing tools in, e.g., plastic extruder in order to increase their lifetime and to improve the surface properties of the final parts. New coating deposition techniques such as high-power impulse magnetron sputtering (HPPMS) can provide more parameters to control the coating mechanical properties, therefore they result in producing coating layers with better performance and perhaps higher damage resistance. In order to be able to compare the effect of different parameters on damage behaviour of the coatings, a cohesive zone (CZ) element model has been applied. The fracture modes are divided into an intergranular fracture inside the coating and delamination between the coating layer and the substrate. The developed numerical model allows predicting the damage initiation and propagation within various types of coating systems in different setups such as nanoindentation. Numerical studies of nanoindentation tests show that the intergranular cohesive tractions, residual stresses, elastic and plastic properties and the grain morphology of the coating layers are the most effective parameters in order to produce stronger coatings.

New Horizons in Coatings and Thin Films
Room Royal Palm 1-3 - Session F2-2

HiPIMS, Pulsed Plasmas and Energetic Deposition

Moderators: Tiberiu Minea, Université Paris-Sud, Tomas Kubart, Uppsala University, Angstrom Laboratory, Sweden

1:50pm **F2-2-2 HPPMS Deposition from Composite Targets: Effect of Two Order of Magnitude Target Power Density Changes on the Composition of Sputtered Cr-Al-C Thin Films***, **Holger Rueß**,* RWTH Aachen University, Germany*; M to Baben,* GTT-Technologies, Germany*; L Shang,* RWTH Aachen University, Germany*; P Polcik, S Kolozsvári,* Plansee Composite Materials GmbH, Germany*; M Hans,* RWTH Aachen University, Germany*; D Primetzhofer,* Uppsala University, Sweden*; J Schneider,* RWTH Aachen University, Germany

Magnetron sputtering techniques are widely used to synthesize a large number of coatings either from elemental, compound or composite targets. Coatings synthesized by direct current magnetron sputtering (DCMS) from the latter two targets often exhibit a considerable compositional deviation from the target composition, in particular, for targets containing constituents with significant mass differences [1,2]. However, for high power pulse magnetron sputtering (HPPMS), where in contrast to DCMS, a large fraction of film forming species is ionized, the magnitude of compositional deviations has not been investigated.

Hence, the effect of target power density on the composition of sputtered thin films from a Cr–Al–Cr_3C_2 composite target, as Cr, Al and C exhibit significant mass differences, was studied by utilizing DCMS (2.3 W/cm²) and HPPMS (162 and 373 W/cm²) at various substrate bias potentials and temperatures. Independent of the applied power density at the target, all Cr–Al–C thin films deposited at floating substrate potential showed no differences in composition. As the target power density was increased and a substrate bias potential was applied, aluminum deficiencies of up to 18.3 at.% were measured. Based on the measured ion currents at the substrate, preferential re-sputtering of aluminum was suggested to cause the dramatic Al depletion. As the substrate temperature was increased with an applied substrate bias potential of -100 V, the Al concentration was reduced by 8.4 at.% compared to the room temperature deposition. This may be rationalized by thermally induced desorption in addition to the afore mentioned re-sputtering effect.

[1] J. Neidhard, S. Mráz, J. M. Schneider, E. Strub, W. Bohne, B. Liedke, W. Möller, C. Mitterer, J. Appl. Phys. 104 (2008) 063304.

[2] S. Mráz, J. Emmerlich, F. Weyand, J. M. Schneider, J. Phys. D: Appl. Phys. 46 (2013) 135501.

2:10pm **F2-2-3 Adherent and Hard DLC Coatings Deposited by HiPIMS in Deep Oscillations Magnetron Sputtering (DOMS) Mode**, ***Fábio Ferreira,*** University of Coimbra, Portugal*; A Aijaz, T Kubart,* Uppsala University, Angstrom Laboratory, Sweden*; A Cavaleiro, J Oliveira,* University of Coimbra, Portugal

Diamond-like carbon coatings (DLC) make up the largest proportion of thin film coating solutions applied in the automotive industry, notably for engine applications, drivetrain components and transmission parts. DLC combine high hardness with low friction coefficient, chemical inertness, high thermal conductivity and high refractive index, making them very attractive for a wide range of other applications. In order to comply with the current trends of rising operating temperatures and lower viscosity oils, component manufacturer are currently seeking to develop a new generation of DLCs coatings, with improved properties. The main limitations of the existing DLC solutions stem from high internal stresses and limited thermal stability. The stresses, often in excess of 10 GPa, limit the maximum achievable thickness of hard H-free DLCs due to adhesion problems. H containing DLC coatings, on the other hand, have lower hardness and are typically restricted to operating temperatures below 350^{o}C. The main objective of this work is to develop a new generation of significantly improved well-adherent and hard DLC coatings, with high sp3/sp2 ratio and good temperature stability. DLC films were deposited by deep oscillation magnetron sputtering (DOMS), a variant of high power impulse magnetron sputtering (HIPIMS). The bombardment energy was controlled by changing the substrate bias. In order to improve the film's adhesion an interlayer was deposited. In this work, the microstructure of the films was characterized using scanning electron microscopy, Raman spectroscopy and X-ray reflectivity. The mechanical properties (Hardness and Young´s modulus) of the films were also characterized.

2:30pm **F2-2-4 Variation of Local Chemical Compositions of (Ti, Al)N Films on Inner Wall of Small Hole deposited by High Power Impulse Magnetron Sputtering**, ***Hidetoshi Komiya,*** *T Shimizu,* Tokyo Metropolitan Univeristy, Japan*; Y Teranishi, K Morikawa, M Yang,* Tokyo Metropolitan Industrial Technology Research Institute, Japan

To enhance the tool life as in industrial scale, thin films with anti-adhesive and high wear toughness are required to deposit uniformly on the three-dimensional complicated shape structure. Focusing on the great possibility of high power impulse magnetron sputtering (HiPIMS), the authors have demonstrated its availability and advantages for the industrial applications [1-3]. For the further improvement of film quality the present study focused on controlling chemical composition of thin film at inner wall of sub-millimeter scale small hole, which is specifically important for the crystal phase and mechanical properties. The small hole structure was realized by clamping the comb-shaped stainless steel plate with two flat silicon wafer substrates. To characterize the films properties at different position of inner wall depth, the several analytical techniques were performed. Surface morphology and cross-sectional microstructure of the films on the inner wall were observed using field emission scanning electron microscopy (FE-SEM). Cross-sectional SEM observation was prepared by focused ion beam (FIB). Additionally, the local chemical composition of the (Ti,Al)N films at each position of inner wall depth was analyzed by energy dispersive X-ray spectroscopy coupled with FE-SEM (SEM-EDX), which can achieve the local elemental analysis at micrometer-scaled area on the inner wall. As results, increasing tendency of atomic composition ratio of Ti and that of N / (Ti+ Al) were shown at deeper position of the inner wall. The role of ionization degree of sputtered species and its transportation and distribution into the small-hole structure are discussed by comparing with the film deposited by conventional dc magnetron sputtering.

References

[1] T.Shimizu, H.Komiya et al., *Surface and Coatings Technology*, 250 (2015) pp.44-51

[2] T.Shimizu et al., *Thin Solid Films*, 581 (2015) pp.39-47

[3] T.Shimizu, H.Komiya et al., *Thin Solid Films*, In Press (http://dx.doi.org/10.1016/j.tsf.2016.09.041)

2:50pm **F2-2-5 A Feasibility Study on the Large-area Graphene Growth by using High Power Impulse Magnetron Sputtering (HIPIMS)**, *C Pandey, M Po, D Liou, M Chen, Y Chen,* ***Ju-Liang He,*** Feng Chia University, Taiwan

High Power Impulse Magnetron Sputtering (HIPIMS), known to produce high density plasmas, is utilized to energize carbon ions from graphite substrate as cathode. for growth of large area graphene.

In this work, we aimed at depositing graphene on Copper and Silicon wafer using HIPIMS at temperatures up to 500^{o}C and substrate bias up to -800V. Vacuum pressures of 0.1 – 0.4 mTorr and deposition times of 5 minutes and 10 seconds were used. At 500^{o}C and the substrate bias set at -800V, a 7-8 layered graphene film on Copper was obtained for a deposition time of 5 seconds. An interesting feature observed using Optical Emission Spectroscopy showed that increasing the peak power increased the presence of Carbon-ion species in the plasma.

Raman spectroscopy and Raman mapping were carried out to analyze the G, D and 2D band information and I_{2D}/I_G ratios for the samples for qualitative analysis of the graphene layers respectively.

The construction of the synthesized graphene was analyzed through TEM micrographs. At zero substrate bias, amorphous carbon film was deposited on the copper substrate whereas when biased at -800V, multiple layers of graphene were deposited with a thickness of 0.33 nm .

This study showed that modifying the substrate temperature and the biasing voltage has a significant effect on the deposition of carbon atoms on the surface of copper or silicon even at low temperature of 500^{o}C as compared to the high temperatures used in CVD techniques.

New Horizons in Coatings and Thin Films
Room Royal Palm 1-3 - Session F5

Additive-manufacturing-based Methods and Surface Engineering

Moderators: Ramana Chintalapalle, University of Texas at El Paso, Sven Ulrich, Karlsruhe Institute of Technology (KIT)

3:30pm **F5-7 3D-Painted Metals and Alloys: A New Approach to Metal and Alloy Advanced Manufacturing**, *A Jakus, S Taylor,* ***Nicholas Geisendorfer,*** *D Dunand, R Shah,* Northwestern University, USA

We present a alternative technology to traditional laser and e-beam based metal and alloy additive manufacturing (AM) approaches that utilizes room-temperature extrusion of particle-based liquid inks comprised of metal oxide powder(s), elastomeric binder, and graded volatility solvents to create self-supporting, complex constructs that can be thermochemically reduced and sintered, resulting in metallic constructs. This particular ink formulation results in 3D-printed green bodies that, although comprised of up to 90 vol.% metal, alloy, and/or metal compound particles, can be bent, rolled, folded, cut, and even fused with other similar materials using the ink as an adhesive. The inks may also be used to rapidly create flexible, conformal films via dip-coating and other non-3D-printing methods. We demonstrate that this process can be applied to a variety of ferrous and non-ferrous primary metal and alloy systems to create objects as small as a single cubic millimeter and as large as many cubic centimeters, comprised of structural features as small as 100 µm. In this manner, nano- and micron-scale oxide powders, which are generally far more economical than their metallic or pre-alloyed powder counterparts, can be utilized to rapidly create large scale, user-defined architectures. Mechanical testing of 3D-printed oxide green bodies reveals that tensile and compressive strengths and moduli depend heavily on the concentration of particles within the construct, as well as the size of the comprising particles. None of the green bodies tested, including those comprised of 90 vol.% particles, catastrophically fail under compressive loads, but rather, plastically deform. Inks comprised of a variety of metals - including but not limited to those of iron, nickel, copper, tungsten - are presented along with inks comprised of mixed oxides corresponding to desired final binary and ternary alloy compositions. Oxide green bodies are thermochemically reduced in pure H_2 atmosphere at elevated temperatures to metals and alloys, which then continue to be sintered in H_2 or inert atmosphere. The resulting metallic constructs, although volumetrically reduced due to sintering and to oxide-to-metal density changes, retain their originally shapes without warping, cracking, or sagging. Metallographic and electron microscopic analyses of the resulting metal and alloy structures reveal near fully dense metallic constructs can be achieved with the majority of the systems tested. Finally, we show how this process can be extended towards creating complex, multi-metal/alloy constructs through co-3D-printing of multiple liquid oxide inks.

3:50pm **F5-8 3D Printing of 2D Materials**, *A Juhl,* Materials and Manufacturing Directorate, Air Force Research Laboratory, USA*; A Stroud,* Institute for Micromanufacturing/Physics Program, Louisiana Tech University, USA*; W Lai,* University of Dayton/Sensors Directorate, Air Force Research Laboratory, USA*; S Kim,* Human Effectiveness Directorate, Air Force Research Laboratory, USA*; N Glavin, R Berry, G Leuty,* Materials and Manufacturing Directorate, Air Force Research Laboratory, USA*; R Naik,* Human Effectiveness Directorate, Air Force Research Laboratory, USA*; M Durstock,* Materials and Manufacturing Directorate, Air Force Research Laboratory, USA*; P DeRosa,* Institute for Micromanufacturing/Physics Program, Louisiana Tech University, USA*; E Heckman,* Sensors Directorate, Air Force Research Laboratory, USA*;* ***Christopher Muratore****,* University of Dayton, USA

Alternative materials and fabrication techniques are necessary to revolutionize the performance of large scale flexible electronics. Direct printing of electro-optical devices is a promising new fabrication approach, especially for integration of emerging two dimensional (2D) materials which have uncommon and useful combinations of properties, such as tunable band gaps, mechanical flexibility and optical transparency. However, challenges in conventional printing of suspended 2D particles and low performance of printed circuits remain. Here we describe a printing technique based on a novel a selective molecular attachment (SMA) approach for integration of 2D and other materials into printed circuits or devices. Peptide molecules have been identified via phage display techniques that adhere selectively to semiconducting few-layer MoS_2 flakes and graphene. These peptides are dissolved in 'ink' and printed on insulating surfaces to print transistors and other devices. The printed substrates are then dipped in suspensions of graphene and MoS_2 and the particles stick only to the peptide printed surfaces. Simulations of the peptide surface interactions reveal the specific amino acids that bind to substrate and particle. For example we observe that for the HLL peptide adsorbed on MoS_2, the phenylalanine ring had the closest binding position of any amino acid. The other ring residue structures, histidine and the two prolines, were also shown to very close to the surface. The n-term, c-term, and arginine residues were seen to migrate away from the surface. This knowledge enables design of peptides for enhanced adhesion and also for sensing of target molecules in vapor or solution phase. It is anticipated that the exotic combinations of properties found in 2D materials will add unique functionality to devices over standard printed materials and architectures. Here we demonstrate the technique and explore the peptide-surface interactions in SMA processes.

4:10pm **F5-9 Direct Laser Deposition of High Entropy Alloy Coatings on High Temperature Alloys***, Daniel Fabijanic, Q Chao,* Deakin University, Australia*; T Jarvis, X Wu,* Monash University, Australia*; P Hodgson,* Deakin University, Australia

High entropy alloys (HEAs) are relatively a new alloy system comprising of a minimum of 5 principle alloy elements at a concentration between 5-35 atomic percent. Contrary to phase rule prediction many HEA compositions form simple solid solutions. HEAs have attractive properties as bulk or coating materials in elevated temperature applications: high resistance to thermal softening, thermally stable microstructure, low inter-diffusion, and high oxidation resistance. Limited studies have explored the formation of HEA coatings on steel substrates by laser surface melting a static layer of pre-alloyed powders. This technique is restricted to horizontal surfaces, limiting practical implementation. To clad complex shapes an appropriate technique is "blown powder" additive manufacturing (Direct laser deposition, DLD) where powder is delivered to a focused laser on a controllable head. The formation of HEA coatings by this technique is unreported in the literature. This work addresses two main research questions; *Can chemically homogenous coatings be manufactured by the DLD of a blend of 5 elemental powders?* and *Can the DLD process parameters be controlled to eliminate the dilution effect of the substrate?*.

$Al_xCoCrFeNi$ (x=0.3, 0.6 and 0.9) HEA coatings of were produced by single-pass DLD on 253MA austenitic steel and Inconel 600 superalloy using a mixture of blended elemental powders. A three-level parametric study was performed on key variables: laser power, scan speed, spot size, powder feed rate, focal offset and hatch distance. Through thickness elemental composition (GDOES) and phase analysis (XRD) was determined. The coating microstructure (SEM, AsB detector), local homogeneity (EDS) and properties (microhardness) were obtained in cross-section. Increasing Al mole fraction from 0.3 to 0.6 and 0.85 resulted in a change in HEA coating crystal structures from FCC, FCC/BCC and BCC. The compositional mixing between the deposited layer and the substrate was quantified using a proposed mixing factor, which was significantly influenced by the deposition variables, chiefly powder feed rate. Homogenous HEA coating compositions were obtained at a relatively higher powder feed rate.

4:30pm **F5-10 In-situ Impedance Spectroscopy Evaluation of Electrolytic Plasma Polishing Process for Stainless Steels***, V Mukaeva, E Parfenov, R Nevyantseva,* Ufa State Aviation Technical University, Russian Federation*; A Matthews,* ***Aleksey Yerokhin****,* University of Manchester, UK

Electrolytic Plasma Polishing (EPPo) is currently attracting increasing attention due its ability to provide excellent surface finish to components manufactured by various methods, including 3D printing parts of stainless steels, Ti, Cu and Ni alloys. The method is based on anodic dissolution of metals combined with sputtering by glow discharge which is developed in the Vapour Gaseous Envelope (VGE) formed at the surface of the working electrode under the conditions of high-voltage electrolysis. However, how these two different material removal mechanisms coexist and interact with each other remains unclear. To elucidate these relationships in-situ impedance spectroscopy studies of the EPPo process of AISI 420 stainless steel have performed. The impedance spectra have been acquired for the treatments carried out at voltages and temperatures ranging from 250 to 350 V and 70 to 90 ^oC respectively. Based on the analysis of impedance spectra, an equivalent circuit was developed, including three kinetic processes with different time constants representing charge transport through the VGE by normal conduction and plasma discharge mechanisms followed by charge transfer across the interface with the metal anode. Physical meanings of the circuit elements have been discussed and dependencies on processing parameters established. These dependencies have been correlated with kinetic characteristics of material removal and quality of surface finish achieved. As a result, optimum conditions for EPPo treatment of AISI 420 stainless steel have been established.

Coatings for Use at High Temperatures
Room Sunrise - Session A2-2

Thermal and Environmental Barrier Coatings

Moderators: Lars-Gunnar Johansson, Chalmers University of Technology, Sweden, Kang Lee, NASA Glenn Research Center, USA

8:00am **A2-2-1 La-Sr-Mn Based Chromium Barrier Coatings for Interconnectors in Pressurized Steam Electrolysis on Exposure to Pure Oxygen and Water Vapor**, ***Vladislav Kolarik***, *M Juez Lorenzo, V Kuchenreuther-Hummel,* Fraunhofer Institute for Chemical Technology ICT, Germany*; M Pötschke, D Schimanke,* Sunfire GmbH, Germany

Power-to-liquids processes converting electric power from renewable energy sources into liquid fuels are of forward-looking interest. For achieving high process efficiency, it is envisaged to run the steam electrolysis under pressures up to 30 bar at temperatures around 850°C. The impact of such severe conditions on the behavior of the interconnector coatings designed to retain evaporating chromium is a crucial issue and needs detailed understanding to ensure a reliable operation.

The commercially available interconnector materials Crofer 22 H, Sanergy HT pre-coated by a thin Co layer and the Mn-free ITM were coated by a La-Sr-Mn based oxidic coating (LSM). The coatings were deposited by thermal spraying and by slurry roll coating. For simulating both opposite extremes of the possible process atmospheres, pure water vapor and pure dry oxygen were selected for the study. The experimentation under a pressure of 30 bar at 850°C was conducted in laboratory test autoclaves from Alloy 602 with exposure times up to 1000 h in water vapor and up to 3000 h in dry oxygen. Post-oxidation analysis was performed by field emission scanning electron microscopy (FE-SEM) with EDX element analysis and XRD.

In water vapor the oxide scales on the interconnector materials with LSM coating are notably thinner than on the uncoated material. However, the coating decomposes with the time to a coarse-grained lanthanum-rich phase in the surface area as well as in vicinity of the oxide scale and to a manganese-rich phase concentrated between them. The thermally sprayed LSM coating is more efficient in oxide scale thickness reduction, probably to its higher density, and it shows a less pronounced decomposition into the two phases.

The effect of reducing the oxide scale thickness on the interconnector alloy is in pure oxygen notable only after 3000 h. The structure of the LSM coating remains homogeneous after exposure to pure oxygen with higher porosity in the case of the slurry roll coating. Chromium is detected in the LSM coating, obviously evaporated from the interconnector alloy. In the case of the slurry roll coated LSM it is equally distributed in the whole coating, whereas with the thermally sprayed LSM a dense Cr-rich phase formed on top, consisting of the semi-conducting $SrCrO_4$.

8:20am **A2-2-2 Investigation of the Adhesion of Glassified Sand/salt Deposits on Thermal Barrier Coatings Exposed to High-temperature Combusted Gas Flows**, ***Michael Walock***, *B Barnett, A Nieto, W Gamble, A Ghoshal, M Murugan,* US Army Research Laboratory, USA*; D Zhu,* National Aeronautics and Space Administration, USA*; J Swab, M Pepi,* US Army Research Laboratory, USA*; R Pegg, C Rowe,* US Navy Naval Air Systems Command, USA*; K Kerner,* US Army Aviation and Missile Research, Development, and Engineering Center, USA

Advanced gas turbines are used in commercial/military aviation, ship propulsion, and industrial power generation. However, degraded environments that contain sand, dust, ash, soot, and/or salt can significantly affect their durability and performance. Specifically, accumulation and infiltration of contaminants, upon melting and subsequent solidification, can significantly reduce the operational life of hot-section components through physical and chemical changes. In this study, standard and advanced thermal barrier coatings (TBCs) were deposited onto engine-relevant substrates, such as Inconel 718 and Rene N5. Prior to molten contaminant exposure, the TBCs are evaluated using non-destructive and destructive techniques, such as scanning acoustic microscopy, scanning electron microscopy, scanning auger electron microscopy, optical microscopy, thermal property testing, erosion testing, and adhesion testing, to elucidate relevant processing-property relationships. After which, the coatings were exposed to sand and salt particle-laden flows (independently and mixed) in a unique hot particulate ingestion rig, under engine-relevant conditions. This environment leads to molten sand/salt particles, enabling the evaluation of melt infiltration and glassy deposit accumulation on TBCs. Post-test evaluations follow the same protocol as the pre-test so as to ascertain the physical and chemical changes that result from sand/salt accumulation and/or infiltration.

8:40am **A2-2-3 Effect of Nanostructure and Composition on the Transient Oxidation Behavior of Nanograined Alloys**, ***Pralav Shetty***, *J Krogstad,* University of Illinois at Urbana-Champaign, USA

Nanograined alloys possess impressive mechanical properties mediated by their high grain boundary density but suffer from poor high temperature stability. To overcome this, alloying has often been used to pin and stabilize the grain boundaries. As the implementation of such alloys in commercial high temperature applications becomes more viable, it is important to understand the effect of grain boundary structure and alloying on their oxidation behavior. In this study, the transient oxidation behavior of far from equilibrium dc magnetron sputtered NiCrAl films has been investigated. Even though the transient oxide forms quickly and makes up a very small volume fraction of the overall scale, it can dictate several key properties like the chemistry, morphology, and growth kinetics. Moreover alloying elements like yttrium (Y) which have a large positive enthalpy of mixing and a higher affinity for oxygen compared to the base element Ni, can have beneficial effects on both the stability and oxidation behavior of the alloy. Through the use of controlled oxidation of free standing sputtered films at 900°C and complimentary scanning transmission electron microscopy elemental analysis, we show an anomalous oxidation behavior compared to previous literature in this system. The columnar sputtered nanostructure seems to enhance the diffusion of preferred species like Cr and Al, to and along the grain boundaries to quickly nucleate a chromia or alumina scale which then proceeds to grow uniformly. Even minute Y additions seems to improve the scale adhesion and density as supported by the oxide growth rate estimated from thermogravimetric analysis. These insights will help in the development of a more complete grain boundary-dominated physics based model of nanograined oxidation and may ultimately influence the way in which oxidation resistant alloys are designed.

9:00am **A2-2-4 CrAlSiYN Coating with AlSiN Intermediate Layers for Enhanced Thermal Stability and Oxidation Resistance at Elevated Temperatures**, *S Liu,* Singapore Institute of Manufacturing Technology, Singapore*; Y Yang,* Data Storage Institute, Singapore*; F Ng,* Singapore Institute of Manufacturing Technology, Singapore*; R Ji,* Data Storage Institute, Singapore*;* ***Xianting Zeng***, Singapore Institute of Manufacturing Technology, Singapore

In this paper, the role of Y and Si doping in the thermal stability and oxidation resistance of CrAlN based coatings are investigated, with the mechanisms of coating oxidation characterized for different temperatures. Y and Si doped CrAlN coatings were deposited in a hybrid HIPIMS and magnetron sputtering disposition system, and their chemical compositions and mechanical properties were studied by EDX and nanoindentation respectively. The as deposited coatings were annealed in Ar and air for 1 hour at a range of temperatures, and the change in coating composition and microstructures were characterized by GIXRD, and cross-sectional FIB/SEM imaging and EDX mapping.

It was found that high level of Y addition is beneficial for the coatings thermal stability, but has a detrimental effect on their oxidation resistance. The enhancement in thermal stability could be attributed to the role of Y in suppressing the diffusional decomposition of CrAlN. However, at the same time, Y doping suppressed the formation of a dense oxide protection layer and facilitated the inward propagation of O_2 due to the low formation of Y_2O_3, giving rise to deteriorated oxidation resistance. In order to achieve concurrent enhancement of coating thermal stability and oxidation resistance, a novel structure of CrAlSiYN coating with AlSiN intermediate layers was developed, which exhibited significant enhancement in both high temperature thermal stability and oxidation resistance, as the presence of AlSiN layers effectively suppressed diffusion processes both within the coating and at its interface with air and the substrate.

9:20am **A2-2-5 Metallic Coatings on Copper for High Heat Flux Application in Rocket Engines**, ***Torben Fiedler***, *J Rösler, M Bäker,* Technische Universität Braunschweig, Germany

The copper wall of regeneratively cooled liquid-fuel rocket combustion-chambers is exposed to high thermomechanical loads. Despite the cooling, surface temperatures of more than 800 °C on the hot-gas side are reached. This results in a high thermal gradient in the copper wall. This gradient leads to thermal stresses which may cause damage of the chamber wall, for example by the so called dog-house effect, where the cooling channels tend to buckle and fracture. To avoid this damage, the temperature in the copper wall can be lowered by applying a thermal barrier coating system. This coating system could also protect the copper surface against oxidation.

Due to the high cooling heat flux in the copper wall, a high thermal gradient and therefore high in-plane stresses as a result of different thermal expansion can be expected. On the hot side of the wall, these stresses are compressive in the heating phase and become tensile after cooling if the compressive stresses relax at high temperatures. To investigate the influence of these loads and to test possible coating systems for the use in rocket engines, laser-cycling experiments were carried out. The laser test facility consists of a 3.3 kW diode laser with a special optics, producing a broad focal point. The laser spot can heat the coating surface up to 1500 °C in less than 0.5 s. The short heating-time leads to a high thermal gradient in the sample, representing the conditions in the rocket combustion-chamber. The temperature is kept constant for a few seconds and the coatings are quenched in water after each laser cycle.

Previously, a coating system consisting of a NiCuCrAl bond-coat and a Ni-superalloy top-coat has been developed. In the laser cycling experiments, three different damage mechanisms were observed:

1. Buckling of the coatings occurs due to the thermal gradient and thus a larger thermal expansion in the hotter coating than in the substrate.

2. Vertical cracks are caused by tensile stresses in the coatings, which form due to relaxation of the compressive stresses at high temperatures after longer heat exposure and subsequent rapid cooling.

3. Coating delamination is caused by the different coefficient of thermal expansion between substrate and bond coat in the roughness profile at the interface.

To gain a better understanding of the damage mechanism and to qualify a coating system for the application in experimental subscale test chambers, finite element simulations were carried out. These simulations may help to identify critical loads in the coatings that may lead to a failure during the laser tests or in the rocket engine and to set up a detailed failure model of the coatings.

9:40am **A2-2-6 Mechanical Properties of ZrO_2-Y_2O_3 Thermal Barrier Coatings by Isothermal Heat Treatment**, ***Byung-Koog Jang,*** National Institute for Materials Science, Japan*; K Yasuda,* Tokyo Institute of Technology, Japan*; K Lee,* Kookmin University, Republic of Korea*; S Kim, Y Oh, H Kim,* Korea Institute of Ceramic Engineering and Technology, Republic of Korea

Thermal barrier coatings (TBCs) have received a large attention because they increase the thermal efficiency of gas turbine engines by increasing the gas turbine inlet temperature and reducing the amount of cooling air required for the hot section components. To optimize TBCs for integration into gas turbines,characterization of the relationship between microstructure and thermal-mechanical properties of the coatings is necessary. The purpose of this work is to investigate the influence of the microstructure as well as porosity on mechanical properties of ZrO_2-4mol%Y_2O_3 (YSZ) coatings deposited by air plasma spray (APS) or EB-PVD (electron beam-physical vapor deposition).The mechanical properties of YSZ coatings were evaluated by three-point bending method and nano indentation. The bending strength, Young's modulus and residual stress of plasma sprayed specimens depend on microstructure as well as coating distance. The hardness & Young's modulus of EB-PVD samples show direct proportion to isothermal heat treatment time during 2~100h at 1200°C.

10:00am **A2-2-7 Estimation Of The Mechanical Properties Of Thermal Barrier Coatings With Porous And Dense Vertically Cracked Microstructures By Modified Small Punch Tests**, ***Pierre Planques,*** Cirimat - Safran Helicopter Engines, France*; V Vidal, P Lours,* Mines Albi, ICA (Institut Clément Ader), France*; V Proton, F Crabos,* Safran Helicopter Engines, France*; J Huez, B Viguier,* CIRIMAT, France

Cyclic oxidation failure of Atmospheric Plasma Sprayed Thermal Barrier Coatings (APS TBCs), commonly used to insulate hot sections in gas turbines, usually results from the spallation of the ceramic top coat. In order to predict such spalling phenomena, understanding the mechanisms for cracks initiation and propagation in thermal barriers is a major issue for engine-makers. Failure of the TBC is strongly related to the thermal and mechanical properties of each component of the multi-materials system (substrate, bond coat and ceramic) but also to the response of the TBC as a whole. The purpose of the work is to assess the mechanical behaviour of thick TBC using both experimental and computer simulation approaches for two TBC microstructures, i.e. standard lamellar, porous and micro-cracked (classically obtained through APS coatings), and Dense Vertically Cracked (DVC).

The experimental characterisation of the mechanical behaviour of the TBCs and their elementary components is addressed using three points bending (3PB) tests and Small Punch Testing (SPT). For this purpose, a modified instrumented non-standard SPT setup has been designed, allowing mechanical testing of the materials in natural air in the temperature range 25°C-1000°C. This allowed measurements of true material properties, like strength and fracture toughness, of both standard and DVC APS TBCs following various isothermal heat treatments at 1100 °C and 1200 °C. Specifically, the bottom deflexion is measured and specimens are not clamped as usual in the standard configuration of SPT, referred to as "Drawing Punch Test". This last point is crucial for brittle fracture behaviour with little or even no plastic deformation.

The evaluation of strength and stress intensity factors is based on Finite Element (FE) calculations in order to determine the material constitutive parameters by minimizing the difference between simulated and experimental small punch force–displacement curves.

10:20am **A2-2-8 Comparison of Damage Evolution in High Purity Nano and a Conventional YSZ Thermal Barrier Coating during Thermal Cycling**, ***Krishna Praveen Jonnalagadda,*** *R Eriksson,* Linköping University, Sweden*; K Yuan,* Beijing General Research Institute of Mining and Metallurgy, China*; X Li,* Siemens Industrial Turbomachinery, Sweden*; X Ji, Y Yu,* Beijing General Research Institute of Mining and Metallurgy, China*; R Peng,* Linköping University, Sweden

Sintering of the top coat at high temperatures is considered to accelerate the damage development in thermal barrier coatings (TBCs) during thermal cycling. To counter sintering and thus enhance the resistance to thermal cyclic fatigue, a nano structured high purity yttria stabilized zirconia (YSZ) has been developed and in this work, its damage evolution with thermal cycling is studied and compared to that of a conventional YSZ coating. The coatings were deposited by atmospheric plasma spraying (APS). The TBC samples were thermally cycled between 100 °C and 1100 °C with a hold time of 1h at 1100 °C. The results showed that the high purity nano YSZ coating exhibited roughly half the cyclic life compared to the conventional YSZ coating. The difference in the life time is explained with the help of analysis of micro cracking observed on cross sections of the thermally cycled TBC samples. Influence of other factors such as fracture toughness and elastic modulus of the top coats were also studied. Furthermore, finite element modelling was used to understand the crack growth paths in both the materials and their contribution to the final failure.

10:40am **A2-2-9 Non-reactively Sputtered Ultra-High Temperature Hf-C and Ta-C Coatings**, *H Lasfargues, T Glechner, C Koller,* TU Wien, Institute of Materials Science and Technology, Austria*; V Paneta, D Primetzhofer,* Uppsala University, Angstrom Laboratory, Sweden*; S Kolozsvári,* Plansee Composite Materials GmbH, Germany*; D Holec,* Montanuniversität Leoben, Austria*;* ***Helmut Riedl****, P Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

Transition metal carbides (TMC) are known for their exceptional thermal stability and mechanical properties, notably governed by the carbon content, degree of crystallinity, and the prevalent vacancies on the non-metallic sublattice. Especially, the binaries Hf-C and Ta-C as well as their ternary mixture Ta-Hf-C are highly attractive due to their ultra-high melting points and their strong tendency to form carbides in the preferred face centered cubic structure. However, when using reactive deposition techniques, the formation of amorphous C-containing phases is often observed.

Therefore, we study in detail the influence of the deposition parameters on the structure and morphology, mechanical properties, as well as thermal stability of non-reactive sputtered Hf-C and Ta-C thin films. The carbon content within the coatings strongly correlates with the target-to-substrate alignment, the deposition temperature, as well as bias voltage applied. For example, in the case of Ta-C maximum values of $TaC_{0.81}$ could be reached applying a $TaC_{0.97}$ target and a substrate temperature of 700 °C combined with a bias potential of -100 V. A further increase could be only achieved through co-sputtering of pure carbon for both systems. Nevertheless, all HfC_y films are single-phase face-centered cubic, whereas the TaC_y films also contain small fractions of the hexagonal Ta_2C phase, which decreases with increasing C contest. The highest hardness and indentation modulus among all coatings studied is obtained for $TaC_{0.78}$ with H = 43.7±0.65 GPa and E = 495.8±8.9 GPa.

Ab initio calculations predict an easy formation of vacancies on the C-sublattice, especially in the Ta-C system, and a temperature driven stabilization of defected structures at high temperatures, with fewer vacancies on the C sublattice for Hf-C than Ta-C. The predicted phase stability is proven up to 2400 °C for both systems by annealing experiments

in vacuum, also with stabilization of the hexagonal fraction after 1625 °C in Ta-C films.

11:00am **A2-2-10 Impact of Substrate Surface Morphology on APS Ceramic Coating Adhesion Measured by Laser Shock Test (LASAT)**, *H Sapardanis, V Guipont, A Koster,* ***Vincent Maurel,*** Mines ParisTech, France

The aim of this study is to analyze different surface morphology of Haynes 188 Co base superalloys before coating. The surface was alternatively grit blasted, grit blasted and oxidized, processed by electro-discharge machining, or processed by shotpeening. Then pure alumina was deposited using conventional air plasma spray. The use of laser shock adhesion test (LASAT) has shown strong differences in the resulting interfacial toughness of the obtained coating [1-2]. Size of delamination was measured by an original use of infra-red thermography, image analysis and final cross-section analysis. Finally, it has been evidenced that LASAT was able to provide a continuous evolution of the size of the delaminated area as a function of the laser flux with a very high level of results reproducibility. Then a ranking of the quality of the interface could be yielded from this methodology. The combination of the LASAT, in-situ measurement of buckling and finite element analysis of residual stresses is finally used to determine interfacial toughness. The experimental measurement of in-plane displacement field and out-of-plane buckling evolution leads to an accurate description of both boundary condition of FEA and yields to a crosscheck analysis of the interfacial toughness between FEA and experiment.

References

[1] Guipont, V., Jeandin, M., Bansard, S., Khor, K. A., Nivard, M., Berthe, L., ... & Boustie, M. (2010). Bond strength determination of hydroxyapatite coatings on Ti-6Al-4V substrates using the LAser Shock Adhesion Test (LASAT). Journal of Biomedical Materials Research Part A, 95(4), 1096-1104.

[2] Sapardanis, H., Maurel, V., Köster, A., Duvinage, S., Borit, F., & Guipont, V. (2016). Influence of macroscopic shear loading on the growth of an interfacial crack initiated from a ceramic blister processed by laser shock. Surface and Coatings Technology, 291, 430-443.

11:20am **A2-2-11 Influence of Pt Concentration on Structure of Aluminized Coatings on a Ni Base Superalloy**, *E Pauletti,* ***AnaSofia D'Oliveira,*** Universidade Federal do Paraná, Brazil

">Aluminum diffusion coatings have been processed by chemical vapor deposition techniques. Particularly, pack cementation is a procedure frequently used to process competitive oxidation resistance coatings on Ni based alloys operating at high temperatures. The superior oxidation resistance is associated with the presence of a NiAl layer that supplies Al to maintain an α - Al_2O_3 continue and adherent film at the surface of coatings. Further enhancements on the performance of alloys are gained when a layer of Pt is deposited on the Ni based alloy before pack aluminization. Under these conditions a (Ni,Pt)Al layer forms to act as an efficient diffusion barrier. To achieve high efficiency it is important to understand role of Pt in aluminized coatings. This work assessed the influence of Pt concentration on the structure of aluminized coatings on a precipitation harden Ni alloy. Electroplating was used to deposit Pt layers with different thicknesses (2, 3 and 7 µm) were on a Ni superalloy NI 183. Subsequently, heat treatment at 900 °C for 90min in argon atmosphere was carry out to promote the stress relief of the electroplated Pt layer and to promote the interdiffusion of Pt and the Ni alloy. Aluminization at 1100ºC for 5 hours used out of the pack cementation procedures avoiding direct contact between samples and the pack mixture. X ray diffraction identified phases at the top surface of coatings and scanning electron microscopy analysis showed that aluminized coatings are composed of two main regions a layer of β – NiAl and a interdiffusion zone (IDZ). The aluminide layer is a hipostoichiometric β – NiAl ordered matrix with Pt in solid solution. Pt concentration in this matrix increases the distortion in the ordered crystal structure of NiAl as confirmed by the displacement of XRD peaks towards higher 2θ. Increasing thickness of Pt electroplated layer causes an increase on the total thickness and alters features within the coating. The higher the Pt content the smoother the Al gradient in coatings and the lower the Kirkendall porosity. These features are a consequence of the impact of Pt on vacancy concentration in the NiAl lattice contributing to a higher atomic mobility in the NiAl layer. The concentration of Al in the IDZ followed the Pt thickness and accounts for a change on the alloy solubility hence microstructure. The thinner 2µm Pt layer induced the formation of a $(Ni,Pt)_3Al$ inspite of the processing conditions. Results showed that for the processing parameters tested, oxidation performance at high temperature is improved with Pt electroplated thickness.

Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B2-2
CVD Coatings and Technologies

Moderators: Michel Pons, University Grenoble Alpes, SIMAP, CNRS, Makoto Kambara, The University of Tokyo

8:00am **B2-2-1 Investigation of Ti-based Hard CVD Coatings on Various Metals Suited as Alternate Binder Phase for WC-Co Cutting Tools**, ***Linus von Fieandt,*** Uppsala University, Angstrom Laboratory, Sweden*; E Lindahl,* Sandvik Coromant R&D Materials and Processes, Sweden*; T Larsson,* SECO Tools, Sweden*; M Boman,* Uppsala University, Angstrom Laboratory, Sweden

Titanium based CVD coatings such as TiN, TiC and Ti(C,N) have been successfully applied as wear resistant coatings on WC-Co cutting tools for almost six decades. Recent research activities for WC based tools aims towards replacement of the Co binder phase, being a suspected carcinogenic. Other metals e.g. Ni and Fe are therefore suggested as possible candidates to replace Co as binder phase.

It is expected that CVD Ti based coatings grown on WC tools with e.g. Fe or Ni as the binder phase will show different nucleation and texture development compared to a conventional WC/Co substrate. The difference in nucleation and initial growth is believed to be attributed to the catalytic properties and reactivity of the binder phase. As such, it is fair to assume that the growth process of the coating needs to be altered in order to facilitate a growth of a controlled morphology and orientation.

Another aspect to be addressed is the coating adhesion. Adhesion is promoted by a low chemical reactivity and a limited diffusion between the binder phase and the coating. Salt like reaction products and brittle intermediate phases are examples of reaction products that can cause poor adhesion.

In this study Ti – based coatings were deposited on various metallic substrates such as; Fe, Ni, Co and Cr using a hot wall CVD equipment. Nucleation, orientation evolution and composition of the deposited layers were investigated. It was found that deposition on pure Ni resulted in a sponge like porous morphology. Deposition on Cr yielded a bimodal morphology with standing platelet crystallites. The coated Fe substrate showed presence of Fe in the deposited coating, which is believed to be caused by substrate corrosion. The conclusions from the experimental results have been supported by thermodynamic calculations.

8:20am **B2-2-2 Hot Filament CVD Diamond Coatings on Cutting Tools for Hard to Machine Materials**, ***Michael Woda,*** *W Puetz, M Frank, B Mesic, W Koelker, C Schiffers, O Lemmer,* CemeCon AG, Germany

Low-pressure thin film CVD diamond synthesis using either microwave or hot filament excitation is a well suited deposition technique for pure sp3 bonded polycrystalline diamond coatings with a large number of various applications on an industrial scale. Most prominent, hot filament CVD diamond coated tools with complex geometries are typically applied at cutting of a certain class of hard to machine materials. Various case studies addressing deposition technology, coating properties and tool performance on some of these materials including graphite, glass-epoxy substances for printed circuit boards (PCB), silicon containing aluminum alloys (with Si larger ≈ 9%), carbon fiber reinforced plastics (CFRP), sintered ceramics or cemented carbides are presented in the scope of this presentation.

8:40am **B2-2-3 Nanocluster Assisted Mesoplasma Epitaxial Bridging**, *R Yamada,* The University of Tokyo, Japan*; S Wu,* Chinese Academy of Sciences, China*;* ***Makoto Kambara,*** The University of Tokyo, Japan

Silicon epitaxial films can be deposited by mesoplasma CVD at rates faster by one order of magnitude than the conventional thermal CVD. In this process, Si source gas is first decomposed completely in the mesoplasma and Si nanoclusters form during rapid condensation as actual deposition precursors just before arriving on the film growth surface [1,2]. Owing to the nanoclusters' unique loosely-bound structure, Si nanoclusters are plausibly deposited on a film with high sticking probability to lead to high deposition rate, while maintaining epitaxial film formation as a result of spontaneous and instantaneous rearrangement of constituent Si atoms upon impingement on substrate. Fast rate epitaxy is also observed covering the SiO_2 mask on Si wafer, suggesting that nanoclusters can also be the growth precursors for lateral epitaxial overgrowth (LEO), i.e. the lateral extension of the epitaxial film. This allow us to anticipate that Si substrate with concave grooves with certain appropriate width could be covered by the epitaxial film that overgrows epitaxially from the adjacent Si region. In this work, we have first employed molecular dynamic (MD) simulation to

evaluate the feasibility of the epitaxial film coverage over the nano-sized trench by the cluster assisted mesoplasma CVD for the potential epitaxial bridging. Secondly, Si epitaxial film depositions were also attempted on the Si wafers with porous surface under the typical epitaxial condition.

In brief, in the MD simulation, Si cluster that forms during rapid condensation of high temperature Si vapors is injected from the top at random position and impinges on the nanosized trench with a 100% sticking. It is seen that the Si clusters form the projecting edge from each trench wall and eventually these edges meet and create continuous film, leaving an open space underneath, as expected generally from the coverage phenomena of the trench with high-sticking species. It is however interesting that the film atomic structure preserves the epitaxial relationship from the side single crystal trench wall, indicating the possibility of epitaxial bridging and thus the feasibility of epitaxy over nothing (EON). In addition, smooth epitaxial films are actually deposited on the Si substrate having porous structure that is created by anodic etching, which could be an experimental evidence of feasibility of nanoclusters assisted fast rate epitaxial bridging.

9:00am **B2-2-4 Low Pressure Chemical Vapor Deposition of hex-BN: Relationship between Gas Phase Chemistry and Coating Microstructure**, *P Carminati,* LCTS-CNRS, France*; T Buffeteau, N Daugey,* ISM-CNRS, France*; G Chollon,* LCTS-CNRS, France*; F Rebillat,* LCTS-University of Bordeaux, France*;* ***Sylvain Jacques,*** LCTS-CNRS, France

In the last few years, BN has become the most promising alternative to pyrocarbon as an interphase material in non-oxide ceramic matrix composites (CMCs) for the next generation of aircraft engine parts. Indeed, the use of BN interphases should improve the mechanical properties and lifetime of SiC-based CMCs under oxidative environment at high temperature. Such BN coatings are often deposited by low pressure chemical vapor deposition (LPCVD) from BCl_3–NH_3 gas system. But in this case, an insufficient degree of crystallization can make the obtained boron nitride too unstable to environment. Furthermore, little is known about the deposition mechanisms and their impact on the BN microstructure.

In the present work, the effects of deposition temperature and total flow rate on the microstructure of BN coatings deposited from BCl_3–NH_3–H_2 gas mixtures at low pressure have been studied. From X-ray diffraction measurements and transmission electron microscopy observations, the coatings appear heterogeneous, i.e. made of a mixture of poorly and highly crystallized domains on a very local scale. The structural homogeneity, as well as the degree of crystallization depends on the deposition chemistry (diluent gas, depletion of gaseous species...). For two given sets of deposition parameters, a comparison with BCl_3–NH_3–Ar system was made and the examined coatings exhibit a higher degree of crystallization and a better structural homogeneity than those deposited with H_2 as the diluent gas.

Ex-situ Fourier transform infrared (FTIR) measurements have been carried out on the residual gas mixture at the outlet of the LPCVD reactor in order to detect the species leading to poorly or highly organized BN. The measurements were coupled with ab initio vibrational mode calculations and they allowed the detection and identification of an effective gaseous precursor for highly crystallized BN ex-BCl_3 deposition. The concentration evolutions of the species into the residual gas mixture were also studied as a function of the deposition temperature and total gas flow rate. The NH_3-free system with hydrogen has also been studied by FTIR and results have shown the formation of $BHCl_2$, even at temperatures lower than BN deposition temperatures. This species seems to be an intermediate molecule that reacts further with NH_3 to also form BN. It is thus suspected of being be the source of poorly crystallized domains into BN coatings deposited from BCl_3–NH_3–H_2 gas mixtures. Finally, assumptions have been put forward to identify the main reaction paths leading to BN.

9:20am **B2-2-5 High-speed Structural Control for Functionalization of Various Oxide Films**, ***Akihiko Ito,*** Yokohama National University, Japan **INVITED**

We have demonstrated that an intense laser field enhances chemical vapor deposition (CVD) process and the developed process achieves not only a **high-speed deposition** but also a **significant orientation growth** in various kinds of ceramic coatings. In addition, the developed coating technology produces **unique nanostructures**, which exhibit outstanding properties. For example, Al_2O_3, TiO_2 and ZrO_2 are traditional engineering ceramics, but they are still highly valued as practical materials. Functionalization of their films with the control of orientation and microstructure is of great interest in both of academic and industrial aspects.

This talk will introduce you to recent topics on high-speed structural control for functionalization of various oxide films with CVD technology, including orientation control of α-Al_2O_3 films, feather-like structures in β-Al_2TiO_5 films, nanodendrite formation in Al_2O_3–ZrO_2 nanocomposite films, superstructure in Ba β-alumina films, high-speed epitaxial growth of transparent CeO_2 thick films, H_2 generation in $NaTaO_3$ photocatalytic films, and development of Yb–Si–O environmental barrier coatings for SiC/SiC composite in a gas turbine engine.

This work was supported in part by KAKENHI, Japan Society for the Promotion of Science, and Cross-ministerial Strategic Innovation Promotion Program (SIP), "Structural Materials for Innovation, SM^4I (Funding agency: JST)".

10:00am **B2-2-7 Protective Coatings Enabled by Atomic Layer Deposition Processing**, ***Christopher Oldham,*** *J Daubert, G Parsons,* NC State University, USA

Thin film materials for corrosion mitigation is an ongoing area of research and development. Recently several groups have explored using atomic layer deposition (ALD) as a process to form highly conformal protective coatings for metal surfaces. ALD offers unique advantages for depositing uniform coatings in high aspect ratio designs. For corrosion protection applications ALD has been used to protect metal surfaces using common metal oxides materials such as alumina and titania. However, for protection in aqueous environments some ALD coatings etch or dissolve. Other issues with poor nucleation on metal surfaces leads to coatings with high porosity that can compromise the underlying metal surface in corrosive environments. In this presentation we will discuss results on protecting copper and other metals with metal oxide and multi-layer structures deposited by ALD. Results from the surface morphology and electrochemical performance will be presented along with a discussion of using ALD coatings to protect metallic surfaces with challenging coating geometries.

10:20am **B2-2-8 Chromium Carbide Growth at Low Temperature by a High Efficient DLI-MOCVD Process in Effluent Recycling Mode**, *A Michau,* ***Francis Maury,*** CIRIMAT, France*; F Schuster,* CEA Saclay, France*; R Boichot, M Pons,* SIMaP, University of Grenoble Alpes, CNRS, France*; E Monsifrot,* DEPHIS, France

For a better control of production cost of manufactured objects that comprise CVD coatings, the improvement of the economic productivity of deposition processes is a challenge. The increasing use of metalorganic precursors is a way to improve the economy of the process because this greatly lowers the deposition temperatures leading to substantial energy savings. When expensive molecular precursors as for precious metals are used the by-products are collected at the exit of the CVD reactor then the leading recyclers and traders develop in parallel complex effluent treatments to refine and reused the collected precursors after removing trace contaminants. This approach is also applied in high volume CVD production facilities. For instance a hydrogen recycle system was proposed for CVD of poly-Si. Also in the growth of Si for solar cells the exhaust gases (H_2, HCl, chlorosilanes) were collected, separated and recycled. Generally these strategies reduce the production cost but they did not act directly on the CVD process.

To develop large-scale CVD processes using expensive reactants direct recycling of precursor become necessary to achieve a high conversion yield. However direct recycling of effluent using metalorganic precursors was not reported because the quality of the layers strongly depends on the metal source and these compounds undergo complex decomposition mechanisms producing many unstable metal-containing by-products.

The bis(arene)M precursors, where M is a transition metal in the oxidation state zero (Cr, Mo, W, V, Nb, Ta) are an important family of CVD precursors for low temperature deposition of carbides, nitrides and even the metal. A greater knowledge of the growth mechanism, a modeling approach and the use of direct liquid injection (DLI) to feed the MOCVD reactor has led us to study the effect of direct recycling of effluents on the quality of chromium carbide coatings using bis(ethylbenzene)chromium(0). The results are compared with those obtained using a fresh solution of precursor. Interestingly, both coatings are amorphous in the temperature range 400-550°C; they exhibit a smooth surface morphology, a dense structure, the same chemical composition (close to Cr_7C_3) and a high hardness (23-29 GPa). The main criteria for the selection of MOCVD precursors enabling a successful direct recycling are discussed. It was demonstrated that direct recycling of effluents for instance in a recycle loop is an efficient route to improve the economy of DLI-MOCVD which makes this process very

competitive for the deposition of this important class of carbide protective materials.

10:40am **B2-2-9 Growth and Characterization of SiO_x Thin Film Deposited by Plasma Enhanced CVD on a Magnesium Alloy**, ***Hyunju Jeong,*** *J Cho,* POSCO (Pohang Iron and Steel Company), Republic of Korea

Magnesium alloys have good properties such as low density and high thermal conductivity, but their applications are still limited due to their poor surface quality and corrosion resistance. Even though many studies have been suggested to characterize their surface properties and protect the surface using a variety of techniques, it is necessary to furthermore undertake investigations in order to apply them into various industrial applications, resulting in the improvement of surface properties.

In some industrial application, it is required to employ coating techniques which fabricate transparent coating layers which also act as barrier coating layer against gas and vapor permeation. Chemical vapor deposition (CVD) is known as one of promising coating techniques to form good quality thin films such as passivation films in various industrial areas. Most of all, low temperature processes have advantages of cost reduction, productivity and substrate stability. It is well known that plasma enhanced chemical vapor deposition (PECVD) is less dependent on substrate temperature than conventional CVD, leading to good quality films at relatively low temperature below 300°C.

In the present work, Si*Ox* films as transparent and passivation layers were fabricated on the surface of a magnesium alloy using a PECVD technique. Particularly, magnesium and magnesium alloys have material properties such as high surface activity and high thermal conductivity. Such characteristics possibly have an influence on growth of films as well as interface of the films and substrates during PECVD. Therefore, we undertook an investigation to characterize growth and characterize the interface of Si*Ox* films and a magnesium alloy. FETEM results displayed thin films grown at the interface of a Si*Ox* film and magnesium alloy at substrate temperature of 50 and 300 °C where the thin films tended to be grown as deposition time. XPS analysis revealed that an outer layer close to Si*Ox* films was mainly composed of SiO2 and $Mg(OH)_2$ whereas an inner layer close to magnesium substrates consisted of $Mg(OH)_2$ and MgO.

The structures on the surface were evaluated using field emission scanning electron microscopy (FESEM). The cross sectional compositions and structures were examined by field emission transmission electron microscopy (FETEM), scanning transmission electron microscopy-energy dispersive spectroscopy (STEM-EDS). The detail compositions at the interface of films and AZ31 magnesium alloy were discussed using X-ray photoelectron spectroscopy (XPS) measurements.

Keywords: thin films; SiO_x; PECVD ; Magnesium alloys

11:00am **B2-2-10 Electrochemical Behavior of Graphene Coatings Deposited on Copper Metal by Electrophoretic Deposition and Chemical Vapor Deposition**, ***Mohsin Ali Raza,*** *A Ali, F Ali Ghuari, A Aslam, K Yaqoob, A Wasay,* University of the Punjab, Pakistan*; M Raffi,* National Institute of Lasers and Optronics, Pakistan

Graphene gains utmost importance for electronics, composites, sensors and biological applications due to its remarkable properties. The attributes such as two dimensional morphology, chemical inertness, high specific surface area and aspect ratio make graphene a promising candidate for anticorrosive coatings. Graphene has ability to retard electrochemical reactions occurring at metal-electrolyte interfaces by acting as a barrier to aggressive ions. This work aims to compare electrochemical performance of graphene coatings deposited on copper metal (Cu) by electrophoretic deposition (EPD) and chemical vapor deposition (CVD) technique. In the CVD process, graphene coatings were deposited on Cu by passing vapors of sodium ethoxide and argon gas (carrier gas) through a quartz tube at a temperature of 900 °C. In the EPD process, graphene was deposited on Cu, made as anode, from a suspension of graphene oxide and water. The EPD deposition process partially reduced graphene oxide and further reduction was achieved by heating coated samples at 200 °C or by treating coatings with hydrazine solution. The coatings were characterized using Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), X-ray diffraction (XRD), atomic force microscopy (AFM) and Raman spectroscopy. FTIR analysis revealed that graphene coatings produced by EPD had more oxygen bearing functional groups compared to coatings deposited by CVD. CVD-based graphene coatings had higher adhesion to the substrate than that of EPD-based coatings. AFM images showed that thickness of coatings increased as a function of deposition time. The electrochemical behavior of coatings was studied using tafel analysis and electrochemical impedance spectroscopy techniques in 3.5% NaCl solution. The CVD-based graphene coatings performed better than that of EPD coatings and reduced corrosion rate of Cu. The CVD coatings remained intact even after aggressive corrosion testings, while EPD based coatings showed some damage. The comparative study of the electrochemical behavior of graphene coatings clearly demonstrates that graphene coatings deposited by CVD process using sodium ethoxide as percursor are superior to coatings deposited by EPD process using graphite oxide as precursor.

11:20am **B2-2-11 Characterization of Coated Silane Compounds on Aisi 304 Stainless Steel Using Plasma-Oxide Vapour as Adhesion**, ***Damilare Baruwa,*** University of Johannesburg, South Africa*; P Oladijo,* Bostwana International University of Science and Technology, Botswana*; J Chinn,* Integrated Surface Technologies, Inc., USA*; N Maledi,* University of the Witwatersrand, South Africa*; E Akinlabi,* University of Johannesburg, South Africa

Quest for safe, low cost and reliable coating has led to the alternative development of various chemical compounds of silane in order to mitigate corrosion process and reduce the risk of carcinogenic compounds that have been previously employed in hexavalent chromium-based coating materials. Silane is a hydrophobic and hydrophilic chemical compound, but with contact angle above 110° is hydrophobic. The present study was conducted to determine the influence of silane coating on AISI 304 stainless steel. In this study, three different saline-based coatings of composition [Tris(Trimethylsiloxy)silyethyl]dimethylchlorosilane (Alkyl); Tridecafloro-1,1,2,2-tetrahydrooctyltrichlorosilane (FOTS) and Henicosyl-1,1,2,2-tetrahydrododecyltricholrosilane (FDDTS) were deposited on 304 stainless steel. The surface of the substrate was grit-blasted by plasma oxide (vapour) adhesion by using nano-composite structures with a hybrid Atomic Layer Deposition (ALD) and Chemical Vapour Deposition (CVD) process. This investigation present results on microstructure (Optical microscopy, SEM/EDX), mechanical test (EMCO Hardness Tester, ultimate tensile strength, yield strength), chemical phase content (XRD), porosity and the electrochemical corrosion behavior of different silanes coating on AISI 304 stainless steel. The results showed that the coating characterization and their corrosion behavior were different to that of AISI 304 stainless steel which was addressed in the study.

Hard Coatings and Vapor Deposition Technologies
Room California - Session B4-3

Properties and Characterization of Hard Coatings and Surfaces

Moderators: Ulrich May, Robert Bosch GmbH, Diesel Systems, Chau-Chang Chou, National Taiwan Ocean University, Taiwan, Farwah Nahif, eifeler-Vacotec GmbH

8:00am **B4-3-1 Aspects of Thermal Stability of TiAlN and ZrAlN**, ***Magnus Odén,*** Linköping University, (IFM), Sweden **INVITED**

Today TiAlN material system is the industrial standard for arc deposited protective coatings of metal cutting inserts. A striking feature of this system is that is possible to produce kinetically stabilized while thermodynamically unstable solid solutions inside its miscibility gap by for example arc deposition. A beneficial segregation at elevated temperatures results in improved mechanical properties while a too high temperature causes a detrimental phase transformation to w-AlN. ZrAlN is a related material system with a larger miscibility gap and consequently a stronger driving force for segregation.

In this presentation I will review our efforts to extend the working envelope to higher temperatures. In particular I will discuss the influence of external parameters such as temperature [1] and pressure [2] on the rate of decomposition, and also means to affect the decomposition rate and route. The latter includes aspects of internal interfaces [3], additional alloying elements [4], and nitrogen vacancies [5].

[1] N. Shulumba et al. Phys Rev. Lett. (2016) & A. Knutsson et al. J. Appl. Phys. (2013).

[2] N. Norrby et al. J. Appl. Phys. (2013) & N. Shulumba et al. Phys Rev B. (2016).

[3] K. Yalamanchili et al. Acta Mater. (2016) & F. Wang et al. Phys. Rev. B. (2016).

[4] H. Lind et al. Appl. Phys. Lett. (2011).

[5] I.C. Schramm et al. Acta Mater. (2016).

8:40am **B4-3-3 Effects of Treatment Temperature and Gas Blow Velocity of IH Nitriding on Microstructure of Titanium Alloy**, ***Shogo Takesue***, Keio University, Japan; *S Kikuchi,* Kobe University, Japan; *H Akebono,* Hiroshima University, Japan; *K Fukazawa,* Netsuren Co., Ltd., Japan; *J Komotori,* Keio University, Japan

We have recently developed a gas-blow induction heating (IH) nitriding system, which is a combination of IH and blowing nitrogen gas onto a specimen in a nitrogen atmosphere. This system is capable of nitriding titanium alloys within a few minites, a process that normally requires tens of hours. We previously reported that the nitriding process caused an increase in the surface hardness and wear resistance, but a degradation of the fatigue properties of the alloys. The latter was attributed to grain coarsening and a phase transformation due to an elevated treatment temperature of 900°C. The aim of the present study was to examine the possibility of suppressing these effects by varying the nitriding temperature. The surface properties were analyzed using an X-ray diffractometer, an optical microscope and a scanning electron microscope. In order to characterize the surface modified layers, the surface roughness and micro-Vickers hardness of the specimens were measured. The results showed that grain coarsening and phase transformations were suppressed when the nitriding process was carried out at a lower treatment temperature of 700°C. A high hardness nitrided layer was formed on the surface of the specimen when the gas blow velocity was increased through the use of a smaller diameter gas blow nozzle. The wear resistance of the nitrided specimen at a low temperature and a high gas blow velocity was better than that of the untreated specimen.

9:00am **B4-3-4 Oblique Angle Deposition of Nanostructured ZrC Thin Film by Reactive Magnetron Sputtering and its Effect on Structure and Mechanical Property**, ***SathishKumar Shanmugam***, *A Sharma, M Gowravaram, S Suwas,* Indian Institute of Science, India

Zirconium carbide films were grown from a Zr target in a mixture gas of Ar/CH_4 on Si (100) substrate by oblique angle reactive magnetron sputtering technique. The influence of glancing angle (α= 0˚ to 75˚) induced anisotropic growth rate of crystallographic planes and the mechanism involving the morphological development of oblique angle deposited zirconium carbide films have been investigated. The crystalline structure and the composition were determined by XRD and XPS, respectively. The changes in morphology, surface roughness in oblique incidence have been further investigated by HRSEM and AFM, respectively. The relative intensity of (111), (200) and (311) X-ray Diffraction peaks of fcc crystal structure vary significantly with deposition angle. The mean crystallite size of the obliquely sputter deposited films was found to be larger than that of the films sputter deposited conventionally. Anisotropic growth rate of crystallographic planes during oblique incidence lead to the evolution of faceted growth in the film with subsequent increase in RMS surface roughness. The hardness and Young's modulus decreased with increase in deposition angle, due to highly porous microstructure. Correlation was drawn between the film's hardness and reduced Young's modulus obtained by nanoindentation with changes in the microstructure.

9:20am **B4-3-5 The Influence of Al Content on Characteristics of CVD-Aluminum Titanium Nitride Films**, ***Kenichi Sato***, *S Tatsuoka, K Yanagisawa, T Ishigaki, K Yamaguchi, S Nishida,* Mitsubishi Materials Corporation, Japan

Recently, Aluminum Titanium Nitride ($Al_xTi_{1-x}N$) films deposited by thermal CVD method using ammonia gas has been paid much attention to because some papers have reported their good results in milling of alloy steels and cast irons. One of the biggest characteristics of these films is the amount of Al. It is higher than that of AlTiN films deposited by PVD method. It is well-known that conventional AlTiN films deposited by PVD method have cubic structure in the range of Al content lower than about x=0.7, while they obtain hexagonal structure in the range of Al content higher than x=0.7. However, CVD-AlTiN films keep cubic structure in Al content higher than 0.7, which prevents their cutting properties from getting worse. The amount of Al is one of the most important factors which determine cutting properties, because it affects mechanical properties such as hardness, adhesion and so on. We have focused on the influence of Al content of AlTiN films deposited by thermal CVD method using ammonia gas on their characteristics such as hardness and microstructure.

In this research, CVD-AlTiN films whose Al content were different from each other were deposited and evaluated. It was clarified that each CVD-AlTiN film deposited in this research had nano-size particles and showed high (100) orientation from observation by Scanning Electron Microscopy and X-ray Diffraction. Also, they have lamellar structure due to change of Al content. From the nano-indentation test, it was found that the hardness increased as the amount of Al increased although AlN film showed low hardness because it has hexagonal structure softer than cubic structure. In addition, the result of micro scratch tests showed there was no detachment of each CVD-AlTiN film loaded up to 30N and this result implied that CVD-AlTiN films have good adhesion to substrate of WC-Co alloys. Finally, some cutting tests of these films and conventional CVD and PVD films were performed and CVD-$Al_{0.8}Ti_{0.2}N$ film showed the best result.

9:40am **B4-3-6 Wear Resistance Capabilities of B-C-W Coatings**, ***Heidrun Klostermann***, *M Friedemann,* Fraunhofer FEP, Germany; *M Ottersbach, D Schraknepper,* Fraunhofer IPT, Germany; *J Poetschke, M Mayer,* Fraunhofer IKTS, Germany; *F Fietzke, O Zywitzki,* Fraunhofer FEP, Germany

The present study deals with the evaluation of B-C-W coatings as potential candidates for wear resistance in the cutting of cemented carbides. Comprising different hard materials like boron carbide B_4C, tungsten carbide WC, tungsten boride WB as well as a certain solubility of tungsten in B_4C, deposition of coatings from this material system seems promising for wear resistant applications. Especially, these coatings can combine high hardness, high resistance to crack formation and crack propagation, good thermal stability and low friction. In search for wear resistant layers that are suitable for the cutting of difficult to cut materials like high temperature alloys or cemented carbides,coatings in the system B-C-W have been synthesized by pulsed magnetron co-sputtering of boron carbide (B_4C) and tungsten (W), where the tungsten content can be varied by adjusting the duration of sputtering pulses. Whereas coatings with low tungsten content of up to 25 at-% exhibit high hardness but are prone to oxidation, increasing tungsten content to 30…65 at-% results in stable coatings. Such coatings have been deposited on special analogy tools as well as on polished reference samples made of ultrafine cemented carbides both.

With the coated tools, analogy machining experiments are conducted on a specially developed orthogonal cutting test bench for tool analysis with an integrated force measurement unit and a high speed video camera. With this setup it is possible to gain relevant process data about the potentials of the newly developed coating systems for cutting of a coarse grain WC-25Co cemented carbide by evaluating the chip formation mechanisms of the workpiece, the cutting forces and the wear behavior of the tools. Conclusions are drawn regarding the relation between coating composition, coating structure and the performance in cutting processes.

10:00am **B4-3-7 Micromechanical Properties and Wear Resistance of Quaternary TiAl(X)N Alloys (X=Nb, Cr or V)**, ***Yu-Hsiang Chen***, *L Rogström,* Nanostructured Materials, IFM, Linköping University, Sweden; *J Roa,* Universitat Politècnica de Catalunya, Spain; *M Johansson-Jõesaar,* SECO Tools, Sweden; *M Anglada,* Universitat Politècnica de Catalunya, Spain; *M Odén,* Nanostructured Materials, IFM, Linköping University, Sweden

Hard coatings consisting of alloys such as TiAlN have been extensively studied and are widely used for high-speed cutting applications due to their superior high temperature properties. The thermal stability can be further improved by designing multi-component alloys via adding a forth element into the TiAlN coating [1]. The mechanical behavior of the coating is essential for improving the tool life in its cutting applications. However, the influence of the forth element on the coating's mechanical and tribological properties has not been fully studied.

In this study, $Ti_{0.33}Al_{0.50}(X)_{0.17}N$ coatings (X=Nb, Cr or V) were deposited by cathodic arc deposition to a thickness of 2-3 µm and analyzed with respect to their mechanical properties at different length scales in order to induce different stress levels to the coating system. All coatings exhibit a solid solution NaCl cubic structure with a columnar microstructure. Nanoindentation results show that TiAl(Nb)N presents the highest hardness among the quaternary alloys. Moreover, micro-scratch tests show similar critical load (~ 60 N) for the first appearance of decohesive coating damage (i.e. spallation of the coating system). However, there is a change in failure mechanism between the coatings, where the Cr and V alloyed coatings fails by recovery spallation, indicating relatively brittle coatings. While TiAl(Nb)N exhibits the most ductile behavior resulting in less damage on the coating surface. With increased scratch load (100 N), the TiAl(Nb)N coating also shows less cracks at the edges of the track. In addition, linearly reciprocating ball-on-flat sliding wear tests were done to investigate the wear resistance of coatings. The quaternary coatings show similar wear rates (~ 1.5×10^{-6} mm^3/Nm), while the reference alloy $Ti_{0.5}Al_{0.5}N$ presents a higher wear rate (4×10^{-6} mm^3/Nm). In summary, the TiAl(Nb)N coatings shows a combination of high hardness and a low wear rate in comparison to the other quaternary and the reference TiAlN coating. The results are discussed in terms of elastic properties, fracture toughness and wear

behavior [2] of the coatings to determine the most promising quaternary coating system for cutting applications.

[1] Holec et al. / J. Appl. Phys. 113, 113510 (2013)

[2] A. Leyland et al. / Wear 246, 1–11 (2000)

10:20am **B4-3-8 High Resolution Lateral Force-displacement Measurements as a Tool for the Determination of Lateral Contact Stiffness and Poisson's Ratio***, Thomas Chudoba,* ASMEC GmbH, Germany

High resolution normal force-displacement measurements are used since more than 30 years for nanoindentation experiments to investigate indentation hardness and modulus perpendicular to the surface. However conditions in an application are often more complex and the understanding of surface or coating failures also requires the consideration of lateral forces. Further the Poisson's ratio, internal stresses or lateral inhomogeneity cannot be extracted from normal measurements alone. The Poisson's ratio of coatings is mostly not known and only an assumption is used to convert the reduced modulus (that is measured by nanoindentation) to the indentation modulus.

Since few years a lateral force unit can be used in combination with nanoindentation technique to measure lateral force-displacement curves also with nanometer resolution. This unit is not only a tool for friction force measurements. An internal actor like in a nanoindentation head allows the application of lateral forces without any requirement of lateral movement between indenter and sample beside a small elastic deformation. The transition between full sticking, the reduction of the contact area due to increasing shear stresses and the begin of sliding can be fully resolved. This transition range between sticking and sliding friction, which is typically connected with a lateral elastic deformation below 100nm, can be used to measure the lateral contact stiffness. The ratio of lateral and normal contact stiffness was used by Lukas et al. in a publication from 2004 [1] to derive the Poisson's ratio for several materials, but the results could not be confirmed by another group.

It will be shown that it is also possible to derive the Poisson's ratio for hard and smooth materials from a fit of the lateral curves in the reversal points when friction coefficient and contact area are accurately known. Finally some prospects will be given for further test options that result from the combination of high resolution normal and lateral force-displacement measurements.

[1] B.N.Lucas, J.C. Hay, W.C. Oliver, Using multidimensional contact mechanics experiments to measure Poisson's ratio, J. Mat. Res. 19 (2004) 58-65

10:40am **B4-3-9 Influence of a-Si:H Interlayer on the Adherence of a-C:H Coatings Deposited on Different Metallic Surfaces***, G Capote,* National University of Colombia, Colombia*; D Lugo,* Institute for Space Research, Brazil*; J Gutiérrez,* National University of Colombia, Colombia*; **VladimirJesus Trava-Airoldi,*** Institute for Space Research, Brazil

Amorphous hydrogenated carbon (a-C:H) films have been used as protective coatings in many applications due to their attractive properties. These hard coatings have relatively low adherence to metallic surfaces, caused by their high total compressive stress. In order to overcome this low adhesion, a thin amorphous hydrogenated silicon (a-Si:H) interlayer was used as an interface.

The influence of a-Si:H interlayer on the adherence of a-C:H coatings deposited on different metallic surfaces is presented in this investigation. Six metallic materials widely used in industry were used as substrates: (1) AISI M2 molybdenum high-speed tool steel; (2) AISI **D2 tool steel; (3)** AISI 304 stainless steel; (4) Nickel-based alloy INCONEL 718; (5) Nitinol alloy; and (6) Titanium alloy Ti6Al4V. The interlayers and the coatings were deposited employing an asymmetrical bipolar pulsed-DC PECVD system with an active screen. This active screen functioned as an additional cathode and allowed depositing the films at very low pressure in an almost collision-less regime with high plasma density. Silane gas was used as a precursor for interlayer depositions, while the acetylene gas was employed as a precursor for a-C:H film depositions. The interlayers were synthetized varying the applied negative pulse amplitude from -0.8 kV to -10 kV, keeping their thickness constant at 250 nm.

The adhesion of the a-C:H coatings was evaluated using the critical load of failure determined by a classical scratch test. Raman spectroscopy was used to analyze the films' atomic arrangements and for the hydrogen content calculation. The total compressive stress was determined through the measurement of the substrate curvature before and after the film deposition with a stylus profilometer, while nanoindentation experiments allowed determining the films' hardness and elastic modulus. The friction coefficients and the wear rates were measured using a tribometer in unlubricated sliding friction experiments, while the corrosion resistance was evaluated via electrochemical potentiodynamic polarization techniques.

The results showed high values of critical loads, suggesting a high degree of adherence of the a-C:H coatings to all metallic surfaces. The highest critical load values (≥ 25 N) resulted when the a-Si:H interlayers were deposited using the highest negative voltage (from -6 kV to -10 kV). The best adhesion was obtained for the Nitinol alloy surfaces. A combination of a modified pulsed-DC PECVD system with an active screen and a-Si:H interlayer allowed depositing hard, adherent, low-stress, high wear, and corrosion-resistant a-C:H coatings on different metallic surfaces.

11:00am **B4-3-10 Reactive Magnetron Sputtering of Transition Metal Nitrides for Electronic and Opto-Electronic Applications***, **Amber Reed,*** Air Force Research Laboratory, USA*; H Smith,* University of Dayton and Air Force Research Laboratory, USA*; M McConney, D Look, D Abeysinghe, V Vasilyev, J Cetnar, B Howe,* Air Force Research Laboratory, USA

With their inherent high temperature stability, hardness, abrasion resistance, and potential complimentary metal-oxides semiconductor process compatibility, transition metal nitrides are a promising material system for next generation electronic and opto-electronic devices. Two materials of specific interest are titanium nitride (TiN) and scandium nitride (ScN). Due to its higher thermo-mechanical robustness and lower losses compared to gold, titanium nitride (TiN) is an ideal material for plasmonic applications, while ScN has integration potential into gallium nitride - based devices due to its close lattice matching with GaN (< 1% lattice mismatch), high carrier concentrations (up to 10^{21} cm^{-3}) and low resistivity (<10^{-4} Ω cm^{-2}). The crystalline quality of these materials greatly affects their performance with low defect single crystals having higher figures of merit for both applications.

In this work, we demonstrate the synthesis of high quality epitaxial TiN and ScN films deposited on (001)-oriented magnesium oxide (MgO) and (0001)-oriented sapphire single crystal substrates using a newly built up controllably unbalanced reactive magnetron sputter epitaxy tool at AFRL. We investigate the role of deposition power, nitrogen gas fraction and ion flux impingement on crystallinity (i.e. degree of orientation, lattice constant and strain) and subsequently the films' optical and electronic transport properties. Films are characterized using x-ray diffraction (XRD), atomic force microscopy, transmission electron microscopy (TEM), Hall measurements and ellipsometry. Films are remarkably smooth (~100pm RMS roughness) and indicate step flow growth with little or no domain boundaries. XRD and TEM further demonstrate the exceptional film quality of epitaxial films on both MgO and sapphire substrates. Hall measurements of the TiN reveal mobilities (μ_H) > 20 $cm^2/(V*s)$, carrier concentrations (N) >10^{23} cm^{-3}, resistivities (ρ) < 14 Ω-cm and metallic behavior. The crystallinity of the ScN films is strongly dependent on sputtering power; the highest quality films are obtained at 50 W. The electrical transport properties of the ScN are strongly affected by crystalline quality and film orientation. Films with a (001)-orientation have μ up to 85 $cm^2/(V*s)$ while for the (111)-oriented ScN μ< 10 $cm^2/(V*s)$.

11:20am **B4-3-11 Comparative Investigation of Zr-B-(N), Zr-Si-B-(N), and Zr-Al-Si-B-(N) Hard Coatings***, **Philipp Kiryukhantsev-Korneev,*** *M Lemesheva, I Yatsyuk, D Shtansky, E Levashov,* National University of Science and Technology "MISiS", Russian Federation

ZrB_2-based coatings demonstrate relatively high hardness and wear resistance, low friction coefficient but have low working temperature limited by 700-800^{0}C. It's well known that oxidation resistance of the boride coatings can be enhanced by Si and Al alloying. The goal of this work is a complex investigation of the Zr-B-(N), Zr-Si-B-(N), and Zr-Al-Si-B-(N) coatings, including estimation of high-temperature tribological characteristics, thermal stability, oxidation resistance, and diffusion barrier properties.

The ZrB_2, ZrSiB, and ZrAlSiB cathodes produced by self-propagation high-temperature synthesis technology were subjected to magnetron sputtering either in a pure Ar and N_2 atmosphere, or in a gaseous mixture of Ar+15%N2. Molybdenum, quartz, alumina, NiCrAlW and WC-Co alloys were used as substrate materials. To evaluate the high-temperature oxidation resistance the coatings were annealed in air atmosphere at various temperatures range from 500 till 1500^{0}C. The structure of as-deposited and heat-treated coatings was studied by means of X-ray diffraction, scanning and transmission electron microscopy, glow discharge optical emission spectroscopy, Raman and FTIR spectroscopy. The mechanical properties of the coatings were measured by nanoindentation and scratch-testing. The

tribological properties were evaluated using impact-tester and high-temperature ball-on-disc tribometer. Optical and electrical properties of coatings were also examined.

Results obtained show that Zr-Si-B-(N) and Zr-Al-Si-B-(N) coatings deposited at low nitrogen partial pressure consist of nanocrystallites of hexagonal ZrB_2-phase, 1-3 nm in size (3-5 times smaller compared to undoped coating) and amorphous regions. N-rich coatings exhibit fully amorphous structure. The maximum hardness 26 GPa, Young's modulus 260 GPa, and elastic recovery 60% were determined for Zr-Si-B-(N) coatings deposited in Ar-15%N2. The addition of nitrogen significantly increased wear resistance in sliding and impact conditions. Maximal oxidation resistance (Tox>1400°C) was achieved for low-nitrogen Zr-Si-B-(N) coatings. High protective properties of Zr-Si-B-(N) coatings are due to formation of dense SiO_2 top-layer reinforced with ZrO_2 nanoparticles which impedes penetration of oxygen into the depth of coating. The mechanical properties and oxidation resistance of Zr-B-(N) and Zr-Al-Si-B-(N) coatings were markedly lower compared to Zr-Si-B-(N) deposited at the same nitrogen partial pressure. Combination of relatively high hardness, good tribological properties, and high oxidation resistance makes Zr-Si-B-(N) coatings promising candidates for protective purposes to be used in high-temperature applications.

11:40am **B4-3-12 Multiphysics Modelling and Experimental Investigation on the Characteristics of Laser Deposited Al-Sn-Si Coatings on Ti6Al4V Alloy**, ***Olawale Fatoba,*** University of Johannesburg, South Africa*; A Popoola,* Tshwane University of Technology, South Africa*; E Akinlabi,* University of Johannesburg, South Africa

Corrosion and wear phenomenon has been responsible for the gradual deterioration of components in industrial plants. This deterioration of components results in loss of plant efficiency, total shutdown and aggressive damage in a number of industries. Hence, surface modification and coating technique with enhanced surface properties is desirable. The investigation of Al-Sn-Si coatings by laser deposition technique is aimed at enhancing the properties of Al-Sn-Si coatings on Ti6Al4V alloy. A 3 kW continuous wave ytterbium laser system (YLS) attached to a KUKA robot which controls the movement of the alloying process was utilized for the fabrication of the coatings at optimum laser parameters. The fabricated coatings were investigated for its hardness, corrosion and tribological properties. The corrosion behaviour was investigated in 1M H_2SO_4 and 3.65wt.% NaCl solutions at 28°C via Eletrcochemical Impedance Spectroscopy (EIS) and Potentiodynamic Polarization techniques. The optical microscope (OM), field emission scanning electron microscope equipped with energy dispersive spectroscopy (SEM/EDS) were used to study the morphology of the fabricated coatings and X-ray diffractometer (XRD) for the identification of the phases present in the coatings . The improved hardness and wear resistance performance were attributed to hard intermetallic compounds like Ti_3Al, Ti_6Sn_5 and Sn_3Ti_5. The coatings were free of cracks and pores with homogeneous and refined microstructures. The enhanced anti-corrosion performance was also attributed to monolithic Ti_5Si_3 phases formed. The experimental results correspond with COMSOL multphyics model used in this research.

Keywords: Corrosion rate; wear; Hardness; Al-Sn-Si coatings; multi-physics modeling, temperature fields.

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces

Room San Diego - Session E2-2

Mechanical Properties and Adhesion

Moderators: Gerhard Dehm, Max-Planck Institut für Eisenforschung, Etienne Bousser, The University of Manchester, Fan-Bean Wu, National United University, Taiwan

8:00am **E2-2-1 Study of Bauschinger Effect in Ni Thin Metallic Films Submitted to Cyclic Deformation**, ***Pierre-Olivier Renault,*** *W He, P Godard, E Le Bourhis, P Goudeau,* Universite de Poitiers, France

The lifetime of flexible electronic devices is strongly dependent on their mechanical performance as they are submitted to complex thermo-mechanical cyclic loadings during service. As an elementary substructure inside such devices, metallic thin films are often supported by a polymer substrate.

A substantial amount of experimental work has shown that the plastic response of a thin metal film can be very different from that of its bulk counterpart. The yield stress, flow stress and hardening rate of thin films depend on film thickness. During cyclic deformation of a material, the plastic deformation in one direction can affect the plastic response in reverse direction; one consequence is the decrease of the yield strength of a metal when the direction of strain is changed, i.e. a reduced elastic limit at reversal straining. Such Bauschinger effects have been reported on different metallic thin films in the last ten years.

In this communication, an experimental method using uniaxial tensile testing is used to study the Bauschinger effect in thin metal films deposited on pre-stretched polyimide substrate. Thanks to our new pre-stretch setup based on previous work [1], the metallic thin films can be deformed alternatively from tension to compression within a strain domain of a few % (depending on the elastic range of the polymer substrate). The elastic intra-granular strain of polycrystalline thin films and true strain of substrates are measured in situ during tensile-compressive loading by X-ray diffraction (XRD) and digital image correlation (DIC) techniques. A complete strain transfer through the interface is observed in the elasto-plastic regime as the interface is strong enough thanks to the thin film elaboration PVD technique (namely ion beam sputtering) [2]. From lattice strain-true strain curves, the mechanical response of thin film/substrate set is analyzed in view of the complete loading history.

[1] Renault P.-O., Faurie D., Le Bourhis E., Geandier G., Drouet M., Thiaudiere D., Goudeau P., "Deposition of ultra-thin gold film on in situ loaded polymeric substrate for compression tests", Materials Letters **73**, 99-102 (2012).

[2] Geandier G., Renault P.-O., Le Bourhis E., Goudeau Ph., Faurie D., Le Bourlot C., Djemia Ph., Castelnau O., Cherif S. M., Elastic-strain distribution in metallic film-polymer substrate composites, Applied Physics Letters 96, 041905 (2010).

8:20am **E2-2-2 Mo-Re Thin Films for Flexible Display Applications**, *F Hauser, T Jörg,* Montanuniversität Leoben, Austria*; M Cordill,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria*; R Franz,* Montanuniversität Leoben, Austria*; H Köstenbauer, J Winkler,* Plansee SE, Austria*;* ***Christian Mitterer,*** Montanuniversität Leoben, Austria

Sputtered Mo films are nowadays widely used as thin films in flat panel display applications, e.g., for gate and source/drain electrodes or signal and data bus-lines. However, due to their brittleness, usability in future flexible displays is limited. In order to overcome this disadvantage, a strategy to improve the ductility of brittle Mo thin films by alloying with Re is explored within this work. A series of Mo-Re thin films with 50 nm thickness were grown on 50 µm thick polyimide substrates by magnetron co-sputter deposition from pure Mo and Re targets. Up to ~25 at.% Re, a solid solution with the body-centered cubic structure of Mo was obtained. In-situ characterization methods were applied to determine the electro-mechanical behavior of the films during deformation. Uniaxial tensile tests were performed under the light microscope to directly observe the fragmentation process and to determine the crack onset strain. In addition, the electro-mechanical response was evaluated by measuring the change in the electrical resistance during straining. After tensile straining, pure Mo thin films exhibited straight through-thickness cracks, which are usually observed for brittle films, while the Mo-Re films showed a wavy crack path, indicating a more ductile behavior. The addition of Re also has a significant effect on the electro-mechanical response of films, where the rise of the resistance indicated a crack onset strain three times higher than for pure Mo. In summary, alloying of Mo thin films with Re is a promising strategy to improve their ductility, which in turn can enable their utilization in flexible displays.

8:40am **E2-2-3 Rate Sensitive and Creep Behavior of Thin Metallic and Oxide Films: on Chip Testing and Activation Volume Analysis**, ***Thomas Pardoen,*** *G Lemoine, H Idrissi,* Université Catholique de Louvain, Belgium*; D Schryvers,* University of Antwerpen, Belgium*; M Ghidelli,* Université Catholique de Louvain, Belgium, Italy*; M Coulombier, R Vayrette, L Delannay,* Université Catholique de Louvain, Belgium*; S Gravier,* Grenoble INP, France*; J Raskin,* Université Catholique de Louvain, Belgium **INVITED**

Creep and viscoplastic deformation mechanisms are generally amplified in thin films compared to bulk systems due to various factors related to the dominance of the free surfaces and/or to the abundance of internal defects and interfaces. A series of experimental investigations on freestanding thin metallic, metallic glass and oxides films using an on chip uniaxial test method will be reviewed, focusing on the creep/relaxation behavior. The generic approach to tackle with thermally activated mechanisms through the activation volume mechanics framework is applied to rationalize the measurements. These measurements are supplemented by in or ex situ transmission electron microscopy analysis and micromechanical models to

unravel the origin of the dominant deformation mechanisms in connection with the microstructure. The commonalities and specificities among these systems will be discussed. An important common characteristic is the improved ductility associated to a enhanced rate sensitivity.

9:20am **E2-2-5 Intrinsic Stresses - New Methods to Evaluate Them Using Enhancing Indentation Methods and New Models to Optimize Them**, ***Nick Bierwisch***, *N Schwarzer,* SIO, Germany

In many d eposition processes intrinsic (or residual) stresses can't be avoided during the coating creation. Mostly because of bias or high deposition temperatures and the mismatch in the coefficients of thermal expansion for the various materials. The intrinsic stresses can have a big influence on the material behavior in contact situations.

In one way they can help fighting against your critical external loads and reducing the created stresses. On the other way they can also weaken the material compound when producing to much stresses in a weaker part of the system. Both sides can also have an effect on the adhesion strength between the different coatings. So gaining knowledge about these intrinsic stresses could help a lot in the field of modeling or simulating your worst case application scenarios.

This talk will show 2 new methods to evaluate the intrinsic stresses using extended indentation measurements and new mathematical models. One method applies a mixed load indentation by adding a lateral load component to the applied normal load. The other new measurement uses a reference probe with known intrinsic stresses. With this new measurement methods and new mathematical models the intrinsic stresses within your material can be evaluated.

The second part of the talk will focus on a new model, which allows you to optimize the intrinsic stress distribution to increase the performance in a given worst case application. Nowadays more and more production processes allow to steer the intrinsic stresses during the coating deposition process. This allows a new degree of freedom in the development process and can speedup the development. You can save a lot time because you don't need to search for new materials which also can improve the performance. So knowing how to build up the intrinsic stresses before the deposition process will speedup the development and optimization process of your new material compound a lot. You can save a lot of prototypes and therefore much development time and costs. This work is part of the EU project IStress [1] and within this project this model was implemented into the software package FilmDoctor [2]. It allows you to define your later application and the software will find an intrinsic stress distribution within your coatings which will decrease the resulting stresses in your worst case contact in your later application.

References:

[1] www.stm.uniroma3.it/iSTRESS

[2] [http://www.siomec.de/FilmDoctor]

9:40am **E2-2-6 Investigation of Buckling Driven Delamination of DLC Coatings for Evaluation of Adhesion Strength**, ***Richard Braak***, *U May, L Onuseit, G Repphun,* Robert Bosch GmbH, Diesel Systems, Germany*; M Guenther, J Emmerlich,* Robert Bosch GmbH, Germany*; C Schmid, K Durst,* Physical Metallurgy, TU Darmstadt, Germany

Diamond like carbon coatings (DLC) are widely used as wear-resistant coatings, e.g. in the automotive industry for Diesel injection systems. Their exceptional properties, as high hardness and high modulus are the result of the ion bombardment during the plasma coating process. In addition the thin films sustain substantial residual compressive stresses which can be a problem with respect to the adhesion: The in-plane compressive stress can lead to buckling driven delamination. It occurs in different shapes: Circular, straight-sided or worm-like blisters or even big-area delamination. The type of appearance is closely linked to the mode-dependent fracture toughness of the interface.

In the current work, ta-C coatings (tetragonal amorphous carbon) with different kinds of adhesion layer design are investigated. As the mechanical properties of the whole coating system do have influence on the buckling behavior, depth profiles of the layered structures are taken via nanoindentation on a small angle cross section (SACS). The intrinsic stresses are determined with two separate methods: The curvature test and via a focused ion beam (FIB) in combination with digital image correlation (DIC).

In the first part of the paper commonly used indentation and nanoscratch tests are discussed, the latter with constant and increasing load. The created damages are investigated thoroughly via SEM-imaging (Scanning Electron Microscopy). The findings lead to a novel adhesion test which is presented in the second part. A ranking of the adhesion strength of the different adhesion systems can be done with the suggested method. The ranking is used to show the range of application of the common scratch and indentation tests.

10:00am **E2-2-7 Characterization of Thin Films by Nanoindentation: Avoiding Mistakes during the Measurement and Data Analysis**, ***Esteban Broitman***, Engineering Consulting, Sweden

Nowadays, nanoindentation has become a routinely technique for the mechanical characterization of thin films and small-scale volumes. Thanks to the development of friendly analysis software and advances in high sensitive instrumentation, it feels like the measurement and calculation of hardness and elastic modulus can be done automatically by just *"the pushing of one button."* However, the consequences of the easy procedures have led many researchers to publish erroneous data [1].

In this paper, common mistakes in the measurement and data analysis during the nanoindentation of thin films will be critically reviewed, and the possible ways to correct them will be discussed: 1) the misuse of the 10%-thickness *"rule of tomb"* to avoid the effect of the substrates; 2) the lack of thermal drift correction in long-term duration experiments; 3) the wrong data conversion from Vickers microindentation to Berkovich nanoindentation; 4) the ignorance of pile-up effects; 5) the misinterpretation of indentation size effects at low penetrations; 6) the wrong determination of tip area functions; 7) the lack of load frame compliance correction during the characterization of very hard coatings; 8) the confusion of thermal drift with creep and viscoelastic effects; 9) the misinterpretation of pop-ins and pop-outs; 10) the preconceptions about a direct relationship between hardness and tip penetration; 11) the preconceptions about a direct relationship between elastic modulus and hardness; 12) the lack of considering surface roughness influence; 13) the possible change of surface mechanical properties during sample preparation; 14) the use of dirty or damaged tips; 15) the natural differences in the results when using spherical, cube-corner, or Berkovich indenters; 16) ignoring the influence of indentation loading rate; 17) the interpretation of elastic recovery in very elastic or very plastic films; 18) the confusion of load-penetration nanoindentation curves with stress-strain compression diagrams; 19) the difference in the results between load-controlled and depth-controlled indentations; and 20) the lack of knowledge about possible work/strain hardening effects or phase transformations during indentation.

The origins of the aforementioned mistakes will be elucidated from the lack of understanding on contacts mechanics theory, the limits and validation of Oliver and Pharr's method, and preconceptions transmitted from generation to generation of nanoindentater users. At the whole, it will be stressed that it is not enough to know *"how to push the button"* in order to measure the nanoscale mechanical properties of thin films.

[1] E. Broitman, Tribology Letters 65 (2017) 23.

10:20am **E2-2-8 Plasma Electrolytic Oxidation Coatings on AZ31 Magnesium Alloys with Si_3N_4 Nanoparticle Additives**, ***YiYuan Lin***, *J Lee, C Tseng,* Ming Chi University of Technology, Taiwan*; B Lou,* Chang Gung University, Taiwan

The magnesium AZ31 alloys have been used in a wide range of lightweight applications such as aerospace, automotive and personal computers due to its unique properties. However, high chemical reactivity, poor corrosion and wear resistance limit their widespread uses in many fields. The plasma electrolytic oxidation (PEO) process can produce protective oxide layer on the magnesium alloy to improve its mechanical property, wear resistance and corrosion resistance. In this work, the silicon nitride (Si_3N_4) nano particles were added into the electrolyte of PEO treatment on AZ31 alloy to improve the mechanical and anticorrosion properties of oxide coating. Surface and cross-sectional structure of the oxide layers was studied by scanning electron microscope (SEM). Energy dispersive spectrophotometry (EDS), X-ray diffraction (XRD) techniques were employed to determine the phase structure and chemical composition of the layers. The adhesion and mechanical properties of coating were analysis by scratch test, pin-on-disk wear test and hardness test, respectively. Potentiodynamic polarization tests were employed to investigate the electrochemical corrosion behavior of PEO treated AZ31 alloy. Effects of Si_3N_4 addition concentration on the microstructure, mechanical and anticorrosion properties were further discussed in this work.

10:40am **E2-2-9 Fractures, Wrinkles and Buckles in Brittle Multi-layers on Flexible Substrate**, ***Davy Dalmas,*** Laboratoire de Tribologie et Dynamique des Système (LTDS), Ecole Centrale de Lyon, France*; I Ben Cheikh, G Parry, R Estevez,* SIMaP – Univ. Grenoble Alpes, CNRS, SIMaP, France

Polymer film coated with stacks of thin layers (metal, oxides or organic) are more and more used in many industrial applications such as flexible and opto microelectronics (screens, OLED, Photovoltaic applications...). Maintaining the mechanical stability of these coated systems requires both to control the cohesion of the coating and its adhesion to the substrate for various mechanical loadings. As the mechanical behaviour of these systems is highly dependent on both the properties of the substrate (modulus, thermal expansion coefficient, glass transition temperature ...), and of the coating (deposition conditions, the residual stresses,…), it is essential to develop dedicated characterization methods and idealized model experiments to understand the mechanical stability of those thin films deposited on flexible substrates.

In this Study, fracture propagation of TiO_2 and Ag layers of various thicknesses coated on a PET substrate is investigated during simple traction tests. During those tests, two phenomena can be observed. Firstly, at low strain, channel crack starts to appear in the coating. We show that the crack density undergoes a transition from a statistic failure distribution classically observed for brittle material and well-described by Weibull distribution to a deterministic sequence of failures set by the elastic mismatch between the film and the substrate. At high strain, the crack density saturates more rapidly than expected (i.e. for distance between two consecutive cracks one order of magnitude higher that he film thickness). Secondly, we observed a second transition from wrinkling to buckling of the coating in the transverse direction to Poisson effect. We show that the transition between those two phenomena is driven by the composition of the coating.

Finally, we propose a two-dimensional model of a film bonded to an elastic substrate to describe the evolution of crack density with the applied strain in the case of large elastic mismatch between the film and the substrate. We then extend this model to an elasto-plastic one in order to account for the plasticity in the substrate. This plasticity is experimentally evidenced by in-situ AFM imaging and numerical validation by FEM that both show the localisation of strain in the substrate during fracture process. We propose that this localisation is responsible of the early saturation of crack density observed at high strain.

11:00am **E2-2-10 Combined XPS and Adhesion Studies of Metal - Polymer Interfaces for Space Applications**, ***Barbara Putz,*** Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Monanuniversität Leoben, Austria*; G Milassin, Y Butenko, C Semprimoschnig,* European Space Research and Technology Centre (ESTEC), The Netherlands*; M Cordill,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Monanuniversität Leoben, Austria

Good adhesion of metal-polymer interfaces is crucial for the reliability of a vast number of high-tech and everyday applications, such as multilayer insulation for satellites as well as flexible and rigid microelectronic devices. Of special interest for space applications is how stable these interfaces are chemically and mechanically with respect to the extreme thermal cycling the devices undergo in operation. In low earth orbit a spacecraft typically encounters 6000 thermal cycles of +/- 100°C during one year in operation. In this study, mechanical adhesion measurements are combined with X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) in order to relate the interface strength to the interface chemistry and structure for the Aluminium-Polyimide (Al-PI) system. This material system is used as a multilayer insulator for satellites currently in orbit. The interfacial adhesion energy was measured using tensile induced delamination before and after a thermal cycling treatment of +/- 150°C up to 200 thermal cycles. In order to assess the chemistry of the interface, an 180° peel test was used to provide access to the metal side and the polymer side of the interface. Peeling allows the interface of interest to be evaluated without any additional etching or sputtering steps that would alter the interface chemistry. XPS survey scans and relevant high resolution core levels were recorded on both sides of the peeled interfaces to identify and understand relevant interfacial bonding and to distinguish between adhesive failure of the interface and cohesive failure in the substrate. TEM cross-sections were used to examine the interface structure as a function of thermal cycling and related to the mechanical adhesion measurements. It was determined that the Al-PI system initially has very good metal-polymer adhesion which does not degrade due to the thermal loads caused by the sun during orbit. The combination of mechanical adhesion measurements, structure and chemistry evaluation of the interfaces allows for an improved understanding of how thermal treatments can influence interfacial behaviour between metals and polymers. This new knowledge will help improve design and reliability of the materials used in space applications and can also provide vital information for flexible and rigid microelectronics used on earth.

11:20am **E2-2-11 Mapping Adhesion Energy of Tungsten Based Barrier Layers with Scratch Induced Buckling**, ***Andreas Kleinbichler,*** *J Zechner,* KAI - Kompetenzzentrum Automobil- und Industrieelektronik GmbH, Austria*; M Cordill,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria

Diffusion barrier layers provide microelectronic devices with chemical and mechanical stability, thus ensuring the reliability during service. The barrier layer prevents the contamination of the conductive metallization due to Si diffusion in a certain temperature range while also acting as an adhesion layer to the underlying substrate providing mechanical stability. However, the interface adhesion may change due to temperature gradients present during sputter deposition and result in a radius dependent adhesion across the wafer. Tungsten-titanium (WTi) alloys have been demonstrated to be very important barrier materials in copper based microelectronic devices as they exhibit thermal stability up to 800°C and good adhesion behavior to silicon oxide substrates. The adhesion of WTi to Borophosphosilicate glass (BPSG) is of special interest in modern metal–oxide–semiconductor field-effect transistors (MOSFET) since the strength of this kind interface is usually weak. A reliable way of assessing the adhesion quantitatively is required to properly map the adhesion across the wafer surface and for the different temperatures the wafer is exposed to during the production process and later during its lifetime. The adhesion of a 300nm WTi film with an 800nm BPSG substrate on top of a 700µm Si wafer has been investigated using scratch testing. The scratches induce buckles in the film which are used to quantitatively calculate the film/substrate-adhesion and can easily be performed as a function of the position over the wafer. From the different positions a map of the adhesion energy of the WTi-BPSG interface can be constructed. The adhesion map will help identify areas on the wafer that might have been influenced by the thermal gradient present during production.

New Horizons in Coatings and Thin Films
Room Royal Palm 1-3 - Session F4-1

Functional Oxide and Oxynitride Coatings

Moderators: Michael Stueber, Karlsruhe Institute of Technology, Anders Eriksson, Oerlikon Balzers, Oerlikon Surface Solutions AG

8:00am **F4-1-1 Development of Microstructure, Phase Composition and Residual Stresses during Plasma Electrolytic Oxidation (PEO) of Aluminium Alloys**, ***Etienne Bousser,*** *A Yerokhin,* The Univ. of Manchester, UK*; T Schmitt,* École Polytechnique de Montréal, Canada*; A Gholinia, J Donoghue,* The Univ. of Manchester, UK*; D Asquith,* Sheffield Hallam Univ., UK*; A Jarvis,* Univ. of Sheffield, UK*; P Withers, A Matthews,* The Univ. of Manchester, UK

Aluminium alloys are widely used for their high specific strength but because of their lower hardness, these alloys often present a less than ideal resistance to surface degradation. In order to improve the tribo-mechanical behaviour of these materials, Plasma Electrolytic Oxidation (PEO) has been shown to offer better wear performance through increased hardness due to the formation of hard crystalline phases during the oxide growth process at near-to-ambient bulk metal temperatures. Indeed, these coatings are typically non-uniform with a shallow porous top layer which sits on a thicker, dense layer comprising of a mixture of polycrystalline and amorphous oxide phases. In this paper, we investigate the evolution of microstructure, phase content and residual stress states in Al_2O_3 layers formed on aluminium alloys using Pulsed Bipolar PEO processes.

In order to understand the evolution of surface layer microstructure and phase composition during PEO treatments, the layers formed at different process durations were evaluated. In order to characterise appreciable changes in microstructure and crystallography of the formed oxide phases over a small range, the surface layers were characterised by cross-sectional Scanning Electron Microscopy (SEM) while the phase composition and strain states were evaluated by laboratory- and synchrotron-based depth-resolved Grazing Angle X-Ray Diffraction (GAXRD) measurements. Moreover, in order to observe the effects of thermal gradients during coating deposition on the occurrence, size and distribution of the different alumina phases (alpha, gamma and amorphous phases) within the coating

microstructure, high resolution Electron Back-Scattered Diffraction (EBSD) was carried out on the coating cross-sections prepared by Xe^+ ion Plasma FIB serial-sectioning and broad Ar^+ ion beam milling.

In this study, we will show that the microstructure and phase content is strongly dependent on the processing method through variations in temperature flux within the forming oxide layer. In addition, the complex distribution of residual stresses as a function of depth and phase content is presented. We will show that overall low compressive residual stresses are present in the coating and are balanced by tensile stresses in the substrate. Finally, it appears that the gamma to alpha phase transformation, which occurs in the inner region of the coating, leads to relaxation of internal stresses in the gamma phase matrix.

8:20am **F4-1-2 Influence of Transition Metal Dopants on the Reactive Sputtering Process of Al_2O_3 Thin Films and their Oxidation Resistance**, ***Bernhard Kohlhauser***, *H Riedl, C Koller,* Institute of Materials Science and Tech., TU Wien, Austria*; S Kolozsvári,* Plansee Composite Materials GmbH, Germany*; V Paneta, D Primetzhofer,* Uppsala University, Sweden*; H Hutter,* Institute of Chemical Technologies and Analytics, TU Wien, Austria*; P Mayrhofer,* Institute of Materials Science and Tech., TU Wien, Austria

The pursuit of longer lasting workpieces is pushing materials to their limit. To meet the ever growing mechanical and chemical demands, the aid of protective coatings is developing from a surface improvement to an essential necessity. One of the coating materials, that attracts particular attention due to its outstanding oxidation resistance, thermo-mechanical stability and chemical inertness is Al_2O_3. While the thermodynamically stable α–Al_2O_3 (corundum) is limited to high deposition temperatures, the cubic γ-Al_2O_3 can be deposited by DC pulsed or RF reactive sputtering at more workable temperatures but lower growth rates. Reactive DC sputtering yields higher deposition rates but struggles with non-stable deposition conditions due to the formation of isolating Al_2O_3 at the target surface.

To improve the reactive DC sputtering process, we study the influence of small amounts of transition metal dopants such as M = Cr, Nb, Mo, and W on the deposition process as well as the properties of the deposited $(Al_{1-x}M_x)_2O_3$ thin films. The selected concentrations of the dopants in the targets were 2 and 5 at.% each. Resulting dopant concentrations in the thin film were investigated via a combination of energy dispersive x-ray spectroscopy and time-of-flight recoil detection analysis. In comparison to the non-alloyed Al target a significantly improved process stability was observed. The morphology of all coatings is highly dense, smooth and partly columnar with cubic γ-Al_2O_3 crystalline structure. The mechanical properties of the low level Cr, Mo, and W containing coatings are slightly enhanced, e.g. hardness values of about 25 GPa. Transmission electron microscopy is applied to evaluate the influence of the dopant atoms on the morphology and the crystal structure. As a result of the enhanced process stability, the oxidation protection capabilities can be clearly improved by alloying W, Mo, or Cr compared to pure Al_2O_3 thin films, as proven by differential scanning calorimetry and secondary ion mass spectroscopy of isotope tracers.

8:40am **F4-1-3 On the Phase Evolution of Al-Cr-based Intermetallics and Oxides Formed by Cathodic Arc Evaporation**, *V Dalbauer,* ***Christian Koller***, *R Raab,* CDL-AOS TU Wien, Austria*; S Kolozsvári,* Plansee Composite Materials GmbH, Germany*; J Ramm,* Oerlikon Surface Solutions AG, Liechtenstein*; M Bartosik, P Mayrhofer,* TU Wien, Austria

The protection of tools and components by only several microns thick hard coatings has evolved to an indispensable element of today's manufacturing and forming process chain. This particular type of surface treatment not only guarantees for enhanced performance of components facing severe mechanical and thermal load, or higher resistance against chemical attacks, but also makes the production cycles more efficient by increasing the duty-cycle and simultaneously lowering material consumption. Owing to their outstanding properties in oxidising and chemically hazardous environments Al-Cr-based oxide coatings represent ideal candidates for the protective application at elevated temperatures. However, the strong dependence of these properties on the microstructure and crystallographic composition in combination with the formation of metastable phases at synthesis temperatures of less than 600 °C still pose a considerable challenge to materials scientists.

We therefore address the phase formation of cathodic arc evaporated $(Al_xCr_{1-x})_2O_3$ coatings with Al-contents x ranging from 0.90 to 0.25 as a function of oxygen partial pressure. Coatings synthesised with a constant oxygen process pressure are compared to gradually-structured films, for which the oxygen flow was slowly increased throughout the deposition process. The growth of metallic films and their transition to oxide phases with M_2O_3 stoichiometry are discussed based on cross-sectional transmission electron microscopy and X-ray nano-beam studies.

9:00am **F4-1-4 Synthesis of Local Epitaxial α-$(Cr_{1-x}Al_x)_2O_3$ Thin Films ($0.08 \leq x \leq 0.16$) on α-Al_2O_3 Substrates by R.F. Magnetron Sputtering**, *Y Gao, H Leiste, M Stüber,* ***Sven Ulrich***, Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM-AWP), Germany

(0001) oriented nanocrystalline α-$(Cr_{1-x}Al_x)_2O_3$ ($0.08 \leq x \leq 0.16$) thin films with a thickness of ~270 nm were grown on *c*-plane α-Al_2O_3 (0001) single crystal substrates at 400˚C by non-reactive reactive radio frequency magnetron sputtering from a segmented ceramic target. The stoichiometric composition of all films was verified by electron probe micro-analysis (EPMA). Only (*000l*) reflections of the films and the substrates were identified from X-ray diffraction (XRD) in Bragg-Brentano geometry. The reflections of the films shift to larger diffraction angle with increasing Al concentration. The mosaic spreading of the (0006) reflex of the films was analyzed to determine the misorientation of the individual crystals with respect of *c*-axis in the films. Transmission electron microscopy (TEM) was carried out in order to study the microstructure and further confirm the orientation and epitaxial relationship of $[0001]_{film}$ // $[0001]_{substrate}$ and $[10\text{-}10]_{film}$ // $[10\text{-}10]_{substrate}$. More information such as lattice parameters *a* and *c*, strain relaxation and epitaxial quality of partial crystal tilting was obtained by reciprocal space mapping (RSM). Further, Raman spectra show a significant shift of phonon frequency with Al concentration. The band gap of the films is between 2.72 eV and 2.85 eV, calculated from visible light absorption spectra. The films nano-indentation hardness and the reduced Young's modulus are in the range of 25.6 - 30.8 Gpa and 216 - 339 Gpa respectively, which vary dependent on the Al concentration.

9:20am **F4-1-5 Thermal Stability of Arc Evaporated Oxide, Nitride, Oxinitride, and Oxide/Nitride Coatings within the Systems Al-Cr-N and Al-Cr-O**, ***Robert Raab***, CDL-AOS TU Wien, Austria*; C Koller,* TU Wien, Austria*; S Kolozsvári,* Plansee Composite Materials GmbH, Germany*; J Ramm,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P Mayrhofer,* TU Wien, Austria

The most common industrially used material systems synthesised by cathodic arc evaporation are nitrides or oxides. Among these, Al-Cr-based films are particularly suitable for a multitude of applications, which not only required a balanced and tailored property spectrum up to 1000°C (and beyond), but also the capability to withstand oxidising and chemically invasive environments. However, increasing demands for higher application temperatures and extended duty cycles, require improvements even for already well-established coatings.

In this regard, we have studied the thermal stability of $Al_xCr_{1-x}N/(Al_xCr_{1-x})_2O_3$ multilayer coatings and compared them with the homogenously grown counterparts $Al_xCr_{1-x}N$, $(Al_xCr_{1-x})_2O_3$, as well as its combination in terms of quaternary Al-Cr-O-N. Therefore, $Al_xCr_{1-x}N$ and $(Al_xCr_{1-x})_2O_3$ multilayers as well as mixtures thereof were synthesised by reactive arc evaporation using powder metallurgically prepared $Al_{0.7}Cr_{0.3}$ targets. By careful adjustment of deposition time and reactive gas configuration, the multilayers could be designed with different bilayer periods and interface types. By reducing the time per layer during the deposition (thus increasing the total number of bilayers), the $(Al_xCr_{1-x})_2O_3$ and $Al_xCr_{1-x}N$ layers have different thicknesses, resulting in decreased bilayer periods from 175 to 30 nm. The quaternary Al-Cr-O-N coatings, were synthesised with different O to N ratios to achieve a similar chemical composition compared to the multilayers.

We used a combination of differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), X-ray powder diffraction (XRD), and hardness investigations after annealing the samples up to 1500 °C in vacuum for one hour to investigate the decomposition of the Al-Cr-based oxide, nitride, oxinitride, and oxide/nitride coatings.

According to DSC/TGA results we can conclude that the thermal stability increases, with increasing total number of layers. We observed a transition from a two-step process of the Al-Cr-based multi-layered coatings with higher bilayer periods as well as the oxinitride coatings with higher N contents, to a one-step process of the $Al_xCr_{1-x}N/(Al_xCr_{1-x})_2O_3$ multilayers with the lowest bilayer periods and the oxinitride coatings with highest O content.

Based on our results we can conclude that a multi-layer arrangement with optimized bilayer period is superior to the monolithically grown $Al_xCr_{1-x}N$, $(Al_xCr_{1-x})_2O_3$, and quaternary Al-Cr-O-N.

9:40am **F4-1-6 Structural Evolution in Reactive RF Magnetron Sputtered $(Cr,Zr)_2O_3$ During Annealing**, ***Ludvig Landälv,*** Linköping Univ., IFM, Thin Film Physics Div. and Sandvik Coromant R&D, Sweden*; J Lu,* Linköping Univ., IFM, Thin Film Physics Div., Sweden*; S Spitz, H Leiste, S Ulrich,* Karlsruhe Institute of Technology (KIT), Inst. for Applied Mat. (IAM-AWP), Germany*; M Johansson-Jõesaar,* Linköping Univ., IFM, Nanostructured Mat. And SECO TOOLS, Sweden*; M Ahlgren, E Göthelid,* Sandvik Coromant R&D, Sweden*; B Alling,* Linköping Univ., IFM, Thin Film Physics Div. and Max-Planck-Institut für Eisenforschung GmbH, Sweden*; L Hultman,* Linköping Univ., IFM, Sweden*; M Stüber,* Karlsruhe Institute of Technology (KIT), Inst. for Applied Mat. (IAM-AWP), Germany*; P Eklund,* Linköping Univ., IFM, Thin Film Physics Div., Sweden

Physical vapor deposited binary oxide alloys has drawn attention in the past years, often focusing on the Al-Cr-O system [1,2]. The interest for this material system stems from the possibility to stabilize the desired corundum phase, α-Al_2O_3, by introducing other elements to the alloy such as Cr in α-$(Al,Cr)_2O_3$.The corundum structure is stabilized by means of a template growth; Cr forms escolaite Cr_2O_3 which is isostructural with corundum. Exchanging Al with Zr, which is used in many other ceramic alloy systems, creates a new and interesting oxide system with the retained stabilization from Cr, despite Zr's one higher valence than Al and being significantly larger in size. Spitz et al. mapped the Cr-Zr-O system over a wide range of Cr/Zr composition by reactive RF-magnetron sputtering [3], obtaining different phases: solid solution in corundum structure at low Zr-content, cubic-$(Zr,Cr)O_2$ based solid solutions at ~50 at % Zr, and monoclinic/tetragonal solid solution $(Zr,Cr)O_2$ for higher Zr-content. A recent in-situ synchrotron X-ray diffraction study showed the increase in crystallization onset temperature of α-$(Cr,Zr)_2O_3$ and tetragonal $(Zr,Cr)O_2$ from as-deposited amorphous Cr-rich Cr-Zr-O films during vacuum annealing with increasing Zr content

(3-15 at %) [4].

In the present study, $Cr_{0.28}Zr_{0.10}O_{0.61}$ coatings were synthesized at 500 °C by reactive RF-magnetron sputtering, to a thickness of about 5 µm. The as-deposited coatings were then vacuum annealed at 750°C, 810 °C, and 870 °C for 5 h each. The microstructure development of the binary oxide compound after annealing was characterized through high resolution state of the art HRSTEM and HREDX-maps, revealing the segregation of Cr and Zr on the nm scale.

The as-deposited films comprise of α-$(Cr,Zr)_2O_3$ solid solutions with a Zr-rich $(Zr,Cr)O_x$ amorphous phase distributed as elongated, in the growth direction, alternating domains. After annealing to 750°C tetragonal ZrO_2 nucleates and grows from the amorphous phase. The ZrO_2 phase is stabilized in its tetragonal (t) structure at these fairly low annealing temperatures, possibly due to the small grain size (<~30 nm). Correlated with the nucleation and growth of the t-ZrO_2 phase is an increase in hardness, with a maximum hardness after annealing to 750 °C, followed by a decrease in hardness upon grain coarsening, bcc metallic Cr phase formation and loss of oxygen during annealing to 870 °C.

[1] Ramm, J., et al., Surface & Coatings Technology, 2007, **202**(4–7): p. 876-883

[2] Khatibi, A., et al. Acta Materialia, 2013, **61**(13): p. 4811-4822

[3] Spitz S., et al. Thin Solid Films, 2013, **548**: p. 143-149

[4] Rafaja D., et al, Thin solid Films, 2016, **516**: p. 430-436

10:00am **F4-1-7 Ternary Oxide Coatings as High-temperature Solid Lubricants**, ***Samir Aouadi,*** *J Gu, D Stone,* University of North Texas, USA*; Y Gao, A Martini,* University of California Merced, USA **INVITED**

This talk will provide an overview of the latest research developments on binary and ternary oxide coatings that have the potential to be used as solid lubricants at elevated temperatures. The review focuses on understanding the major mechanisms that lead to a reduction in friction and/or wear in high temperature lubricious oxides. Changes in the structural, chemical, and electronic properties of these oxides as a function of temperature will be correlated to their mechanical and tribological performance using a range of experimental tools in addition to simulations based on ab initio calculations and molecular dynamics simulation methods. The incorporation of these oxides in adaptive coating designs will also be discussed. Adaptive mechanisms include metal diffusion and formation of lubricant phases at worn surfaces, surface contact tribe-chemical evolution to form phases with low melting point, and the formation of easy-shear oxides. This review also includes a discussion of the industrial applications of these coatings as well as of potential improvements to the coating design and other anticipated future developments.

10:40am **F4-1-9 High-rate Reactive High-power Impulse Magnetron Sputtering of Hf-O-N Films with Tunable Composition and Properties**, ***Jaroslav Vlcek,*** *A Belosludtsev, S Haviar, J Houška, R Čerstvý, J Rezek,* University of West Bohemia, Czech Republic

Oxynitrides are a class of materials with yet unexplored physical, chemical and functional properties, and a great potential for industrial applications.

In this work, reactive HiPIMS with a feed-back pulsed reactive gas (oxygen and nitrogen) flow control and an optimized location (high-density plasma) of the reactive gas inlets in front of the target and their orientation toward the substrate made it possible to produce high-quality Hf-O-N films with a tunable elemental composition, structure and properties at very high deposition rates ranging from 240 nm/min for HfO_2 films [1] to 175 nm/min for HfN films. Basic principles of this method will be given.

The depositions were performed using a strongly unbalanced magnetron with a planar hafnium target of 100 mm diameter in argon-oxygen-nitrogen gas mixtures at the argon pressure of 2 Pa. The nitrogen fractions in the reactive gas flow were in the range from 0 % to 100 %. The repetition frequency was 500 Hz at a fixed deposition-averaged target power density of 30 Wcm^{-2} with the voltage pulse duration of 200 µs (duty cycle of 10 %). The substrate temperatures were less than 140 °C during the depositions of films on a floating substrate at the distance of 100 mm from the target. All films were nanocrystalline and their elemental compositions were varied gradually from HfO_2 to HfN. We present a gradual change of hard (18 GPa), highly optically transparent (extinction coefficient of $5x10^{-4}$ at 550 nm), electrically insulating and hydrophobic (water droplet contact angle of 101°) HfO_2 films into harder (25 GPa), optically non-transparent, electrically conductive (electrical resistivity of $3.2x10^{-6}$ Ωm) and more hydrophobic (water droplet contact angle of 107°) HfN films.

[1] Vlcek, A. Belosludtsev, J. Rezek, J. Houska, J. Capek, R. Cerstvy, S. Haviar, High-rate reactive high-power impulse magnetron sputtering of hard and optically transparent HfO_2 films, Surf. Coat. Technol. 290 (2016) 58.

11:00am **F4-1-10 Thin Films in the M-Si-O-N Systems**, ***Sharafat Ali,*** Linnæus University, Sweden*; P Biplab, R Magnusson, G Greczynski, E Broitman,* Linköping University, (IFM), Sweden*; B Jonson,* Linnæus University, Sweden*; J Birch, P Eklund,* Linköping University, (IFM), Sweden

Thin films in the M-Si-O-N systems (Where M= Mg, Ca), were deposited on commercial soda-lime silicate float glass, silica wafers and sapphire substrates by RF magnetron co-sputtering from Mg/Ca and Si targets in an $Ar/N_2/O_2$ gas mixture. Chemical compositions, optical and mechanical properties of the films were investigated using X-ray photoelectron spectroscopy, spectroscopic ellipsometry and nanoindentation. Thin films in the M-Si-O-N system are composed of N and M contents up to 80 at. % and 50 at. %, out of anions and cations respectively. This is very rare in the bulk form. The films were found to be homogeneous and transparent in the visible region. Mechanical properties like hardness and reduced elastic modulus show high values, up to 20 GPa and up to 160 GPa respectively, and show similar compositional dependencies i.e. increase with the N content. The refractive indices range from 1.60 to 2.02 at wavelength 633 nm and is found to increases with increasing N and M contents.

11:20am **F4-1-11 Diffusion between Silica Thin Film Deposited by Reactive Magnetron Sputtering and Glass Substrate during Annealing at High Temperature**, ***Jean-Thomas Fonné,*** *E Gouillart, E Burov, H Montigaud, S Grachev,* Joint unit CNRS/Saint-Gobain UMR 125 - Surface of Glass and Interfaces, France*; D Vandembroucq,* UMR 7636 CNRS/ESPCI/Paris 6 UPMC/Paris 7 Diderot - Physics and Mechanics of Heterogeneous Media Laboratory, France

Industrial processes often involve annealing and/or tempering glass panels coated with thin films. Diffusion of alkali ions from the substrate to the active layers is typically observed during these treatments and can modify properties of these thin films. In order to understand the kinetics and mechanisms of this phenomenon, amorphous silica thin films (pure or doped with aluminum) deposited by magnetron sputtering under reactive atmosphere onto glass substrates have been studied after annealing above the glass transition temperature (Tg). Various techniques such as SIMS, SEM, AFM, XPS, EPMA and Raman Spectroscopy were used for the evaluation of the composition depth profile and the microstructure characterization.

Our investigations show that annealing commercial soda-lime glass substrates coated with silica thin films above Tg leads to migration phenomena between silica and glass with two essential steps:

- A fast migration of alkali ions (especially sodium and potassium) from the substrate to the film is first observed. This transport phenomenon is shown to strongly depend on aluminum doping in silica layers. In particular the alkali ions concentration obtained in the silica layer after annealing scales linearly with the initial aluminium concentration in the silica layer.

- A slow homogenization then takes place at the interface between the silica thin film and the glass substrate. This second phenomenon is controlled by the interdiffusion of the st of all elements. We observe a gradual thinning of the silica layer with the square root of time.

Differents annealing durations and temperatures were studied since these phenomena depend on elements mobility and activity. Moreover the impact of deposition conditions was also studied (like the deposition pressure) since these parameters can have an influence on the silica layer properties.

11:40am **F4-1-12 Investigation of Sputtered Zirconium Oxide Thin Films Deposited at Different Oxygen Partial Pressure**, ***Nicky Patel,*** Sardar Patel College of Engineering, India*; K Chauhan,* Chandubhai S. Patel Institute of Technology (CSPIT), Charotar University of Science and Technology (CHARUSAT), India*; S Rawal,* McMaster University, Canada

Reactive magnetron sputtering was used to deposit zirconium oxide thin films by using argon as inert gas and oxygen as reactive gas. The oxygen partial pressure was increased from 17% to 50% and its effect on structural, wettability and tribological properties of deposited zirconium oxide thin films are investigated. The structural characterization by X-ray diffraction confirms formation of (111) peak for zirconium oxide thin films whose intensity decreases with increase in oxygen partial pressure. Atomic force microscopy results indicate increase in surface roughness values with increase in oxygen partial pressure. The average transmittance values of around 80% within wavelength range of 300 nm to 700 nm was observed which proves that zirconium oxide thin films are transparent. Contact angle measurement done for water and formamide liquids indicate zirconium oxide thin films are hydrophobic. The maximum contact angle observed on zirconium oxide thin films are 102.6°and 101.3° for water and formamide liquids respectively. Tribological investigation shows that zirconium oxide thin films coated pins had a reduction of wear when compared to the uncoated pins.

Advanced Characterization Techniques for Coatings and Thin Films

Room Royal Palm 4-6 - Session H3-1

Characterization of Coatings in Harsh Environments

Moderators: David Armstrong, University of Oxford, Jeff Wheeler, Laboratory for Nanometallurgy, ETH Zürich

8:00am **H3-1-1 Small-Scale Mechanical Testing on Ion Beam Surface-Modified Engineering Materials**, ***Peter Hosemann,*** University of Californa at Berkeley, USA **INVITED**

Ion beam irradiation has been utilized to enhance surface properties of materials but also as a surrogate for neutron irradiation damage which is a truly harsh environment. Due to the limited penetration depth of ion beam irradiation, small scale mechanical testing is required in order to evaluate mechanical properties in the region on interest. In this work we present small scale mechanical test data on ion beam irradiated steels. We will feature nanoindentation, microcompression testing as well as micro tensile testing. We find that while nanoindentation and microcompression testing provides a good measures of hardening and yield strength the tensile testing gives inside into the plasticity. The load drops occurring during the testing are able to provide inside into localized failure and dislocation activity to the point where semi quantitative load drop analysis can be used as a parameters for slip channel formation. In addition a new method of Helium implantation using the ORION Nanofab He ion beam microscope is presented with subsequent mechanical property measurements of the implanted region.

8:40am **H3-1-3 High Temperature Nanoindentation up to 800°C: Experimental Optimization**, *N Randall, M Conte,* Anton Paar TriTec, Switzerland*; J Schwiedrzik, J Michler,* EMPA, Switzerland*;* ***Pierre Morel,*** Anton Paar, USA

One of the primary motivations for development of instrumented indentation was to measure the mechanical properties of thin films. Characterization of thin film mechanical properties as a function of temperature is of immense industrial and scientific interest. The major bottlenecks in high temperature measurements have been thermal drift, signal stability (noise) and oxidation of the surfaces. Thermal drift is a measurement artefact that arises due to thermal expansion/contraction of indenter tip and loading column. This gets superimposed on the mechanical behavior data precluding accurate extraction of mechanical properties of the sample at elevated temperatures. Vacuum is essential to prevent sample/tip oxidation at elevated temperatures.

This talk will summarize the latest design of the UNHT^3 HTV nanoindentation system that can perform reliable load-displacement measurements up to 800°C. The sample, indenter and reference tip are heated separately and the surface temperatures matched to obtain drift rates as low as 1nm/min at 800 °C, without any correction. Particular focus will be placed on recent developments which are of high importance in being able to accurately analyze high temperature nanoindentation data. These include the validation of instrument calibration across the entire temperature range, the determination of indenter area function and modelling of the temperature transfer between the sample surface and the tip, as well as compliance considerations. It is only by solving these issues that truly accurate mechanical properties can be calculated from high temperature load-depth data.

9:00am **H3-1-4 Size-dependent Nanoscale Plasticity in Oxidation-strengthened Zr/Nb Multilayers**, ***Mauro Callisti,*** University of Southampton, UK*; M Monclus,* IMDEA Materials Institute, Spain*; J Llorca,* Polytechnic University of Madrid, Spain*; J Molina-Aldareguía,* IMDEA Materials Institute, Madrid, Spain*; T Polcar,* University of Southampton, UK

Nanoscale metallic multilayers (NMMs) represent a relatively new class of heterogeneous materials often used to understand the relationship between intrinsic materials properties (grain size, interfaces, etc.) and the corresponding mechanical properties. Among the possible combinations, Zr/Nb (*hcp/bcc*) NMMs were investigated in this study, as the strengthening mechanisms and the oxidation behaviour of Zr/Nb NMMs are not understood. Furthermore, Zr-Nb alloys are widely employed in nuclear industry; therefore, in view of the positive role of interfaces against radiation damage, Zr/Nb NMMs could represent a promising candidate material for the future nuclear industry.

In this study, Zr/Nb multilayers with a periodicity (L) ranging between 10 – 75 nm were deposited by magnetron sputtering and subsequently annealed at 350 for different annealing times (2 – 168 hrs). Analytical electron microscopy, *in-situ* XRD and nano-mechanical testing were combined to reveal the oxidation process as well as the deformation mechanisms in pristine and annealed samples.

The oxidation process occurred in a selective way in Zr/Nb NMMs, where Zr rapidly transformed into monoclinic ZrO_2, while Nb progressively oxidised at a much lower rate to form a Nb_2O_5 phase. The sequential oxidation of Zr and Nb layers was key for the oxidation to take place without rupture of the layered structure. Micropillar compression tests revealed that in Zr/Nb NMMs with L = 10 nm the deformation mechanism was mostly governed by shear bands formation in softer non-oxidised regions. Conversely, for larger periodicities (L = 75 nm) the mechanical properties of individual layers played a more dominant role on the deformation mechanism. In particular, in the as-deposited Zr/Nb co-deformation of Zr and Nb occurred, although Nb layers were slightly extruded out between Zr layers. On the other hand, in the annealed Zr/Nb NMMs (L = 75 nm) both Nb and Nb_2O_5 layers were found to control the deformation mechanism.

9:20am **H3-1-5 High Temperature Mechanical Properties Characterization of DLC Films**, *M Rouhani,* National Chung Cheng University, Taiwan*; F Hong,* National Cheng Kung University, Taiwan*;* ***Yeau-Ren Jeng,*** National Chung Cheng University, Taiwan

Thermal stability of various DLC films is an important factor determining their application range. Up to know, all the studies on the thermal stability of DLC films were limited on the annealing of the films at elevated temperature and then characterization of the changes in material structure and properties at room temperature. In this study, we have used special equipment which allows us to do in-situ characterization at elevated temperatures in order to understand materials behaviour close to service conditions. In order to investigate the effect of temperature on the mechanical properties of DLC films, three series of DLC films were successfully deposited on Si substrates using filtered cathodic arc vacuum (FCVA) deposition system. All the deposition parameters for these three series were kept constant; except Ar pressure (P_{Ar}) which varied from 0.5 to 1 and finally to 1.5 mTorr. The hardness and modulus of the films were measured at 21, 40, 60, 80, 100, 120, 140, 180, 200, 250, 300, 350, 400, 450 , 500°C using a nanoindenter. At room temperature the film deposited

at the lowest P_{Ar} (0.5 mTorr) shows the highest hardness (36 GPa), followed by the film deposited at P_{Ar}=1 mTorr with hardness of 26 GPa, while the film deposited at the highest P_{Ar} shows the lowest hardness (18 GPa). The microstructure of the films at room temperature was characterized using Raman spectroscopy and the findings confirm the reduction in sp^3/sp^2 ratio by increasing the P_{Ar} during the deposition process. Increasing the temperature during the hardness measurement, results in hardness reduction of all the films, and at temperatures above the 350°C some of the films start to delaminate. More interestingly, for annealing temperature lower than 300°C, when the substrate temperature is returned to room temperature, the hardness of the DLC films rise again close to the hardness values measured originally at room temperature, although small reduction is noticeable which may be due to stress reduction. To investigate the mechanism behind the hardness dependence on the temperature test, several nano-wear tests were carried out at room temperatures and elevated temperatures and we could see changes in worn area and its surroundings using Raman spectroscopy. Overall, our in-situ experiment coupled with annealing tests may explain why previous reports could not see significant reduction in hardness after annealing, while in close to service conditions, the harness of the DLC films significantly reduces at elevated temperature.

9:40am **H3-1-6 Aluminide Coatings on Thin-Walled Sheets – Mechanical Properties and Thermocyclic behaviour**, ***Johannes Bauer***, DECHEMA-Forschungsinstitut, Germany; *H Ackermann,* Oel-Waerme-Institut, Germany; *M Galetz,* DECHEMA-Forschungsinstitut, Germany

Sheets in industrial furnaces and oil burners are exposed to high temperatures and aggressive atmospheres. For service conditions involving temperatures below 900°C and low mechanical stresses, relatively inexpensive heat-resistant steels are usually used. For higher exposure temperatures, currently cost-intensive Ni-based alloys have to be employed even for low stress applications. Aluminized austenitic steels are a suitable alternative. Under service conditions Al diffuses not only outwards to form the protective α- Al_2O_3 scale, but also inwards to the substrate because of the concentration gradient. Simultaneously, the substrate elements e.g. Fe, Cr and Ni diffuse outwards. As a consequence the thickness and the microstructure of the diffusion zone (DZ), interdiffusion zone (IDZ) and the substrate are altered. In the case of thin-walled components the microstructural evolution of the coated system and the subsequent change of the mechanical properties cannot be neglected and have a strong influence on the lifetime of the system.

In this study, heat-resistant austenitic steels (X15CrNiSi20-12 and X15CrNiSi25-21) were aluminized via pack cementation with coating thicknesses varying between 40-130 µm to enhance their corrosion resistance up to 1000°C. Uncoated samples were investigated for comparison. Thermocyclic exposure tests were performed and the alteration of the microstructure of DZ, IDZ and substrate was analyzed. Furthermore tensile tests at room temperature and creep-rupture tests in burner exhaust atmosphere were conducted to show the influence of the coatings on fundamental mechanical properties.

The results reveal the influence of the coating on the overall mechanical behavior and corrosion resistance of the coated system.

10:00am **H3-1-7 Variable Temperature Micropillar Compression Transient Tests on Nanocrystalline Palladium-Gold: Probing Activation Parameters at the Lower Limit of Crystallinity**, ***Juri Aljoscha Wehrs***, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

The plasticity of nanocrystalline metals is governed by a complex ensemble of deformation mechanisms which strongly depends on the materials grain size. Smaller grains are less effective in generating dislocations and hence their ability to interact across intercrystalline domains is reduced. Therefore it is instructive that, in particular for that case that grain sizes approach the limit of crystallinity towards the amorphous regime, grain boundary-mediated deformation processes gain influence while dislocation-mediated processes fade. Mechanisms which essentially emerge from the core regions of grain boundaries, such as grain boundary sliding, grain boundary migration, dislocation nucleation and shear transformation zones are under debate. Consequently, both thermally activated and inelastic, stress-driven deformation processes can be simultaneously operative in these materials. All of these mechanisms contribute towards the increased time dependent plasticity of nanocrystalline metals, manifesting itself as a high degree of strain-rate sensitivity and susceptibility to load relaxation and creep even at room temperature.

In this study we explore the strain rate sensitivity and the load relaxation properties of a highly pure nanocrystalline $Pd^{90}Au^{10}$ alloy with an extremely fine nominal grain size of d~10nm by means of dynamic micropillar compression experiments at variable temperatures. First we briefly review and discuss the testing technique, our experimental considerations and data analysis methods. Then we focus on the applicability of this type of micromechanical experiment for probing activation parameters in nanocrystalline materials. The extracted activation parameters (i.e. strain rate sensitivity, activation volume and activation energy) are discussed and compared to literature data to gain insights into the possible rate controlling deformation mechanisms at the lower limit of crystallinity.

10:20am **H3-1-8 High Temperature Micro-Mechanical Testing of Aluminide Coatings**, ***James Gibson***, *H Reuß, J Schneider, S Korte-Kerzel,* RWTH Aachen University, Germany

The effect of thin film composition and temperature on the elastic, plastic and fracture properties of transition metal nitride and oxynitride coatings was invested by nanoindentation, micro-cantilever bending and micro-pillar compression. Vanadium aluminium nitride (VAlN) and vanadium aluminium oxynitride (VAlON) coatings were manufactured by high-power impulse magnetron sputtering on silicon substrates. A focused ion beam was used to cut notched micro-cantilever beams to determine values of fracture toughness and micro-pillars were cut to observe plastic deformation in otherwise brittle coatings. Tests were carried out to 500°C in-situ using a Nanomechanics inSEM system.

A room temperature fracture toughness measurement of 2.3 and 2.6 MPa√m was measured in the VAlN and VAlON, respectively.

10:40am **H3-1-9 Temperature-dependent Interfacial Layer Formation during Sputter-deposition of Zr Thin Films on Al_2O_3(0001)**, ***Koichi Tanaka***, *J Fankhauser,* University of California, Los Angeles, USA; *M Sato,* Nagoya University, Japan; *D Yu, A Aleman, A Ebnonnasir, C Li,* University of California, Los Angeles, USA; *M Kobashi,* Nagoya University, Japan; *M Goorsky, S Kodambaka,* University of California, Los Angeles, USA

Zirconium thin films are attractive as protective layers in nuclear reactors and in chemical processing plants owing to its mechanical and corrosion-resistant properties. Relatively little is known concerning the growth-related aspects of Zr thin films. Here, we present results from investigation of the effect of substrate temperature (600 °C ≤ T_s ≤ 900 °C) on microstructure of Zr thin films grown on Al_2O_3(0001) via dc magnetron sputtering in an ultra-high vacuum deposition system with base pressure < 5×10^{-10} Torr. ~220-nm-thick Zr films are deposited at a rate of ~0.06 nm/s from Zr target (99.1 wt.% pure with 0.8 wt.% Hf) in 10 mTorr Ar (99.999%) atmosphere. The as-deposited layers are characterized using x-ray diffraction, cross-sectional transmission electron microscopy along with energy dispersive spectroscopy. At 600 °C ≤ T_s ≤ 700 °C, we obtain hexagonal close-packed structured Zr(0001) thin films. At T_s < 750 °C, the layers are dense with smoother surfaces. At T_s ≥ 750 °C, the Zr layers are highly textured with {0001} as the preferred orientation. The films are increasingly porous with highly corrugated surfaces. We find that the Zr/Al_2O_3 interfaces are not abrupt but that there exists an additional layer whose thickness increases with increasing T_s from 10 ± 4 nm at 600 °C to 116 ± 4 nm at 900 °C. These interfacial layers are primarily composed of Zr and Al and their relative concentrations vary with T_s.

Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B3-1

Deposition Technologies and Applications for Diamond-like Coatings

Moderators: Frank Papa, Gencoa Ltd., USA, Klaus Böbel, Bosch GmbH

2:10pm **B3-1-3 New Pathways for Improving Adhesion of DLC on Steel in Low Temperatures**, *L Leidens,* UCS and CAPES, Brazil*; Â Crespi,* UCS, Brazil*; F Alvarez,* IFGW-UNICAMP, Brazil*;* ***Carlos Figueroa****,* UCS, Brazil

Diamond-like carbon thin films (DLC) are state-of-art coatings that can have properties which are object of interest such as ultra-low friction coefficient, chemical inertness and low wear rates. Despite of its strident properties, the use of DLC is not yet fully widespread due to the poor adhesion of the film in some substrates, for example, plain and low-alloy steels. In order to improve DLC adhesion on steel, different interlayers have been proposed. On one hand, hybrid technologies containing a step of PVD deposition of a metal/metal nitride interlayer are industrially used, although its costs are high for several applications. On the other hand, PECVD technologies can produce silicon-containing interlayers, although the deposition temperatures that prompt adhesion as high as 300ºC. Previous works have pointed out that oxygen atoms act as terminator species in silicon-containing interlayers that diminish DLC adhesion on steel.

The aim of this work is to investigate new pathways of reaching high DLC adhesion by using silicon-containing interlayers in low deposition temperatures. In order to explore alternatives, a hydrogen plasma etching effect was analyzed in two different set of samples. [3] The first set look at analyzing the physicochemical processes due to hydrogen plasma interaction in the silicon-containing interlayer and, consequently, the interlayers were deposited with HMDSO at a constant temperature and time of 300°C and 10 min, respectively, varying the hydrogen etching time (0 to 10 min) at 85°C on AISI 4140 low-alloy steel. The second set look at analyzing the adhesion in low deposition temperatures and, consequently, the interlayers were obtained at different deposition temperatures (80 to 180°C) and the hydrogen plasma etching was performed at a constant temperature and time of 85°C and 6 min, respectively.

The samples were characterized by SEM, GDOES, adhesion tests, and profilometry. One can see that the interlayer thickness decreases with the increasing of the hydrogen plasma etching processing time. The etching mechanism suddenly changes at a processing time of 4 minutes. Whereas shorter etching times than 4 min remove roughly constant contents of carbon, silicon and oxygen, longer etching times than 4 min remove more silicon and oxygen than carbon. Moreover, the hydrogen etching process prompts to good adhesion of the DLC on low-alloy steel as low temperature as 85ºC. We propose a mechanism where the outermost interface (DLC/interlayer) is constituted by more carbon than silicon and oxygen atoms after the hydrogen etching process enabling more carbon-carbon chemical bonds than before, which increase the adhesion.

2:30pm **B3-1-4 Stress Evolution of Diamond-like Carbon Films via Controlled Metal Doping**, ***Aiying Wang****, X Li, L Sun, P Guo,* Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, China

>It is well known that, being one family member of carbon-based solid materials, diamond-like carbon (DLC) films own more comprehensive advantages over diamond, carbon nanotube, even as well as very recently the blooming graphene, due to their superior physiochemical properties, facile synthesis with low cost over large uniformity, and amorphous smooth surface etc. In particular, DLC films enable the possibility to apply the eco-friendly surface engineering to satisfy the strong demands of energy saving and emission reduction to update. In this talk, we will introduce our study on the stress controlling of DLC films via metal doping, where the feature and concentration of doped metal were controlled. Specifically, the mechanism to understand the stress reduction originated from the various doped metals will be addressed in view point of combined experimental and theoretical studies. Further synergistic effect of co-doped metals on the microstructure and properties of Me-DLC films will be discussed, which provide a new concept to fabricate the DLC films with comprehensively high performance for wide range of industrial applications.

2:50pm **B3-1-5 Influence of Alloying Metals on Tribological Properties of Diamond-like Carbon Films Synthesized by Metal Plasma Activated Deposition Process**, *D Wang,* ***Wei-Yu Ho****, M Shih, W Chen,* MingDao University, Taiwan*; J Wang, J Hung,* Aurora Scientiftic Corp, Canada

The metal plasma activated diamond-like carbon (mpa-DLC) film has been commercially adopted by manufacturing industries for its superior tribological and functional properties to prolong tools and components service life. The multi-layered and gradient mpa-DLC coating consists of a metallic interface layer, a metal nitride/carbide transition layer and the outmost DLC film, which was synthesized by breaking down of acetylene feed gas. The whole process can be categorized as an integrated and PVD-activated CVD synthesis of DLC coatings. TiN and CrN are among the common starting and supporting materials between the substrate and the top DLC layer. This research looked into the strengthening mechanism of the interface bonding and the intrinsic tribological property of the mpa-DLC coating by adding second and/or third metal elements such as Al, Cr, or Si to the TiN and CrN base lattice. The electron states of carbon and the chemical bonding configuration will be studied by using ESCA-SIMS. The tribological properties will be investigated by using ball-on-disk tribo-meter, nano-indentation, and scratch tester. The thermal property will be examined by using TG/DT. Results of this research will provide a mechanism to further improve the mpa-DLC coatings.

Keywords: metal plasma, DLC, tribology, PVD coating

3:10pm **B3-1-6 Thick Diamond Like Carbon Coatings Deposited by Deep Oscillation Magnetron Sputtering for Automotive Applications**, ***Jianliang Lin****, P Lee, R Wei, K Coulter,* Southwest Research Institute, USA

Hydrogenated diamond like carbon (DLC) coatings with thicknesses up to 20 µm have been deposited by sputtering a graphite target in Ar and acetylene (C_2H_2) mixture using a two-step process including plasma enhanced magnetron sputtering (PEMS) and deep oscillation magnetron sputtering (DOMS). The PEMS technique was used for substrate ion cleaning and sputter deposition of the Ti/TiN bond layer, while the DOMS technique was used to sputter graphite in an Ar+C_2H_2 environment to form the top DLC layer. The effects of the C_2H_2 flow rate (f_{C2H2}) on the deposition rate, adhesion, surface roughness, mechanical and tribological properties of the coatings were studied by means of scanning electron microscopy, Raman spectroscopy, HRC indentation, nanoindentation, dry ball-on-disk test, and block-on-ring test in SAE 10W-30 engine lubricant. Appropriately introducing C_2H_2 (e.g.10 sccm, 4% of the total gas flow) increased the deposition rate, the sp^3/sp^2 ratio, and hardness and wear resistance of the DLC coatings. In contrast, higher C_2H_2 flows (>30 sccm, 12% of total gas flow) showed detrimental effects on the adhesion as well as the mechanical properties of the coatings. These thick hydrogenated DLC coatings exhibited low dry sliding COF in the range of 0.07 to 0.12 in the ambient air, and low friction in SAE 10W-30 engine lubricant in the range of 0.08 to 0.090.

3:30pm **B3-1-7 Deposition of ta-C by Filtered and Unfiltered Laser-arc Technique – Actual Status**, ***Volker Weihnacht****, G Englberger, A Leson,* Fraunhofer IWS, Germany **INVITED**

Due to their unique combination of superhardness and low friction properties tetrahedral amorphous carbon films (ta-C) are very attractive as tribological coatings e.g. on automotive sliding components like piston pins, piston rings, and valve-train parts. In contrast to conventional DLC films (a-C:H), ta-C cannot be deposited by PECVD or magnetron sputtering techniques. The only effective technique for mass production of ta-C coatings is arc evaporation of graphite. As the arc spot movement on graphite is very difficult to control, a laser triggered pulsed arc evaporation technique was developed at Fraunhofer IWS.

This contribution will show how the laser-arc technique has developed from an idea and first prototypes to an industrially upscaled technology used for mass production of ta-C coatings. Special emphasis will be put on the issue of deposition rate versus ta-C coating properties and possibilities how to modify the coating architecture to deposit well-adhering ta-C coatings with thickness of even more than 10 µm.

Furthermore, the issue of arc-induced particle emission and defects in the ta-C coatings will be addressed. It will be shown how plasma filtering specifically developed for the laser-arc technique will suppress the particle transmission from the cathode to the substrate and hence reduce the defect density and roughness of deposited coatings.

4:10pm **B3-1-9 Wear Behavior of CoCrMo Alloy Coated with Highly Adhesive N-Doped DLC by ICP-CVD**, ***Jesus Corona Gomez***, *Q Yang,* University of Saskatchewan, Canada

Coating the joint surfaces with diamond like carbon (DLC) is a promising way to increase the service lifetime of hip joints made of CoCrMo alloy. However, the weak adhesion of DLC on the alloy presents problems for this application. This work aims to improve the adhesion of DLC on CoCrMo alloy with Nitrogen doping and nanodiamond incorporation. Nanodiamond particles with different densities was synthesized on CoCrMo alloy sheets by microwave plasma enhanced chemical vapor deposition and nitrogen doped DLC thin films were then deposited on them by Inductively Coupled Plasma assisted Chemical Vapor Deposition (ICP-CVD). The effect of nitrogen doping and nanodiamond incorporation on the film adhesion was investigated by scratch testing and wear behavior of the samples were studied using ball-on-disc testing. Results showed that Nitrogen doping and nanodiamond incorporation could improve the film adhesion significantly and thus the wear performance. The excellent tribological performance of the coated samples is attributed to the graphitization of the top layer of the DLC according to the Raman spectrum analysis. The wear resistance of the DLC coated CoCrMo alloy was superior to the bare CoCrMo alloy due to the high adhesion of DLC on the alloy. The results have demonstrated that the modified DLC films are promising for total hip joint replacement application.

4:30pm **B3-1-10 Carbon-Based Coatings on Nanofabric by Using HIPIMS for Possible EAOPs Applications**, ***Pi-Wei Wang***, *C Tsen, C Liu, J He,* Feng Chia University, Taiwan

Nanofibers, capable of providing extra functions in contrast to regular-size fibers due to vary high specific surface area. This has brought a large opportunity for the nanofibers to utilize in form of nanofibrous membranes as air and water filtration materials. In combination with advanced coating technique such as high power impulse magnetron sputtering (HIPIMS), it would be able to develop new form of filtration materials for better purifying performance. In this study, carbon-based coatings were deposited on nanofibrous membranes by using HIPIMS (where high density plasma favorites sp3-containing carbon film growth at low-temperature) to achieve additional functions for use as membrane electrode of an electrochemical advanced oxidation processes (EAOPs). Experimental results show that mixed sp2/sp3 carbon film can be obtained, through the result of Raman spectroscopy analysis. The deposited nanofibrous membrane can be electrical conductive for EAOPs purpose. Degradation efficacy for specific organic substance can vary depending on the deposition parameters and were discussed.

Hard Coatings and Vapor Deposition Technologies
Room California - Session B4-4

Properties and Characterization of Hard Coatings and Surfaces

Moderators: Ulrich May, Robert Bosch GmbH, Diesel Systems, Chau-Chang Chou, National Taiwan Ocean University, Taiwan, Farwah Nahif, eifeler-Vacotec GmbH

2:10pm **B4-4-3 Coatings Selection Criteria for WC/Co Cutting Tools**, ***Aharon Inspektor***, *P Salvador,* Carnegie Mellon University, USA **INVITED**

Internet of Things (IoT), where all objects have unique identifiers and incessant internet connectivity, will fundamentally change the world we live in and the manufacturing industry. In this paper we will examine the impact of the forthcoming 4th Industrial Revolution on machining industry, the anticipated changes in metal cutting procedures and the emerging new generation of cutting tools.

The use of embedded sensors, fast connectivity and intelligent feedback in metal cutting has the potential to increase material removal rates at significantly tougher thermal and mechanical conditions at the cutting edge. Successful implementation of the new technologies will require similar progress in cutting tools. We will first review and analyze current trends and machining strategies in leading workshops. Then, we will discuss key criteria for the design of new cutting tools, and guidelines for the development of new functional coatings. The coating selection criteria will be based on the current and on the anticipated machining wear-maps that chart the optimum machining conditions for various workpiece materials. The paper will include examples from machining High Temperature Alloys, Stainless Steel and Carbon Composites.

2:50pm **B4-4-5 Investigation of the Plasma Electrolytic Oxidation Mechanism of Titanium**, ***Golsa Mortazavi***, *E Meletis,* University of Texas at Arlington, USA

Plasma electrolytic oxidation (PEO) is an environmentally friendly technology capable of forming coatings with excellent adhesion strength. Total applied current to the oxide, in this process, is composed of electronic current caused by sparking and ionic current caused by diffusion of electrolyte ions into the oxide. Correlation between the ionic/electronic current contribution rate at different current densities and the oxide layer characteristics is utilized to understand the coating growth mechanism during the PEO stages. In this study, titania films were produced via PEO on commercially pure titanium in an alkaline phosphate electrolyte at various current densities i.e. 30, 40, 50, 60, 80, 100, and 110 mA/cm^2. Voltage-time (V-t) behavior has been investigated to elucidate the contribution of ionic and electronic current and different stages of PEO process. The V-t response showed that at low current densities, voltage attained relatively constant values, due to the dominance of the electronic current that is mainly due to sparking and as such is independent of the film resistance. High density of plasma discharge at this condition, forms large number of discharge channels and increases the porosity and surface roughness of the coating. Also, these plasma discharges provide enough energy to raise temperature facilitating formation of both rutile and anatase. At high current densities though, the ionic current dominates enhancing ionic diffusion through the oxide resulting in a dense, thick anatase film. The present results show that the V-t response can be utilized to elucidate the oxide growth mechanism during PEO process.

3:10pm **B4-4-6 Lessons Learned from Sputtering Icosahedrally Bonded Borides**, *O Hunold, P Keuter, P Bliem, D Music, F Wittmers, A Ravensburg,* RWTH Aachen University, Germany*; D Primetzhofer,* Uppsala University, Sweden*;* ***Jochen Schneider***, RWTH Aachen University, Germany

We have systematically studied the effect of transition metal valence electron concentration (VEC) of amorphous $T_{0.75}Y_{0.75}B_{14}$ (a–$T_{0.75}Y_{0.75}B_{14}$, *T*= Sc, Ti, V, Y, Zr, Nb) on the elastic properties, bonding, density and electronic structure using *ab initio* molecular dynamics. As the transition metal VEC is increased in both periods, the bulk modulus increases linearly with molar- and mass density. This trend can be understood by a concomitant decrease in cohesive energy. *T′* = Ti and Zr were selected to validate the predicted data experimentally. A–$Ti_{0.74}Y_{0.80}B_{14}$ and a–$Zr_{0.75}Y_{0.75}B_{14}$ thin films were synthesized by high power pulsed magnetron sputtering. Chemical composition analysis revealed the presence of up to 5 at.% impurities, with O being the largest fraction. The measured Young's modulus values for a–$Ti_{0.74}Y_{0.80}B_{14}$ (301±8 GPa) and a–$Zr_{0.75}Y_{0.75}B_{14}$ (306±9 GPa) are more than 20% smaller than the predicted ones. The influence of O incorporation on the elastic properties for these selected systems was theoretically studied, exemplarily in a–$Ti_{0.75}Y_{0.75}B_{12.75}O_{1.25}$. Based on *ab initio* data, we suggest that a–$Ti_{0.75}Y_{0.75}B_{14}$ exhibits a very dense B network, which is partly severed in a–$Ti_{0.75}Y_{0.75}B_{12.75}O_{1.25}$. Upon O incorporation, the average coordination number of B and the molar density decrease by 9% and 8%, respectively. Based on these data the more than 20% reduced Young's modulus obtained experimentally for films containing impurities compared to the calculated Young's modulus for a–$Ti_{0.75}Y_{0.75}B_{14}$ (without incorporated oxygen) can be rationalized. The presence of oxygen impurities disrupts the strong B network causing a concomitant decrease in molar density and Young's modulus. Very good agreement between the measured and calculated Young's modulus values is obtained if the presence of impurities is considered in the calculations. The implications of these findings are that prediction efforts regarding the elastic properties of amorphous borides containing oxygen impurities on the at.% level are flawed without taking the presence of impurities into account.

3:30pm **B4-4-7 Ductile Behavior of Hard MoBC and WBC Nanolaminates**, ***Petr Vašina***, *P Soucek, S Mirzaei, L Zabransky,* Masaryk University, Czech Republic*; J Bursik,* IPM, Academy of Science, Czech Republic*; V Perina,* NPI, Academy of Science, Czech Republic*; V Bursikova,* Masaryk Univerisity, Czech Republic

State-of-art ceramic materials nowadays used as protective coatings such as TiN, TiAlN, c-BN etc. generally exhibit high hardness and high stiffness. These positive features are often accompanied by negative brittle deformation behaviour. To overcome this limitation a new generation of materials with high hardness and moderate ductility is desired. Recently, there has been an increased interest in boron and carbon based nanolaminates such as Mo_2BC [1] which exhibit a very similar structure to the MAX phases. According to the ab-initio models, these materials were predicted to exhibit unusual combination of high stiffness and moderate ductility [1]. The coatings were deposited either by DCMS at extremely high

substrate temperature of 900°C [1] or at moderate temperature of 380°C employing HiPIMS [2]. In our research, co-sputtering of Mo (W), C and B_4C targets to finely tune the coating composition of Mo_2BC and W_2BC was used. Mid-frequency pulsed DC plasma excitation was employed to enhance the ion flux on the substrate by factor of 3 compared to DCMS case which promoted the crystallization of Mo_2BC. Coatings with the same XRD patterns as those deposited by HiPIMS at the same substrate temperature were prepared. The moderate deposition conditions resulted in grown of partially crystalline Mo_2BC coatings with nanocomposite structure where small Mo_2BC crystallites of approx. 10 nm size were embedded in an amorphous matrix. These coatings showed high hardness of 31.6 ± 0.8 GPa and extremely high fracture toughness – it was even impossible to form a crack in these coatings at extremely high indentation load with cube corner indenter where both the coatings and the underlying hard-metal substrate were severely plastically deformed. Only a shear/slip plane defects typical for ductile materials were detected. This required ductile behavior of hard coating observe for partially crystallite Mo_2BC with nanocomposite structure is hard to be met with other commercial coatings tested by similar manner.

1. J. Emmerlich, D. Music, M. Braun, P. Fayek, F. Munnik, J.M. Schneider, J. Phys. D: Appl. Phys, 2009 42 185406 (6pp).

3:50pm **B4-4-8 Coating Characterization with Surface Acoustic Waves***, **Martin Zawischa**, D Schneider, M Leonhardt, S Makowski, V Weihnacht,* Fraunhofer IWS, Germany

Measuring film properties is essential for understanding and designing coating systems and for controlling quality in coating manufacturing.

For more than ten years now, the laser-induced surface acoustic wave technique has been proven as a fast and non-destructive way to characterize coating and surface properties. Several parameters influence the velocity of the waves like Young's modulus, coating thickness, porosity, subsurface damage or hardening zone. Due to the fact, that the penetration depth of propagated waves depends on wave frequency, a bundle of information about the above mentioned parameters can be obtained from the measured dispersion curve of the detected waves. Once the dispersion curve has been measured, a physical model of the coating system is fitted to the measured data to derive the information of interest.

Fields of applications in both research and industrial environments are PVD and CVD coatings, thermal-sprayed coatings, semiconductors, low-k films and bulk materials.

Up to now, the physical model was limited to a single layer or to multilayers with two alternating materials. In this work, an implementation of a more advanced model is presented, which accounts for up to five individual layers with full data set. By means of examples, fitting of some multi-layer systems is demonstrated. In one example several variants of a DLC coating system with a chromium interlayer deposited on a silicon wafer are measured. The number of obtainable parameters is discussed with respect to the shape of the dispersion curve. Different measurement strategies can be deduced from these finding and extend the possibilities of the laser-induced surface acoustic wave method.

4:10pm **B4-4-9 Anti-Corrosion Performance and Wear Behaviour of Laser Deposited Ni-Ti-Zn Coatings on UNS G10150 Steel.***, **Ayanda Xulu,*** Tshwane University of Technology, South Africa*; O Fatoba,* University of Johannesburg, South Africa*; A Popoola,* Tshwane University of Technology, South Africa*; S Pityana,* Council for Scientific and Industrial Research (CSIR), South Africa

The untimely failure of engineering steels when exposed or used in harsh working environment is attributed to low hardness, poor tribological behaviour and corrosion resistance and this invariably restricting its applications. Since the durability of steel is determined by its deterioration over time which is affected by the environment, tailoring of the surface composition and microstructure through laser deposition becomes very vital. The investigation of Ti-Zn-Ni coatings by laser deposition technique is aimed at enhancing the properties of Ti-Zn-Ni coatings on UNS G10150 steel. A 3 kW continuous wave ytterbium laser system (YLS) attached to a KUKA robot which controls the movement of the deposition process was utilized for the fabrication of the coatings. The fabricated coatings were investigated for its hardness, corrosion and wear resistance performance at different laser processing parameters. The corrosion behaviour was investigated in 1M H_2SO_4 and 3.65wt.% NaCl solutions at 28°C via Electrochemical Impedance Spectroscopy (EIS) and Potentiodynamic Polarization techniques. The optical microscope (OM), field emission scanning electron microscope equipped with energy dispersive spectroscopy (SEM/EDS) were used to study the morphology of the fabricated coatings and X-ray diffractometer (XRD) for the identification of the phases present in the coatings . The improved hardness and wear resistance performance were attributed to hard Ti_2Ni intermetallic compound, martensitic TiNi and TiZ_{16} phases. The coatings were found to have uniform and fine microstructures free of cracks and pores. The enhanced corrosion resistance was also attributed to NiTi and TiO_2 phases formed.

4:30pm **B4-4-10 Effect of V Addition on the Thermal Stability, Oxidation Resistance and Tribological Performance of Self-lubricant TiSi(V)N Coatings Deposited by HiPIMS in DOMS Mode***, **Filipe Fernandes**, R Serra, A Cavaleiro,* SEG-CEMUC, University of Coimbra, Portugal

Effective lubrication and wear protection at high temperature and in cyclic environments are continuing challenges that are crucial for energy efficiency in turbomachinery, machining tools and aerospace applications. In recent years, various self-lubricating coatings have been developed by combining hard and wear resistant binary or ternary coatings (such as TiN, TiAlN, CrN, CrAlN, YSZ) with specific elements (e.g. Ag, V) that reduce friction by diffusing to the surface and/or forming a low friction tribolayer on the wear surface. Despite the improvement in friction and wear resistance, the quick depletion of the lubricious specie from the coating system by rapid out diffusion and consequently loss of improved tribological behavior delayed their upscaling to the industry. A promising approach for controlling diffusion of the lubricant element is the use of a diffusion barrier layer. This is the case of the TiSiN coating system, which deposited as nanocomposite structure the amorphous Si-N phase can work as an antidiffusion barrier. Thus the aim of this work is to evaluate the effect of V additions on the structure, thermal stability, oxidation resistance and tribological performance of TiSiN films deposited with dissimilar Si contents, with emphasis on the development of selflubricant coatings with control release of the lubricious phase. TiSi(V)N coatings with different vanadium and Si contents were deposited by DOMS. Temperature effect on the structure of the V rich coating was characterized in open air in-situ by hot-XRD device in the range of 500 °C to 750 °C. Thermal stability was studied in a protective atmosphere in the range of 500 °C to 1000 °C. The oxidation behavior of coatings was studied by thermogravimetry (TGA). Bright field scan transmission electronmicroscopy STEM/EDX maps and elemental profiles along the cross section of the oxidized coatings were acquired to understand the kinetics of ions diffusion and oxide scale growth. Tribological behaviour of coatings was characterized in a high temperature tribometer. After wear tests, the wear tracks and wear debris were characterized by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS) and Raman spectroscopy. Oxidation resistance of coatings decreased with V additions. Tribological tests showed that friction and wear rate of coatings decreased progressively with increasing vanadium content.

4:50pm **B4-4-11 Wear Study of PVD AlTiN Coatings with High Al Content***, **Joern Kohlscheen**, C Bareiss,* Kennametal GmbH, Germany*; C Charlton, D Banerjee,* Kennametal Inc., USA

AlTiN coatings are widely used as protective coatings in the cutting tool industry. It is generally accepted that increasing the aluminum content from 50 to about 65 at. % (metallic fraction of the compound) improves the tool performance in many applications. However, for high hardness the coating structure needs to remain essentially cubic (fcc). If deposition parameters are not optimized or the Al content is increased further, considerable amounts of the soft hexagonal phase will be deposited and wear resistance of the film is reduced. We present a study of AlTiN coatings with compositions near an elemental ratio of 2:1 (Al:Ti). Carbides samples were coated by arc PVD using a commercial system. Phase change in the films was promoted with selected variants by annealing up to 1000 degree C under vacuum. Structural analysis was done by SEM and XRD (BB and GI mode). Basic mechanical properties were determined by universal hardness testing. The wear behavior of the coatings was studied by cyclic indentation on the macro and micro scale and the resultung wear is described in detail. As expected, aluminum contents above 65 at. % lead to rapid decrease in wear resistance. Formation of the undesired hexagonal phase could be delayed by suitable deposition parameters (magnetic field at the arc source). Annealing for extended periods of time reduce coating performance again as more hexagonal phase is formed. The wear behavior in the laboratory test generally reflects the results obtained under more complex loading situation (dry milling of ductile cast iron).

5:10pm **B4-4-12 Tribological Behavior of MoBCN-MoSx Coating under Elevated Temperature**, ***Xiaodong Zhu***, *Q Li, L Qiu, K Xu,* Xi'an Jiaotong University, China

To extend the utilization of tribological coatings, people have designed adaptive or "chameleon" coatings which reduce friction and wear by changing surface chemistry and microstructure in response to the change of environment and loading. In these coatings, a wear-resistant phase was chosen as the main phase and some lubricating phase as assistants. The wear-resistant phase usually has a high friction and large amount of lubricant is necessary to reduce the coefficient of friction, and thus leads to low hardness and reduced oxidation resistance . MoBCN coating was found to have low friction coefficient from room temperature to 600 ℃ . By adding lubricating phases of MoS_2, the MoBCN/MoS_2 composite coating may possess better tribological propertiesfor wide temperature range.

In this study, MoBCN/MoS_x coatings were prepared by ion beam enhanced magnetron sputtering from a Mo/B_4C /MoS_x composite target. The content of boron and sulfur was controlled by the number of the corresponding mosaic targets. The friction and wear behaviors of these composite coatings were evaluated by ball-on-disc wear test at different temperatures. The introduction of sulfer reduces the coefficient of friction and wear rate at room temperature. However, it is oxidized into MoO_3 and loses its character of lubrication at elevated temperature, accordingly its oxidation tendency increases. It is shown that more content of boron may reduce the negative effect of sulfur on the oxidation resistance, and thus its tribological behavior at elevated temperature is improved. Therefore, boron is proved to be the key element in enhancing tribological performance of MoBCN/MoS_x coating at elevated temperature.

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces
Room San Diego - Session E3

Tribology of Coatings for Automotive and Aerospace Applications

Moderators: Sébastien Guimond, Oerlikon Balzers, Oerlikon Surface Solutions AG, Nicolas Argibay, Sandia National Laboratories, Pantcho Stoyanov, Pratt & Whitney, USA

1:50pm **E3-2 Bending Fatigue Property Enhancements of Metallic Substrates by Thin Film Metallic Glass Coatings**, ***Chia-Hao Chang***, *J Chu,* National Taiwan University of Science and Technology, Taiwan

Thin film metallic glasses (TFMGs) possess extraordinary mechanical properties such as high strength, high toughness, large elastic limit as well as excellent wear and corrosion resistances. Thus, they have attracted industrial interests for the potential applications with their superior mechanical properties. In this presentation, 200-nm-thick TFMG and TFMG/ceramic multilayer coatings were deposited on the 316L stainless steel, Ti6Al4V alloy and ZK60 Mg alloy specimens using radio frequency magnetron sputtering system for four-point-bending fatigue test at room temperature. Fatigue properties of either TFMG-coated or TFMG/ceramic multilayer-coated samples were improved significantly. The hardness of TFMGs and multilayer, their excellent adhesion to the substrate, and the resulting reduction in surface roughness are believed to account for the enhanced fatigue characteristics.

2:10pm **E3-3 Optimization of the Tribological Contact between Piston Ring and Cylinder Wall with Oxide Coatings**, *C Bohnheio, P Ernst, P Luethy,* Oerlikon Metco AG, Switzerland*; J Ramm, H Rudigier,* ***Florian Seibert***, *B Widrig,* Oerlikon Surface Solutions AG, Liechtenstein

Strategies to further improve the efficiency of modern combustion engines resulted in the development of so called downsized engines operating at higher power densities and operation temperatures. This implies improved stability of material surfaces in the contact between piston ring and cylinder wall. The piston group contributes also significantly to the energy loss in the powertrain of a combustion engine. Therefore, reduced friction losses are another demand in engine development. The selection of appropriate coatings for the piston ring and the liner surface may respond to both challenges.

Two coating technologies were investigated: physical vapour deposition (PVD) for the piston rings and atmospheric plasma spray (APS) for the cylinder bore surfaces. In a first step, these coatings were applied to test substrates and investigated by a reciprocating wear test (SRV®). The tests were performed under dry and lubricated conditions and for room temperature and temperatures up to 160°C. Wear of the coating and the ball (counter-part) was measured by confocal microscopy. It could be shown that the tribological contact between hard PVD and APS oxide coatings and the alumina counter-part did not only show excellent wear behavior for different surface finishing, but had also the highest stability for elevated temperatures. In a next step, the most promising coating combinations were tested in a motorbike engine configuration and compared with standard materials like CrN for the piston ring and a number of standard coatings for the liner. The tests demonstrated for one oxide-oxide combination an increase of the power output of the engine by 1.5%.

2:30pm **E3-4 Mechanical Characterization of the Glaze Layer formed by Fretting Wear in a Ceramic versus Metallic Alloy Contact**, *A Viat,* ***Gaylord Guillonneau***, *S Fouvry,* Ecole Centrale de Lyon, France*; G Kermouche,* Ecole des Mines de Saint-Etienne, France*; J Michler,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

In a simplified aeronautic blade disk contact, between ceramic and Haynes 25 (cobalt-based alloy) flats, high temperature fretting wear induces third body formation. This third body, called "glaze layer", is created from compacted and sintered debris. Nanocrystalline structure and composition have been described in a previous paper [1]. The glaze layer adhering on both alloy and ceramic counterparts contains counterface material, as observed for ductile contacts [2]. However, the glaze layer does not behave like a ductile material at first sight: under ambient temperature, it is brittle and harder than the two respective substrates.

In-situ SEM micropillar compression at temperatures between ambient and 500 °C have been performed in the glaze layer and its substrates in cross section. This approach focuses on the mechanical behavior at temperatures where the glaze layer is created and is operational for wear protection. The device used is an Alemnis/EMPA high temperature SEM micro-tester [3]. Micropillar compression enables to obtain directly the mechanical response of material surfaces in terms of elasticity, yield stress / hardness and work hardening. Also, the deformation behaviour can be directly observed by SEM images. Firstly, the tribological contact and the device used for in-situ microcompression will be presented. Then the mechanical properties will be detailed and discussed in terms of elasticity and plasticity as a function of temperature. Finally, a discussion about the relation of the glaze layer mechanics with its formation and lubricious properties is proposed.

References

[1] Viat A, De Barros Bouchet M-I, Vacher B, Le Mogne T, Fouvry S, Henne J-F. Nanocrystalline glaze layer in ceramic-metallic interface under fretting wear. Surf Coat Technol.

[2] Rigney D.A., 2000. "Transfer, mixing and associated chemical and mechanical processes during the sliding of ductile materials", Wear 245, pp 1-9

[3] Rabe R, Breguet J-M, Schwaller P, Stauss S, Haug F-J, Patscheider J, et al. Observation of fracture and plastic deformation during indentation and scratching inside the scanning electron microscope. Thin Solid Films 2004;469–470:206–13

2:50pm **E3-5 Sequence of Stages in the Microstructure Evolution in Copper under Reciprocating Tribological Loading**, ***Christian Greiner***, Karlsruhe Institute of Technology (KIT), Germany **INVITED**

Tailoring the surface properties of a material for low friction and little wear has long been a goal of tribological research. Since the microstructure of the material under the contact strongly influences tribological performance, the ability to control this microstructure is thereby of key importance. However, there is a significant lack of knowledge about the elementary mechanisms of microstructure evolution under tribological load. To cover different stages of this microstructure evolution, high-purity copper was investigated after increasing numbers of sliding cycles of a sapphire sphere in reciprocating motion. Scanning electron and focused ion beam (FIB) microscopy were applied to monitor the microstructure changes. A thin tribologically deformed layer which grew from tens of nanometers to several micrometers with increasing number of cycles was observed in cross-sections. By analyzing dislocation structures and local orientation changes in the cross-sectional areas, dislocation activity, the occurrence of a distinct dislocation trace line and the emergence of new subgrain boundaries could be observed at different depths. These results strongly suggest that dislocation self-organization is a key elementary

mechanism for the microstructure evolution under a tribological load. The distinct elementary processes at different stages of sliding identified here will be essential for the future modelling of the microstructure evolution in tribological contacts.

3:30pm **E3-7 Effect of Test Atmosphere on the Tribological Behaviour of the Fluorinated Tetrahedral Amorphous Carbon (ta-C-F) Coatings against Steel**, ***MuhammadZafarUllah Khan***, *S Bhowmick, A Alpas,* University of Windsor, Canada

Carbon based coatings exhibit low coefficient of friction (COF) in sliding contact against steel, but the resulting COF is highly sensitive to environmental conditions. This study examines the tribological properties of a fluorinated tetrahedral amorphous carbon (ta-C-F)coating containing 12 at. % F (ta-C-F) tested against a 52100 grade steel at 2.0 N and 5 cm/s in ambient air (53% RH), in dry oxygen and in dry N_2 atmospheres with relative humidity reduced to less than 4%. The ta-C-F coating exhibited low and stable steady state COF (μ_s) under ambient (0.25), dry oxygen (0.27) and N_2 (0.22) atmospheres conditions. It was suggested that a carbonaceous transfer layer passivated by F atoms was responsible for low and stable μ_s under all testing conditions as revealed by X-ray photoelectron and micro-Raman spectroscopy. However, the running-in COF (μ_R) varied with the testing atmosphere. The highest running-in COF (μ_R = 0.56) was observed under ambient condition which was reduced to 0.48 in dry oxygen and 0.40 in N_2. The presence of N_2 played an important role in stabilizing carbonaceous transfer layer by limiting the formation of abrasive iron oxide particles.

3:50pm **E3-8 Laser-based Process for Polymeric Tribological Coatings on Lightweight Components**, ***Hendrik Saendker***, *J Stollenwerk,* Fraunhofer Institute for Laser Technology, Germany*; P Loosen,* Chair for Technology of Optical Systems TOS, Germany

Multiple applications, especially in the automotive sector and in mechanical engineering, are predominantly affected by friction and wear stress and, therefore, represent a substantial challenge for the components being used. Oftentimes, the endurance and the efficiency of these components can be enhanced by means of application-specific tribological coatings. For engine components like pistons or bearing shells made of light metals like Aluminum, current coatings based on sliding lacquer do not meet increasing requirements, particularly regarding temperature resistance and wear protection. Coatings based on high-temperature resisting thermoplastic polymers like PEEK (polyether ether ketone) represents an alternative to conventional tribological coatings. An outstanding challenge results from using temperature-sensitive Aluminum alloy which show structural changes above temperatures of 140 - 180°C, hence below the melting temperature of PEEK of approximately 340°C. In Comparison to conventional oven processes, laser-based processes provide a reduced thermal load of the workpiece. Therefore, the investigated coating process comprises four consecutive steps: a laser-based pre-treatment of the components (1), the preparation of a hydrous dispersion based on PEEK powder (2), the deposition of the dispersion by e.g. spray coating (3), and the melting of the PEEK powder by means of laser radiation (4).

The current investigations are primarily focused on the investigation of the influence of different pre-treatments on the adherence of the coating and the influence of different temporally temperature profiles during laser melting on the properties of the coatings, e.g. relative density, crystallinity, surface roughness and structural changes of the base material. The pre-treatments comprise the processing of the component by means of pulsed laser radiation. For the laser melting of the PEEK powder, different lasers operating in the continuous wave mode are used.

By means of this new coating process, dense and adherent tribological coatings can be applied on Aluminum substrates. The adherence is significantly increased by the laser-based pre-treatment of the metallic substrates.

4:10pm **E3-9 Long-term Tests of Tribological Properties of HVOF-sprayed WCCoCr Carbide Coatings of Ultra-fine Powders with a View to Applying Them to Sliding Rings of Mechanical Seals**, ***Aleksander Iwaniak***, *R Swadzba,* Silesian University of Technology, Poland*; G Wieclaw,* Certech Sp. z o.o., Poland*; L Norymberczyk,* ANGA Uszczelnienia Mechaniczne Sp. z o.o., Poland

This paper describes tests aimed at exploring the tribological properties of thermal-sprayed coatings. The coatings were deposited onto the face areas of cylindrical metallic specimens whose shape approximated that of sliding rings used in mechanical seals. Long-term (over 400 hours of continuous operation) frictional wear tests of the coated samples were performed at a specialized workstation simulating the operation of a mechanical seal. The wear of the specimens was evaluated by 3D scanning. After the tests, the specimen surfaces were examined by means of a 3D profilometer and a scanning electron microscope (SEM, EPMA). The tests show that WCCoCr coatings sprayed using ultra-fine powders (less than 10 µm) ensure the effectiveness of a friction pair and are characerised by a low degree of frictional wear in comparison with coatings sprayed using powders having coarser particles (25 µm). The highest degree of wear was identified for CrCNiCr-type coatings. The tests indicate that metallic sliding rings covered with WCCoCr carbide coatings of ultra-fine particle powders can be used in certain types of mechanical seals in which solid tungsten carbide (WC) rings are currently used.

Financial support by The National Centre for Research and Development (NCBiR) in Warsaw, Poland - Project No INNOTECH-K2/IN2/2/181798/NCBR/13 is gratefully acknowledge.

4:30pm **E3-10 Role of Oxygen in High Temperature Sliding Behaviour of W Containing Diamond-like Carbon (W-DLC)**, *S Bhowmick, M Lou, A Alpas,* ***MuhammadZafarUllah Khan***, University of Windsor, Canada

W-containing diamond-like carbon (W-DLC) coating is of interest to the manufacturing industry, as they showed low coefficient of friction (COF) against aluminum at elevated temperatures. The low COF values at 400 ˚C (0.18) and 500 ˚C (0.12) could be attributed to the formation of the transfer layers made of lubricious tungsten oxide WO_3. However, at intermediate temperatures between 100 ˚C and 300 ˚C, a high COF of 0.60 was recorded. In this work, the friction reduction mechanisms of W-DLC coatings were investigated in dry oxygen atmosphere and studied as a function of testing temperature up to 500 ˚C against an Al alloy. The purpose of maintaining an oxygen rich environment was to increase the propensity of WO_3 formation at the sliding surfaces. An average steady state COF (μ_s) of 0.11 was observed at 25 ˚C and low friction values were maintained up to 500 ˚C where μ_s was 0.13. Micro-Raman and X-Ray photoelectron spectroscopy (XPS) revealed that at room temperature the transfer layers were rich in carbon, whereas between 100 ˚C to 500 ˚C the transfer layers primarily consisted of tungsten oxide. The presence of sufficient oxygen in testing atmospheres led to the formation of tungsten oxide rich transfer layers which reduced the COF between 100 ˚C to 500 ˚C. This work shows the importance of compositional characterization and study of mechanisms of transfer layer formation during sliding friction of 319 Al tested against W-DLC coatings.

New Horizons in Coatings and Thin Films
Room Royal Palm 1-3 - Session F4-2

Functional Oxide and Oxynitride Coatings

Moderators: Michael Stueber, Karlsruhe Institute of Technology, Anders Eriksson, Oerlikon Balzers, Oerlikon Surface Solutions AG

1:50pm **F4-2-2 After-arc Plasma Technique to Modify Chemical States of Surface and Grain Boundaries of 50-nm-thick Conductive ZNO Films to Achieve a Fast-response Hydrogen Sensor**, ***Tetsuya Yamamoto***, *J Nomoto, H Makino,* Kochi University of Technology, Japan*; H Kitami, T Sakemi, Y Aoki,* Sumitomo Heavy Industries, Ltd., Japan*; K Kobayashi,* Kochi University of Technology, Japan*; S Kishimoto,* Kochi National College of Technology, Japan

We report a high-response hydrogen gas sensor based on a 50-nm-thick conductive Ga-doped ZnO (GZO) polycrystalline films. The GZO films were deposited on amorphous glass substrates at a temperature of 200 Celsius by ion plating with direct-current arc discharge. The Ga_2O_3 content in the ZnO targets were 4 wt.%. Control of chemical states of adsorbed oxygen atoms on the ingrain surface and at grain boundaries and of oxygen-related point defects such as oxygen vacancies in the vicinity of the ingrain surface is essential to achieve hydrogen gas sensors showing a very strong and *immediate response* to this gas. We, thus, have been developing a novel after-arc plasma technique to generate electronegative oxygen ion (O^-) for the control of the density and chemical states of the different type of defects above. The analysis of the data obtained by X-ray photoelectron spectroscopy measurements for as-deposited GZO films indicated the presence of oxygen vacancies, O^-, hydroxyl, oxygen molecule and water molecule. On the other hand, XPS study on the GZO films after the exposure to the O^- revealed that the intensity of the peak to the O^{2-} ions on the wurtzite structure of the hexagonal Zn^{2+} ion array increased, whereas the intensity of the peak associated with the O^{2-} ions that are in oxygen

deficient regions within the ZnO matrix decreased. The above changes in the intensity of this component may be in connection with the variation in the concentration of the oxygen vacancies. This implied that some of the doped oxygen species should adsorbed on the surface of grain boundaries, trapping carrier electrons. This lead to the formation of a high and narrow energy barrier at a grain boundary in addition to the energy barrier owing to the nature of the grain boundaries such as discontinuity and disorder. In this study, we assume the chemical reaction limiting the performance of hydrogen gas sensors can be as follows: the reaction of hydrogen gas (H_2) with an O^- ion adsorbed on a grain boundary produces water molecule together with a free electron, resulting in a decrease in the electrical resistivity. We confirmed the distinctly enhanced performance of the hydrogen gas sensors with *fast response* within 1 second at a temperature of 330 Celsius. The use of extrinsic O^- ions exposure with the after-arc plasma technique would be an effective way for the achievement of H_2 sensors exhibiting at lower temperature. We will propose a theoretical model of the H_2 sensing mechanism limiting the properties of the H_2 sensor.

2:10pm **F4-2-3 Microstructure and Corrosion Resistance of PVD Hf-coated Mg Alloy after Thermal Oxidation Treatment***, D Zhang, Z Qi, B Wei,* ***Zhoucheng Wang,*** Xiamen University, China

Hf coatings are fabricated on Mg alloy by PVD magnetron sputtering and further submit to thermal oxidation treatment at temperature of 200℃, 300℃ and 400℃, respectively. The surface analysis indicates that new shallow grain boundaries are appeared on the coating surface when the treatment temperature is over 300℃. These changes in microstructure inhibit the permeation of corrosion media into the substrate and decrease the diffusion rates of corrosion products. Moreover, the thickness of the hafnium oxide film resulted from surface oxidation is increased with increasing the treatment temperature. As a result, surface densification and oxidation of the coating induced by the post treatment significantly decreased its susceptibility to corrosion. In addition, the release of the residual stress produced by the post treatment suppresses the delaminating of the coating as Mg is corroded. Consequently, the Hf coating post-treated with 400℃ exhibits more positive corrosion potential, lower corrosion current density and higher polarization resistance than that of the other coating in electrochemical test. However, salt spray test reveals that the Hf coating post-treated with 300℃ provides the most efficient long-term protection for Mg alloy. Scratch test reveals that it was mainly due to the poor adhesion strength resulted from the big difference in thermal expansion coefficients between coating and substrate during the high treatment temperature (400℃).

2:30pm **F4-2-4 HiPIMS Deposition of Ta-O-N Coatings with Modified Surface by Cu Nanoclusters for Water Splitting Application***, Jiří Čapek, Š Batková, S Haviar, J Houška,* University of West Bohemia, Czech Republic

As reported in [1], Ta-O-N material can provide appropriate properties (i.e., band gap width and alignment) for splitting of water into H_2 and O_2 under visible light irradiation (without any external voltage). This could bring a great possibility to convert the solar light into a useful chemical energy. However, it is still impossible to prepare the Ta-O-N electrodes by conventional (chemical) methods at the temperatures less than 500°C without post-annealing. Moreover, the efficiency of this material for water splitting is limited due to fast recombination rate of photogenerated electrons and holes.

Recently, we have demonstrated [2] in our laboratory that high-power impulse magnetron sputtering is a suitable technique for low-temperature (less than 250 °C) and high-rate (higher than 150 nm/min) deposition of Ta-O-N coatings with tunable elemental composition and optical band gap width. In this work, we focus on a further optimization of deposition conditions (e.g., average pulse target power density, working gas pressure, substrate bias and temperature) in order to reach proper crystal and electronic structures of Ta-O-N coatings with respect to the water splitting application. Moreover, we propose to modify the surface of the coatings by Cu nanoclusters in order to enhance the efficiency of water splitting due to a reduced recombination rate of electrons and holes. For this purpose, we have designed a unique dual magnetron-based system combining the reactive high power impulse magnetron sputtering with a source of metallic nanoclusters. The results of our experiments including the coating properties investigated using atomic force microscopy, spectroscopic ellipsometry and high-resolution SEM and preliminary data on photocatalytic activity are presented in detail.

[1] R. Abe, J. Photochem. Photobiol. C Photochem. Rev. 11 (2010) 179.

[2] J. Rezek et al., Thin Solid Films. 566 (2014) 70.

2:50pm **F4-2-5 New Oxides and Oxynitrides for Thermoelectrics and Hard, Transparent Coatings***, Per Eklund,* Linköping University, IFM, Sweden **INVITED**

I present an overview of our experimental and theoretical investigations of $Ca_3Co_4O_9$- and $CaMnO_3$-based systems by reactive magnetron sputtering for thermoelectrics and amorphous oxynitride M-Si-O-N coatings as hard, transparent coatings. We have introduced a two-step sputtering/annealing method for the formation of highly textured virtually phase-pure $Ca_3Co_4O_9$ thin films by reactive co-sputtering from Ca and Co targets followed by an annealing process at 730 °C under O_2-gas flow.The thermally induced phase transformation mechanism was investigated by *in-situ* time-resolved annealing experiments using synchrotron-based 2D x-ray diffraction as well as *ex-situ* annealing experiments and standard lab-based x-ray diffraction [1] . By tuning the proportion of initial CaO and CoO phases during film deposition, the method enables synthesis of $Ca_3Co_4O_9$ thin films as well as Ca_xCoO_2. The same approach is used to synthesize $CaMnO_3$ and $CaMn_xNb_{1-x}O_3$ perovskite oxides on Al_2O_3 (0001), (1-100) and (1-102). Furthermore, amorphous thin films in the Mg/Ca-Si-O-N systems were deposited by reactive RF magnetron co-sputtering from Mg(Ca) and Si targets in $Ar/N_2/O_2$ gas mixtures [2]. The films were found to be homogeneous and transparent in the visible region with high hardness of 21 GPa and elastic modulus of 166 GPa.

3:30pm **F4-2-7 Reactive Magnetron Sputter Deposition of NbO_x Thin Films***, Roland Lorenz,* Montanuniversität Leoben, Austria*; M O'Sullivan, D Sprenger, B Lang,* Plansee SE, Austria*; C Mitterer,* Montanuniversität Leoben, Austria

Within this work, niobium oxide thin films were deposited on silicon and glass substrates by reactive dc magnetron sputtering from niobium targets prepared by cold gas spraying. The oxygen partial pressure in the oxygen/argon atmosphere was varied while the overall gas pressure and the applied target current were kept constant. The applied pulsed d.c. substrate bias voltage was set to -50 V and several pulse conditions were used. Scanning electron microscopy was used to investigate the topography of film surface and fracture cross-section. To examine the crystalline structure, X-ray diffraction and Raman spectroscopy was applied. Further, X-ray photoelectron spectroscopy and energy dispersive X-ray spectroscopy were used to measure the oxygen content within the films and to illuminate the chemical bond structure. The optical properties of the films were determined by their reflexion and transmission spectra, while the electrical thin film resistivity was measured by four point probe. With increasing oxygen partial pressure the film growth rate decreases, while the oxygen content within the films increases. All films grown show a smooth surface and their amorphous microstructure is reflected by both, the fracture cross-sections and the X-ray diffractograms. The increasing oxygen content within the films leads to a transition from non-transparent films to nearly fully-transparent films. This transition is linked to an increase of the electrical resistivity, where films grown at the highest oxygen content show insulating properties.

3:50pm **F4-2-8 Electrical Properties of BiNbO Thin Films Deposited by Dual Co-sputtering***, Osmary Depablos-Rivera, J Pérez-Alvarez,* Instituto de Investigación en Materiales-UNAM, Mexico*; S Charvet, M Lejeune,* Université de Picardie Jules Verne, France*; S Rodil,* Instituto de Investigación en Materiales-UNAM, Mexico

The bismuth oxide-based materials have been gaining interest because their optical and electrical properties are suitable for applications, such as opto-electronic devices, catalysts in photo-induced processes and clean energy generation areas. The bismuth niobium oxides (BiNbO) system is one of this materials group, and they have been reported as possible candidates for solid electrolytes and high-k dielectric materials for capacitors. In such applications, their synthesis as thin films is desirable. In this work, we propose the use of the dual magnetron co-sputtering technique for the synthesis of the different compounds of the BiNbO system controlling the composition and structure by adjusting the deposition parameters of the two independently driven targets. The films were deposited from an α-Bi_2O_3 and Nb targets; the power applied to the ceramic target was fixed at 30 W (radio frequency), and the power applied to the Nb was varied between 20 and 150 W (DC). The deposition was done under $Ar:O_2$ (20 volume % O_2) reactive atmosphere. The substrates were borosilicate glass pieces, which were heated at 150 °C. The films deposited at Nb power above 50 W were amorphous, then they were annealed at 600 °C for 2 h in air. The identification of the obtained different phases was done correlating the structural and compositional results by x-ray diffraction and energy dispersive x-ray spectroscopy/x-ray photoelectron spectroscopy, respectively. Four different structures were obtained: solid

solutions with different Nb concentrations and defective fluorite-based structure, Bi_3NbO_7, $Bi_5Nb_3O_{15}$ and $BiNbO_4$. The electrical conductivity of the films was measured as a function of the temperature by both DC and AC (impedance spectroscopy) two-probe methods, using Pt electrodes on the film surface and a ring electrode configuration. From the analysis of the data, it was possible to estimate the activation energy for the ionic and or electronic conduction processes. The films presenting the fluorite solid solution structure and the Bi_3NbO_7 phase showed ionic conductor behavior, while the other phases were insulators.

Acknowledgements: The research leading to these results has received funding from the BisNano project (125141), PHOCSCLEEN (318977) and the CONACYT (251279), DGAPA-PAPIIT (100116). ODR thanks to CONACYT for the scholarship during the PhD study.

4:10pm **F4-2-9 Structure and Properties of Magnetron-sputtered Manganese Ferrite Films**, ***Fred Fietzke***, *O Zywitzki,* Fraunhofer FEP, Fraunhofer Institute for Organic Electronics, Germany

Mixed oxides of iron with other metals like zinc, nickel, or manganese have already been used for a long time because of their magnetic properties, especially in electrical engineering as core material of coils and current transformers.

The fabrication of the bodies needed for these applications is usually carried out by sintering technique, in which the details of process management affect the characteristics of the finally produced material in decisive way.

Ferrites as thin film material so far have been little investigated but more and more come into focus of interest for potential applications as electromagnetic shielding or optical absorber.

In the work to be presented, manganese ferrite films with and without the addition of chromium have been produced by reactive pulsed magnetron sputtering of alloyed targets.

Primarily, the influence of substrate temperature and oxygen content in the gas atmosphere on structure and optical properties of the deposited layers have been investigated. The evaluation of the magnetic properties is of more complex nature and will be published at a later date.

Layers with thicknesses between one and two microns have been deposited onto flat samples of polished stainless steel and borosilicate glass. The substrate temperature was in the range from 150°C (without additional heating) to 600°C.

All deposited films show a dark anthracite or black appearance in reflected light and a more or less pronounced transmittance in the infrared region, where the transmission factor is determined by the oxygen content and the onset wavelength of transmission by the metal composition.

Whereas at lower substrate temperatures smooth amorphous films with distinct residual reflectivity are formed, at temperatures above 500°C matt crystalline layers with an absorption coefficient of more than 95% over the whole wavelength range of visible light arise.

The crystalline layers exhibit spinel structure and a surface roughness of more than 100 nanometers. XRD spectra, SEM pictures, and GD-OES profiles will be presented, and the mechanism of layer growth in the different temperature regions will be discussed.

4:30pm **F4-2-10 A Combined Optical and Electronic Structure Analysis of ZnO:Al Films: Bandgap Renormalization and the Burstein – Moss Effects**, ***Neilo Trindade,*** Sao Paulo Federal Institute, Brazil*; N Marana, M Junior, J Sambrano, A Tabata, J Silva, J Bortoleto,* Sao Paulo State University, Brazil

ZnO and ZnO:Al are wide-bandgap semiconductors which have many applications, mainly as transparent conducting films. ZnO is one of the most promising candidates to replace ITO because of its low toxicity, availability and low production cost. To reduce the electrical resistivity of this material different types of dopants have been used. The Al3+ ion (0.54 Å) is considered one of the best dopants because it has ionic radius close to the radius of the ion Zn2+ (0.74 Å). As a conductive transparent oxide, ZnO doped with Al (AZO) shows great promise for applications such as emitters in the range UV / blue, photodetectors, transparent electronics and solar cells. Thin films of these compounds were deposited onto glass and silicon substrates by RF magnetron sputtering for the investigation of structural and optical characteristics. In order to produce ZnO:Al, the target composition consisted of 95.3 at.% zinc and 4.7 at. % aluminum. The XRD results show that the films present wurtzite structure and that the crystallinity is significantly improved with the Al incorporation. A high degree of orientation texture with the [001] axis perpendicular to the substrate surface is observed in the doped samples. The Al incorporated films exhibited optical transmittance above 80% in the visible spectrum and a clear absorption band in the infrared due to free carriers. Additionally, the optical band gap around 3.5 eV is significantly above the values for the intrinsic ZnO (~ 3.3 eV). Photoluminescence (PL) measurements showed a broad emission band in the visible region. Narrower PL emission lines at 3.32 and 3.37 eV showed up in Al incorporated films, and were related to excitonic emissions. The experimental results were interpreted using computational modeling based on the Density Functional Theory. The results show that the Burstein-Moss effect plays a central role in determining the optical characteristics of the doped material. In addition, the electronic structure analysis show the dominant effect related to Al incorporation in the films, and that the contribution of aluminum atoms affects mainly the conduction band and Fermi level. The authors would like to thank the financial support of the Brazilian agencies FAPESP (2008/53311-5) and CNPq (555774/2010-4).

Surface Engineering - Applied Research and Industrial Applications
Room Sunrise - Session G2

Components Coatings

Moderators: Kenji Yamamoto, Kobe Steel Ltd., OsmanL. Eryilmaz, Argonne National Laboratory, USA, Jolanta Ewa Klemberg-Sapieha, Polytechnique Montreal

1:50pm **G2-2 Advanced Metal/Ceramic Nano-multilayers for Joining Applications: Interplay between Nano-confinement, Stress Relaxation and Environmental Conditions**, ***Mirco Chiodi,*** *C Cancellieri, F Moszner,* Empa, Laboratory for Joining Technologies & Corrosion, Switzerland*; M Andrzejczuk,* Warsaw University of Technology, Poland*; J Janczak-Rusch, L Jeurgens,* Empa, Laboratory for Joining Technologies & Corrosion, Switzerland

The industrial demand to manufacture complex, heterogeneous devices has grown exponentially. Such devices typically comprise various materials with different heat sensitivities and thermal expansion coefficients. Thus, novel approaches towards joining of complex multi-materials at ever-reduced temperatures are emerging. Among the others, a promising strategy involves the use of nanostructured brazing fillers in the form of coatings consisting of Nano-MultiLayers (NMLs) of metallic brazing filler and a chemically inert barrier. The interplay between spatial confinement, internal stress gradients and the processing environment can stimulate phase-transitions and/or enhanced kinetics associated with a significant outflow of the confined metallic brazing filler to the surface at reduced temperatures. This phenomenon could be exploited for joining materials well below the melting point of the bulk constituents.

Here, we present a comprehensive investigation of the microstructural evolution of (Ag/AlN)5nm/10nm NML coatings upon heating in air. SEM/TEM results evidence the strong migration of Ag from the inner part of the NML to the surface. Silver particles as large as 1 µm are found after a heat treatment in air up to 420 °C. XRD characterization and pole figures confirm that Ag and AlN are initially strongly textured. The in-plane texture is partially lost upon heating in air, as a consequence of the Ag migration and the partial oxidation of AlN. The microstructural evolution of the Ag/AlN NML during annealing was monitored by real-time XRD collected at the synchrotron. Beyond this temperature, a strong increase in the Ag coherency domain is registered. Such increase correlates with the Ag particle appearing on the surface and subsequently coarsening. The average stress state in the Ag layers has been qualitatively evaluated using the real-time XRD data. The results indicate an accumulation of (thermal) stress between 200-280 °C which is then released at higher temperatures, triggering the massive Ag migration. Identical experiments carried out in vacuum or in absence of multilayered structure indicate that no Ag migration takes place. To elucidate the crucial role of oxygen on the Ag mobility at low temperatures, an extensive XPS analysis was carried out on samples heated at different temperatures (from 200 °C to 420°C). The results indicate that oxygen is penetrating through the NML structure and (partially) reacting with both AlN (forming AlOx) and Ag (being adsorbed and/or incorporated at Ag layers surface). The adsorption and dilution of oxygen in Ag can strongly enhance its atomic mobility, thus further easing its relocation on the NML surface.

2:10pm **G2-3 Coatings for the Aerospace Industry***, Jeffrey Lince,* The Aerospace Corporation, USA **INVITED**

Coatings are of critical importance to both aircraft and spacecraft. However, environmental requirements for coatings between the two vary considerably. Coatings used to protect turbojet engines must operate in air at a wide range of temperatures from ambient to greater than 1200°C. In contrast, coatings used on spacecraft may be required to achieve their function in air during prelaunch storage, and also on orbit, i.e., in vacuum, at lower temperatures, and in a potentially radiation-rich environment. This talk will provide a survey of coatings techniques for aircraft and spacecraft, concentrating on areas where improvements are needed. For example, superalloys are used to maintain strength at elevated temperatures in aircraft applications, but compatible coatings are required to form thermal barriers, and to minimize corrosion and fatigue. Thermal spray coatings are being used extensively for this purpose. In addition, thermal spray and PVD coatings are used to coat ceramic fiber cloth with metals to form advanced metal-matrix composites (MMCs) that are low weight and exhibit superior materials properties. Solid lubricating/antiwear coatings in aircraft and space applications often involve different materials: CaF_2 and metal oxides provide low friction and wear in air at elevated temperatures, while MoS_2 is preferred at low temperatures in vacuum. Chromate coatings are used for corrosion protection on both aircraft fuselages and spacecraft surfaces, but improved performance can be met with more modern coating materials like rare earth salts, sol gel organic-inorganic composites, and resin composites. In this talk, current research being done in order to push coating performance to meet continually increasing requirements will be discussed.

2:50pm **G2-5 Triboactive CrAlN+X Hybrid dcMS/HPPMS PVD Nitride Hard Coatings for Friction and Wear Reduction on Components***, K Bobzin, T Brögelmann,* ***Christian Kalscheuer****,* Surface Engineering Institute - RWTH Aachen University, Germany

Increasing environmental awareness and energy costs are major driving forces behind the development of energy efficient machines. Simultaneously, increased energy efficiency often leads to higher power densities. The consequences are load spectra which often exceed the load carrying capabilities of the base material and therefore higher wear rates and reduced life times. Therefore, coatings for the application on highly loaded components were developed. Besides diamond-like carbon (DLC) coatings, nitride hard coatings deposited by physical vapor deposition (PVD) show a high potential for wear reduction on machine components. However, regarding friction reduction in lubricated tribological contacts, nitride hard coatings still exhibit a high demand for research since state-of-the art lubricants are tailored to interact with steel surfaces in order to form friction reducing tribolayers. Therefore, the addition of tribo effective elements (X) into nitride hard coatings is a promising approach to enhance tribological interactions with lubricants and to reduce friction. In order to deposit PVD coatings on complex geometries with increased mechanical properties, the high power pulsed magnetron sputtering (HPPMS) technology shows high potential. The aim of the paper is the analysis of the tribological interaction between the nitride hard coating (Cr,Al)N+Mo and lubricants. Therefore, a mineral base reference oil and a mineral oil doped with a sulphur additive were investigated regarding interactions with the coatings under tribological conditions. The coatings were deposited in a low temperature T ≤ 200 °C hybrid PVD coating process on case hardened steel AISI5115 (16MnCr5E). Hybrid PVD coating processes allow the combination of direct current magnetron sputtering (dcMS) and HPPMS. The coating and compound properties were investigated. The tribological behavior of the coatings was tested in a pin on dics (PoD) tribometer against inert ceramic Si_3N_4 counter bodies to ensure that tribologial interactions can only occur due to reactions between the coatings and the lubricant. The uncoated case hardened steel AISI5115 (16MnCr5E) and a (Cr,Al)N coating were investigated as reference. The tests were conducted at temperatures T = 90 °C and T = 130 °C at Hertzian contact pressures $p_H \approx$ 1,600 MPa and $p_H \approx$ 1,900 MPa. Under the given tribological conditions a friction reduction was achieved by adding the tribo effective element Mo into the coatings. Raman spectroscopy revealed that MoS_2 was formed in-situ during the tribological tests. The investigated (Cr,Al)N+Mo coatings are therefore a promising approach for friction reduction in highly loaded tribological systems.

3:10pm **G2-6 Tribological Performance of PTFE Based Composite Seal Materials Against Diamond Like Carbon and Catalytically Active Nitride Based Nano-composite Coatings***, OsmanL. Eryilmaz, G Ramirez, A Erdemir,* Argonne National Laboratory, USA

Natural gas (NG) consumption has been grown rapidly during the last decade, and NG production is projected to further increase by 44% through 2040. Consequently, the potential for methane emission (which can deter GHG benefits of using NG) is also expected to increase throughout the supply chain. Accordingly, the NG industry is facing tough challenges toward mitigating methane emissions in the form of not only adopting new low-emission gas compression technologies but also upgrading or enhancing the currently installed compressors in the field. NG industry uses two types of compressors in the production, delivery and storage of NG. Most common one is the reciprocating NG compressors which account for the largest amount of leakage of methane. Primary leak source of those compressors are wear and scratches on rod and seal material surfaces in piston rod packing systems. One approach is to apply hard coatings onto rod surfaces to prevent wear on the rod side, however it could be detrimental on the delicate Teflon based counter face seal side.

New coatings and surface modification techniques are in need to prevent wear on both surfaces. One approach would be to develop a hard coating that generates tribo-films that beneficial to Teflon based seal side as well, this would minimize wear on both sliding surfaces, or another approach would be to use already known solid lubricant coating such as diamond like carbon. Accordingly, in this paper, we concentrate on the friction and wear performance of DLC, and catalytically active nano-composite nitride based coatings against PTFE type seal materials filled with different fillers (Carbon, MoS2, glass, etc.). A series of vanadium nitride – copper nano-composite, and hydrogenated DLC films were prepared using high power impulse magnetron sputtering (HPIMS). The films were grown on 52100 steel substrates for tribological tests. X-Ray Diffraction (XRD), raman Spectroscopy, nano-indentation techniques were used to characterize the structural, mechanical and chemical nature of the resultant coatings. Bench-top tribological tests were conducted by using oil lubricated reciprocating test rig. Overall, the effect of sliding speed, contact pressure, type of PTFE fillers on the tribolocigal behavior of coatings were investigated. Both nitride and carbon based coatings improved the wear performance of the system depending on the type PTFE composite counter-face used. At the end of each test, confocal raman was used to evaluate sliding interfaces and any structural changes resulting from the tribological tests to shed more insight into the possible mechanisms responsible.

Surface Engineering - Applied Research and Industrial Applications

Room Sunrise - Session G6

Application-driven Cooperation between industry and Research Institutions

Moderators: Hamid Bolvardi, Oerlikon Balzers, Oerlikon Surface Solutions AG, Kirsten Bobzin, Surface Engineering Institute - RWTH Aachen University, Germany

3:30pm **G6-7 Research Behind a High Performance Metal Cutting Tool***,* ***Jacob Sjölén****,* SECO Tools, Sweden **INVITED**

The research and development of metal cutting tools has over the last century led to incredible improvements in manufacturing. Cost efficient solutions, more advanced materials and super-alloys are key-words in a modern machine shop, meaning demands on increased productivity and new solutions for machining of difficult materials. This, in turn, generates extreme conditions at the cutting tool edge, comprising e.g. high pressure, high thermal load and chemical interaction.

To meet the demand of endurance at these circumstances, there is a need for a deep material understanding combined with the continuous development of material properties, tool design and cutting process. Thus, this requires combined efforts over the entire R&D-chain covering activities from fundamental research to field testing, including co-operations over the borders between academia and industry and compiling all this knowledge into a High Performance Metal Cutting Tool.

This work will present examples of how such collaboration between academia and industry leads to an increased understanding of existing conditions, improved productivity of new tools and technology platforms for the development of next generation metal cutting tools. More

specifically, how application driven research of the wear properties in the metal cutting processes connects to the thermal, chemical and mechanical behavior, which further relates to synthesis, composition and structure of materials used for metal cutting tools, for detailed understanding of the whole system in order to continuously push the limits for the tools.

4:10pm **G6-9 Residual Stress Measurement Technique for Static and Dynamic Coating Processes using Micro-machined Stress Sensors for Scientific and Industrial Applications***, L Banko,* ***Dario Grochla****, A Ludwig,* Ruhr-Universität Bochum, Germany

The mechanical behavior of the thin film-substrate compound strongly correlates with residual stress especially with respect to the hardness, adhesion and tribological performance. The film stress is affected by different contributions like interfacial stress or different coefficients of thermal expansion as well as dislocations, impurities, voids and grain boundaries. Several stress components are related to the film´s microstructure and can indicate the presence of phases. Failure mechanisms like buckling or cracking often can be ascribed to intrinsic and/or extrinsic film stress.

Quantitative determination of thin film stress can be challenging, especially for very thin films, e.g. optical or barrier coatings < 100 nm. XRD strain measurement might fail because of low intensity or texture. Curvature stress measurements base on the Stoney equation to calculate the stress knowing the substrate thickness, film thickness and the radius of curvature. However, in thin coatings the bending force might not be strong enough to deflect standard available substrates that are usually 200 – 500 µm thick. The appropriate selection of the substrate thickness is the key to control the sensitivity of the curvature method. By adequate tuning of the substrate thickness a high measurement resolution (few MPa) can be obtained in any film thickness range.

Micro-machined cantilever stress sensors (6.55 x 7.4 mm^2) have been developed to meet this criterion. Sensors were fabricated with a substrate thickness in the range of 30 – 120 µm. The Sensors were validated in several research and industrial type plasma-based depositions with film thicknesses ranging from < 10 nm to 3 µm and have been applied in static as well as dynamic coatings processes. The small sensors allow localized stress determination in different places of the deposition chamber. The combination of the stress sensor and an optical holography test stand, provides a fast and easy point-and-click measurement to quantify residual stress. Additionally, the coefficient of thermal expansion can be calculated by thermal cycling of the sensors on a heating platform as the Young's modulus is known. Furthermore, it will be shown, how residual stress measurements can help to understand different thin film behaviors and reveal non-uniformities in the coating processes. The stress sensors can be used as an indicator (figure of merit) in industrial deposition processes, to easily monitor thin film quality over long time periods.

Acknowledgment: SFB-TR 87

4:30pm **G6-10 Improvement of Thermal Stability and Oxidation Resistance of Molybdenum Nitride***,* ***Fedor F. Klimashin****,* CDL-AOS TU Wien, Austria*; M Arndt,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P Polcik,* Plansee Composite Materials GmbH, Germany*; H Euchner, N Koutná,* TU Wien, Austria*; D Holec,* Montanuniversität Leoben, Austria*; P Mayrhofer,* TU Wien, Austria

The ever-growing industry demands challenge researchers to develop ever-better performing materials. Evidently, the industry–university collaboration, implying funding for the research activities and monetization of the developed cutting-edge technologies, is mutually beneficial, and one of the most effective ways of engaging the knowledge exchange between industry and research institutions is a direct research collaboration of both.

The present research – conducted in cooperation with Oerlikon Balzers AG and Plansee Composite Materials GmbH – aimed at improving thermal stability and oxidation resistance of the cubic-structured molybdenum nitride γ-MoN_x. The refractory metal Mo is successfully used as alloying element (for nitrides in particular) for the purpose of improving hardness[1], toughness[2,3], friction coefficient[4], while the application of γ-MoN_x – though high-temperature allotropy – is strongly limited to 300–500 °C unless an oxygen-free atmosphere is provided. Optimizing the composition of alloying elements (able to form a dense oxide scale at elevated temperatures, e.g. Al and Cr) and vacancies (inherent in Mo-based nitrides), superhardness (over 40 GPa) combined with high resistance to plastic deformation (~0.4 GPa) and significantly improved thermal stability and oxidation resistance (both > 900 °C) could be achieved.

References:

1 Endrino, J. L. & Derflinger, V. The influence of alloying elements on the phase stability and mechanical properties of AlCrN coatings. *Surface and Coatings Technology* **200**, 988-992 (2005).

2 Sangiovanni, D. G., Hultman, L. & Chirita, V. Supertoughening in B1 transition metal nitride alloys by increased valence electron concentration. *Acta Materialia* **59**, 2121-2134 (2011).

3 Zhou, L., David, H. & Mayrhofer, P. H. Ab initio study of the alloying effect of transition metals on structure, stability and ductility of CrN. *J. Phys. D: Appl. Phys.* **46**, 365301 (2013).

4 Glatz, S. *et al.* Influence of Mo on the structure and the tribomechanical properties of arc evaporated Ti-Al-N. *Surface and Coatings Technology* (2017).

4:50pm **G6-11 Empirical Alloys-by-design Theory Calculations to the Microstructure Evolution Mechanical Properties of Mo-doped Laser Cladding NiAl Composite Coatings on Medium Carbon Steel Substrates***, C Lin,* ***Wei-Yu Kai****,* National Taipei University of Technology, Taiwan

An experimental investigation is performed into the microstructure and mechanical properties of Mo-doped (0, 3, 6, 9,12 and 15wt% Mo) NiAl coatings deposited on medium carbon steel substrates with a laser cladding process. It is shown that as the Mo content increases, the density of the Mo-rich phase network structure increases and the grain size of the laser-clad coating reduces. Furthermore, the hardness and wear test results indicate that a higher Mo addition not only increases the strength of the NiAl coating, but also improves its toughness and wear resistance. On the other hand, the underlying mechanism of phase formation and elements diffusion has been firstly studied by first principle simulation and DICTRA corresponding to the SEM micrographs of cross-section and coating-substrate interface. It is presented that pure NiAl and Mo phase exist a lowest formation enthalpy complying with the results of Thermocalc simulation. What more, the diffusion of Fe from substrate controlled by the addition of refractory element of Mo and the solid or liquid state of coatings during cladding process. Thus, with a combination of alloy design, the role of laser cladding process, and the theoretical calculation, this study provides a potential guideline for evolution and practical application of intermetallic compound in the future. In general, with a combination of alloy design, the role of laser cladding process, and the theoretical calculation in this study provide a useful source of reference for extending the applications of NiAl composite coatings in the aerospace field and other advanced industries.

Advanced Characterization Techniques for Coatings and Thin Films

Room Royal Palm 4-6 - Session H3-2

Characterization of Coatings in Harsh Environments

Moderators: David Armstrong, University of Oxford, Jeff Wheeler, Laboratory for Nanometallurgy, ETH Zürich

2:10pm **H3-2-3 Recent Advances in Nanomechanical Testing of Thin Films: Variable Temperature, Ultra-high Strain Rates, in-situ EBSD Experiments***, J Best,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; J Wheeler,* Laboratory for Nanometallurgy, Department of Materials Science, ETH Zürich, Switzerland*; J Wehrs, J Schwiedrzik, G Mohanty, J Ast, X Maeder, K Thomas,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; M Morstein,* Platit Ag, Switzerland*;* ***Johann Michler****,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland **INVITED**

We've developed two recently two platforms for variable temperature nanomechanical testing. The first platform allows for variable temperature and variable strain rate testing of micropillars in situ in the scanning electron microscope. By utilizing an intrinsically displacement-controlled micro-compression setup, which applies displacement using a miniaturized piezo-actuator, we've recently extended the attainable range of strain rates to up to~ 10^4 s^{-1}, and enabled cyclic loading up to 10^7 cycles. Stable, variable temperature indentation/micro-compression in the range of -150°C to 600°C is achieved. Combination with in situ EBSD allows for the determination of crystallographic orientation with sub-100 nm spatial resolution. Thereby, it provides highly localized information on phenomena such as elastic bending of the micropillar or the formation of deformation twins and plastic orientation gradients. A second system allows for measurements at lower loads ex-situ in a dedicated vacuum chamber in the range of -150 °C to 700 °C.

Using these new capabilities, we examine the plasticity and fracture of thin films. Variable strain rate and variable temperature micro-compression experiments on metal multilayers were performed. Activation parameters such as activation energy and activation volume were determined and discussed in view of the most probable deformation mechanism. To study fracture and fatigue behavior of nanocrystalline ceramics thin films several different small-scale fracture toughness geometries were compared and impact testing using a flat punch was performed, respectively. It was found that notching using a focused gallium source influences small-scale toughness measurements and can lead to an overestimation of the fracture toughness values for chromium nitride (CrN) thin films. Impact testing at 500 Hz up to temperatures of 500 °C showed increased CrN plastic behavior at high temperatures, and demonstrated the usefulness of the equipment for performing accurate small-scale impact tests. Finally, during a more measurement method oriented research project, we explored in-situ HR-EBSD to estimate the size of the plastic zone underneath the crack tip during micro-cantilever fracture tests in tungsten single crystal. We demonstrate the mapping of the evolution of the stress field around the notch tip and the estimation of the GND density in the plastically deformed zone.

2:50pm **H3-2-5 Combined Size and Texture-dependent Deformation and Strengthening Mechanisms in Zr/Nb Nano-multilayers in Harsh Environments**, ***Tomas Polcar***, *M Callisti,* University of Southampton, UK

A combination of transmission electron microscopy analyses and nanomechanical measurements was performed to reveal deformation and strengthening mechanisms occurring in sputtered Zr/Nb nanoscale metallic multilayers (NMMs) with a periodicity (*L*) in the range 6 – 167 nm. Electron diffraction analyses revealed a change in the crystallographic orientation of α-Zr when *L* 27 nm, while Nb structure retained the same orientations regardless of *L*. For *L* > 60 nm, the strengthening mechanism is well described by the Hall-Petch model, while for 27 < *L* < 60 nm the refined CLS model comes into picture. A decrease in strength is found for *L* < 27 nm, which could not be simply explained by considering only misfit and Koehler stresses. For *L* 27 nm, plastic strain measured across compressed NMMs revealed a change in the plastic behaviour of α-Zr, which experienced a hard-to-soft transition. Further decrease in L led to crystallographic orientation change of α-Zr with a consequent change of the dominant slip system. The actual strength at these smaller length scales was effectively quantified by taking these structural aspects into account in the interface barrier strength model. Then the multilayers were subject to irradiation (gamma) and high energy implantation (He, C, Si, Cu) and the effects of radiation damage on mechanical properties were studied in detail.

3:10pm **H3-2-6 The Oxidation Resistance of ZrO_2-Coated and Vacuum Annealed ZrN-Coated Zircaloy-4**, ***I-Sheng Ting***, *J Huang, G Yu,* National Tsing Hua University, Taiwan

The purposes of this study were to evaluate the oxidation resistance of ZrO_2-coated Zircaloy-4 (Zry-4) and investigate the effect of vacuum heat treatment on ZrN-coated Zry-4. Oxidation is a crucial problem for the Zry-4 fuel cladding of light water nuclear reactor. Ceramic coatings, such as CrN, SiC, and Si_3N_4 have been proposed for increasing the corrosion resistance of Zry-4. In general, when reacting with water, Zry-4 will spontaneously form a surface oxide layer that is composed of both tetragonal and monoclinic ZrO_2. Nevertheless, the oxide layer is only several nanometers, which is insufficient to protect the substrate from the severe environment in reactor. Therefore, this study aimed to compare the oxidation resistance between directly deposited ZrO_2 thin film about 500 nm on Zry-4 using unbalanced magnetron sputtering (UBMS) and those formed by vacuum annealed ZrN-coated Zry-4 at 1000 °C for 1 h. After the deposition of ZrO_2 thin films and vacuum annealing of ZrN thin films, X-ray diffraction (XRD) was used to characterize the structure. The residual stresses in the ZrO_2 and annealed ZrN thin films were respectively determined using $\cos^2\alpha\sin^2\psi$ XRD method. Our preliminary study showed that the contact angle of ZrN thin film on Zr metal is about 50° and that of ZrO_2 thin film on AISI 304 stainless steel is roughly 86°. Both results indicated high contact angles between the coatings and substrates, which accounting for adhesion problems. It was also found that the poor wettability between ZrO_2 and AISI 304 stainless steel even resulted in poor corrosion resistance. Therefore, the wettability of ZrO_2 on Zry-4 and ZrN on Zry-4 was evaluated in this study through contact angle tests. Thermogravimetric analyzer (TGA) and focused ion beam (FIB/SEM) were used to characterize the oxidation behavior and observe the oxide thickness, respectively. The compositional depth profiles were determined by Auger electron spectroscopy (AES). Based on the experimental results, the feasibility of the oxidation protective coatings was evaluated.

3:30pm **H3-2-7 Effect of Using Dissimilar Substrate Materials on Interfacial Properties of HVOF Deposited Inconel 718 Alloy**, ***Sahar Abualigaledari***, *M Salimijazi, F Azarmi, Y Huang,* North Dakota State University, USA

Coating and substrate interfacial properties highly influence the characteristics and performance of the entire coating system. Thus, it has been a primary concern especially in the case of repairing components using thermal spraying process. Due to the nature of thermal spraying deposition, it is speculated that stronger interface will form in the case of similarity between substrate and coating material. This work is an attempt to evaluate the bonding strength of the thermal spray coatings deposited on similar and dissimilar substrate materials. To this end, Inconel 718 was deposited on Inconel 718 and Steel substrates using High Velocity Oxygen Fuel (HVOF) technique. Microstructural characteristics, phase, and elemental distribution of the coatings were studied by Scanning Electron Microscopy (SEM), Electron Dispersive Spectroscopy (EDS), and X-ray Diffraction (XRD). Vickers indentation technique and lap shear test were employed to investigate the mechanical properties of coating-substrate interface and coating layers. The resulted hardness values were applied in an empirical model known as Palmqvist method to assess the fracture toughness and bonding strength of the coatings. Residual stress distribution analysis was also implied across the coatings, using XRD technique, to validate the data. The results indicated better interfacial strength of Inconel 718/Inconel 718 since its shear strength and fracture toughness were higher than that of Inconel 718/Steel sample.

3:50pm **H3-2-8 Sublimation and Self Freezing of Planar Surfaces in Rarefied Atmospheres**, ***Rahul Basu***, Adarsha Institute of Technology, India

A simulation of phase transformations in planar geometries under various boundary conditions is performed. The case of ablation, accretion and self freezing under rarefied atmospheres and application of external heating is looked at for the ice-water-vapor and naphthalene systems. Consideration of ablation is important in applications with space shields in space flight under radiation and heat sources along with near vacuum conditions. Recent Non invasive methods in cryogenic surgery also rely on production of extreme cold in subcutaneous layers by surface ablation. In this paper, sample calculations for water-ice and naphthalene give the velocities of the freezing and vaporization fronts under various parameter combinations, assuming isotropic properties in each phase. It is shown that considerable difference exists between the cases of self freezing, ablation and accretion. For instance in the case of water, rates of self ablation without heat sources and self accretion (as in the formation of ice crystals directly from vapor) differ by an order of Magnitude

Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B3-2

Deposition Technologies and Applications for Diamond-like Coatings

Moderators: Frank Papa, Gencoa Ltd., USA, Klaus Böbel, Bosch GmbH

8:00am **B3-2-1 Tribological Behavior of Unlubricated Sliding between Steel Ball and Si-DLC Deposited by Ultra-high-speed Coating Employing MVP Method**, *T Nakano, K Yamaguchi,* ***Ippei Tanaka****, H Kousaka,* Gifu University, Japan*; H Hashitomi,* Cnk Co., Ltd., Japan

Recently, with increasing demands for energy saving by friction reduction and lifetime extension by wear reduction, the application of DLC (Diamond-Like Carbon) is spreading gradually and steadily. In this field, higher-speed coating method with applicability to 3-dimensional shapes is strongly desired. Plasma CVD is a promising candidate for such demands due to its excellent capability for coating 3-dimensional shapes; however, typical coating speed of DLC with conventional plasma CVDs is not so high, ~1 μm/h; in addition, further drastic increase of the coating speed is not expected due to the use of low-density (ne~10^8–10^{10} cm^{-3}) DC or RF plasma in such conventional methods. The use of higher-density plasma is considered to be essential for increasing the coating speed. Thus, we have proposed a high-speed coating method of DLC with a novel plasma CVD employing much higher-density plasma (ne~10^{11}–10^{13} cm^{-3}), which is sustained by microwave propagation along plasma-sheath interface on metal surface. In our previous work, a considerably high deposition rate of 156 μm/h and hardness of 20.8 GPa was obtained. In this work, we investigated the effect of film composition on friction property of Si-containing a-C:H films in such ultra-high-speed DLC coating.

Si-containing a-C:H films (one type of DLC) were deposited on steel substrates by different 2 methods: DC plasma and microwave-excited high-density near plasma, or our newly proposed method, where the gas composition of Ar, CH_4, C_2H_2, and TMS in source gas flow was changed. Friction tests were conducted in a ball-on-disk apparatus under dry condition, where a SUJ2 ball 8 mm in diameter contacted to a DLC-coated disk at a normal load of 1 N. Sliding test was conducted for 60 minutes at a rotation speed of 250 rpm. The atomic composition of the films was evaluated by XPS for C, O, and Si, and RBS-ERDA for H/C.

The hydrogen and silicon contents were from 25 to 35 at% and from 7.76 to 28.43 at%, respectively. Friction coefficient of Si-containing a-C:H films was decreased from 0.12 to 0.025 with decreasing oxygen content from 0.75% to 4.15%. This result indicates the possibility of decreasing friction coefficient by oxygen content in Si-containing a-C:H films .

8:20am **B3-2-2 Tribological Behavior of DLC Coatings on AISI 4340 Steel Deposited in PECVD DC-Pulsed Technique with Additional Cathode for Automotive Applications**, ***MarcoA. Ramirez R.****, D Lugo,* National Institute for Spacial Research INPE, Brazil*; N Fukumasu, I Machado,* Surface Phenomena Laboratory - Polytechnic School - University of Sao Paulo - Brazil, Brazil*; E Mitma P., V Trava-Airoldi,* National Institute for Spacial Research INPE, Brazil

Diamond-Like Carbon (DLC) coatings have attracted significant attention due to its low friction, high hardness, high wear resistance, among others. These films meet conditions that can be used in some mechanical applications in aerospace and automotive industries. The major disadvantage of these coatings is the low adhesion on metallic substrates, caused by elevated compressive residual stresses after deposition. Some plasma conventional methods require a high consumption of energy that are used to grow DLC films, resulting in a high level of temperature and pressure during the deposition, which affects the adhesion of the film to the substrate. The use of PECVD-DC Pulsed with additional cathode, allows to grow DLC films in extremely low pressure and temperature. In this work, DLC coatings were deposited employing an asymmetrical bipolar pulsed-DC PECVD with additional cathode at temperature as low as 90 C and pressure as low as 0.1 Pa, which allowed a collisionless regime and a higher plasma density. Acetylene gas was used as a precursor. In order to overcome low adhesion of DLC films on steel substrate, a thin amorphous silicon interlayer was deposited as an interface. Resulting coatings were analised with SEM-FEG and Raman scattering spectroscopy in terms of morphology and atomic arrangement,respectively. The total residual stress was evaluated by the curvature method. The tribological behavior (friction and wear) was analyzed by reciprocating wear tests at room temperature. Adhesion was evaluated in accordance with the VDI3198 norm, based on a Rockwell C indentation test. XPS analyses, will also be used in order to get a relationship among the adhesion and the silicon interface on set nucleation parameters. The elevated coating hardness (higher than 25 GPa) promoted good wear resistance. These results suggest that the PECVD-DC Pulsed with additional cathode and acetylene as a precursor gas to grow DLC films on engineering steels may represent a new alternative to improve the mechanical behavior in automotive applications.

8:40am **B3-2-3 Structural Evolution and Temperature-sensitivity of W-containing Diamond-like Carbon Films Deposited by a Hybrid Linear Ion Beam Systems**, ***Peng Guo****, L Sun, P Ke, A Wang,* Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, China

In present study, W-containing diamond-like carbon (W-DLC) films (0.3~70.4 at.%) were fabricated by a hybrid beams system consisting of a DC magnetron sputtering and a linear ion source. The influence of composition and microstructure on the room temperature (300 K) resistivity and temperature coefficient of resistance (TCR, 300~400 K) of the W-DLC films were also investigated. As evidenced by XPS, XRD, TEM and Raman measurements, the microstructure of W-DLC films evolved from amorphous carbon matrix with dissolved W atoms into composite materials made of WC_{1-X}/W_2C nanocrystallites embedded in amorphous carbon matrix with increasing W concentration. The electrical resistivity of the temperature of all the films exhibited a negative TCR. The mechanism of the temperature sensitivity in the W-DLC films was also discussed.

9:00am **B3-2-4 Effects of Carbon Content and Argon Flow Rate on the Triboperformance of Self-lubricating WS_2/a-C Sputtered Coating**, ***Huatang Cao****, J Th.M De Hosson, Y Pei,* University of Groningen, Netherlands

Layered transition metal dichalcogenides (TMD) such as WS_2 are materials well-known for their solid lubrication properties [1]. However, the lubricating property degrades through oxidation or moisture and it is also limited by its low hardness and low load-bearing capacity. In contrast amorphous diamond-like carbon (DLC) films are reported to have many features that contribute to excellent tribological characteristics, such as high hardness, anti-wear property with both low friction coefficient and low wear rate[2]. The present research aims at depositing WS_2/a-C nanocomposite coatings by magnetron co-sputtering method. The effects of carbon content and argon flow rate on the microstructure and mechanical performance were investigated. The WS_2/a-C nanocomposite tribocoating was scrutinized by electron microscopy and mechanical testing. Transmission electron microscopy reveals feathery WS_2 platelets, randomly distributed in the amorphous carbon matrix. The nanocomposite coating turns out to be more amorphous-like with increasing carbon content. Nanoindentations tests show that the hardness and elastic modulus of the coating increase with increasing carbon addition while decreasing with a higher argon flow from 10 sccm to 25 sccm.

Ball-on-disk tribotests (100Cr6 steel ball as a counterpart) show that the coefficient of friction can be as low as 0.017 in a dry environment (<5% relative humidity). It reaches 0.15 in a high humidity surrounding and remains stable within 20000 sliding cycles.

References:

1. S. Prasad, J. Zabinski. Super slippery solids, Nature 387, 761-763(1997).

2. A. Nossa, A. Cavaleiro, N.J.M. Carvalho, B.J. Kooi, and J.Th.M. De Hosson, On the microstructure of tungsten disulfide films alloyed with carbon and nitrogen, Thin Solid Films 484 (1-2), 389-395(2005).

9:20am **B3-2-5 Industrial Development of Carbon-based Coatings**, ***Ruud Jacobs****, G Fransen, R Tietema, D Doerwald, J Landsbergen,* IHI Hauzer Techno Coating B.V., Netherlands **INVITED**

In this presentation an overview will be presented on the developments of carbon-based coatings for applications in automotive technology.

Initially the introduction of high pressure diesel injection technology required the introduction of wear resistant coatings to protect the steel parts against wear to prevent leakage of pressure and damage to components. In the earliest phase of development, metal doped DLC's produced by sputtering were applied, soon however because of a demand for higher wear protection followed by the introduction of hydrogenated DLC's produced in hybrid sputter/PECVD processes. Due to the improved fuel efficiency, power densities increased causing strain on other components in the engine, as well as in the valve and power train, consequentially leading to a demand for wear protection coatings on those parts as well.

In the last decade the requirement for reduced emissions of CO_2 gave a strong boost to the market for components. Reduced friction, reduced weight and increased efficiency in fuel combustion were necessary to meet the new demands.

Developments in lubricants tend to go in the direction of lower viscosity. Hybrid technology and start-stop engines increase the operating time of the engine in mixed-mode lubrication. Both trends in automotive development direct to increasing wear resistance requirements. This has been leading to large scale introduction of ta-C (tetrahedral carbon) coatings produced by arc technology after 2010. These ta-C coatings are offering for many cases an optimum of highest hardness in combination with lowest friction, but a post-treatment is required to optimize the surface quality of the coated components. Newest developments in tribological contacts tend to go in the direction of higher operating temperatures combined with high wear resistance and minimum friction, whereas also the cost of the system plays an important role.

10:00am **B3-2-7 Glow Discharge and Deposition of Thick DLC Film in Cage-shaped Hollow Cathode System with Adjustable Bias**, ***Xiubo Tian,*** *M Wu, C Gong,* Harbin Institute of Technology, China*; R Wei,* Southwest Research Institute, USA

Diamond-like-carbon (DLC) has been widely utilized in related industries to tribological, optical, electrical applications, etc. A cage-shaped hollow cathode discharge (C-HCD) has been utilized to produce high-density plasma for deposition of DLC films. To further optimize the microstructure and surface properties of the DLC films, a new approach is proposed, in which the energy of ions incident to the sample surface can be independently controlled by an additional bias between the samples and the metal cage (mesh). The samples are biased with a voltage from 0V to -500V with respect to the cage biased with 1000-4000V (pulse). The internal sample bias has a critical effect on the cage hollow cathode discharge. Generally the glow discharge of C-HCD system is enhanced by the sample bias. However with a higher C-HCD current, there exists a certain sample bias which weakens the glow discharge. It is attributed to the competing effect of both self-discharge and ion consumption induced by negatively-biased sample. Compared to conventional method, additional bias effectively removes thecarbon contamination and some macro-burring on the sample surface. And the bias also leads to the formation of the surface protuberances with nanoscale size. The clean surface and mechanical lock structure have effectively improved the adhesion between the film and substrate. Si-DLC films have been synthesized with a mixture of Ar, C_2H_2 and tetramethylsilane (TMS). The results demonstrate that the DLC films have been deposited with a higher rate (4~6um/h) due to higher plasma density produced by high-current pulse in the mesh cage. The intense ion bombardment significantly densified the microstructure and reduced the H contents, and consequently increased the nanohardness (*H*) of DLC films. As an example, a DLC film was deposited on HSS with thickness of 40um and critical load of ~100N. Our results have proven that this novel set up may be a very effective tool to fabricate DLC films with high deposition rate and excellent surface properties with denser microstrcture.

10:20am **B3-2-8 Enhanced Adhesion Of Hard Dlc Coatings On Metallic And Insulating Substrates**, ***Ivan Fernandez,*** Nano4energy Sl, Spain

Diamond-Like Carbon (DLC) coatings have been recognized as one of the most valuable engineering materials for various industrial applications including manufacturing, transportation, biomedical and microelectronics. Among its properties, DLC has good frictional behaviour combined with high surface hardness, offering an elevated protection against abrasive wear.

As the industrial success of DLC films in tribological contacts is strongly dependent on their adhesion properties, two different approaches were used to enhance DLC coating adhesion onto both metallic and insulating substrates.

- HiPIMS metal ion etching and implantation with both Ti and Cr plasmas was used to pre-treat the M2-HSS metallic substrates, obtaining Rockwell HF1 values and critical loads in the macro-scratch tests above 100N .

- Positive ion-assisted pre-treatment [1] was used to etch glass substrates and promote strong adhesion of thin DLC layers. Taber abrasion tests were performed to evaluate the pre-treatment process effect on the coating adhesion. A significant DLC coating adhesion improvement was observed.

10:40am **B3-2-9 Low Friction of Graphene Nanocrystalline Embedded Carbon Nitride Coatings Prepared with MCECR Plasma Sputtering**, ***Pengfei Wang,*** Institute of Nanosurface Science and Engineering, Shenzhen University, China*; W Zhang,* Xi'an Jiaotong University, China*; D Diao,* Shenzhen University, China

The excellent mechanical and tribological behaviors of amorphous carbon nitride coatings, especially the super-low friction performance (friction coefficient of less than 0.01 in dry nitrogen gas environment) made them good candidates as solid lubrication coatings in advanced engineering applications. However, the low friction mechanism of carbon nitride coatings in nitrogen gas environment is still not yet clearly understood. The objective of this research is to clarify the key factors of atomic composition and structure of the carbon nitride coating itself in achieving the low friction in nitrogen gas environment.

In this work, graphene nanocrystalline embedded carbon nitride (GNECN) coatings were fabricated with the mirror confinement electron cyclotron resonance (MCECR) plasma sputtering method under low energy electron irradiation. It is clearly observed that the deposition rate, internal stress, surface roughness and hardness of the prepared GNECN coatings change with the variation of the flow ratio of argon and nitrogen gas in the operating gas under a pressure of 0.04 Pa. Moreover, graphene nanocrystalline structure was identified in the amorphous carbon nitride matrix from the analyses of TEM, XPS and Raman spectroscopy. Furthermore, stable and low friction coefficient of less than 0.05 of GNECN coating was achieved after a short run-in period when slid against Si_3N_4 ball in nitrogen gas environment. A uniform transfer film was formed on the worn surface of counterpart ball material according to the optical image. It is believed that the introduction of graphene nanocrystalline structure plays a key role in achieving low and stable friction coefficient of GNECN coatings, which could help us better understanding the low friction mechanism of CNx coatings in nitrogen gas environment from the viewpoint of the composition and structure of the coating. Moreover, the clarification of the relationship between the low friction behavior and electric output property of the contact surfaces is beneficial for understanding the tribo-electrification principle as well as exploring the application of GNECN coatings in tribo-energy field.

Fundamentals and Technology of Multifunctional Materials and Devices

Room Royal Palm 1-3 - Session C3-1

Thin Films for Energy-related Applications

Moderators: Jim Partridge, RMIT University, Martin Allen, University of Canterbury

9:20am **C3-1-5 Solar Photovoltaic Energy Generation in Thermal Insulation Glazing**, ***David McKenzie,*** The University of Sydney, Australia **INVITED**

There is renewed interest in combining solar photovoltaic technologies with thermally insulating glazings. Modern cities have multi storey buildings with large areas of glazed facades that represent the majority of the building envelope. These facades have large energy exchanges with the environment that must be managed efficiently in order to avoid major energy wastage. The combination of PV technologies with thermal insulating glazings is a novel approach with potential to increase the harvesting of solar energy while minimising unwanted energy exchanges. New technologies for PV such as perovskite cells have shown good efficiency while allowing for some useful residual light transmission with an options for a choice of colour. There is a synergy with double glazed insulating units, first because of the local generation of energy while minimising losses, and second because the perovskite cells are moisture sensitive. In a synergistic design the thermal insulating glazing can act as a protective encapsulation of the cells. Recent advances and the current status of available technologies in this area will be discussed in this paper .

10:00am **C3-1-7 Effects of Annealing on Thermochromic Properties of W-doped Vanadium Dioxide Thin Films Deposited by Electron Beam Evaporation**, ***Shao-En Chen,*** National Cheng Kung University, Taiwan*; H Lu,* National Chin-Yi University of Technology, Taiwan*; S Brahma, J Huang,* National Cheng Kung University, Taiwan

Thermochromic vanadium dioxide (VO_2) undergoes a fully reversible semiconductor-metal transition (SMT) at a critical temperature T_t of ~68 °C with a dramatic change in electric and optical properties, which makes it an attractive candidate for use in smart windows. Switchable VO_2 and W-doped vanadium dioxide ($W_xV_{1-x}O_2$) thin films are grown successfully over quartz substrates via electron beam evaporation technique by using VO_2 / $W_xV_{1-x}O_2$ as targets at room temperature (RT) followed by a post annealing process at different temperatures. The films were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, scanning electron microscopy (SEM) and optical transmittance measurement. The XRD analysis shows that the as-deposited films are amorphous, and that transform into (011)-preferred orientation

of monoclinic VO_2 (VO_2(M)) after annealing at 500 °C under vacuum. Moreover, (011) peak of W-doped VO_2 films shifts to a lower diffraction angle as compared with un-doped VO_2 films which confirm the incorporation of W ions into the VO_2 lattice. Temperature dependent optical transmittance (T-T) measurement demonstrates the thermochromic properties, with a reduction in the phase transition temperature (T_t) as observed in W-doped VO_2 films, which is attributed to the variation of electron structure in VO_2 due to doping.

10:20am **C3-1-8 Fabrication and Characterization of Titanium Doped β-Ga_2O_3 Thin Films for Application in Oxygen Sensors**, ***Sandeep Manandhar,*** *E Rubio, R Chintalapalle,* The University of Texas at El Paso, USA

The electrical conductivity changes in metal oxides when exposed to atmosphere have attracted considerable interest in the field of gas sensing. Several candidate metal oxides (SnO_2, ZnO, TiO_2 and Ga_2O_3, WO_3) have high sensitivity to gases. Among these metal oxide, Gallium oxide (Ga_2O_3), the stable oxide of gallium, finds attractive applications in luminescent phosphors, high temperature sensors, antireflection coatings, and solar cells. Ga_2O_3 has been recognized as a deep ultraviolet transparent conducting oxide (UV–TCO), which makes the material a potential candidate for transparent electrode applications in UV optoelectronics. Ga_2O_3 thin film has proven to detect the presence of oxygen at high temperatures (>700 °C). However, recent trends and demand for reliable oxygen sensors imposed restrictions on the response time and sensitivity. In this work, we proposed and investigate to modify the properties of Ga_2O_3 by selectively doping with titanium (Ti). Ti doped β- Ga_2O_3 thin films with variable Ti content were deposited by co-sputtering of the Ga-oxide ceramic and Ti metal by varying the sputtering power to these targets. The effect of Ti on the crystal structure and electronic properties of β- Ga_2O_3 thin films is significant. The results will be presented and discussed in the context of utilizing these materials in oxygen sensor applications.

10:40am **C3-1-9 Bombardment of Tungsten Oxide Thin Layers by Low Energy of He and D Ions**, ***Hussein Hijazi,*** *Y Addab,* Aix-Marseille Université, France*; A Maan, J Duran, D Donovan,* University of Tennessee-Knoxville, USA*; C Pardanaud, M Cabié,* Aix-Marseille Université, France*; F Meyer, M Bannister,* Oak Ridge National Laboratory, USA*; R Pascal, C Martin,* Aix-Marseille Université, France

Tungsten is the plasma-facing material for next fusion reactors (e.g. ITER divertor) due to its high melting temperature, high thermal conductivity and low erosion yield. As a drawback, tungsten has a strong chemical affinity with oxygen and native oxide is naturally present on tungsten surfaces, which leads to the formation of tungsten oxide layers. In order to study the effect of oxidation on tungsten properties, the behavior of WO_{3-x} layers under deuterium/helium bombardment and thermal cycling effect in divertor-like conditions, we have produced, by thermal oxidation, thin layers of WO_{3-x} on W substrates which mimic the possible oxidation of tungsten plasma facing components. The produced tungsten oxide layers were characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy and X-ray diffraction (XRD) techniques. The thickness of the colored oxide thin layer δ, measured by SEM using focused ion beam cross-section (FIB), follows a parabolic law as a function of the oxidation time. A set of those oxide tungsten thin film samples were separately exposed, at PIIM laboratory (Marseille-France) and in collaboration with the University of Tennessee UT (Knoxville-USA) and Oak Ridge National Laboratory ORNL (Oak Ridge-USA), to D and He plasma beams with energy range from 20 eV to 320 eV and total fluence ~ 4.10^{21} m^{-2} and sample temperatures RT-673 K. At RT, due to D implantation (which has high affinity to bond formation) followed by its deep diffusion [1], preliminary results show a phase transition in the WO_{3-x}, change in the layer color as well as formation of tungsten bronze (D_xWO_3) have been observed. However, the He implantation (that has high affinity to induce the creation of bubbles, holes and nanostructure morphology on W [2]) neither causes surface morphological change on the oxide of tungsten nor changes in its color. However, at 673K, an erosion effect was observed due to He implantation in the oxide layer. Deep analysis on the process of structural damage in surface/bulk and estimation of the erosion rate will be described for both exposures using the coupling of Raman spectroscopy and SEM approaches.

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces
Room San Diego - Session E1-1

Friction, Wear, Lubrication Effects, and Modeling

Moderators: Albano Cavaleiro, University of Coimbra, Carsten Gachot, Vienna University of Technology, Giovanni Ramirez, Argonne National Laboratory, USA

8:00am **E1-1-1 Stress and Friction Modelling for Improved Nano-scratch Testing of Hard Coatings**, ***Ben Beake,*** Micro Materials Ltd, UK*; V Vishnyakov,* University of Huddersfield, UK*; T Liskiewicz,* University of Leeds, UK

Nano- and micro-scale scratch tests have significant benefits over the more traditional macro-scale tests with 200 micron end radius diamond indenters. By employing smaller loads and sharper probes it is possible to greatly increase the sensitivity of the test to coating properties. Nevertheless, interpretation of the results can be complex without further analysis. In this paper we present (i) analytical modelling to assess the main stresses acting at the coating-substrate interface (von Mises, tensile and shear stresses) (ii) simulation of load-dependent friction. The modelling has been applied to different coating systems such as DLC on hardened steels and hard nanocomposite TiSiN on silicon. The stress modelling has been able to explain dramatic experimental differences in failure mechanisms with coating mechanical properties due to differences in tensile stresses at the interface and whether plastic flow initiates in coating or substrate. It has been possible to deconvolute the interfacial component of friction from the ploughing contribution and to accurate simulate the total frictional force by additionally considering the load-dependent transfer of load support to the front half of the probe as the deformation becomes less elastic in nature.

8:20am **E1-1-2 Wear Resistance and Solid Lubricity of Nanolayered Molybdenum Containing Nitride Coatings Deposited using Cathodic Arc Technique**, ***Qi Yang,*** National Research Council of Canada, Canada

Molybdenum containing MoTiN, MoCrN, MoZrN and MoAlTiN nanolyered coatings, were deposited on the 17-4 PH stainless steel substrate by using cathodic arc evaporation technique. Pin-on-disc dry sliding tests were performed to investigate the coatings' wear resistance and solid lubricity. All these coatings, particularly MoTiN and MoAlTiN coatings, demonstrated wear resistance superior to and coefficient of friction significantly lower than the corresponding Mo-free TiN, CrN, ZrN and AlTiN coatings. For example, the specific wear rate of the MoAlTiN coating is less than 0.15% of that of AlTiN while its coefficient of friction is only 0.28 when compared to 0.60 of the AlTiN coating. The excellent tribological performance is contributed to the formation of the surface MoO_3 layer on the wear track due to the tribo-oxidation process. Further wear tests of the MoTiN and MoAlTiN coatings against Al_2O_3 ball revealed less improvement in wear resistance and less reduction in coefficient of friction. When tested against Si_3N_4 ball, both coatings, though showing noticeably better wear resistance than their corresponding Mo-free coatings, did not demonstrate low coefficient of friction. The scanning electron microscopy (SEM) and the energy dispersive X-ray spectroscopy (EDS) analyses of the wear track surfaces illustrated the importance of retaining a stable MoO_3 surface layer in order to maintain the beneficial effect of Mo on the tribological performance of the coatings.

8:40am **E1-1-3 Exploring Tribological Interactions – from Molecules to Engineering Applications**, ***Daniele Dini,*** Imperial College London, UK **INVITED**

Tribological phenomena are governed by events and mechanisms which find their roots at the small scales, even more so in environments where mechanical and chemical effects are intimately coupled. For example, nano-scale thermal and particle emission events control the formation of antiwear additive films and oxidation; surface damage, such us crack initiation and wear, results from the accumulation of strain at dislocations level; corrosion events are triggered and controlled by molecular interactions. The key challenge addressed in this talk is the need for the development of robust methodologies for the integration of the skills and techniques recently developed by our modelling team at different scales (see e.g. [1-7]) to capture physical, chemical and mechanical processes and interactions across the scales via a multi-physics modelling strategy. Example of modelling methodologies developed and employed to solve problems at specific length- and time-scales will be presented before concentrating on coupling strategies to be adopted to shed light on macro-

scale tribological events while zooming-in to understand their governing mechanisms.

References

[1] Bodnarchuk, M.S., Heyes, D.M., Breakspear, A., Chahine, S., Edwards, S., Dini, D., "Response of Calcium Carbonate Nanoparticles in Hydrophobic Solvent to Pressure, Temperature and Water", **J. Phys. Chem. C** (2015), 119(29), pp. 16879–16888.

[2] Putignano, C., Carbone, G., Dini, D., "Mechanics of Rough Contacts in Elastic and Viscoelastic Thin Layers", **Int. J. Solids Struct.** (2015), doi:10.1016/j.ijsolstr.2015.04.034.

[3] Gurrutxaga-Lerma, B., Balint, D.S., Dini, D., Eakins, D.E., Sutton, A.P., "Attenuation of the Dynamic Yield Point of Shocked Aluminum Using Elastodynamic Simulations of Dislocation Dynamics", **Phys. Rev. Letters** (2015), 114(17), 174301.

[4] Smith, E.R., Heyes, D.M., Dini, D., Zaki, T.A., "A localized momentum constraint for non-equilibrium molecular dynamics simulations", **J. Chem. Phys.** (2015), 142 (7), 074110.

[5] Medina, S., ,Dini, D., "A numerical model for the deterministic analysis of adhesive rough contacts down to the nano-scale", **Int. J. Solids Struct.** (2014), 51(14), pp. 2620–2632.

[6] Gattinoni, C., Heyes, D.M., Lorenz, C., Dini, D., "Traction and non-equilibrium phase behaviour of confined sheared liquids at high pressure", **Phys. Rev. E**, 88, (2013), 052406.

[7] Bertocchi, L., Dini, D., Giacopini, M., Fowell, M.T., Baldini, A., "Fluid film lubrication in the presence of cavitation: a mass-conserving two-dimensional formulation for compressible, piezoviscous and non-newtonian fluids", **Tribol. Int.**, 67, (2013), pp. 61–71.

9:20am **E1-1-5 Mechanical Stability under Sliding Contact of Thin Multilayer with Weak Adhesion***, **Aymar Quarré de Boiry**,* Joint unit CNRS/Saint-Gobain UMR 125 - Surface of Glass and Interfaces, France*; D Dalmas,* École Centrale de Lyon – Laboratoire de Tribologie et Dynamique des Système, France*; J Faou, J Teisseire,* Saint-Gobain Recherche, France

To modify the surface properties of the flat glass (optical, thermal, electrochemical...), thin film deposition by magnetron sputtering is a technique increasingly widespread. For example, low emissivity glasses which are produced by Glass industry for many years allow reducing energy losses by blocking infra-red. An essential part of those functionalized glasses is a thin silver layer (ten nanometers) deposed by cathodic pulverization. However, these coatings have often low mechanical resistance toward contact loading (scratch) which can happen during manipulation or washing. Scratches are due to contact loading (friction) and are influenced by mechanical properties of the stack (modulus, toughness, adhesion …) [1]. However, a quantitative analysis of the damages is tough because of the complexity and the thinness of the layers (few nanometers). The idea developed during this study is to extend the understanding of the scratch phenomenon in order to improve the scratch resistance of thin multilayers by a method of interfacial patterning. Indeed, it has been recently showed that an alternation of weak adhesion areas (with silver) and strong adhesion areas (without silver) allows improving adhesion [2, 3].

In this study, the objective is to perform ball on plan tests to analyze and understand scratch mechanisms on multilayers thin film with low adhesion deposited on glass. Indeed, the glass transparency allows a direct visualization of scratching process during the tests. First, we focused on homogenous samples with a weak interface and we shows that the scratch is strongly influenced by the presences of brittle layers in the stack. Then, a photolithography protocol is used to pattern a ten nanometers silver layer inside a multilayer stack. In order to understand the scratch phenomenon and the contact between the ball and the layers, many parameters have been measured and their influences and evolution will be discussed: distance between the surface and the sphere, generation of debris, initiation morphology or width of the scratch.

[1] X. Geng, Z. Zhang, E. Barthel, D. Dalmas, Mechanical stability under sliding contact of thin silver film embedded in brittle multilayer, Wear 276–277 (2012) 111– 120

[2] D. Dalmas, E. Barthel, D. Vandembroucq, "Crack front pinning by design in planar heterogeneous interface", J. MECH. PHYS. SOLIDS 57 (2009) 446

[3] Patinet, S., Alzate, L., Barthel, E., et al., Finite size effects on crack front pinning at heterogeneous planar interfaces: Experimental, finite elements and perturbation approaches, J. MECH. PHYS. SOLIDS, 61, Issue: 2 (2013) 311-324

10:00am **E1-1-7 Tribochemical Investigation of Hydrogenated DLC Films of Different Roughness by Means of Vacuumtribology Accompanied by Mass Spectrometry***, **Matthias Kachel**,* Fraunhofer Institute for Mechanics of Materials IWM, Germany

Shot peening prior to deposition allows to effectively create rough DLC coatings and give them a specific topography. While the effect on the coatings adhesion has been discussed earlier, the main objective of this work is to investigate how a strongly increased roughness influences the tribochemistry of hydrogenated diamond-like carbon coatings (a-C:H).

The shot peening treatment was performed on steel bearing rings using globular shot of WC/Co-88/12 with a grain size of 70 µm. By varying the shot peening parameters, different surface topographies were prepared whose relevant parameters as well as spectral information (PSD) were determined using atomic force microscopy (AFM). The tribological experiments were carried out in a vacuum tribometer (ball on disc) that was equipped with a mass spectrometer. Thus, beside the coefficient of friction, the emission of different hydrocarbons and hydrogen for dry and lubricated conditions were detected. The wear of the ball and the coating was measured after the tribological test via profilometry and was then related to the Z-transition of the ball during the experiment. The structural change of the coating was evaluated using Raman spectroscopy.

The investigantions revealed that the signals obtained by the mass spectrometer correlate directly with the chemical composition of the DLC coating and are therefore a measure of gaseous wear. The ratio of gaseous and solid wear was strongly dependent on the particular surface topography which was found to be responsible for the developement of the COF over time. For the lubricated system, gaseous wear originating from the coating and the oil was detected, giving a measure for oil degradation. In total, the friction coefficient was found to be a function of roughness affecting gaseous and solid wear which both influence the chemical transformation of the coating and the formation of a transfer layer.

10:20am **E1-1-8 Plasma-Assisted Lubrication for the Sliding between Polymer and Diamond-Like Carbon***, S Okumura,* Nagoya University, Japan*; T Hibino, **Hiroyuki Kousaka**,* Gifu University, Japan*; N Umehara,* Nagoya University, Japan

Diamond like carbon (DLC) has widespread applications in many fields due to its excellent mechanical properties such as high hardness, low friction, chemical inertness. Recently, DLC is applied to machine parts as coating to reinforce the surface property. On the other hand, the use of polymer parts made of engineering plastics is increasing instead of metal ones because polymer is light, low cost and easily processed. It is expected in the future that the application of DLC to metal comes to be more frequent in order to further improve the sliding property between metal-polymer contact in sliding parts. For that reason, it is important to clarify the characteristic of friction between DLC and polymer. In this research, silicon doped DLC (a-C:H:Si), which is coated by plasma enhanced chemical vapor deposition (PECVD) on a steel disk (SUS304, JIS) 25 mm in diameter, was used as a mating material of sliding against Polyoxymethylene (POM) which is an engineering plastic. Friction tests were conducted in a roller-on-disk apparatus under dry condition, where the side surface of POM roller 5 mm in diameter and 5 mm in height was contacted to DLC-coated disk at a normal load of 1 N. Sliding test was onducted for 20 minutes at a rotation speed of 200 rpm, where the rotation radius of the roller changes from 5.5 to 10.5 mm along the roller axis. During the total sliding distance of 200 m, helium gas flow and helium plasma flow were irradiated for 50 to 100 m, and 100 to 150 m, respectively. Friction coefficient observed for the first 50 m without any irradiation was around 0.2, which was not changed by the following helium gas irradiation. Then, plasma irradiation caused seriously instable and high friction coefficient (around 1.0); however, after stopping the plasma irradiation, the friction coefficient rapidly fell down to around 0.066 and was stabilized. This result indicates the possibility of plasma-assisted lubrication for the sliding between polymer and DLC. (The authors gratefully acknowledge the funding by JST CREST, Japan.)

10:40am **E1-1-9 Integrated Multiscale Material Modelling of Topographical Effects on Wear and Friction in Sliding DLC Contacts**, *K Holmberg, A Laukkanen,* VTT Technical Research Centre, Finland; ***Timo Hakala,*** VTT Technical Research Centre of Finland Ltd, Finland; *H Ronkainen,* VTT Technical Research Centre, Finland; *G Stachowiak, P Podsiadlo, M Wolski,* Curtin University, Australia; *M Gee,* NPL National Physical Laboratory, UK; *C Gachot,* Vienna University of Technology, Austria; *L Li,* Hong Kong City University, Hong Kong

In wear studies, surface topography is typically characterized by standard 2D roughness parameters such as R_a and R_q values. These parameters tend to work well with isotropic surfaces but they are not able to provide full information about surface anisotropy and roughness at different scales of measurement. This limitation of commonly used standard parameters is crucial since most real engineering surfaces are anisotropic and multi-scale objects. Computational modelling and simulation of changes occurring in a material due to surface loading, and calculations of stress and strain in loaded contacts is a research area that is rapidly evolving today. Modelling and simulation of a tribocontact help to understand the mechanisms that result in surface cracking, wear particle formation and wear evolution. Numerical simulations can be carried out on several spatial scale levels, from nano size to macro size, by using software representing the material structure from atomic and even sub-atomic to continuum macro and component level.

The effect of surface roughness and topographical orientation on surface stresses influencing wear has been investigated for diamond like carbon (DLC) coated steel surfaces with three levels of surface roughness (R_a) in the range of 0.004 – 0.11 µm, and with topographical orientations of grinding marks (grooves) at 0°, 45° and 90°. A novel multiscale numerical finite element method (FEM) model was developed to integrate the layered and microstructural material features with the orientation of surface topographical features (VTT Propertune). A fractal geometry and surface voxelisation based approach were utilised to derive representative 3D topography. The simulations show the details of the main topographical orientation effects on local stresses affecting wear as they appear at a single scratch by a diamond ball and in a self-mated sliding contact between two rough surfaces. The 45º sliding direction to the grooves resulted in a mixed state of surface loading in contact during the scratch test. The complex state of stress-strain within the roughness peaks decreased the overall tensile stress state and resulted in a greater surface resistance to cracking compared to 0º and 90º directions. Model based calculations showed that the surface structure was about four times more rigid in the direction of grooving compared to the more flexible behaviour in the direction perpendicular to the grooving. This behaviour was confirmed experimentally. The macro-topography had a dominating effect on surface cracking, influencing on both wear and friction, while the micro-topographical features contributed to surface cracking by less than 40 %.

11:00am **E1-1-10 A Comparative Study of Fatigue Properties of TiVN and TiNbN Thin Films Deposited On Different Substrates**, ***Hikmet Cicek,*** Erzurum Technical University, Turkey; *O Baran,* Erzincan University, Turkey; *A Keles, Y Totik, I Efeoglu,* Ataturk University, Turkey

Transition metal nitrides, especially ternary phase films attract attention due to its high mechanical and tribological features. Besides these, fatigue properties play a very important role on the performance in service life of these type films. TiVN and TiNbN films were deposited on M2 and H13 steel substrates by reactive magnetron sputtering system. Fatigue properties of the films were characterized via multipass scratch tests. 100, 250 and 500 cycle with two directions multipass tests were conducted at room temperature under the 20 N constant load. Structural properties determined with X-ray diffraction, scanning electron microscopy and energy dispersive spectroscopy. Mechanical features of the films were observed with nano hardness tests. Fatigue behaviors, deformation types, coefficient of frictions of the films and effect of different substrates were discussed comparatively. According to the results, TiNbN films showed much better fatigue resistance than TiVN films although critical adhesion load value of TiNbN was less than TiVN film. TiVN films generally showed brittle type cracks at the edge of the tracks though TiNbN films showed more ductile type cracks. Additionally, the films deposited on M2 substrates exhibited better strength than H13 substrates.

11:20am **E1-1-11 The Mechanical and Tribological Properties of Nanocomposite CrMoSixN Coatings**, ***Yu-Chu Lu,*** *J Duh,* National Tsing Hua University, Taiwan

The CrMoN coatings has been found to have superior mechanical and tribological properties, such as high hardness and low friction due to the solid solution strengthening and the formation of lubricating molybdenum oxide. In this study, the mechanical and tribological properties of CrMoN with various Si content was investigated. With Si contents ranged from 0 at. % to 13.0 at. % , the quaternary $CrMoSi_xN$ coatings were deposited on silicon wafer and Inconel 718 by RF magnetron sputter. Through nanoindentation, the hardness and the H^3/E^{*2} ratio of $CrMoSi_xN$ coatings were obtained. The results showed that mechanical characteristics in $CrMoSi_xN$ coatings were strongly influenced by Si contents. The CrMoSixN coating exhibited highest values in hardness and H^3/E^{*2} ratio with 11.0 at.% Si doped, in which columnar grains turned into nanocomposite structure. The strengthening mechanism of nanocomposite structure was attributed to grain refinement and prevention of direct penetration of cracks. Futhermore, the tribological behavior of CrMoSixN coatings were investigated by ball-on-disc tribometer in atmosphere at room temperature, 500 °C, and 750 °C respectively. The results indicated that the tribological properties of CrMoSixN coatings could be significantly improved with the Si addition due to protective oxide formation on wear tracks and the cooperation of MoO_3 as solid lubricant. At high temperature, MoO_3 contributed to low friction coefficient, while the low wear rate was owing to the presence of SiO_2. With 11 at.% Si doping, the $CrMoSi_xN$ coatings showed superior mechanical and tribological characteristics, leading to potential applications for wearproof and self-lubricating dry cutting tools at elevated temperature.

11:40am **E1-1-12 Comparative Studies on Tribological Behaviors of a Magnetron Sputtered CrSiN Coating Under the Environments of Air and Water**, ***Fangfang Ge,*** *J Congcong, S Tao, L Peng, H Feng,* Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, China

Tribological behavior of a magnetron sputtered CrSiN coating with 12.5 at.% Si was studied by ball-on-plate sliding tests in three environments, including air ambient, deionized water, and 3.5 wt.% NaCl water. Then in-situ microscopic examinations on the wear tracks were followed by the combination of scanning electron microscopy (SEM) and a focused ion-beam system. Under the air ambient the coating exhibited a friction coefficient of ~0.47 and a specific wear rate of 1.2×10^{-16} m^3/N m, corresponding to a mild wear process mainly dominated with tribo-oxidation. The tribological behavior of the coating appeared similar features under deionized water and 3.5 wt.% NaCl water. The friction coefficients were relatively lower (~0.24) whereas the specific wear rates increased almost an order of magnitude. It was observed that cracks had formed initially during the running-in period, which might be due to chemical reactions between the coating and the water, resulting more wear of the coating under the environments of deionized water and 3.5 wt.% NaCl water.

12:00pm **E1-1-13 The Mechanical and Tribological Properties of Ti [Nb, V] N Films on the 2024 Al-alloy**, ***Ozlem Baran,*** Erzincan University, Turkey; *A Keles,* Ataturk University, Turkey; *H Cicek,* Erzurum Technical University, Turkey; *Y Totik, I Efeoglu,* Ataturk University, Turkey

Al and Al alloys exhibit low wear resistance altough they were used wide range of automobile and aerospace industries. Therefore, in this study, transition metal nitride films were deposited on this light metal alloy in order to improve the wear resistance. The structural properties of the films were analyzed by XRD, SEM and EDS. The hardnesses of the films were determined with a nanohardness test. A pin-on-disc tribometer was used to determine of friction and wear behaviour of the films under different conditions; 50% RH and argon gas. Ti[Nb, V]N films on the Al alloy exhibit a very dense and columnar microstructure. The highest film thickness and the hardness values were obtained as 440 nm and 12 GPa from TiNbVN films. Also, TiNbVN films exhibited the lowest friction coefficent values under different tribo-test conditions. The thickness and the hardness values of TiNbN films are 400 nm and 9.6 GPa, respectively. TiVN films with the lowest thickness (360 nm) and hardness (6 GPa) have the highest friction coefficents under both conditions. The indenter penetration values are 18.75%, 26.4% and 15.23% for TiNbN, TiVN and TiNbVN, respectively. Wear behaviours of the films were affected from the film thickness, hardness and friction coefficent values, significantly.

Surface Engineering - Applied Research and Industrial Applications

Room Sunrise - Session G4

Pre-/Post-Treatment and Duplex Technology

Moderators: Hiroshi Tamagaki, NIRO (The New Industry Research Organization), Wan-Yu Wu, Da-Yeh University, Chris Stoessel, Eastman Chemical Company, Inc., USA

8:40am **G4-3 Nitriding and DLC Coating of Aluminum Alloy Using High Current Pressure-Gradient-Type Plasma Source**, ***Akio Nishimoto***, Kansai University, Japan; *E Furuya, K Kousaka,* Chugai Ro Co., Ltd., Japan

The low hardness and poor tribological performance of aluminum alloys restrict their wide applications in automotive fields. However, protective hard coatings deposited onto aluminum alloys are effective for overcoming their poor wear properties. In this study, a diamond-like carbon (DLC) film followed by a nitriding layer was deposited onto an aluminum alloy via a pressure-gradient-type plasma source using nitrogen and acetylene gases. This pressure-gradient-type plasma source is operated at a low discharge voltage of 60-100 V and a high current of 60-130 A. An aluminum alloy EN AW-5052 sample was plasma nitrided for 4 h at 520 ºC under 0.09-1.1 Pa. DLC was then coated with an acetylene gas after plasma nitriding using the same apparatus. The Vickers microhardness of the surface nitrided at 0.51 Pa reached approximately 340 HV from 125 HV. In addition, glow discharge optical emission spectrometry (GD-OES) revealed that nitrogen was concentrated at the surface region. After the DLC coating, the sample was reddish brown in color. GD-OES results demonstrated that a carbon-rich region formed in the top surface region (DLC film), followed by the formation of a nitrogen-rich region (nitriding layer). Nanoindentation test showed that the hardness of the top surface (DLC film) was 10.3 GPa. The DLC coating also exhibited good tribological performance in a ball-on-disk wear test, with friction coefficients of approximately 0.17, which was characterized as low value of DLC. In addition, aluminum nitride (AlN) interlayer was deposited on the nitriding layer by ion plating method in order to enhance adhesion between the DLC film and the substrate. Rockwell indentation indicated good adhesion. Hardness, roughness, and structure of the DLC film deposited on the AlN interlayer was investigated.

9:00am **G4-4 Towards Hard yet Tough Ceramic Coatings**, ***Sam Zhang***, Nanyang Technical University, Singapore

Over the past decades, hard and super hard ceramic coatings have been developed and widely used in various industrial applications. Meanwhile, an increasing number of studies have realized that the toughness is just as crucial, if not more, than hardness especially for ceramic coatings. However, hardness and toughness do not go naturally hand in hand. In other words, hard coatings usually are brittle and less durable while toughened coatings are of lower strength. For practical engineering applications, it is more desirable to have coatings with high hardness without sacrificing toughness too much. In this talk, a review is presented on continuous progress to realize hard-yet-tough ceramic coatings from an angle of hardening as well as toughening.

9:20am **G4-5 Flash Lamp Annealing (FLA) for Post-deposition Treatment at High Throughput**, ***Thoralf Gebel***, University of Applied Sciences Mittweida, Germany; *M Neubert,* ROVAK GmbH, Germany; *W Skorupa,* Helmholtz Zentrum Dresden-Rossendorf, Germany **INVITED**

Today's deposition processes for large area / large volume applications are strongly influenced by cost saving issues, by environmental regulations and by aspects of improved throughput. Especially in the case of thermal processing steps (e.g. for transparent conductive oxide (TCO) layers for displays on flexible glass) this becomes a very important aspect: substrates which need to be heated during or after the deposition process require sophisticated handling systems, and the moving substrates heated to elevated temperatures require cooling zones which may limit the throughput. A promising approach to overcome these problems are novel ultra-short time thermal processes with treatment times in the (sub)millisecond range. By using pulsed photonic treatment (e.g. by means of laser or flash lamp annealing) only the surface layers of the substrate materials are heated and therewith the thermal budget is strongly reduced. The work presented here focuses on investigations of such new thermal processes by using simulations and providing energy & cost saving models. Aspects of process design and overlapping issues and their influence to homogeneity will be discussed.

10:00am **G4-7 Evaluating the Effect of Titanium-Based PVD Metallic Thin Films on Nitrogen Diffusion Efficiency in Duplex Plasma Diffusion/Coating Systems**, ***Gorkem Yumusak***, *A Leyland,* University of Sheffield, UK; *A Matthews,* University of Manchester, UK

Titanium is a very popular engineering metal due to its outstanding properties, such as low density and high specific strength. However, the wear resistance of titanium is very poor in many industrial environments. Wear resistant hard coatings can be used to increase the service lifetime of manufactured products but the effectiveness of these coatings on titanium is sometimes weak due to poor load bearing capacity of the substrate. Therefore, titanium alloys need certain pre-treatments before the Physical Vapour Deposition (PVD) of ceramic hard coatings.

In this work, triode plasma nitriding (TPN) has been applied in order to increase the load bearing capacity of titanium alloys. It is known that the adhesion between titanium alloy substrates and PVD hard coatings can be increased significantly after substrate diffusion treatment [1]. TPN treatments were used in this work because the diffusion of the nitrogen can be achieved more easily at lower temperatures and shorter times, without the need for hydrogen in the gas mixture.

The efficiency and effectiveness of triode-plasma diffusion treatment can be increased by applying a thin PVD metallic layer on titanium alloy substrates, before plasma nitriding [2, 3]. In this context, different compositions of β-titanium coating (stabilized by addition of Nb) were produced on α+β Ti-6Al-4V and β Ti-15Mo substrate materials; the formation of β phase in Ti-Nb coatings before nitriding (and of nitride phases after TPN treatment at 500-700ºC) was analysed.

[1] G. Cassar, S. Banfield, J.C. Avelar-Batista Wilson, J. Housden, A. Matthews, A. Leyland, Wear 274 (2012) 377.

[2] G. Cassar, A. Matthews, A. Leyland, Surf Coat Technol 212 (2012) 20.

[3] B. Attard, A. Matthews, A. Leyland, G. Cassar, Surf Coat Technol 257 (2014) 154.

10:20am **G4-8 Properties of Surface Passivation at Si/Al_2O_3 Interface Annealed in Different Gas Ambient**, *C Yang,* National Chung-Hsing University, Taiwan; ***Chun-Wei Huang***, *C Hsu,* Da-Yeh University, Taiwan; *C Kung,* National Chung-Hsing University, Taiwan; *S Lien,* Da-Yeh University, Taiwan; *W Zhu, X Meng, X Zhang,* Xiamen University of Technology, China

Efficient surface passivation is crucial in most electronic devices, especially in solar cells, where the generated electron-hole pairs need to be collected by contacts before recombining at the surfaces. Aluminum oxide (Al_2O_3) film synthesized by atomic layer deposition system (ALD) offers a high level of surface passivation for p-type passivation emitter and rear cells (PERC). The high passivation quality of Al_2O_3 is related to high negative charge combined with low interface density. The post-annealing process after the deposition of Al_2O_3 films can effectively activate the passivation. The objective of this work is to optimize the passivation performance by hiring different annealing temperature and atmosphere containing air, nitrogen, oxygen, and forming gas (95 % N_2+5 % H_2) inside the furnace.

The silicon wafers used in this study is mono-crystalline p-type commercial-grade CZ silicon wafers with a thickness of 200±20 μm and a resistivity of 0.5 to 5 Ω-cm. The original lifetime of bare wafer is under 5 μs. Initially silicon wafers are cleaned through a standard Radio Corporation of America (RCA) cleaning process and textured using 6 % KOH solution. After that, the uniform 25 nm Al_2O_3 films are prepared by non-vacuum spatial atomic layer deposition on double sides of wafers. Post annealing process in air, nitrogen, oxygen, and forming gas ambient are performed to the samples at 350°C to 650°C for 30 min using a furnace. To characterize the passivation quality of Al_2O_3 films, effective carrier lifetime (τ_{eff}), negative fixed charge (Q_f) and interface trap density (D_{it}) are measured and determined. The result shows that as the annealing temperature increasers, the τ_{eff} increases first and then decreases after peak τ_{eff} of around 152 μs at 450°C. It indicates that appropriate annealing temperature can activate the passivation effect of Al_2O_3, but τ_{eff} may decline rapidly when the temperature over 600°C due to the crystallization of Al_2O_3. The trend of τ_{eff} value can be further explained by the fixed negative charge and D_{it}. The highest Q_f of -1.07×10^{12} cm^{-2} and lowest D_{it} of 7.5×10^{12} $eV^{-1}cm^{-2}$ that can effectively reduce recombination on the Si/Al_2O_3 interface are determined from the capacitance-voltage curve at 450°C, hence increasing the lifetime of carriers before trapped by defects. For gaining higher τ_{eff}, the samples are annealed in various atmosphere for 450°C. The better τ_{eff} of around 180 μs is acquired while annealed in forming gas. This is probably attributed to the extra chemical passivation effect via filling dangling bonds on the Si surface by hydrogen atom. The results of this study can able be used for high efficiency PERC cells.

10:40am **G4-9 High Performance Solar Selective Coatings based on TiNxOy**, ***Cho-Yen Lee***, *J Ting,* National Cheng Kung University, Taiwan

In this work, a series of TiNxOy films have been investigated for used as solar selective absorbers due to their remarkable optical, mechanical, and electronic properties. The films were deposited using a reactive magnetron sputtering technique. A pure titanium target was used and the deposition took place in different mixtures of oxygen, nitrogen, and argon. The obtained TiNxOy was then coated with an anti-reflection layer, consisting of metal or non-metal oxides with desirable refractive index. The TiNxOy films and the resulting multilayer coatings were analyzed for the material characteristics. Effects of the material characteristics on the optical performance is presented and discussed. We demonstrate that the resulting multilayer coatings make a breakthrough on the limitation of traditional absorbers' monotonous color appearance which is expected to be desirable in many applications.

11:00am **G4-10 Diagnostics of Surface Roughness during Electrolytic Plasma Polishing Pre-treatment for Stainless Steels**, *V Mukaeva, E Parfenov, R Farrakhov, M Gromova,* Ufa State Aviation Technical University, Russian Federation; ***Aleksey Yerokhin***, The University of Manchester, UK

Pre-treatments of steel surface constitute an important step for successful physical vapor deposition of commercially used protective coatings such as TiN, Ti and other. Electrolytic plasma polishing (EPPo) provides several effective pre-treatment operations such as deburring, cleaning and polishing which can be combined in one process. The EPPo has found its industrial scale applications in treatment of stainless and high carbon steels, nickel, copper, titanium and aluminum alloys. This process has high efficiency, and it meets modern environmental requirements, but its drawbacks include process non-linearity and high power consumption.

To investigate into the process mechanism and to overcome its drawbacks, a novel acoustic emission study has been performed, and a diagnostic approach providing estimation of the surface roughness during the treatment has been proposed. A source of the acoustic emission during the EPPo is a vapor gaseous envelope (VGE) boiling around the workpiece connected as an anode. The EPPo is usually carried out at high voltages in the range from 200 to 500 V applied between the anode and cathode. These conditions promote an appearance of the VGE with a glow discharge intensively modifying the surface. The experimental study has been dedicated to the EPPo of stainless steel BS420S29. The acoustic emission oscillations were measured by a waterproof piezoelectric hydrophone which was *immersed* into the electrolyte and located 6…12 cm away from the workpiece. A data acquisition system consisted of a computer and an analog-to-digital converter, which were controlled by a Labview based program. It was shown that an informative frequency range from 500 to 2000 Hz has characteristic spectral features which help to estimate the surface roughness during the process.

Finally, a new method of the surface roughness diagnostics was designed and introduced into automated EPPo equipment, increasing the process efficiency by 5-7%

Surface Engineering - Applied Research and Industrial Applications

Room Sunrise - Session G5

Atmospheric Plasma Applications

Moderators: Hana Barankova, Uppsala University, Sweden, Sang-Yul Lee, Korea Aerospace University

8:00am **G5-1 Radiofrequency Cold Plasma Jets Generated at Atmospheric Pressure: from Principles to Applications**, ***Gheorghe Dinescu***, *E Ionita, M Ionita, M Teodorescu, V Marascu, A Lazea-Stoyanova,* National Institute for Lasers, Plasma and Radiation Physics, Romania **INVITED**

We present the principles and various discharge configurations for producing cold radiofrequency plasmas at atmospheric pressure, like plasma jet sources of DBD (Dielectric Barrier Discharges) and DBE (Discharges with Bare Electrodes) types and their utilization in engineering, biomedicine, environment, and nanotechnology. The applicative potential of those plasmas is exemplified with: polymer surface modification in order to control the wettability, carbon cleaning and silicon etching, patterning the cells growth on surface, promoting the adhesion of dental prostheses, operation in liquid phase for chemical decomposition and functionalization of nanomaterials, and synthesis of metallic nanoparticles.

Advanced Characterization Techniques for Coatings and Thin Films

Room Royal Palm 4-6 - Session H2-1

Advanced Mechanical Testing of Surfaces and Coatings

Moderators: Benoit Merle, Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Marco Sebastiani, University of Rome "Roma Tre"

8:00am **H2-1-1 Controlling Disorder in Vapor-deposited Metallic Thin Films and its Influence on Mechanical Behavior**, *D Magagnosc,* University of Pennsylvania, USA; *G Balbus,* University of California Santa Barbara, USA; *G Feng,* Villanova University, USA; ***Daniel Gianola***, University of California Santa Barbara, USA **INVITED**

The nonequilibrium nature of kinetically frozen solids such as metallic glasses (MGs) is at once responsible for their unusual properties, complex and cooperative deformation mechanisms, and their ability to explore various metastable states in the rugged potential energy landscape. These features coupled with the presence of a glass transition temperature, above which the solid flows like a supercooled liquid, open the door to thermoplastic forming operations at low thermal budget as well as thermomechanical treatments that can either age (structurally relax) or rejuvenate the glass. Thus, glasses can exist in various structural states depending on their synthesis method and thermomechanical history. Despite the ability to make MGs in bulk form (cm-size or larger) and their appealing properties, the full spectrum of structural states in MGs and the corresponding mechanical behavior is relatively unknown, stymying the tuning of MG properties via informed processing and synthesis routes. Recent reports of organic glasses synthesized by physical vapor deposition show a degree of control not available in bulk materials and the occurrence of ultrahigh kinetic stability – so-called ultrastable glass formation.

Here, we use sputter deposition while varying the substrate temperature, to isochemically control the structural state and concomitant mechanical response in a Pd-based MG thin film at the time of glass formation. Increasing the deposition temperature from 333 K to 461 K results in a 33.5% increase in hardness to 9.69 GPa for amorphous films. Further increasing the temperature leads to a decrease in hardness, indicating low and high temperature deposition regimes where increased surface mobility allows access to a more relaxed and more rejuvenated structure, respectively. Through this mechanism we access the range of achievable structural states, from ultrastable to highly liquid-like glasses.

8:40am **H2-1-3 Influence of Microstructure on the Cyclic Electro-mechanical Behavior of Ductile Films on Polymer Substrates**, ***Megan Cordill***, *O Glushko,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences and Monanuniversität Leoben, Austria; *D Többens,* Helmholtz-Zentrum Berlin für Materialien und Energie, Germany; *C Kirchlechner,* Max-Planck-Institut für Eisenforschung GmbH, Germany

In order to advance flexible electronic technologies it is important to study the combined electro-mechanical properties of thin metal films on polymer substrates under mechanical load. Ductile films and lines are an integral part of flexible electronics because they allow current flow between semiconducting islands and other operating features. When ductile films on polymer substrates are strained in tension the substrate can suppress the catastrophic failure that allows for their use in flexible electronics and sensors. However, the charge carrying ductile films must be of an optimum thickness and microstructure for suppression of cracking to occur. In order to improve mechanical and electrical properties of these complex material systems, more work at characterizing the processing-structure-property relationships should be performed. Studies of strained films on polymer substrates tend to emphasize only the electrical properties and thickness effects more than the role of film microstructure or deformation behavior. The microstructure of the film not only determines the mechanical behavior but also influences the electrical behavior and could be optimized if studied in connection with the mechanical behavior. To address both the electro-mechanical and deformation behavior of metal films supported by polymer substrates, in-situ 4 point probe resistance measurements were performed with in-situ confocal scanning laser microscopy imaging of the film surface during cycling. The 4 point probe resistance measurements allow for the examination of the changes in resistance with strain, while the surface imaging permits the visualization of localized thinning and crack formation. Furthermore in-situ synchrotron tensile tests provide information about the stresses in the film and show the yield stress where the deformation initiates and the relaxation of the film during imaging. The combination of electrical measurements, surface imaging, and stress measurements allow for a complete picture of electro-mechanical behavior

needed for the improvement and future success of flexible electronic devices.

9:00am **H2-1-4 Crystalline/Amorphous Metallic Multilayers – from Dislocations to Shear Bands***, **Marlene Mühlbacher**,* Montanuniversität Leoben, Austria*; C Gammer,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria*; F Spieckermann, C Mitterer, J Eckert,* Montanuniversität Leoben, Austria

Amorphous metallic coatings have recently emerged as promising thin film materials - thin film metallic glasses - due to their excellent chemical stability, good wear resistance and exceptionally high strength. Their mechanical behavior, however, is fundamentally different from their crystalline counterparts, due to the disordered structure lacking dislocations as carriers of plastic deformation. To investigate the different deformation and failure mechanisms, we have synthesized Zr- and Pd-based crystalline/amorphous multilayers with a total thickness below 1 µm and individual layer thicknesses below 100 nm by unbalanced dc magnetron co-sputtering from elemental targets. The microstructural variation is achieved by a change of deposition temperature or a change of composition (e.g. crystalline $Pd_{0.69}Si_{0.31}$ /amorphous $Pd_{0.80}Si_{0.20}$) established by different powers applied to the magnetrons. Nanomechanical samples are prepared in a focused ion beam instrument. Mechanical properties and their dependence on layer thickness and arrangement of the multilayers are investigated with a particular emphasis on *in-situ* tensile testing in the transmission electron microscope. This approach allows for a direct comparison of plastic deformation through the movement of dislocations and shear bands in the crystalline and glassy layers, respectively. Strategies for the prevention of sudden failure of the thin film metallic glass, e.g. by the confinement of shear bands between crystalline layers, are evaluated.

The tensile tests are complemented by *in-situ* and conventional nanoindentation and put into context with glass transition and crystallization temperatures of the thin film metallic glasses obtained by differential scanning calorimetry, thus presenting a comprehensive picture of the crystalline/amorphous multilayer system.

9:20am **H2-1-5 A Novel Method for the Preparation of Tensile Thin Film Specimens for In-situ Mechanical Testing in the TEM***, **Benoit Merle**, J Liebig, M Göken,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany

A novel method was developed for the preparation of thin film micro-tensile specimens. Unlike most previous techniques, it does neither require the availability of a cleanroom nor that of expensive photolithographic equipment. It is based on a combination of focused ion beam (FIB) milling and electron-beam-assisted etching with xenon difluoride precursor gas. In contrast to existing FIB-based preparation approaches, the area of interest is never exposed to ion beam irradiation and a pristine microstructure is preserved. This is achieved by using a special shadow milling geometry with a thin silicon membrane simultaneously serving as a substrate and protective layer for the thin film of interest. A great advantage of the new method is that it enables the target preparation and mechanical testing of individual microstructural defects. The method was applied to nanotwinned Cu-Al as well as Au thin films. The fabricated tensile specimens were mounted on a push-to-pull conversion device and subsequently tested in-situ in the transmission electron microscope (TEM).

[1] Liebig, J. P., Göken, M., Richter, G., Mačković, M., Przybilla, T., Spiecker, E., Pierron, O.N., Merle, B.: A flexible method for the preparation of thin film samples for in situ TEM characterization combining shadow-FIB milling and electron-beam-assisted etching. Ultramicroscopy, 171:82-88 (2016).

9:40am **H2-1-6 Liquid Metal Embrittlement at the Micro-scale: Gallium FIB vs. Xenon FIB***, Y Xiao,* Laboratory for Nanometallurgy, ETH Zurich, Switzerland*; **Jeff Wheeler**,* Laboratory for Nanometallurgy, ETH Zürich, Switzerland

Micromechanical testing of structures fabricated using focused ion beam (FIB) has allowed significant progress to be made in understand the deformation and properties of small volumes of materials. However, the vast majority of FIB structures are machined using Gallium, which is known to embrittle many metals (e.g. Al, Cu and Fe) by weakening their grain boundaries. This has recently been shown to have a significant negative effect on the strength of micropillars of polycrystalline aluminum. Here we extend upon that work to investigate the effect of Ga FIB on the deformation and fracture properties of grain boundaries of several materials by comparing structures (micro-pillars and -cantilevers) made using both Xe FIB and Ga FIB.

10:00am **H2-1-7 Quantum Contact Mechanics for Tribology, Wear and Erosion***, **Norbert Schwarzer**,* SIO, Germany

Erosional or tribological models and simulations do not only require a comprehensive mechanical contact model but also need to account for the principle uncertainties residing in the field.

It will been shown that the classical continuum mechanical and thus, also deterministic, concepts are not adequate if one intends to describe tribological processes like erosion, fretting, wear etc.

By incorporating quantum mechanical concepts via a principle scale dependent accessibility with respect to input parameters from measurement, surface roughness or even non-continuous composition, one does not only overcome such flaws in the classical approaches but also automatically incorporates a method to observe and actively control the influence of the uncertainty budget [1].

According to the classical quantum mechanics, the uncertainty is been accounted for by a “Planck” constant, only that this time, depending on the dimension of the problem, we end up with Planck-vectors or tensors instead of the classical scalar.

The way to go is cumbersome at the beginning, because it requires the principle quantization of the line element of a general continuous space, but the outcome is a very compact, rather general and powerful tool to handle practical applications.

As a byproduct, so it seems, also the quantization of the Einstein field equations can be achieved [2].

[1] N. Schwarzer: „Quantum Tribology – Part I: Theory“, www.amazon.com/dp/ B01CI4BI2E

[2] N. Schwarzer: „Recipe to Quantize the General Theory of Relativity“, www.amazon.com/dp/ B01LX664IF

10:20am **H2-1-8 Textile Nanocharacterization: Topography, Phase Imaging, and Nanomechanical Property Investigation of Polyester Yarn Interaction with Silicon Matrix***, B Kim, **Gerald Pascual**, K Lee,* Park Systems Corporation, USA

Textiles research and development is rapidly turning to nanomaterials to create new fabric blends that have increased performance for traits such as damage resistance, breathability, and even self-cleaning. To better inform materials design strategies, it is necessary to have a tool and techniques capable of measuring not only nanoscale topographies of material components, but their nanomechanical properties as well. Atomic Force Microscopy (AFM) is a solution well-suited to explore and characterize these traits. To this end, a silicon gel matrix and polyester yarn sample was prepared for examination with a commercial AFM system, the Park NX10 from Park Systems. Non-contact mode AFM from Park Systems was used to perform topography and phase imaging. Force-distance spectroscopy plus force-volume mapping was used for nanomechanical property characterization. The acquired data reveals that the hardness of the yarn is about 100 times greater than the matrix it is embedded in with forces being measured in nanonewton resolution and distances in micrometers. This investigation of the textiles sample is reflective of AFM’s effectiveness in allowing textiles researchers to explore the root, nanoscale causes of desirable macroscopic traits in novel fabric blends and further improve upon them.

10:40am **H2-1-9 A Nanoindentation System with Equivalent Capabilities in Both Normal to and Parallel to the Sample Surface***, **Warren Oliver**,* Nanomechanics, Inc., USA*; P Phani,* International Advanced Research Centre for Powder Metallurgy & New Materials, India*; K Johanns,* Nanomechanics, Inc., USA*; J Pethica,* CRANN, Trinity College Dublin, Ireland*; K Parks,* Nanomechanics, Inc., USA

An entirely new nanomechanical testing system has been built. The system retains the same measurement capabilities associated with high performance nanoindentation systems from which we have reported results in the past in the direction normal to the surface of the sample and adds the equivalent signals parallel to the surface. The same sensitivity, range and dynamic performance (including frequency specific experiments) are available simultaneously and continuously in both directions. The ability to measure not only load and displacement but stiffness and phase angle at specific frequencies parallel to the surface continuously and simultaneously with these same measurement in the normal direction has resulted in entirely new results concerning the onset of sliding between two bodies in contact. Unique new data concerning the initiation of slip at micro asperities, friction and wear, lubrication, scanning surface topology, mechanical property mapping and multidimensional characterization of structures can now be investigated. Specifics of the dynamic performance

when each axis is actuated separately as well as simultaneously will be presented along with a number of examples of its use. A dynamic model that describes the system's behavior will also be presented.

11:00am **H2-1-10 The Effects of TIP Sharpness and Substrate Properties on Nanohardness Measurement in Thin Hard Coatings by FEM**, ***Frantisek Lofaj***, *D Nemeth,* Institute of Materials Research of SAS, Slovakia

FEM modelling of nanoindentation in the hard coating/softer substrate system revealed strong influence of the sharpness of the indenter tip on the hardness-indentation depth profiles resulting in the limited validity of the general 10% relative indentation depth rule. The result was attributed to the increase of the size of plastic field under the indenter with the increase of tip radius and the limits for the applicability of the nanoindentation tests with real (blunted) indenters were determined. Another important factor strongly affecting the hardness - depth profiles is the difference among the properties of the coating and substrate. These observations were confirmed experimentally on the corresponding depth profiles obtained in the continuous stiffness measurement mode on different W-C coatings deposited on steel and hardmetal substrates by HIPIMS and HITUS. The above limitations of nanoindentation in the determination of the nanohardness of thin films from the corresponding depth profiles are discussed.

11:20am **H2-1-11 Small Punch Testing for Mechanical Characterisation of a Free-standing CoNiCrAlY Coating**, ***Hao Chen***, University of Nottingham, China

In this study, the ductile-to-brittle transition temperature (DBTT) of a high velocity oxy-fuel (HVOF) thermally sprayed CoNiCrAlY (Co-31.7% Ni-20.8% Cr-8.1% Al-0.5% Y (wt%)) coating was investigated. To determine the DBTT, displacement controlled small punch tensile test (SPTT) and multi-step loading small punch test were employed between room temperature (RT) and 750 °C. At low temperatures, evidence of elastic-brittle behaviour was found but at high temperatures extensive yielding and plastic deformation occurred. The yield strength ranged from 1000-1500 MPa below 600 °C to less than 500 MPa above 650 °C and the elastic modulus was found to be approximately 200-230 GPa at 500 °C and 55 GPa above 700 °C, as evaluated via SPTT. The displacements obtained from multi-step loading SPT at each load increment were relatively small and similar at temperatures below 500 °C but a significant increase in displacement was noted at 600 °C. Test results gave a DBTT of this coating of approximately between 500-700 °C. Fractographic investigation showed that the fracture surface at RT exhibited flat, smooth features indicating brittle fracture whereas at 600 °C and above the main fracture mode was dominated by extensive ductile tearing.

Topical Symposia
Room California - Session TS2-1

Thermal, Cold, and Kinetic Sprayed Surface Coatings

Moderators: Pylin Sarobol, Sandia National Laboratories, USA, Charles Kay, ASB Industries, Inc., USA

9:00am **TS2-1-4 Thermally Sprayed Alumina and Ceria-doped-Alumina Coatings on AZ91 Mg Alloy**, ***Sanjeet Kumar***, ITMMEC, Indian Institute of Technology Delhi, India*; D Kumar, J Jain,* Indian Institute of Technology Delhi, India

Present study deals with the development of ceramic based coatings for Mg alloys using thermal spray technique, where Al_2O_3 is doped with CeO_2. Coatings characteristics and other responses were measured using microindenter, nanoindenter, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray Diffraction (XRD) and tribometer. The tribological response is evaluated in terms of specific wear rates and coefficient of friction under lubricated reciprocating sliding condition for different loads and speeds. Ceria doped alumina coatings showed improved responses. The elastic modulus and nano-hardness of CeO_2 doped alumina coating was ~13% and ~53% higher than alumina coating, respectively. Under high load and velocity conditions, ceria doped coating showed ~40% reduction in specific wear rate. Also, the results suggest that ceria doping has helped in lowering the coefficient of friction during sliding. One may attribute this to the development of a new intermetallic phase.

9:20am **TS2-1-5 Langmuir–Blodgett Colloidal Assembly: Challenges and Solutions**, *H Nie,* Donghua University, China*; **Jiaxing Huang**,* Northwestern University, USA

LB assembly has been routinely used in research labs for nearly a century for preparing molecular and colloidal monolayers. Volatile, water-immiscible solvents are convenient for spreading, but they have also been a “pain” in terms of colloidal stability, processability and chemical safety, making scaled up applications difficult. The use of water-miscible spreading solvents would avoid all of these problems, but it tends to lose most materials to water subphase due to intermixing, making such LB colloidal assembly ineffective and hard to standardize or reproducible.

This dilemma can be solved by electrospray spreading, in which the small volume of the microdroplets is readily depleted during initial spreading, leaving no extra solvent for mixing. As is demonstrated with several prototypical colloidal systems, electrospray allows high-yield, high-throughput spreading of colloidal materials on water surface using environmentally benign, water-miscible solvents (even water itself), which liberates this century-old technique from many constrains related to material processing and significantly expands its scope. Electrospray apparatus can be readily automated and fully integrated with existing LB systems, which should help to standardize this technique and scale it up from LB assembly to LB manufacturing.

9:40am **TS2-1-6 Mechanical Properties of Thermal Spray Coatings on Carbon-fiber-reinforced Plastic**, ***Reinhard Kaindl***, Joanneum Research, Austria*; M Kräuter,* Graz University of Technology, Austria*; P Angerer,* Materials Center Leoben Forschung GmbH (MCL), Austria*; W Stöger,* SECAR Technology GmbH, Austria*; M Traxler,* BVT Beschichtungs- und Verschleißtechnik GmbH, Austria*; J Lackner, W Waldhauser,* Joanneum Research, Austria

Due to exceptional properties like high strength and low weight carbon-fiber-reinforced plastic (CFRP) replace steel and aluminum in aerospace and automotive applications. However, the stability of CFRP against mechanical wear, corrosion and thermal load is limited. Thermal spray coatings are routinely used for the protection against extensive wear and/or high temperature, e.g. in power plant turbines, aircraft engines or on pulp rolls in the paper industry. The highly complex relationship between cohesion and adhesion, mechanical properties, structure and composition of course strongly influences the functionality of the compound substrate-coating material. In this contribution, scratch test derived cohesion of thermal spray oxide coatings on CFRP materials and influences of thickness, substrate and coating system will be presented.

Yttrium-stabilized zirconia (YSZ), titanium-aluminum (TiAl) and aluminum-silicon (mullite) coatings with a thickness between 0.15 and 1.4 mm were deposited by thermal spraying on a variety of CFRP materials. Scratch tests were performed using an Anton Paar micro scratch head on cross-sectioned samples embedded in resin. The tests were done with constant loads of 4, 8, 12, 16 and 20 N, scratch length 2 mm, at a speed of 2.4 mm/min with a 100 µm Rockwell C diamond indenter. Images of the cone fracture area were taken immediately after scratching and projected cone areas in μm^2 were calculated.

All cone fractures originated in the coating, confirming that the cohesion was tested. The projected cone area increases with increasing load, in most cases linear but depending upon thickness, substrate and coating system also discontinuous and exponential. This suggests the existence of different failure mechanisms. The lowest areas were observed for a coating thickness around 0.5 mm, both thinner and thicker layers resulted in increased values and decreased cohesion, respectively. The CFRP substrate seems to influence the mechanical properties of the coating. Highest cohesion was found for epoxy and phenolic resin systems. For other systems like sheet moulding compound (SMC), high temperature resins and ceramic particles in the CFRP matrix decrease of cohesion was observed. Differences were also observed for the three coating systems: the highest cohesion was found for TiAl, followed by mullite and YSZ. This is confirmed by the very low, non-economic deposition rates for YSZ during spraying.

In conclusion, scratch tests at constant load allow achieving best functionality against wear and abrasion of thermal spray coatings on CFRP materials by characterizing the cohesion and influences of thickness, substrate and coating system.

10:00am **TS2-1-7 Developments in the Understanding of the Fundamental Growth Mechanisms of Aerosol Deposition**, ***Scooter Johnson,*** Naval Research Laboratory, USA*; D Park,* Korean Institute of Material Science, Korea*; Y Park,* Pukong National University, Korea*; D Schwer, E Gorzkowski,* Naval Research Laboratory, USA **INVITED**

Aerosol deposition is an emerging technologically relevant technique to produce thick polycrystalline films at room temperature. While there have been many materials deposited by this method; including, ceramic, metallic, and even organic compounds for a wide range of applications there is still a very poor theoretical understanding of the mechanics of the film growth. The current theory of film growth is postulated to occur by a mechanism of fracture and plastic deformation of the solid particle as it impacts with the substrate and/or as-deposited particles. This talk will provide an overview of the current understanding of the theory and practice of aerosol deposition along with a comparison between recent experimental results that attempt to correlate film growth, material properties, and deposition parameters.

10:40am **TS2-1-9 Aerosol Deposition as a Method of Room Temperature Thick-Film Deposition**, ***Jesse Adamczyk,*** *P Sarobol, A Vackel, T Holmes,* Sandia National Laboratories, USA*; P Fuierer,* New Mexico Institute of Mining and Technology, USA

Creating thick (>5 µm) films of ceramics and metals typically requires high temperatures or reactive environments, limiting the integration of film/substrate materials possessing drastically different melting points. Thick films of both ceramics and metals can be deposited, using traditional thermal spray techniques. However, particle melting/solidification and splatting lead to a unique microstructure containing splat boundaries, porosity, oxide inclusions, and non-stoichiometric oxide formation. Moreover, melting/solidification can lead to loss of volatile elements, original crystal structure, and associated desired properties (e.g. BaTiO3 will lose its perovskite structure and associated dielectric properties after going through melting/solidification in a plasma spray process). The Aerosol Deposition (AD) process is being utilized to create readily integratable, high density thick-films of ceramics and metals on a variety of substrates at room temperature. In the AD process, thick-films are produced by spraying micron to submicron sized particles out of a nozzle and onto a substrate within a low vacuum chamber. AD takes advantage of the low pressure within the vacuum by allowing sprayed particles to maintain velocity and consolidate in solid-state (no melting/solidification), into a film on impact with the substrate and subsequent film. AD also takes advantage of the small particle size and the ability of ceramic and metallic particles to plastically deform and bond as coatings. Potential applications of aerosol deposition being investigated include direct applied Multi-Layered Ceramic Capacitors (MLCC), electrically conductive electrodes, thermally and chemically resistant barrier coatings, and electrically insulative films.

This work is supported by Office of Electricity and Laboratory Directed Research and Development Program at Sandia National Laboratories. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. DOE's National Nuclear Security Administration under contract DE-AC04-94AL85000.

11:00am **TS2-1-10 Residual Stress Measurement of Aerosol Deposited Films**, ***Andrew Vackel,*** *J Adamczyk, T Holmes, P Sarobol,* Sandia National Laboratories, USA

Aerosol Deposition (AD) is a room temperature, solid state coating process for synthesizing thick films, where sub-micron to micron sized powder is accelerated by a carrier gas through a nozzle towards a substrate within a vacuum environment, forming a coating by particle consolidation. The use of small particles and the reduced drag and bow shock from a vacuum environment allows for normally brittle materials, such as ceramics and carbides, to plastically deform and adhere to the substrate. One of the unique benefits of the AD process is the ability to deposit materials that typically have high melting temperatures or metastable phase compositions at room temperature, allowing material integration that would otherwise be prohibited by the need for high temperatures for processing. Additionally, thermal stress due to expansion mismatches between coating and substrate is eliminated. However, there is still a large degree of residual stress within AD films, due largely to the high kinetic energy impact of particles as the main consolidation mechanism for coating deposition. This talk will explore the use of in-situ substrate curvature measurement to calculate the deposition and residual stresses experienced by different materials in the AD process and how they relate to processing parameters, such as nozzle design, particle size, and process gases, in an effort to better understand and characterize AD coatings.

This work is supported by Office of Electricity and Laboratory Directed Research and Development Program at Sandia National Laboratories. Sandia National Laboratories is a multi-mission laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. DOE's National Nuclear Security Administration under contract DE-AC04-94AL85000.

11:20am **TS2-1-11 Microstructure and Properties of Room Temperature, Aerosol Deposited, Thick $BaTiO_3$ Dielectric Films**, ***Pylin Sarobol,*** *A Vackel, J Adamczyk, T Holmes, M Rodriguez, J Griego, H Brown-Shaklee,* Sandia National Laboratories, USA

$BaTiO_3$ based dielectrics are being explored for high temperature stable capacitor applications to enable high power electrical switching devices. The high sintering temperature of $BaTiO_3$ (T>1000°C) often prevents successful integration with low melting point substrates such as glass, metal, or plastic. In this work, we demonstrate integrated high density $BaTiO_3$ based thick films at room temperature utilizing a novel, solid-state deposition process, Aerosol Deposition (AD). In AD process, high velocity submicron particles impact, deform, and consolidate as coatings on room temperature substrates under vacuum. The aerosol deposited $BaTiO_3$ film crystal structure, grain size, residual strain, and dielectric properties were investigated. Preliminary results showed an in-plane crystallographic strain in our AD films were determined to be ~1% by XRD analysis, which corresponds to an approximate compressive stress of 1GPa. The impact of this significant crystallographic strain on dielectric properties will be discussed. The ability to deposit dielectrics at room temperature will further enable the design, fabrication, and integration of high capacitance devices.

This work is supported by Office of Electricity and Laboratory Directed Research and Development Program at Sandia National Laboratories. Sandia National Laboratories is a multi-mission laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. DOE's National Nuclear Security Administration under contract DE-AC04-94AL85000.

11:40am **TS2-1-12 Dielectrics Produced via Aerosol Deposition**, *E Patterson,* ASEE, USA*; S Johnson,* ***Edward Gorzkowski,*** Naval Research Laboratory, USA

Aerosol deposition (AD) is a thick-film deposition process that can produce layers up to several hundred micrometers thick with densities greater than 95% of the bulk. The primary advantage of AD is that the deposition takes place entirely at ambient temperature; thereby enabling film growth in material systems with disparate melting temperatures. The bonding and densification of the film and film/substrate interface are thought to be facilitated by local temperature rise, high pressure, and chemical bonding during deposition, which leads to a dense nano-grained microstructure. In this talk we present results on the deposition of dielectric and ferroelectric materials deposited by aerosol deposition including the effect of processing parameters on the resultant material properties.

Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B6

Coating Design and Architectures

Moderators: Nina Schalk, Montanuniversität Leoben, Shou-Yi Chang, National Tsing Hua University

1:30pm **B6-1 Radial Symmetry of the Compound Layer Growth in Plasma Nitriding of Pure Iron**, *F Castillo,* ***Joaquin Oseguera****, E Hernánez, J Otero, D Melo-Maximo, A Jimenez,* Instituto Tecnologico y de Estudios Superiores de Monterey, Mexico

Radial symmetry plays a fundamental role in tribological systems, where spinning on axes takes place. This is the case for crankshafts, camshafts and driveshafts among others.Thermochemical treatments, which involve diffusion of one element such as nitrogen, oxygen or boron, produce a concomitant layer growth. Usually, layer growth kinetics has been studied by modeling from a Cartesian coordinate perspective, using plane fronts. The use of thermochemical treatments on radial symmetry surfaces makes relevant to employ different approaches in order to improve the obtained results so far.

The present work proposes a mathematical model which describes the compact layer growth kinetics during plasma nitriding of a pure iron solid cylinder. The erosion effect at the plasma-solid interface due to sputtering is taken into account. The model constitutes a moving boundary value problems, for which radial symmetry solutions are found. The numerical simulation of the model is performed using both finite differences and the Heat Balance Integral Method (HBIM).

1:50pm **B6-2 Self-assembled Nano-lamellar $Ti_{1-x}Al_xN$ LP-CVD Coatings: Development and Analysis**, ***Jakub Zalesak****, J Todt,* Montanuniversität Leoben, Austria*; I Matko,* Institute of Physics, Slovak Academy of Sciences, Slovakia*; M Petrenec,* Tescan Brno s.r.o, Brno, Czech Republic*; B Sartory,* Materials Center Leoben Forschung GmbH (MCL), Austria*; R Pitonak,* Böhlerit GmbH & Co KG, Austria*; R Daniel, J Keckes,* Montanuniversität Leoben, Austria

Recent progress in low-pressure chemical vapour deposition introduced self-organized nano-lamellar $Ti_{1-x}Al_xN$ coating system with outstanding mechanical and thermal properties [1]. This system exhibits a complex three-dimensional ordering of nano-lamellar microstructure, whose composition and period depend on the overall composition. A combinatorial search for optimal process gas flow ratios, to reach dedicated phase composition, microstructure and mechanical properties, was performed using a „graded coating" concept [2]. The analyses of the phasecomposition, microstructure and mechanical properties were performed by using X-ray nanodiffraction, TEM imaging and micromechanical testing of microcantilever beam specimens. Based on the iterative multi-parameter-analysis, refinedprocess gas flow ratios were identified. The optimized cubic self-organized nano-lamellar coating with overall composition of $Al_{0.8}Ti_{0.2}N$ was subsequently heteroepitaxially grown onto a single crystalline 0001 sapphire substrate and subjected to further detailed analyses with the aim to understand the self-organisation mechanisms. For semi-quantitative compositional characterization, EFTEM, EELS and EDX methods were employed. The combination of elemental composition analyses and imaging revealed multi-dimensional periodical compositional oscillations of Ti, Al and N. This singularity, in combination with oriented nano-lamellar microstructure, pointed out that the self-organization effect has its origin in oscillating reactions.

[1] Todt et al. / Surface & Coatings Technology 291 (2016) 89-93

[2] J. Zalesak et al. / Acta Materialia 102 (2016) 212-219

2:10pm **B6-3 Fundamental Properties of TM Nitrides: Materials Design Strategies for Extreme Properties**, ***Joe Greene****,* University of Illinois at Urbana-Champaign, USA **INVITED**

Transition-metal (TM) nitrides exhibit an enormous range of properties; they offer a smorgasbord of opportunities for materials scientists. Cubic TM nitrides have wide single-phase compound fields which can be exploited. We show results for vacancy hardening (not associated with film strain) in 3d Group-IV TiN_x(001) and Group-V VN_x(001); the hardness H of epitaxial layers increases dramatically, while the elastic modulus E and the relaxed lattice constant decrease linearly, as x is decreased from 1.0 to 0.67 and 0.80, respectively. Over the same x range, the resistivity ρ(x) increases linearly due to electron scattering from N vacancies. In contrast, H(x), E(x), and ρ(x) for 5d Group-V TaN_x(001) remain constant due primarily to the presence of isoelectronic antisites.

All Group IV TM nitrides TiN, ZrN, and HfN are very good metallic conductors with room temperature resistivities of 12-14 μΩ-cm. 3d Group-III ScN(001) is a transparent semiconductor with an indirect Γ-X gap of 1.3 eV and a direct X-point gap of 2.4 eV. Reflectivity measurements from $Sc_{1-x}Ti_xN$(001) layers show TiN is strongly reflecting up to the reflectance edge at $\hbar w_e$ = 2.3 eV, while ScN is transparent and $w_e \mu x^{0.5}$. ZrN is intermediate with $\hbar w_e$ = 3.04 eV. Thus, hard decorative coating can be obtained with a wide palette of colors.

Superconducting transitions T_c for the Group-IV TM nitrides range from 10.4 K for ZrN to 9.18 K for HfN to 5.35 K for TiN. For comparison, superconductivity is not observed for the Group-IV rare-earth (RE) nitride CeN. These results are consistent with electron/phonon coupling parameters of 1.11 (ZrN), 0.82 (HfN), 0.73 (TiN), and 0.44 (CeN). The acoustic phonon modes soften monotonically with increasing cation mass; optical mode energies remain approximately constant for the TM nitrides, but are significantly lower for the RE nitride due a lower interatomic force constant.

The extreme range of materials properties available in TM nitrides and related systems can be enhanced through the formation of self-organized superhard nanostructures consisting of commensurate nanolamellae, nanocolumns, nanospheres, and nanopipes. Self-organization strategies include controlled phase separation, surface-induced spinodal decomposition, surface segregation-induced renucleation, strain-induced roughening, surface anisotropy, and dynamic resputter yield amplification.

An issue with superhard ceramic films, however, is that they are typically brittle leading to failure by crack propagation. We show several approaches to obtaining TM nitride layers that are both hard *and* ductile (i.e., tough). Groups IV-V alloys such as $V_{1-x}W_xN$, exhibit metal-atom ordering on adjacent 111 planes in the cation sublattice leading to, in addition to increased hardness, enhanced ductility. Vacancy-induced toughening is also observed in understoichiometric VN_x and $(V,Mo)N_x$ alloys. A final example represents an entirely different approach: designing TM nitride multilayers which are defined not by composition differences, but by bonding differences in alternating layers of essentially the same composition.

2:50pm **B6-5 Stabilisation of Cubic MoN and TaN Systems: the Role Point Defects**, ***David Holec****,* Montanuniversität Leoben, Austria*; N Koutná, F Klimashin, P Mayrhofer,* TU Wien, Austria

Point defects are unavoidably present in materials, either due to thermodynamic reasons (equilibrium) or due to the growth process (non-equilibrium). The latter is the case of physical vapour deposition (PVD), a technique often employed for synthesising nitride-based protective coatings. Both MoN and TaN have recently received attention due their unique mechanical, electrical and chemical properties. The stable variants of both of them are hexagonal structures. However, under specific deposition conditions, they may be prepared in a cubic rock-salt structure. In this contribution we will present our recent *ab initio* based insights into the role of point defects on the stabilisation of these cubic phases. In particular we will show that both materials prefer a presence of vacancies. While in the case of MoN, both Mo and N vacancies possess the same stabilisation effect, in the case of TaN a strong preference for Ta vacancies is demonstrated. Furthermore, we can show that the vacancies are preferably distributed in a disordered fashion in MoN, while both ordered and disordered configurations yield comparable changes of the energy of formation in TaN. Phase diagrams for various deposition conditions will be presented and a relevance to our recent experimental data on N-deficient MoN will be also discussed.

References:

[1] N. Koutná, D. Holec, O. Svoboda, F.F. Klimashin, and P.H. Mayrhofer, J. Phys. D Appl. Phys. **49**, 375303 (2016).

[2] F. F. Klimashin, N. Koutná, H. Euchner, D. Holec, and P.H. Mayrhofer, submitted.

3:10pm **B6-6 Vacancy Induced Mechanical Stabilization of Cubic Tungsten Nitride**, ***Karthik Balasubramanian****,* Rensselaer Polytechnic Institute, USA

First principle calculations are employed to determine the mechanical stability and the formation energies E_f of point defects in rock-salt phase group III B – VI B transition metal nitrides and carbonitrides. Interstitials and antisite defects have relatively high E_f values, in average 3.9 and 9.7 eV higher than those for anion and cation vacancies, such that the latter are the energetically preferred point defects to account for deviations from stoichiometry. The vacancy formation energy decreases when moving towards the right in the periodic table, from E_f = 5.1 to -7.1 eV for anion

vacancies in ScN and WN, respectively, and from E_f = 3.2 to -12.0 eV for the corresponding cation vacancies. This decrease is accompanied by a decrease in the single crystal shear modulus, from c_{44} = 161 for ScN to 164, 126, and -120 GPa, for TiN, VN, and CrN, indicating a transition to mechanical instability of rock-salt nitrides and carbonitrides with increasing valence electron concentration above 5.3. The negative E_f values for both cation and anion vacancies in group VI B nitrides indicate that the rocksalt structure is thermodynamically unstable, despite experimental observations of cubic rock-salt type WN and MoN. We investigate this discrepancy by comparing the energetic and mechanical properties of WN in the experimentally reported rocksalt and theoretically predicted NbO phases. The rocksalt WN is both mechanically and thermodynamically unstable with a formation enthalpy H_f= 0.637 eV per formula unit and a negative c_{44} = -86 GPa while the NbO phase is stable with H_f= –0.825 eV and c_{44}= 175 GPa. Charge distribution and electronic density of states analyses reveal that the mechanical instability of rocksalt WN is due an increased overlap of t_{2g} orbitals upon the application of shear strain along [100], resulting in electron migration from the expanded [110] to the shortened [1-10] direction and a negative shear modulus. The mechanical transition from the unstable NaCl to the stable NbO phase is further explored using supercell calculations of the NaCl structure containing C_v= 0 to 25 % of both cation and anion vacancies. The structure is mechanically unstable for C_v <5 %. At this critical vacancy concentration, the isotropic elastic modulus is zero but increases steeply to 445 GPa for C_v= 10 % and to 561 GPa for the NbO structure with C_v= 25 % which is in good agreement with experimentally measured elastic moduli ranging from 110 – 360 GPa. These results show that the experimental reports of a cubic WN phase can be explained by the mechanical stabilization of the rocksalt phase by a minimum of 5% anion and cation vacancies.

3:30pm **B6-7 Nitrides and the Impact of Entropy on their Phase Stability**, ***Paul H. Mayrhofer***, TU Wien, Austria; *D Holec,* Montanuniversität Leoben, Austria; *F Klimashin, N Koutná,* TU Wien, Austria

Transition metal based nitrides are fascinating materials, owing to their excellent performance against mechanical attack. Since Jien-Wei Yeh's work in 2004 on "Nanostructured High-Entropy Alloys with Multiple Principal Elements: Novel Alloy Design Concepts and Outcomes", research activities on the impact of configuration entropy on the stability of solid solution phases increased. Corresponding to amorphous metals, also high entropy alloys have the potential for increased strength with a combined high fracture, corrosion, and oxidation resistance. Here we discuss in more detail the impact of configurational entropy on the phase stability, mechanical properties and thermal stability of hard ceramic coatings (like Ti-Al-N, Cr-Al-N, Mo-Al-N, Ta-Al-N and combinations thereof). Additionally, we will also treat vacancies (present especially in Mo, W, and Ta containing nitrides) as an important partner for the configurational entropy and discuss their impact on mechanical properties and phase stabilities.

3:50pm **B6-8 Molecular Dynamics Simulations of TiN/TiN(001) Growth**, *D Edström, D Sangiovanni, L Hultman,* Linköping University, IFM, Sweden; *I Petrov, J Greene,* University of Illinois at Urbana-Champaign, USA; ***Valeriu Chirita,*** Linköping University, IFM, Sweden

The Modified Embedded Atom Method (MEAM) interatomic potential is used within the classical Molecular Dynamics (MD) framework to perform simulations of important model materials such as TiN, in order to understand the processes which control TiN growth modes on a fundamental level. We report the results of large-scale simulations of TiN/TiN(001) deposition using a TiN MEAM parameterization which reproduces experimentally-observed surface diffusion trends, correctly accounts for Ehrlich barriers at island step edges [1], [2], and has been shown to give results in good qualitative and quantitative agreement with Ab Initio MD based on Density Functional Theory [3], [4]. We deposit 85% of a monolayer of TiN on 100x100 atom TiN(001) substrates maintained at 1200 K, at a rate of 1 Ti atom per 50 ps, for total simulation times of 212.5 ns. We use N/Ti flux ratios of 1, 2, and 4, and incident N energies of 2 and 10 eV, to probe the effects of N_2 partial pressure and substrate bias on TiN(001) growth modes. We observe nucleation of Ti_xN_y molecules; N_2 desorption; formation, growth and coalescence of mixed <100>, <110>, and <111> faceted islands; as well as intra- and interlayer mass transport mechanisms. For N/Ti flux ratios of 1 at 2 eV incidence energy, films exhibit Ti-rich surface regions which serve as traps to nucleate higher layers, leading to multilayer growth. Increasing the N/Ti flux ratio shifts the growth mode to layer-by-layer and modifies the overall film composition from under- to over-stoichiometric. As the N content of films is increased, N-terminated <110>-oriented island edges become increasingly dominant and the substrate vacancy concentration changes from being N- to Ti-dominated. We discuss the implications of these results on thin film growth and process tailoring.

[1] D. G. Sangiovanni, D. Edström, L. Hultman, V. Chirita, I. Petrov, and J. E. Greene, "Dynamics of Ti, N, and TiNx (x=1–3) admolecule transport on TiN(001) surfaces," *Phys. Rev. B*, vol. 86, no. 15, p. 155443, 2012.

[2] D. Edström, D. G. Sangiovanni, L. Hultman, V. Chirita, I. Petrov, and J. E. Greene, "Ti and N adatom descent pathways to the terrace from atop two-dimensional TiN/TiN(001) islands," *Thin Solid Films*, vol. 558, pp. 37–46, 2014.

[3] D. G. Sangiovanni, D. Edström, L. Hultman, I. Petrov, J. E. Greene, and V. Chirita, "Ab initio and classical molecular dynamics simulations of N_2 desorption from TiN(001) surfaces," *Surf. Sci.*, vol. 624, pp. 25–31, 2014.

[4] D. G. Sangiovanni, D. Edström, L. Hultman, I. Petrov, J. E. Greene, and V. Chirita, "Ti adatom diffusion on TiN(001): Ab initio and classical molecular dynamics simulations," *Surf. Sci.,* vol. 627, pp. 34-41, 2014.

4:10pm **B6-9 Development of Reliable Interaction Potential for and Results of Molecular Dynamics Simulations of ZrO_2 Film Growth**, ***Jiří Houška***, University of West Bohemia, Czech Republic

Thin films of ZrO_2 are of high interest due to a wide range of useful technological properties. In this contribution the growth of ZrO_2 is studied by atom-by-atom molecular dynamics simulations, focused on intrinsic process parameters such as the energy (E) and energy distribution function (EDF) of arriving atoms or the surface temperature (T).

The first part deals with the development of an interaction potential for a realistic description of atom-by-atom ZrO_2 growth. Owing to the fact that for many metal oxides including ZrO_2 only full-charge (Zr^{+4} and O^{-2}) interaction potentials are available in the literature, special attention is paid to the effect of the Zr and O elemental charges. Parameters of the short-range part of the Buckingham interaction potential leading to experimental lattice parameters and formation energies have been identified in a wide range of elemental charges. Simulations reveal that the structures grown using the presently available full-charge interaction potentials are in contradiction with the experiment (the atoms have too low coordination numbers). Correct partial charges and potential parameters leading to experimentally relevant structures (with correct coordination numbers) have been identified [1].

The second part shows how do the film densification, crystal nucleation and uninterrupted crystal growth depend not only on E delivered into the growing films (i) per fast atom (ion) or (ii) per any atom, but especially (iii) on the EDF (namely the fraction of fast atoms in the particle flux) and (iv) on the mass of fast atoms (Zr or O). On the one hand, the nucleation of c–ZrO_2 (the most desired phase) is T-dependent and requires (in order to take place on a short time scale) high E. On the other hand, the growth of previously nucleated (or epitaxial growth of) c-ZrO_2 is much easier, T-independent, and highly dependent on the EDF. Optimum EDFs which allow uninterrupted crystal growth at as low E delivered into the growing films as possible are characterized by (i) narrow EDF and (ii) high momentum delivered into the growing films (i.e. the combination of fast Zr and slow O leads to a better densification and crystallinity than the opposite) [2].

The results (in addition to the methodological importance of the interaction potential development) facilitate defining new synthesis pathways for ZrO_2, and constitute phenomena which may be relevant for other coating materials (isostructural HfO_2 at the first place) as well.

Acknowledgment

Grant Agency of the Czech Republic through Project No. 15-00859Y

References

[1] J. Houska, Comp. Mater. Sci. 111, 209 (2016)

[2] J. Houska, Surf. Coat. Technol. 304, 23 (2016)

4:30pm **B6-10 Experimental Validation of Metal-on-insulator Thin Film Growth Theory**, *B Lü, L Souqui, V Elofsson,* ***Kostas Sarakinos***, Linköping University, Sweden

The current understanding of thin film growth dynamics relies to a large extent on the widely accepted theory of morphology evolution in metal-on-metal homoepitaxial systems which exhibit a strong thermodynamic tendency towards 2D growth. This understanding is, however, challenged when considering the deposition of metal vapor on insulating surfaces; which is governed by a complex interplay between formation, growth, and coalescence of 3D atomic islands. This interplay is described quantitatively by the less established theory for metal-on-insulator (MOI) growth, which

originates from the literature of water vapor condensation and the formation of breath figures, most notably reviewed by Family and Meakin. In contrast to water clusters, 3D atomic islands formed upon vapor condensation, exhibit a size-dependent coalescence rate leading to a so-called elongation transition, which occurs upon sufficient deposition such that coalescing islands become kinetically frozen into elongated shapes. This transition is a key component in the MOI growth theory as it entails information about film growth dynamics encoded in scaling relations between the nominal film thickness (i.e., coverage θ) at elongation, θ_{Elong}, and the rates of vapor deposition, adatom diffusion and 3D island coalescence. While this scaling behavior has been confirmed quantitatively by computer simulations, the lack of a suitable method to measure θ_{Elong} has left experimental proof of the theory ambiguous. In this study, we combine experiments and kinetic Monte-Carlo simulations to develop and implement a method for measuring θ_{Elong} for Ag grown on amorphous SiO_2. Our data confirm the theoretically predicted θ_{Elong} power laws which are then used to calculate the adatom diffusion and coalescence rates for Ag/SiO_2 in good agreement with the literature. The data presented herein constitute a first step towards an experimental validation of the prevailing MOI growth theory and thereby lay the foundation for establishing a universal understanding of thin film growth dynamics. In practical terms, knowledge of the adatom diffusivity and coalescence rates, could facilitate more informed decisions regarding growth manipulation by, e.g., doping, surfactant action or tuning of the deposition rate and growth temperature. This may be of importance for a number of applications where MOI is relevant, such as architectural glazing, microelectronics, catalysis, and the metallization of graphene.

Fundamentals and Technology of Multifunctional Materials and Devices

Room Royal Palm 1-3 - Session C3-2

Thin Films for Energy-related Applications

Moderators: Jim Partridge, RMIT University, Martin Allen, University of Canterbury

1:30pm **C3-2-1 P-type Cu_2O Modified by NiO_x as a Photocathode for Efficient Hydrogen Production in Photoelectrochemical Water Splitting**, ***Ching Lin***, *J Ting,* National Cheng Kung University, Taiwan

First, Cu_2O/NiO_x nanoparticles were synthesized using a hydrothermal method with CuCl and NiO as precursors. Second, Cu_2O/NiO_x nanoparticles were made into a thin film by spin coating method. The NiO_x modified the surface of Cu_2O particles seem to be efficient way as a protective layer in order to enhance the efficiency of H_2 production. The core-shell structure of Cu_2O/ NiO_x nanoparticles were examined with a SEM. Due to an appropriate band energy structure, the photogenerated electrons from Cu_2O are easily transferred to the conduction band of NiO. Therefore, the possibility of the electrons and holes recombination is considerably reduced. XPS spectra revealed that the surface species of NiO_x is a mixture of NiO and $Ni(OH)_2$, which enhances charge separation in photoexcited Cu_2O. The role of NiO and $Ni(OH)_2$ is similar and both were suggested to act as a trap for photoelectrons, therefore retarding charge recombination. We demonstrate that a Cu_2O-based electrode for H_2 evolution can be prepared free of noble metals and we show its utilization in a PEC water splitting cell made solely from earth abundant elements.

1:50pm **C3-2-2 High Temperature Resistant Molybdenum Thin Film Metal Mesh Electrode as Replacement for ITO**, ***Niklas Bönninghoff***, National Taiwan University of Science and Technology, Taiwan

Indium tin oxide (ITO) films are still, despite their disadvantages, the main choice for thin film optoelectronic applications. Indium however is steadily increasing in price. One alternative to ITO is the use of a metal mesh. The most important parameters of a meshed thin film for optoelectronic devices to control are transparency, conductivity and compatibility with industrial processes (e.g. high temperature). Generally, the smaller the mesh dimensions (line width and pitch), the better the device, but the higher the costs.

Two different metal mesh patterns (line grid and hexagonal grid) have been fabricated on a glass substrate, using I-line photolithography to create a pattern on a photoresist, which was used to mask the substrate during DC magnetron sputter deposition. The material used is 5N pure Molybdenum. The deposition parameters (working pressure, DC power and substrate temperature) were chosen to gain a high conductivity film (measured by four-point probe), while still achieving acceptable adhesion (measured by scotch tape test), by usage of a bilayer. The grid pitch has been optimized for a specific device with an area of 15 mm^2.

The mesh's line thickness is 2 microns. The pitch is 300 microns for the line grid and 360 microns for the hexagonal grid, which results in a calculated transparency of 97% and 98% respectively. The transparency however decreases with increasing device size.

In conclusion, a metal mesh with good conductivity, high temperature resistance and an excellent transparency has been fabricated.

2:10pm **C3-2-3 Piezoelectric and Pyroelectric Materials and Systems for Energy Harvesting**, ***Chris Bowen***, *M Xie, Y Zhang, D Zabek, J Roscow,* University of Bath, UK **INVITED**

The continuing need for reduced power requirements for small electronic components, such as wireless sensor networks, has prompted renewed interest in recent years for energy harvesting technologies capable of capturing energy from ambient vibrations and heat. This presentation provides an overview of piezoelectric harvesting system along with the closely related sub-classes of pyroelectrics and ferroelectrics [1,2]. These properties are, in many cases, present in the same material, providing the intriguing prospect of a material that can harvest energy from multiple sources including vibration and thermal fluctuations [3-5].

Examples of modelling and experimental investigations of porous materials for harvesting are discussed including novel freeze cast and sandwich layer structures are described. Pyroelectric layers for thermal harvesting are also described with the use of patterned electrodes to enhance thermal fluctuations and the potential to use pyroelectric charge for water splitting discussed.

[1] C. R. Bowen, H. A. Kim, P. M. Weaver and S. Dunn, Piezoelectric and ferroelectric materials and structures for energy harvesting applications, Energy and Environmental Science, 7, 25-44 (2014)

[2] CR Bowen, J Taylor, E LeBoulbar, D Zabek, A Chauhan, R Vaish, Pyroelectric materials and devices for energy harvesting applications, Energy & Environmental Science 7 (12), 3836-3856 (2014)

[3] J Zhang, C Wang, C Bowen, Piezoelectric effects and electromechanical theories at the nanoscale, Nanoscale 6 (22), 13314-13327 (2014)

[4] C. R. Bowen and M. H. Arafa, Energy Harvesting Technologies for Tire Pressure Monitoring Systems, Advanced Energy Materials 5, 1401787 (2015)

[5] J. Roscow, Y.Zhang, C.R.Bowen et al., Porous ferroelectrics for energy harvesting applications, *Euro. Phys. J. Special Topics.,* 224, 2949-2966 (2015)

2:50pm **C3-2-5 Ion-assisted Growth of Compound Thin Films for Energy-related Applications**, ***Tomas Kubart***, *A Aijaz,* Uppsala University, Sweden

Energy-related applications generally require high quality thin film materials. In many cases, low growth temperatures are desired while the performance is still critical. In this contribution, low temperature ion-assisted growth of compound thin films is discussed using piezoelectric AlN and thermochromic VO_2 as examples.

Using ions instead of neutral atoms provides means for additional energy input which can be readily controlled by externally applied electric fields. We use High Power Impulse Magnetron Sputtering (HiPIMS), a sputtering technique in which a very high ionization degree of the material is achieved due to the pulsed mode operation of the discharge. Low frequency operation with a duty cycle of about 1% is typically used, which leads to two orders of magnitude higher electron densities and corresponding increase in the ionization of the deposition flux.

For piezoelectric AlN films, we have demonstrated a significant enhancement of the AlN texture by using the HiPIMS process [1]. Already at room temperature, films with good texture and low FWHM values of the rocking curve were grown directly on silicon without any seed layer. This is attributed to the high flux of low energy Al and N ions formed in HiPIMS as well as high dissociation of N_2 in the dense HiPIMS plasma. Such films are suitable for electroacoustic devices, microelectromechanical systems, or energy harvesters.

The deposition temperature is also an important factor for thermochromic materials. Vanadium dioxide thin films provide means for controlling solar energy throughput and can be used for energy-saving applications such as smart windows. At present, however, the deployment of VO_2 in thermochromic devices is limited by the high growth temperature, typically above 450°C. Using HiPIMS, we have reduced the growth temperature to

300°C [2]. We have varied the ion energy and found and optimum at 100 eV. Strategies to further reduce the deposition temperature are discussed.

References

[1] M.A. Moreira, T. Torndahl, I. Katardjiev, T. Kubart, Journal of Vacuum Science & Technology A 33 (2015) 021518.

[2] A. Aijaz, Y.-X. Ji, J. Montero, G.A. Niklasson, C.G. Granqvist, T. Kubart, Solar Energy Materials and Solar Cells 149 (2016) 137-144.

3:10pm **C3-2-6 Growth and Characterization of Thin Film $CaMnO_3$ and $CaMn_xNb_{1-x}O_3$ Thermoelectrics**, ***Erik Ekström***, *B Paul, F Eriksson, P Eklund,* Linköping University, IFM, Sweden

Thermoelectrics show great promise as waste heat harvesters in power plants, cars and other applications. This places demands on their physical and chemical properties. They should be non-toxic, have a high conversion efficiency and thermally stable.

In this work, thermoelectric thin film $CaMnO_3$ and $CaMn_xNb_{1-x}O$ perovskite oxides on Al_2O_3 (0001), (1-100) and (1-102) have been investigated. The films were deposited by magnetron sputtering followed by annealing at 800 °C in oxygen [1]. Nb was introduced by co-sputtering. The structural properties of the films were assessed using X-ray diffraction (XRD) by performing q-2q scans and by plan-view scanning electron microscopy studies.

Isothermal annealing was performed in high vacuum using an in situ XRD furnace to study the phase evolution up to 1100 °C. The annealing was done in 100 °C steps, doing a measurement for each step. The structure of the film after the 3 h post deposition heat treatment was orthorhombic $CaMnO_3$. This structure remained stable up to 700 °C, while above 800 °C it decomposed into cubic $Ca_xMn_{1-x}O$. The cubic structure is stable at 800 °C, but at 900 °C the phase changes to orthorhombic MnO_2 and Ca rich cubic $Ca_xMn_{1-x}O$. Additionally, the structure decomposed into a multitude of phases at 1100 °C. X-ray diffraction was also recorded while cooling down, showing that the structure obtained at 1100 °C remained to room temperature.

Scanning electron microscopy revealed that by changing the Ca composition in the rangepower on the Ca magnetron changes the surface structure of the films. A low Ca content resulted in Mn-rich nano-inclusions which are also visible in the XRD. Increasing the Ca content reduces the amount of inclusions and at the ideal composition they disappear. When increasing the Ca content the grain size decreases laterally as seen in SEM and decreases vertically as indicated by an increasing peak width.

Four point probe measurements at room temperature show a decrease in resistivity for the alloyed samples compared to the un-alloyed ones and it is also observed that substrate orientation influences the resistivity. The lowest resistivity for un-alloyed films is 1.70 Ωcm, 1.80 Ωcm and 0.69 Ωcm for (0001), (1-100) and (1-102) orientation, respectively. Having an Nb content of x = 3 results in the lowest resistivity of 0.46 Ωcm, 0.06 Ωcm and 0.10 Ωcm for (0001), (1-100) and (1-102) orientation, respectively. The reduction of resistivity is due to an increase in carrier concentration which has been observed in other studies [2].

1 Paul et al Advanced Electronic Materials **1,** 1400022 (2015).

2Xu et al Solid State Ionics **171,** 147 (2004).

3:30pm **C3-2-7 3D-Painted Solid Oxide Fuel Cells: A New Approach to Functional Multi-Ceramic Construct Fabrication**, ***Nicholas Geisendorfer***, *A Jakus, H Wang, Z Gao, S Barnett, R Shah,* Northwestern University, USA

The fabrication and assembly of solid oxide fuel cell (SOFC) components into an integrated structure, including both support and functional layers, remains one of the primary challenges preventing the widespread adoption of SOFCs as an energy conversion technology. We present an efficient and highly scalable multi-material process for fabricating SOFCs using a combination of 3D-Painting (a room-temperature, liquid extrusion-based 3D-printing process) and dip-coating of particle-laden, liquid-based 3D-inks. 3D-printing is used to sequentially deposit anode and cathode functional layer materials, nickel oxide-yttria stabilized zirconia (NiO-YSZ) and lanthanum strontium manganite (LSM), respectively, without the need to alter printing parameters, allowing unprecedented control over gas channel geometries. Depositing layers thinner than 100 µm using 3D-printing is impractical, so these inks, designed for 3D-printing, are repurposed for the production of mechanically robust, controllably thick, multi-material films via dip-coating to be used as YSZ electrolytes and strontium lanthanum titanate (SLT)/LSM interconnect bilayers. The inks used for both 3D-printing and dip-coating are synthesized through simple, room-temperature mixing of a combination of organic solvents, a biomedical elastomer binder (~10-40 vol.%) and powders of interest (~60-90 vol.%). Vol % powder controls shrinkage and porosity during firing; tailoring the powder vol % for each ink is vital to preventing warping and cracking during cell co-firing and to ensure optimal performance of each component. Fully assembled fuel cell structures are co-fired in air at 1250°C for 4 hours. The microstructural and electrochemical characteristics of fired cells are analyzed and compared with cells produced entirely using tape-casting techniques. We demonstrate that this technique is highly scalable and useful for fabricating monolithic, planar SOFCs of various sizes without the need for cumbersome support materials.

3:50pm **C3-2-8 Nanoengineering Periodically Structured SiCu Thin Film Anodes for Rechargeable LIBs**, ***Billur Deniz Polat Karahan***, *B Bilici,* Istanbul Technical University, Turkey*; O Eryilmaz,* Argonne National Laboratory, USA*; K Amine,* Argonne National Laboratory, USA, United States of America*; O Keles,* Istanbul Technical University, Turkey

In the quest for a radically better lithium-ion battery, a promising direction is suggested so-called “silicon (Si) composite” anodes, in which the negative electrode contains a higher proportion of Si with another material. In the current technology, while the Si composite electrodes have the potential to have far higher energy density, long cycle life and high reversibility are still not satisfactorily provided due to intrinsic properties of Si such as low electrical conductivity and high volumetric changes upon cycling.

Therefore, in this work, to create electron conduction pathway in the electrode and to increase the ductility of the film 10%at. Cu atoms are co-deposited with Si. Then to induce homogeneously distributed interspaces in the electrode structured composite thin film has been engineered by glancing angle electron beam deposition (GLAD) method. This process enables to deposit coatings of any materials without a need of binders or any conductive additives. Plus, various structures from nanocolumns to helices might be deposited by optimizing the evaporation rate of source materials, the incident angle and the azimuthal rotation rate of the substrate.

An innovative approach involving adaptation of ion assistance to GLAD has been also proposed in this study. The well adherent composite nanostructures are expected to provide large reaction area with Li, facile stress relaxation (to prevent electrode pulverization or delamination), effective electrical contacts with the substrate and short Li diffusion distances.

To evaluate the electrochemical performances of the structured composite films, two samples have been deposited on Cu collector with different evaporation rates: quartz crystal microbalances of Cu and Si show 0.4-4 Å/s and 0.9-10 Å/s for Samples 1 and 2, respectively. The morphological analyses show that depending on the evaporation rates of sources the structure of the film changes which affects their performances in cycling.

4:10pm **C3-2-9 A Mesoporous CuAlO2 Hole Transport Layer for Perovskite Solar Cell**, ***Wei-Jie Sun***, *J Ting, P Chen,* National Cheng Kung University, Taiwan

Mesoporous CuAlO2 (CAO) has been investigated for use as a hole transport layer in perovskite based solar cells (PSC) having a p-i-n heterojunctions configuration. CuAlO2 nanopowders (NPs) was first synthesized using a sol-gel method with Cu(NO3)2 and Al(NO3)3 as the precursors. The obtained CuAlO2 NPs were spinning-coated onto indium-tin oxide substrate to form a hole transport layer. The obtained CuAlO2 NPs and layers were examined for the material characteristics, in particular, photoelectrical properties. Effects of the synthesis conditions of these characteristics are addressed and discussed. PSCs having a CuAlO2 transport layer were fabricated. The cell performance was evaluated to demonstrate the advantages of using CuAlO2 as a hole transport layer.

4:30pm **C3-2-10 Fabrication of Hybrid Perovskite Solar Cells based on Low Temperature Solution Process**, ***Tzung-Wei Tsai***, *Y Yu, C Teng,* Ming Chi University of Technology, Taiwan

Organic–inorganic perovskite solar cells have recently emerged at the forefront of photovoltaics research due to its dual electron and hole mobility. Organo-metal halide perovskites were composed of an ABX3 (e.g. $CH_3NH_3PbI_3$) structure in which A represents a cation, B a divalent metal cation (e.g. Pb^{2-}) and X a halide (e.g. F, Cl, Br, I). We used two different materials such titanium dioxide (TiO_2) as the perovskite electron transport layer of the solar cell in this study. The titanium dioxide colloid was prepared by using a ball-milling process with the 50 micrometer zirconia balls in a SiC pot for 8~10h. Then, the titanium dioxide powders were prepared after annealing. The effects of annealing temperature on the properties of perovskite thin film were also investigated. The

organic–inorganic perovskite solar cells with structure ITO/TiO2/Perovskite/Spiro-OMeTAD/Ag were fabricated. The best performance of the prepared solar cells had a photo conversion efficiency of 6.4%, J_{sc} of 12.11 mA/cm^2, V_{oc} of 0.96V, and fill factor of 0.56, respectively.

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces

Room San Diego - Session E1-2

Friction, Wear, Lubrication Effects, and Modeling

Moderators: Albano Cavaleiro, University of Coimbra, Carsten Gachot, Vienna University of Technology, Giovanni Ramirez, Argonne National Laboratory, USA

1:30pm **E1-2-1 Surface Engineering for Increasing Performance of Injection Molding Tools**, ***Lars Pleth Nielsen,*** Danish Technological Institute, Denmark*; S Hengsberger,* Institute of Applied Plastics Research at Engineering College Fribourg, Switzerland*; K Pagh Almtoft, B Hold Christensen,* Danish Technological Institute, Denmark **INVITED**

Injection moulding of high-precision plastic components with high output volumes, using low cycle times without compromising on a high product quality is extremely important in order to increase both the productivity and keeping a competitive edge. At the same time, many moulds are becoming more and more complicated and costly. Hence, it is necessary to increase the lifetime, the wear resistance, minimize the diesel effect, improve the slip properties (ejection force) and the performance of the applied moulds.

The ejection force was quantified in situ during the injection moulding process by incorporating a force sensor. The developed method was found to be so reliable that it was possible to measure a difference between the as machined moulds implying that it was necessary to use each mould as its own reference.

The impact on the ejection force when adding different surface pretreatments to the moulds (as machined, grinded, blasted or laser textured) have been analyzed in combination with different PVD coatings (CrN, HiPIMS CrN, low-temperature pulsed TiAlN) combined with post treatments involving different doses of high-current nitrogen implantation.

The ejection forces were measured for four industrial relevant plastic types (PP, POM, ABS and TPU) before and after adding the wear-resistant coating as well as after ion implantation. The results revealed that the ejection force could be lowered by close to 70% for some of the plastic types by adding a combination of wear-resistant coating and ion implantation. The best performing surfaces were found to be HiPIMS CrN followed by nitrogen ion implantation.

Corrosion and the risk of diesel effect was minimized by Cr ion implantation. The Cr ion implantation was observed to lead to a new phase in the top most 50 nm. The improved corrosion resistance was quantified by cyclic voltammetry.

Thin film characterization of the applied coatings have be addressed based on nanoindentation, SEM and RBS.

The findings will be compared with empirical results from industrial-scale injection moulding.

2:10pm **E1-2-3 Increasing the Lifespan of High Pressure Die Cast Molds Subjected to Severe Wear***, F Silva,* ***Vitor Nunes,*** *M Andrade,* ISEP - School of Engineering, Polytechnic of Porto, Portugal*; R Alexandre,* TeandM - Technology, Engineering and Materials, S.A., Portugal*; A Baptista,* INEGI - – Instituto de Ciência e Inovação em Eng. Mecânica e Eng. Industrial, Portugal

Despite the increasingly incorporation of composite materials on vehicle components, high pressure die casting still remains one of the most useful manufacturing techniques to obtain automotive parts with complex shape in a cost effective way. It is well known that automotive industry requires high production cadency as well as high products quality. Thus, systematic approaches are permanently being done leading to optimize all the production and management aspects.

The aluminum alloys commonly used in automotive parts such as fuel pumps bodies, throttle bodies, EGR valves, support brackets and so on usually contain Silicon which presents high abrasively. The aluminum flow at high temperature and high speed into the mold induces severe wear, sometimes due to a combination of abrasion and erosion effects.

In this study, two molds with typical severe wear problems were selected and the wear mechanisms involved were deeply studied. After that, a careful selection of the best coating for this purpose was done and some of the most critical parts of the mold were coated in order to test possible effective advantages of the coating application, analyzing the wear resistance behavior and wear mechanisms involved. In parallel, tribological tests were also carried out in order to study if a correlation between laboratorial and industrial tests can be drawn. Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy were intensively used to characterize the coatings and the wear mechanisms observed. Laboratorial tribological tests have involved ball scattering and block-on-ring tests, trying to impose low and medium loads on the contact, respectively. Promising results were obtained allowing to conclude that certain coatings present a better behavior than other ones in this field of application.

Keywords: Wear, Abrasion, Erosion, High-pressure die casting, Mold wear, Wear mechanisms, Mold lifespan

2:30pm **E1-2-4 Effect of Cr Additions on the Structure,Oxidation, Tribological and Machining Performance of Multilayered TiAlN/CrAlN Films Deposited by Sputtering***, F Fernandes,* Instituto Pedro Nunes, Portugal*; M Danek,* Czech Technical University, Czech Republic*; T Polcar,* University of Southampton, UK*;* ***Albano Cavaleiro,*** University of Coimbra, Portugal

Machining of hard to cut materials, such as hardened steels or strong materials for high temperature aerospace applications, is nowadays a challenge of modern engineering. In past recent years, different types of coatings have been developed and applied on the protection of machining tools in order to improve their performance and lifetime. TiAlN has been the most widespread coating because of its sufficient thermal stability, up to 900°C, high hardness, oxidation resistance and adhesion resistance. The addition of Cr to this system has been extensively studied; however, at our knowledge the oxidation, high temperature tribology and in-service machining performance of multilayered TiAlN/CrAlN films is still rare. This work focused on the effect of Cr alloying on the structure, oxidation resistance, kinetics of ions diffusion at high temperature and in-service tribological behaviour of TiAlN/CrAlN films. The results were compared with a TiAlN film deposited as reference. The coatings were deposited in an industrial chamber by unbalanced close field magnetron sputtering, onto Si, FeCrAl alloy and WC substrates as well as onto tungsten carbide drills with 5.5 mm diameter. The crystal structure of the films was analyzed by X-ray diffraction. Oxidation of the films was assessed by thermogravimetric analysis (TGA). Tribological experiments were performed in a high temperature pin-on-disc tribometer at RT, 600 and 700 ºC, using Al2O3 balls as counterpart. The tribological experiments were then complemented with in-real machining tests by studying the lifetime of coated drills. The oxidation performance of coatings is improved with Cr additions due to the growth of a more protective Al-Cr-O rich layer in the interface film/oxide. Tribological behavior of Cr rich coatings at room temperature is similar to the one of reference TiAlN film, but at high temperature it is two to three times better. Coatings with high Cr content (Ti0.28Al0.31Cr0.51N) displayed the best oxidation, tribological and machining performance.

2:50pm **E1-2-5 Investigation on Tribological Behaviour of Boron Doped Diamond Coated Cemented Tungsten Carbide for Cutting Tool Applications***, **Ramasubramanian Kannan,** A Narayanaperumal, R Rao,* Indian Institute of Technology Madras, India

In this paper, tribological performance of boron doped microcrystalline diamond (BDD) films and boron doped graded layer diamond thin films (BDD/transition layer/NCD) was studied in detail. The widely used cemented tungsten carbide (WC-Co) was selected as a substrate material for diamond coating. Diamond films was deposited on WC-Co by Hot-filament CVD reactor (HFCVD) setup. Tribology experiment was conducted by using reciprocating tribometer with a normal load of 30 N and a sliding velocity of 10mm/second for a constant wear length of 3 mm. Silicon nitride (Si_3N_4) ball was used as a counter part to study the friction and wear behaviour of diamond films. The surface morphology, topography & roughness of the diamond films were analysed by scanning electron microscope and atomic force microscope respectively. The hardness of the thin diamond films was measured by using berkovich nano indentation test method. The test results found that BDD and boron doped graded layer shows a stable lowest friction coefficient values of 0.004 and 0.003 compared with conventional microcrystalline diamond films (0.007). On the other hand, the wear diameter of the silicon nitride ball for BDD and boron

doped graded layer found to be 620 µm and 785 µm, relatively lower in comparison with microcrystalline diamond films (897 µm). The wear track width was measured by scanning electron microscope and shows that BDD and boron doped graded layer indicates lower wear track width 564 µm and 596 µm compared with microcrystalline diamond films (712 µm). Raman mapping was conducted on the wear track of the diamond films to know about the phase pure diamond (sp^3) and partly graphite phases (sp^2) which in turn contributes for the distinct residual stresses in thin films. The obtained lower friction coefficient for boron doped diamond films on WC-Co cutting tool can be suitable for machining of aluminium based metal matrix composites effectively.

3:10pm **E1-2-6 Influence of Self-lubricating Non-metal Phase on the Erosion and Wear Behavior of Ni-based Abradable Coatings***, **Pantcho Stoyanov**, A Wusatowska-Sarnek,* Pratt & Whitney, USA

In this study, the influence of self-lubricating hexagonal boron nitride (hBN) on the erosion and abradability of Ni-based abradable coatings was investigated. Two coatings of same metallic content, one with and one without hBN, were deposited by means of plasma spray to different densities and consequently hardness values. Subsequently, the coatings were subjected to erosion and abradability testing at room temperature in order to evaluate their performance. In addition, to capture the characteristics of the wear process, a detailed chemical and structural analysis was performed within the near-surface region of the worn specimens (i.e. abradable and blade) by means of Scanning Electron Microscopy (SEM), Transmission Electron Microscopy, and micro-Raman spectrometry.

The erosion resistance of the coatings increased with increasing the density as well as with the addition of hBN, which correlated well with the hardness results. The abradability of the coatings without hBN showed a reverse correlation with erosion capability where the less erosion resistant coatings were more abradable as manifested by the lower blade wear. Similarly, the high density hBN content coatings caused higher blade wear compared to the lower density coatings with hBN. However, the coatings with hBN showed overall better abradability compared to the ones without, which correlated well with slightly lower interface temperatures (i.e. measured by means of thermocouples and IR thermometer) and was attributed to the difference in the particle pull-out mechanism.

3:30pm **E1-2-7 Tuning Run-in Friction Behavior of Carbon Film with Graphene Nanocrystallite Structure***, **Cheng Chen**, S Qiu, D Diao,* Shenzhen University, China

In general, amorphous carbon films always has a high friction stage, so-called “run-in” stage, before reaching low friction steady stage. The causes of the run-in stage have been attributed to removal of surface contaminants, oxide film formation, material transfer, and subsurface microstructure reorientation. Regarding to the low friction application, the run-in stage is undesired and necessary to be shortened or even avoided. However, few effective methods have been proposed for eliminating the run-in stage.

In this study, we demonstrated that the run-in stage of carbon film could be tuned with graphene nanocrystallite structure. Firstly, graphene nanocrystallite embedded carbon films were prepared with low-energy electron irradiation using an electron cyclotron resonance (ECR) plasma sputtering system. The structure of graphene nanocrystallite was varied with electron irradiation energy. Friction behaviors of the films were investigated with a Pin-on-Disk tribometer. Compared with amorphous carbon film, the films with graphene nanocrystallite showed shorter run-in stages. And the run-in stage nearly disappeared for the film with irradiation energy of 40 eV. The steady-stage friction coefficients of amorphous carbon film and graphene nanocrystallite embedded carbon films were all about 0.04. The wear rates of the carbon films in run-in stage were measured with a profilometer. The nanostructures of transfer films were investigated by a Raman spectroscopy. The short run-in stage mechanism was interpreted that graphene nanocrystallite was easier to be worn out than amorphous carbon, and it was beneficial for the formation of nanocrystallized transfer film. Secondly, two layer hybrid films were fabricated by depositing 1~10 nm graphene nanocrystallite layer on a thick amorphous carbon layer. The hybrid films showed short run-in stages and low friction behaviors. This study enables a convenient method to control the run-in stage of carbon film, which is significant for tribology application.

3:50pm **E1-2-8 Study of the Wear Mechanisms and Solutions Regarding Inserts used on Cork Grinders***, F Silva, **Thiago Oliveira**,* ISEP - School of Engineering, Polytechnic of Porto, Portugal*; R Alexandre,* TeandM - Technology, Engineering and Materials, S.A., Portugal*; A Baptista,* INEGI - – Instituto de Ciência e Inovação em Eng. Mecânica e Eng. Industrial, Portugal*; A Alves,* Amorim Cork Composites, S.A., Portugal

Cork was one of the main pillars in the Portuguese economy some decades ago, being nowadays one of the most important natural materials currently exported from Portugal to the entire world. Initially, wine bottle stoppers were almost exclusively the only product extracted from the cork oak hull. However, the high quality required by the bottle stoppers makes unviable the use of some cork hooves and the waste generated by the bottle stoppers extraction also is considerable. Moreover, the traditional Portuguese creativity allows bringing to the market a huge number of products based on cork aggregates as composites, due to the addition of bonding and other materials in order to improve the overall characteristics of those products. Nowadays, cork composites are used in products as distinct as sportive floors, wall memos, lady bags or shoes.

However, these composites need to be processed and one of the first steps to produce the cork granules is its grinding process. Despite the cork presenting a relatively low mechanical strength and hardness, the grade of abrasion generated by cork on grinder inserts during the grinding process is considerable. Companies devoted to cork composites have as main initial operation the cork wastes sorting, separating eventual metallic pieces coming to the process together with the cork. Posteriorly those wastes are driven to the grinders leading to the granules generation and further particle size selection. The inserts used in these grinders as main tools to proceed to the grinding process are severely affected by wear and the increasing competitiveness imposed by the market is forcing to face this concern with care.

This study intends to realize what kind of wear mechanisms are strongly influencing the premature end-of-life of the grinding inserts, which occurs due to reduced cutting efficiency and generation of out of specification cork granules, allowing to determine the best ways to extend their life cycle, improving the cost/benefit ratio and allowing to get a better equipment performance by the increase of the OEE (Overall Equipment Efficiency) of the machines related to this manufacturing operation. Results obtained led to understand the phenomena induced in the inserts and some promising alternative solutions using special materials and coatings were drawn and tested, allowing improve the inserts wear behavior thus making this operation more efficient and profitable.

Keywords: Cork, Cork grinders, Grinders inserts, Inserts wear, Wear mechanisms, Abrasion, Coatings

Surface Engineering - Applied Research and Industrial Applications
Room Sunrise - Session G3

Innovative Surface Engineering for Advanced Cutting and Forming Tool Applications

Moderators: Heidrun Klostermann, Fraunhofer FEP, Holger Gerdes, Fraunhofer Institute for Surface Engineering and Thin Films IST, Ali Khatibi, Oerlikon Balzers, Oerlikon Surface Solutions AG

1:30pm **G3-1 Degradation Mechanisms of Protective Coatings in Precision Glass Molding***, **Marcel Friedrichs**, O Dambon, F Klocke,* Fraunhofer Institute for Production Technology, Germany

Thermo-chemical and thermo-mechanical loads act on molding tools during several hundred cycles of Precision Glass Molding (PGM). Wear protective coatings are used on the molding tools in order to protect the optical surface of the molds against degradation. Therefore, the lifetime of molding tools and thus the process efficiency increase. Precious metal coatings such as platinum-iridium (PtIr) are the most versatile material class used for molding various glass types. Furthermore, diamond-like carbon (DLC) and ceramic coatings are employed in PGM as well.

The presented work investigates the degradation mechanisms of different protective coatings by PGM tests at a service lifetime test bench. Subsequent analyses of coated specimens were performed by white light interferometry, scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS), which proved different degradation mechanisms as diffusion, oxidation, corrosion, glass adhesion and flaking off. Summarizing these observations, a degradation model of the leading

degradation mechanisms for different coating systems has been created, which is currently available for further coating development.

1:50pm **G3-2 Nanolayered Coatings for Advanced Fine Blanking Applications**, ***Marcus Morstein***, *T Schär,* Platit Ag, Switzerland; *B Torp,* PLATIT, Inc., USA, Switzerland; *T Klünsner,* Materials Center Leoben Forschung GmbH (MCL), Austria

A combination of nano- and multilayer structures has proven to provide an optimum combination of wear- and mechanical impact resistance for physical vapor deposition (PVD) coatings used in metal cutting. One field of application where such ceramic coatings are particularly challenged is fine blanking, a versatile metal sheet cutting process able to produce high-quality parts for automotive and general engineering applications, in large quantities. In this process, high compressive and tensile shear forces interact with the coated tool surface, which is additionally challenged by mechanical shock, abrasion and work piece material adhesion.

This paper addresses how using structural design on the nano- and microscale, coatings based on AlCrN and AlCrTiN can be tailored to match the required compromise between wear resistance and toughness. The investigated coatings were produced on two different industrial coating units using lateral (LARC) and central (CERC) cylindrical rotating arc cathodes technology, or a combination of LARC and planar arc cathodes. The nanolayer structure was varied through selection of different target material combinations and different arc currents, and properties relevant to coating adhesion and toughness were measured. In particular, depth resolved internal stress profiles were collected using a modified side inclination XRD technique.

Since wire electrical discharge machining (EDM) is the typical production process for fine blanking punches and dies, pre-treatment methods for substrates made both from powder-metallurgical tool steel and from cemented carbide (WC/Co) were optimized in order to remove surface damage brought in by the manufacturing process and to ensure optimum coating adhesion. Furthermore, a strong coating post-treatment was applied and the beneficial effect of surface smoothness on suppressing workpiece material sticking was illustrated both on the lab scale and in practical fine blanking tests.

Long-term tests in production environment showed that by using the new nanolayered, toughness optimized coatings, controlled wear and thus higher productivity and process stability in fine blanking can be achieved.

2:10pm **G3-3 Growth of Low-defect-density $Ti_{1-x}Al_xN$ Thin Films by Cathodic Arc Evaporation under Industrial Conditions**, ***Marta Saraiva***, *L Johnson,* Sandvik Coromant R&D, Sweden **INVITED**

The metal cutting industry is, nowadays, an extremely competitive market with numerous significant players. In order to stand out and be ahead of the competition, one needs to be proactive and offer products and solutions to customers before their need for them arises. Such achievement requires to carefully listening the market and continuous strive for improvement. Thus, it is crucial to maintain an R&D activity at the upmost level.

The majority of cemented carbide tools used today are coated, with roughly 50% using a Physical Vapour Deposition (PVD) technique. The ability to deliver world class thin films to our products emanates from possessing adequate equipment and knowledge to tweak the process in order to obtain the desired thin film properties, which result in the best product performance for a specific application. Therefore, the control of microstructure is of high importance to tailor the functional performance characteristics of thin films, and in particular, for hard wear-resistant coatings such as TiAlN. Normally, the grain size of TiAlN is strongly correlated to the Al content, with Al as a grain refiner. Therefore it is of high interest to control the microstructure independently of the Al content. One such example is the recent work by Grezynski *et al.* [1], who demonstrated the growth of low-defect TiAlN by a hybrid DC/HiPIMS magnetron sputtering technique using synchronized bias pulsing under laboratory conditions. Here, we report the discovery of growth conditions for low-defect $Ti_{1-x}Al_xN$, deposited by cathodic arc evaporation using a full-scale industrial deposition system under production-ready conditions. By tuning the process parameters, it was possible to change the ordinary cathodic arc hard coating growth mode of defect-rich grains with featureless surfaces, to a mode of feature rich surfaces and low-defect-density.

[1] G. Greczynski *et al.,* Surf. Coat. Technol. 257 (2014) 15.

2:50pm **G3-5 A Contribution to Explain the Mechanisms of Adhesive Wear in the Plastics Processing by the Example of Polycarbonate**, *K Bobzin, T Brögelmann,* Surface Engineering Institute - RWTH Aachen University, Germany; *G Grundmeier, T de los Arcos, M Wiesing,* University Paderborn, Germany; ***NathanChristopher Kruppe***, Surface Engineering Institute - RWTH Aachen University, Germany

In plastics industry, adhesive wear due to flowing hot melt is one of the main damage mechanisms of extrusion tools. Such damages strongly affect the economic efficiency and the product quality. Due to their beneficial properties, Cr-based nitride hard coatings deposited by physical vapor deposition (PVD) are applied as protective coatings. These coatings can prevent the formation of ferric oxides Fe_xO_y, which influence the adhesion and thus the degradation of plastic melt on the tool surface. In the present work, four different CrAl-based nitride and oxy-nitride monolayer coatings were synthesized on tool steel substrate AISI 420 (X42Cr13, 1.2083) by means of a hybrid direct current and high power pulsed magnetron sputtering (dcMS/HPPMS) process. At this, the chemical composition of the nitride and oxy-nitride coatings was varied in terms of the metal ratio Cr/Al. All coatings and one uncoated steel substrate were analyzed before and after long-term annealing in order to investigate it's influence on the chemical composition of the native passive film at the surface by using X-ray photoelectron spectroscopy (XPS). Furthermore, the influence on the wetting behavior of polycarbonate melt by means of high temperature contact angle measurements as well as on the degradation behavior of polycarbonate by fluorescence measurements using Raman spectroscopy were studied. It was shown that the annealing process leads to a significant higher increase of polycarbonate wetting on the uncoated steel compared to the coated samples. Additionally, the coatings with an increased Al content exihibit a significant lower wetting compared to the other coatings and the uncoated steel. The influence of the metal ratio Cr/Al within the nitride and oxy-nitride coatings on the degradation of polycarbonate was quantified and correlated to the high temperature contact angle measurements.

3:10pm **G3-6 Enhanced Replication Ratio of Injection Molded Plastics Parts by using an Innovative Combination of Laser-Structuring and PVD Coating**, *K Bobzin,* Surface Engineering Institute - RWTH Aachen University, Germany; *C Hopmann,* Institute of Plastics Processing, RWTH Aachen University, Germany; *A Gillner,* Chair for Laser Technology, Aachen, Germany; *T Brögelmann, N Kruppe,* ***Mona Naderi***, Surface Engineering Institute - RWTH Aachen University, Germany; *M Orth,* Institute of Plastics Processing, RWTH Aachen University, Germany; *M Steger,* Chair for Laser Technology, Aachen, Germany

One of the fast-growing segments of manufacturing is plastics processing. The properties of plastics products can be optimized by a suitable design of the component surface. One promising method is the usage of molding tools structured in the micrometer range for plastics processing by extrusion and injection molding. Such microstructured, optically functional plastics parts are commonly used in light-field photography, displays and security technology. However, the production of optical functional surfaces demands a high quality of replication from the tool insert. Due to the high density of structures and therefore increased surface area the filling rate during the injection molding is very challenging. The adhesion of the plastics melt on the mold surface during the processing can influence the product quality. One possible approach is the combination of physical vapor deposition (PVD) technology with laser based variothermal injection molding to improve the replication of microstructures. PVD hard coatings, such as ternary chromium based nitride (Cr,Al)N are used as protective coating due to the mechanical, chemical and tribological properties to reduce wear and wetting between mold and plastics. Within the scope of this paper, a laser microstructuring was carried out on an injection mold out of AISI 420. A nitride hard coating was deposited on microstructured mold by means of middle frequency pulsed magnetron sputtering (mfMS). Variothermal injection molding with an external laser beam was used to mold microstructured, coated and uncoated molds. The coating morphology and its chemical composition as well as the mechanical and tribological properties were characterized. Commercial plastics polycarbonate (PC) and two types of polymethyl methacrylate (PMMA) were considered for tribological investigations. Adhesion behavior of molten PC and PMMA on (Cr,Al)N hard coatings was analyzed by means of high temperature contact angle measurements. Wear tests were performed by using pin-on-disc-tribometer measurements at room temperature T = 23 °C and at half of the processing temperature T = 110 °C and T = 150 °C against solid PC and PMMA. The results exhibit a high potential of the investigated nitride coating to be used as protective

coating against abrasive and adhesive wear during processing of polycarbonate and polymethyl methacrylate. A prosperous replication of microstructured and coated mold could be proofed at different molding temperatures. The replication ratio of optical microstructures is increased significantly up to 20-30 % by using mold coating in comparison to uncoated mold.

3:30pm **G3-7 Sophisticated Wear Resistant Coatings used in Cold Sheet Metal Forming of AHSS Sheet Metals**, ***Ali Khatibi***, *M Arndt,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein

Engineering parts made out of high-strength-steel (HSS) sheets are widely used in the structural reinforcement of the car bodies especially where a high impact and crash resistance is required (e.g., passenger compartment, parts of side doors and bumpers). The increasing need for HSS parts in a typical car body (~40 % in 2007 to 75 % in 2015) on the one hand and development of advanced steel grades with very high strengths (>1000 MPa in UHSS) on the other hand demand the utilization of coatings which in combination with state-of-the-art surface treatments (eg nitriding) provide considerable resistance against a variety of failure mechanisms like adhesive and abrasive wear, galling, chipping, and spallation under severe forming loads.

Nitride based coatings like TiN, TiAlN, TiCrN, and AlCrN, which are also used in cutting tool applications have significantly increased the performance of these forming tool applications when compared to non-coated ones. But as the specific requirements in terms of resistance to abrasive and adhesive wear, fatigue, and in some cases corrosion are completely different for metal forming , there is an increasing demand for dedicated and in many cases complex coatings for an additional gain in efficiency.

The present work addresses the development of the wear and fatigue resistant coatings made by physical vapor deposition (PVD) technique to be used for high-scale industrial forming operations of advanced high strength steel (AHSS) and high strength low alloy (HSLA) sheets. Examples of successful implementation of the coatings in some highly challenging industrial forming applications are presented.

3:50pm **G3-8 Performance Evaluation of HSS Cutting Tool Coated with Hafnium and Vanadium Nitride Multilayers, by Temperature Measurement and Surface Inspection, on Machining AISI 1020 Steel**, ***John H. Navarro-Devia***, *W Aperador,* Universidad Militar Nueva Granada, Colombia; *C Amaya,* CDT- ASTIN SENA, Colombia; *J Caicedo,* Universidad del Valle, Colombia

The application of hard coatings onto cutting tools improves lifetime, performance and also quality of workpiece, usually by increasing the wear resistant. Hafnium nitride and Vanadium nitride multilayer coating [HfN/VN]n has mechanical, tribological and physic-chemical properties that have been identified by other authors and are desirable for cutting tools. For the above physical vapor deposition (PVD) of hafnium nitride/vanadium nitride [HfN/VN]n multilayer coating, with 1, 50 and 80 bilayers, were carried out onto High-speed steel (HSS) cutting tools by the Multi-target Magnetron Sputtering technique , using toolbit ASSAB 17 3/8 X 3" as a substrate. Toolbits uncoated and coated with HfN/VN multilayers were used to machine AISI 1020 steel samples at the same turning parameters in a CNC machine.

Cutting efficiency, quality product, and tool wear are influenced by temperature, therefore as evaluation method the temperature of the tool, the steel and the chip were measured by means an infrared sensor, a data acquisition system and data analysis in MatLab to identify mean temperature and temperature rate for each tool. Also superficial roughness (*Ra*) of work pieces were evaluated using a roughness tester and Scanning Electron Microscopy (SEM). Tool rake wear were checked through Optical Microscopy and SEM.

In most of the parameters evaluated differences between the tools were identified, as the temperature at the chip increased, temperature at the tool and temperature rates decreased, the work piece roughness reduced up to 25%, and the wear reduces up to 50%, those were proportional to the bilayers number. Results reveals that on [HfN/VN]n coated tools, occurs less deterioration, due the proportionality between the energy transfer and wear resistance, also improves surface finish of the machined piece; all of them are reflected in changes in process temperatures.

Highlights: This novel method relates three fundamental aspects such as temperature of the components, work piece roughness and tool wear, in order to evaluate the performance of coated cutting tools at in situ tests.

The use of multilayer [HfN/VN]n coating on HSS cutting tools, improves superficial properties by reducing friction coefficient and heat transfer, could increase their lifetime, improve the quality of the workpiece, leading to reduce process time and cost, enhance uniformity of material removal and tool lifetime, getting a manufactured product with a better surface quality.

Acknowledgment: This work was supported by funds for internal calls for projects at Universidad Militar Nueva Granada, contract number ING-2100.

4:10pm **G3-9 High Temperature Oxidation and Cutting Performance of AlCrN, TiVN and Multulayered AlCrN/TiVN Hard Coatings**, ***Shi-Yao Weng***, *Y Chang,* National Formosa University, Taiwan

Transition metal nitrides, such as TiVN and AlCrN, have been used as protective hard coatings due to their excellent tribological properties. In this study, nanostructured AlCrN/TiVN multilayered coatings were deposited periodically by cathodic-arc evaporation (CAE). The AlCrN/TiVN multilayered coatings were post-treated by rapid thermal annealing (RTA). During the coating process of AlCrN/TiVN, TiN was deposited as an interlayer to enhance adhesion strength between the coatings and substrates. The cathode current of both TiV and AlCr alloy cathodes was controlled to produce hard nitride coatings. The microstructure of the thin films was characterized by using a field emission scanning electron microscope (FE-SEM) and transmission electron microscope (TEM), equipped with an energy-dispersive x-ray analysis spectrometer (EDS). Glancing angle X-ray diffraction (XRD) was used to characterize the microstructure and phase identification of the films. The chemical composition and bonding structures were also evaluated. The periodic thickness and alloy content of the deposited coating were correlated with the evaporation rate of cathode materials. A ball-on-disc wear test at room temperature was conducted to evaluate the tribological properties and lubricities of the deposited coatings. To evaluate the cutting performance, end milling tests of 7000 series Al alloys of the deposited tools were conducted at high rotational speed. The TiVN coated tool showed improved tool life as compared to CrAlN and AlCrN because the lubrication effect of TiVN. The design of multilayered AlCrN/TiVN hard coatings is anticipated to inhibit grain growth and improve toughness which expected to increase the mechanical, tribological and oxidation resistance performances of the coatings.

Advanced Characterization Techniques for Coatings and Thin Films

Room Royal Palm 4-6 - Session H2-2

Advanced Mechanical Testing of Surfaces and Coatings

Moderators: Benoit Merle, Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Marco Sebastiani, University of Rome "Roma Tre"

1:30pm **H2-2-1 Mechanical Properties of High-strength Low-weight Truss Structures Fabricated by 3D Direct Laser Writing**, ***Ruth Schwaiger***, Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM-WBM), Germany **INVITED**

Cellular materials with designed architectures are fabricated with the goal to design new materials with high strength and low density. In our approach, polymeric truss structures with characteristic features in the micro-to-nanometer range are fabricated by 3D direct laser writing and then coated using thin film deposition techniques. Annealing treatments as well as deposition of alumina or metal coatings are shown to enhance the strength of the structures.

Nanomechanical testing methods are used to investigate the deformation behavior of the fabricated structures. As demonstrated by push-to-pull tensile tests, annealing can increase the material strength by up to a factor of 10. However, it is found that this increase of strength cannot be fully transferred to architected materials, such as tetrahedral truss structures, because of stress concentrations at the truss nodes. Failure of the truss structures due to buckling and subsequent fracture at the truss nodes as well as a pronounced recovery upon unloading was observed. Cyclic tests showed energy dissipation, which is a function of progressively failing ligaments. Deformation and failure as well as the strategies to improve the properties of 3D microarchitectures will be discussed.

2:10pm **H2-2-3 An improved Nanoindentation Method to Measure Residual Stress and Elastic Moduli of Freestanding Multilayer Thin Films**, ***Marco Sebastiani***, *M Ghidelli,* Roma TRE University, Italy

In this work, we developed an improved nano-mechanical characterisation procedure of freestanding bilayer (Au-TiW) micro-cantilevers and double clamped beams, for applications as Radio Frequency (RF)-switches Micro-

Electromechanical Systems (MEMS). The micro-beams are deflected by using nanoindentation in dynamic stiffness measurement mode, in order to extract the elastic modulus and the residual stresses of both layers. Firstly, the classic beam theory has been implemented for bilayer cantilevers enabling the extraction of elastic moduli. Then, residual stresses are estimated by deflecting double clamped beams, while implementing new analytical models for a bilayer system. The obtained elastic moduli are consistent with the average ones obtained for a single layer micro-cantilever and with nanoindentation results for TiW and Au homogeneous films. The residual stresses are in agreement with the values obtained from the double slot Focused Ion Beam (FIB) and Digital Image Correlation (DIC) procedure, providing an alternative and portable way for the assessment of residual stresses on composite double clamped micro-beams.

2:30pm **H2-2-4 *In Situ* FIB-SEM DIC and Synchrotron XRD Analysis of the Mechanical Degradation of a Uniaxially Loaded Copper-Tungsten Nano-Multilayer***, León Romano Brandt, E Salvati, C Papadaki, H Zhang, S Ying, T Sui, A Korsunsky,* University of Oxford, UK

Thin coatings and multi-layers with individual layer thickness down to a few nanometres enable the design of materials with novel and carefully tailored thermal, mechanical, and functional properties. These properties arise as a consequence of the confinement of inhomogeneous mechanical, chemical and electromagnetic fields within nano-scale strata and nano-grains of material. External mechanical loading can cause structural damage and significantly decrease or undermine the performance of coating systems. It is therefore important to develop methods for quantifying material specific parameters, as well as attain a fundamental understanding of the mechanisms determining the mechanical response of thin films at the micro- and nanoscale and transform this fundamental understanding into generally applicable models.

The analysed copper-tungsten nano-multilayers with individual layer thicknesses of 18/6 nm and a total thickness of 240 nanometres are particularly attractive for applications as heatsinks in microelectronics. The micro- and nano-mechanical analysis of this material requires a variety of complex methods and techniques capable of precisely manipulating and resolving samples at these scales. *In situ* scanning electron microscopy (SEM) image sequences recorded during deformation of samples prepared by focussed ion beam (FIB) milling were interpreted using digital image correlation (DIC) to determine displacement and total strain fields. On this basis, a viable method is proposed for determining fracture toughness of thin nano-multilayers and other key properties of sub-micron thin films.

A very powerful tool for the determination of the elastic strain component of multilayers is synchrotron X-ray diffraction (XRD). We used this technique for *in situ* strain mapping regions of interest while applying stretching to the coating substrate. Based on the obtained strain maps, a description is proposed of the stress-strain state in hard brittle coatings on soft polymer substrates under substrate stretching.

2:50pm **H2-2-5 Synchrotron Nano-diffraction Studies of Ex-situ and In-situ Indented Thin Films: Microstructure and Stress Analysis***, Juraj Todt,* Montanuniversität Leoben, Austria*; C Krywka,* Helmholtz-Zentrum Geesthacht, Germany*; M Burghammer,* European Synchrotron Ratiation Facility, France*; J Keckes,* Montanuniversität Leoben, Austria

Mechanical testing of small features such as thin films and surface regions is a challenging task, especially in the case of microstructurally complex systems exhibiting property gradients at the sub-micrometer scale. Since indentation is a popular technique, there has been considerable effort to model the rather complex underlying mechanical interactions. However, it has been difficult to find experimental validation for these numerical studies, due to the lack of adequate experimental methods.

In recent years cross-sectional scanning X-ray nano-diffraction at synchrotrons has been established as a powerful technique for structural analysis of thin films. Its key feature is a high spatial resolution, usually below 100 nm, offering insight into depth-gradients of phase composition, preferred orientation, morphology and stresses that evolve as a consequence of self-governed film growth or due to deliberate process control.

In the presented work, its capability to assess these sub-micrometer gradients is exploited as a means to study the microstructural changes and stresses induced during the indentation of thin films. This covers the extent, shape and magnitude of multi-axial stress fields during or after their formation, localized reorientation of grains, generation of defects, as well as their relation to the resulting failure modes. Multiple cases of multi-layered and monolithic metallic and ceramic thin films that were indented either ex-situ or in-situ will be discussed. Some of the presented cases will also be compared to respective FE analyses, highlighting areas for their improvement.

[1] Keckes J, Bartosik M, Daniel R, Mitterer C, Maier G, Ecker W, et al. (2012), X-ray nanodiffraction reveals strain and microstructure evolution in nanocrystalline thin films, *Scr Mater* **67**, 748–51.

[2] Stefenelli M, Daniel R, Ecker W, Kiener D, Todt J, Zeilinger A, et al. (2015) X-ray nanodiffraction reveals stress distribution across an indented multilayered CrN/Cr thin film *Acta Mater* **85**, 24-31.

[3] Zeilinger A, Todt J, Krywka C, Müller M, Ecker W, Sartory B, Meindlhumer M, et al. (2016) In-situ Observation of Cross- Sectional Microstructural Changes and Stress Distributions in Fracturing TiN Thin Film during Nanoindentation, *Sci Rep* **6**, 22670.

3:10pm **H2-2-6 Cross-sectional Microstructure and Mechanical Behaviour of As-deposited and Oxidised CVD TiB_2 Hard Coatings Determined by X-ray Nanodiffraction and Micro-mechanical Tests***, David Gruber, M Tkadletz, N Schalk,* Montanuniversität Leoben, Austria*; B Sartory,* Materials Center Leoben Forschung GmbH (MCL), Austria*; C Mitterer, J Keckes,* Montanuniversität Leoben, Austria

In multilayered hard protective coatings used for industrial cutting operations, the functional behaviour depends on the properties of individual sublayers and interfaces.

In this contribution, mechanical properties, residual stresses and the cross-sectional microstructure of TiN/TiB_2 protective coatings on WC-Co substrates are analysed in as-deposited state and oxidised at 700°C in ambient air.

Synchrotron X-ray nanodiffraction is used to investigate gradients of phases and residual stresses as a function of coating depth in order to assess oxidation-induced changes in stress state and observe oxide formation.

In addition, in-situ micromechanical tests on micro-cantilevers, machined by focused ion beam milling of the TiB_2 and TiN sublayers are performed in the scanning electron microscope in order to determine Young's moduli and fracture stresses.

The experimental results indicate a complex nature of oxidation-induced degradation at the coating cross-section and allow to quantitatively evaluate changes in important coating parameters.

3:30pm **H2-2-7 Fundamental Mechanical Properties of Simple- and Pt/Ir-modified-Aluminide Diffusion Coatings after Thermocyclic Exposure***, Ceyhun Oskay, M Galetz,* DECHEMA-Forschungsinstitut, Germany*; H Murakami,* National Institute for Materials Science, Japan

The oxidation protection of Ni-based superalloys under service conditions relies on the mechanical and chemical stability of aluminide diffusion coatings, which provide the necessary Al-reservoir for the protective oxide scale formation. During exposure at high temperatures, the existing chemical gradient between the coating and substrate causes an alteration of the microstructure. Microstructural degradation of such coatings not only affects the chemical lifetime, but also influences the mechanical durability of the system. Therefore determination of the mechanical properties of simple- or modified-aluminide coatings is a significant step for precise lifetime assessment. The change in the microstructure is especially important for thin-walled components, for which the mechanical contribution of the coating gains importance.

In this study, simple aluminide coatings were deposited on four-point-bending flexural test samples of a 2nd generation Ni-based superalloy via a CVD-process. Pt- and Pt/Ir-modified aluminide coatings were manufactured on PWA 1483 samples via a two-step process involving electrodeposition and subsequent pack-aluminizing. Afterwards the samples were exposed to thermocyclic oxidation (1h cycles) at different maximum temperatures (highest 1100°C) for various durations (max. 1000 cycles). Fracture strain, hardness and elastic modulus were determined after the exposure at room temperature (RT) via four-point-bending flexural test with in-situ acoustic emission measurement and nanoindentation respectively. Consequently, the fundamental mechanical properties were correlated with the corresponding Al-concentration.

Al-depletion during thermocyclic exposure causes an increase in the fracture strain. Further depletion triggers the formation of the more ductile γ'-phase, through which the coating becomes able to deform plastically with the substrate at RT, rather than showing premature brittle fracture. Elastic modulus and hardness decrease within the single-phase region. However within the two-phase stability region, the formation of the γ'-phase causes an increase of both properties.

3:50pm **H2-2-8 Fast Nano-mechanical Property Mapping using XPM on Nano-crystalline Structures**, ***Anqi Qiu***, *D Vodnick,* Hysitron, Inc., USA

Surface properties of nano-crystalline materials have been studied intensively using various spectroscopy and microscopy techniques. But due to the sizes of the crystalline structures, it was difficult to map the deformation behaviors of nano-crystalline materials due to the continuum behavior of stress. With the development of ultra low noise XPM technique, nano-mechanical behaviors of nano-crystalline materials show good correlation between the mechanical behavior map and the crystallographic characterization. This gives a new direction of studying nano-crystalline plasticity and grain boundary mediated deformation.

Topical Symposia
Room California - Session TS2-2
Thermal, Cold, and Kinetic Sprayed Surface Coatings

Moderators: Pylin Sarobol, Sandia National Laboratories, USA, Charles Kay, ASB Industries, Inc., USA

1:30pm **TS2-2-1 Influence of Bondcoat and Substrate Chemistry on Lifetime in Suspension Plasma Sprayed Thermal Barrier Coatings**, ***Mohit Gupta***, *N Markocsan,* University West, Sweden; *X Li,* Siemens Industrial Turbomachinery AB, Sweden

A Thermal Barrier Coating (TBC) system is designed to protect gas turbines from high temperatures and harsh environments. Development of TBCs allowing higher combustion temperatures is of high interest since it results in higher fuel efficiency and lower emissions. It is well known that nano-structured TBCs produced by Suspension Plasma Spraying (SPS) have significantly lower thermal conductivity as compared to conventional systems due to their very fine porous microstructure. However they have not yet been commercialised due to low reliability and life expectancy of the coatings.

Lifetime of a TBC system is highly dependent on bondcoat and substrate chemistry as it influences the interdiffusion characteristics and growth rate of Thermally Grown Oxide (TGO) layer. To enhance the lifetime of TBCs, fundamental understanding of relationships between bondcoat-substrate chemistry, TGO growth rate, and lifetime is essential. The objective of this work was to study the effect of TGO growth rate on lifetime in SPS TBC systems by changing bondcoat and substrate materials. Experimental NiCoCrAlY bondcoat powders with different aluminium activity were investigated. High velocity air fuel spraying was used for bondcoat deposition while axial-SPS was used for yttria stabilised zirconia topcoat deposition. Lifetime was examined by thermal cyclic fatigue and thermal shock testing. The failure mechanism in each case will be discussed.

1:50pm **TS2-2-2 *α*-Oxide-Induced Grain Growth in Ligand-Free CZTS Nanoparticle Coatings**, ***Stephen Exarhos***, *E Palmes, R Xu, L Mangolini,* University of California, Riverside, USA

Cu_2ZnSnS_4 (CZTS) is a material of interest for application as the photo-absorber layer in polycrystalline thin film photovoltaic (PV) devices due to its earth abundant, inexpensive, and nontoxic constituents. We have developed a highly scalable synthesis technique for the controllable formation of surface-ligand-free CZTS nanoparticles using aerosol spray pyrolysis. Further, we have developed scalable techniques to generate uniform large-grained polycrystalline thin films from nanoparticle coatings. High quality PV absorber layers are unattainable by sintering our ligand-free particles using traditional methods. We have found that a simple annealing step at moderate temperature (200-300 ºC) in air results in the formation of a thin oxide layer at the particle surface. Powder processed in this manner shows significantly enhanced grain growth kinetics after high-temperature annealing in a low-pressure sulfur atmosphere in concert with alkali incorporation. Most importantly, using these particles and the oxidizing technique, we avoid the introduction of carbon to the system which invariably facilitates the formation of a fine-grain carbon-rich layer between the substrate and the large-grained absorber layer in previously reported nanoparticle-derived films. We also observe structural and compositional inhomogeneity from grain-to-grain in these annealed films, a result previously reported by our group to be found in alternatively processed CZTS films, which allows us to infer possible unknown mechanics of grain growth in the material system. We present extensive characterization of these particles and films in order to understand the role an amorphous oxide layer and phase evolution may play in enhancing grain growth in CZTS nanoparticle coatings.

2:10pm **TS2-2-3 CaviTec HVOF Coatings for Protection against Cavitation Erosion**, ***Sébastien Lavigne***, Polytechnique Montreal, Canada

CaviTec® is an alloy known for its high resistance to cavitation. Under cavitation conditions, this material exhibits a long incubation period before erosion sets-of, and a low erosion rate is observed afterwards. During the incubation period, the material absorbs energy, and a structural transition takes place. In the present work, Cavitec powders were prepared by water atomization followed by HVOF thermal spray. Compared to the bulk alloy, the coatings exhibit a relatively poor cavitation resistance and no incubation period. The defects present in the coatings (intersplat boundaries, pores etc) initiate cracks during erosion, leading to the removal of dense CaviTec particles. However, by ball milling the powder at high energy prior to deposition, the cavitation resistance can be improved by a factor of 2. Moreover, deposition at high velocity leads to a much higher cavitation resistance comparable to that of other well-known cavitation resistant HVOF coatings: For instance, a lower erosion rate than that of WC-CoCr HVOF coatings was achieved, and a longer incubation period than that of Stellite-6 was observed.

2:30pm **TS2-2-4 Experimental and Numerical Investigation on Fracture Toughness of Plasma-sprayed TBCs using a Modified Three-point Bending Method**, ***Jianguo Zhu***, Jiangsu University, China

Determination of interfacial properties of thermal barrier coatings (TBCs) is very important for designing and evaluating the durability of TBCs. In this work, the adhesion of thermal spraying coatings deposited on a NiCoCrAlY bondcoat by the APS process was investigated experimentally. A modified three-point bending test was adopted to initiate and propagate the topcoat/bondcoat (TC/BC) interfacial crack. The fracture surfaces were examined, and images show that the crack plane was just on the TC/BC interface. Furthermore, the displacement and strain fields of the TC/BC interface were obtained using the digital image correlation (DIC) method, and the crack length was accurately determined. Based on the experimental results, the critical strain energy release rate G_c for crack initiation was calculated with Irwin-Kies formula, and the G_c for crack propagation was inversely determined by a finite element model. Results indicate that the G_c can be reliably obtained theoretically and numerically.

2:50pm **TS2-2-5 Process Induced Real-time Residual Stress Measurement of Thermal Spray Coatings**, *W Choi, C Jensen, S Sampath,* ReliaCoat Technologies, LLC, USA; ***Andrew Vackel***, Sandia National Laboratories, USA

INVITED

Thermal spraying (TS) represents a flexible and highly efficient method of materials processing, and applications of protective coatings. Over the last several decades, the thermal spray process has emerged as an innovative and unique means for processing and synthesizing from low melting plastics to complex multi-component alloys and refractory ceramics. TS coatings find extensive applications including, but not limited to aerospace, energy generation, paper and pulp, biomedical implants, earth moving machinery, automotive industries for from thermal barriers for heat shielding to wear/corrosion resistance and reclamation. Despite significant advances in process and materials technology, limitations in coating reliability and repeatability have prevented expanded applicability of thermal spray coatings and, in particular, the use of thermal spray coatings in *prime reliant functions*. One major obstacle to obtaining greater coating performance, repeatability and reliability is the inability to measure relevant coating properties, and to do so in real-time within the production environment.

ReliaCoat Technologies has developed In-situ Coating Property (ICP) sensor, based on bi-layer thermo-elastic beam curvature solutions during and after coating deposition for real time extraction of residual stress evolution, deposition dynamics, and the onset of stress-relief cracking. The sensor distinguishes variation in process condition through resulting residual state of stress and elastic modulus. This real time residual stress analysis can comprehensively be related to both in-flight particle state (temperature and velocity) and booth operational parameters (cooling, spray distance, and deposition rate). Furthermore, monitoring of the residual stress evolution provides a qualitative indication of the stored energy in the layer owing to the intersplat bonding strength (cohesion) and work hardening due to impact (hardness), as well as, energy relief mechanisms including micro/macro cracking, poor cohesion, yielding or creep. Thus, the ICP sensor enables rapid process parametric optimization for design-relevant coating properties within the spray booth.

3:30pm **TS2-2-7 Metallization and Selective Metallization of Silver by Spraying**, ***Koen Staelens,*** Jet Metal Technologies, France

Jet Metal Technologies (France) introduces a green alternative for metallization processes like PVD, electroplating or evaporation.

Two chemical solutions, an oxidant containing the metal salt of the metal that the user wants to deposit, the other the reducing agent, are both water based, solvent, Pd ànd CMR free. Using compressed air and a double nozzle spraying paint gun, the reducing and oxidising agent are simultaneously sprayed onto the substrate surface, starting an oxido-reduction reaction and instantly forming a thin metal layer. The end result of this reaction is a dense and high adherent metallic film on the substrate surface.

The technology is applied on many substrate geometries (small or big, easy or complex, 2D or 3 D shape) and basically all substrate material choices, whether it is an electrically conducting or non-conducting surface. The range of substrates goes from metals, metal alloys, over glass, textiles, ceramics, silicon, leather to a long list of plastics and composites to even wax. The only prerequisite is linked with the use of water based solutions: in order realize an evenly well distributed metal layer over the surface, a good substrate wettability is needed which can be achieved via a pre-treatment step (flaming, plasma or corona). Once the required layer thickness is reached, spraying deionized water stops all reactions and the substrate is dried with the help of compressed air, so no for a curing step.

By adding one more step to the above described process, a selective, conductive pattern can be realized: an alkali sensitive organic ink, used as a negative mask, is printed on the substrate with an ink jet printer. As the oxidant and reducing agent have a pH >10, a loss of adhesion of the printed ink is achieved. During the final step of the process (spraying with deionized water) the ink layer is removed, leaving only metallization where there was no ink printed: a selective coating is achieved, and the result is the exact opposite of the pattern designed with the ink.

Today the technology is used on industrial scale in many application areas where Ag is used. In decorative applications like cosmetic bottles & caps, spirit bottles but also in functional applications like anti-bacterial applications, EMI shielding (500 nm Ag gives 65-70 dB between 10 MHz–10 GHz), intermediate conductive layer (150 nm Ag on a non-conductive surface gives enough electrical conductivity to be followed by electroplating, powder coating, electroforming,).

And with the selective metallization technology the manufacturing processes of e.g. antennas, PCB's, … can be simplified.

Coatings for Use at High Temperatures
Room Grand Exhibit Hall - Session AP

Symposium A Poster Session

AP-2 Fracture Behavior and Thermal Durability of Lanthanum Zirconate Based Thermal Barrier Coatings with Buffer Layer in Thermally Graded Mechanical Fatigue Environments, ***BongGu Kim***, *G Lyu, S Jung, S Lee, Y Jung,* Changwon National University, Republic of Korea*; J Zhang,* Purdue University, USA

The effects of buffer layer on the fracture behavior and lifetime performance of lanthanum zirconate ($La_2Zr_2O_7$; LZO)-based thermal barrier coatings (TBCs) were investigated through thermally graded mechanical fatigue (TGMF) tests, which is designed to simulate the operating conditions of rotation parts in gas turbines. To improve the thermal durability of LZO-based TBCs, composite top coats, consisting of two feedstock powders of LZO and 8 wt% yttria-doped stabilized zirconia (8YSZ), were prepared by mixing in different volume ratios (50:50 and 25:75, respectively). In addition, buffer layers were introduced in layered LZO-based TBCs deposited using an air-plasma spray method. The TGMF tests with a tensile load of 60 MPa were performed until 2000 cycles at a surface temperature of 1100°C for a dwell time of 10 min, and then the samples were cooled at room temperature for 10 min in each cycle. For the single layer TBCs, the thermal durability was enhanced by controlling the LZO:8YSZ ratio as 25:75 vol.%. The TBC with the double buffer layer showed the best thermal cycle performance among all samples, suggesting the buffer layer was efficient in improving lifetime performance. It is noted that failure modes were different in TBC samples. Delamination and/or cracks were created at the interface between the bond and top coats or above the interface in the single-layer TBCs, but the TBCs with the buffer layer was delaminated and/or cracked at the interface between the buffer layer and the top coat, independent of buffer layer species. This study allows us to further understand the LZO-based TBC's failure mechanisms in operating conditions, especially in the thermal and mechanical environments, in order to design reliable TBC systems.

AP-3 Correlation of Thermal Characteristics and Microstructure of 7YSZ/$La_2Zr_2O_7$ and 7YSZ/$Gd_2Zr_2O_7$ Quadruple Layer EB-PVD Thermal Barrier Coatings, *K Bobzin, T Brögelmann, C Kalscheuer,* ***Tiancheng Liang***, *M Welters,* Surface Engineering Institute - RWTH Aachen University, Germany

Referring to the increasing amount of aviation until the year 2030, energy and fuel efficiency as well as the emission of harmful gases are of prime importance to the technological and ecological evaluation of aircraft engines. Minimizing fuel consumption and improving energy efficiency of jet engines can be reached by increased turbine entry temperatures. However, the permitted combustion temperatures are restricted by material-dependent maximum operating temperatures. Nowadays, yttria stabilized zirconia (YSZ) is commonly used as thermal barrier coating (TBC). YSZ generally withstand a permanent surface temperature of T = 1,200 °C, which is limited due to thermally induced phase transformation. Therefore, lanthanum zirconate ($La_2Zr_2O_7$) and gadolinium zirconate ($Gd_2Zr_2O_7$) with their exceptional properties concerning thermal conductivities, melting points and phase stabilities, get into the focus. However, the mismatch of thermal expansion coefficient α of the new ceramic layers and the bond coats or substrates can lead to delamination under thermal load. In recent years, research projects have shown that multilayer systems might be a solution to combine the advantages of different ceramic layers, avoiding detrimental effects such as delamination. In order to assess this potential of multilayer systems, quadruple multilayer systems consisting of 7wt.% YSZ and $La_2Zr_2O_7$ or 7wt.% YSZ and $Gd_2Zr_2O_7$ were deposited on Inconel 600 by electron beam-physical vapor deposition (EB-PVD). To evaluate the long term behavior under thermal cycling and isothermal load, extended thermal cycling tests were conducted at temperatures of T = 1,200 °C and T = 1,300 °C for n = 1,000 cycles as well as isothermal oxidation tests were performed at a temperatures of T = 1,100 °C for t = 50 h. Furthermore, different analyses regarding the basic characteristics of TBC such as thermal conductivity via laser flash method, phase analyses via X-ray diffraction, microstructure analyses via scanning electron microscope and element analyses by means of X-ray spectroscopy were conducted and correlated with each other. The results of the quadruple TBC were compared to those of mono and double layer TBC. These investigations showed a systematic relationship between porosity and thermal conductivity. Moreover, the thermal cycling tests highlight the great advantages of multilayer systems regarding the thermal expansion properties, compared to the monolayer. In this manner, the multilayer systems illustrated the potential of an adapted coating architecture, which leads to an improved TBC lifetimeunder alternating thermal and isothermal load.

AP-5 Oxidation Behavior of Nb–Si–N Coatings, ***Yung-I Chen***, *Y Gao,* National Taiwan Ocean University, Taiwan*; L Chang,* Ming Chi University of Technology, Taiwan

Nb–Si–N coatings were fabricated using reactive direct current magnetron cosputtering on Si substrates. The N contents of Nb–Si–N coatings ranged from 39 to 48 at.% as varying the sputter powers for Nb and Si targets. The Nb–Si–N coatings with a Si content less than 13 at.% exhibited a face centered cubic phase, whereas the coatings with a Si content higher than 17 at.% exhibited near-amorphous. The nanohardness increased from 22.8 GPa for Nb–N coatings to 25.4 GPa for the coating with a 4 at.% Si, and then decreased continuously to 13.3 GPa as increasing the Si content to 23 at.%. The oxidation experiments of Nb–Si–N coatings were conducted at 600 °C in a 1% O_2–99% Ar atmosphere. The results indicated that crystalline Nb–Si–N coatings was oxidized to form Nb_2O_5 after they were annealed for 4 h, whereas no evident oxide scale was observed for the near-amorphous $Nb_{32}Si_{23}N_{45}$ coatings after annealing up to 24 h.

AP-6 Corrosion Behavior of Amorphous and Crystalline Zn-Mg Coating in NaCl Solution, ***JoungHyun La***, *K Bae, S Kim, S Lee, Y Hong,* Korea Aerospace University, Republic of Korea

Recently, Zn-Mg coatings have been studied extensively for the protective coatings of steel sheets due to the excellent corrosion resistance of Zn-Mg coatings compared with pure Zn coatings. However, the structure of Zn-Mg coatings changed with deposition conditions such as power density, pressure, and temperature. In this study, the amorphous and crystalline Zn-Mg coatings were synthesized on the steel substrates using sputtering process at various temperatures. The microstructure, the crystal phase, and corrosion resistance of the Zn-Mg coatings were investigated using the field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), and salt spray test (SST), respectively. The synthesized Zn-Mg coatings at low temperature below 50°C showed the amorphous and featureless microstructure. By contrast, the porous crystalline Zn-Mg coatings were synthesized at the temperature above 100°C. The amorphous Zn-Mg coatings showed the enhanced corrosion resistance in NaCl solution compared to the crystalline Zn-Mg coatings. The featureless microstructure of the amorphous Zn-Mg coatings improved its corrosion resistance by obstructing the direct pathway between a corrosive environment and the substrate as well as inhibiting localized corrosion.

Acknowledgement

This study is financially supported by the Smart Coating Steel Development Center, WPM(World Premier Materials) Program of the Korea Ministry of Knowledge Economy.

AP-7 Nanocomposite Multilayered Coatings with High Thermal Stability and Oxidation Resistance, ***Dmitry Shtansky***, *K Kuptsov, M Golizadeh, P Kiryukhantsev-Korneev,* National University of Science and Technology "MISiS", Russian Federation

High thermal stability and oxidation resistance are important properties for various high-temperature applications. Superhard TiAlSiCN coatings with "comb"-like nanocomposite structure, in which fine (Ti,Al)(C,N) columnar grains were separated by well-developed amorphous SiCN interlayers, recently developed in our group, exhibited the highest thermal stability reported to date for nanocomposite coatings. The main drawback of the TiAlSiCN coating is a relatively large difference in temperatures between its thermal stability (1300 °C) and oxidation resistance (1000 °C), which limits their use at high temperatures.

In this work we applied a multi-layering approach to close the gap between thermal stability and oxidation resistance. The coatings were deposited on Al_2O_3 substrate by reactive DC magnetron sputtering of TiAlSiCN target and ion sputtering of SiBC or Al_2O_3 targets in a gaseous mixture of Ar + 15% N_2. The coatings were annealed in vacuum at 1000, 1300 and 1400°C as well as in air at 1000, 1100 and 1200°C for 1 hour to investigate thermal stability and oxidation resistance. XRD, SEM and EDX studies showed that TiAlSiCN/Al_2O_3 coating mostly lost its multilayer structure already after annealing at 1300°C and experienced significant grain growth, while TiAlSiCN/SiBCN coating maintained its multilayer structure with negligible grain growth. Annealing at 1400°C led to a partial recrystallization of top layers of TiAlSiCN/SiBCN coating, while most of the coating remained its structure. After annealing at 1100°C in air, TiAlSiCN/Al_2O_3 coatings were only partly oxidized due to the formation of a dense Al_2O_3 top layer, while TiAlSiCN monolayer and TiAlSiCN /SiBCN coatings were almost completely

oxidized. However, incorporated amorphous Al_2O_3 layers in TiAlSiCN/Al_2O_3 coating were crystallized to a certain degree, which shortened initial and transient stages of oxidation by providing preferred nucleation sites and facilitating lateral growth of the oxide.

AP-10 Structure, Mechanical, Tribological, And Chemical Properties Of Mo-Si-B And Mo-Al-Si-B Coatings, ***Philipp Kiryukhantsev-Korneev***, *A Sheveyko, A Bondarev,* National University of Science and Technology "MISiS", Russian Federation*; K Kuptsov,* National University of Science and Technology "MISIS", Russian Federation*; E Levashov, D Shtansky,* National University of Science and Technology "MISiS", Russian Federation

Mo-Si-B and Mo-Al-Si-B coatings were deposited by DC magnetron sputtering and ion implantation assisted magnetron sputtering (IIAMS) of the MoSiB and MoAlSiB composite targets fabricated by the self-propagating high-temperature synthesis method. The structure, element and phase composition of coatings were studied by means of scanning and transmission electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, energy-dispersive spectroscopy, and glow discharge optical emission spectroscopy. The mechanical properties of the coatings were measured using nanoindentation. The tribological properties were evaluated in air using impact-tester and high-temperature ball-on-disc tribometer. To evaluate oxidation resistance, the coatings were annealed in air in the temperature range of 1200-1700 °C during different time slots between 10 min and 5 h. The results obtained demonstrate that the Mo-Si-B coatings possess higher hardness, improved oxidation resistance and better thermal stability compared with their Mo-Al-Si-B counterparts. The 7-mm thick Mo-Si-B coatings were shown to withstand successfully oxidation during short-time exposure for 10 min at temperature as high as 1700 °C due to the formation of protective silica scale. The oxidation of Mo-Al-Si-B coatings was accompanied by the diffusion of aluminum to the coating surfaces and the formation of a single Al_2O_3 layer at 1200-1300 °C and a double Al_2O_3-SiO_2 layer at 1500 °C which were less protective against oxidation. The surface oxidation processes were also accompanied by phase transformations inside the oxygen-free part of both Mo-Si-B and Mo-Al-Si-B coatings with the formation of MoB and Mo_5Si_3 phases.

AP-11 Oxidation Resistance of Ta–Si–N Coatings, *Y Chen,* ***Yu-Xiang Gao***, National Taiwan Ocean University, Taiwan*; L Chang,* Ming Chi University of Technology, Taiwan

Ta–Si–N coatings with a high Si content of 18–21 at.% were fabricated using reactive direct current magnetron cosputtering as the sputter power was set at 100W for each target, and these coatings exhibited near-amorphous in the as-deposited state. The N contents of Ta–Si–N coatings increased from 31 to 47 at.% as varying the nitrogen flow ratio from 0.1 to 0.4, accompanied with decrease trends of nanohardness from 20 to 14 GPa and Young's modulus from 220 to 196 GPa. By contrast, Ta–Si–N coatings prepared using substrate-holder rotating speeds of 1–30 rpm and a nitrogen flow ratio of 0.4 exhibited a similar chemical composition, accompanied with a nanohardness of 12–14 GPa and a Young's modulus of 187–199 GPa. The oxidation resistance of Ta–Si–N coatings was evaluated by performing annealing at 800 °C in ambient air, which showed notably oxidation resistance related to TaN coatings because the oxide scales formed with restricted thicknesses. The oxidation behavior of near-amorphous Ta–Si–N coatings was examined using transmission electron microscopy and X-ray photoelectron spectroscopy.

AP-12 Effect of Hot-dip Aluminum Coating on Dissimilar Weldment between Low Carbon Steel and 304 Stainless Steel in NaCl/Na_2SO_4 Mixture Salts Induced Hot Corrosion, ***Huan-Chang Liang***, *K Tsai, C Wnag,* National Taiwan University of Science and Technology, Taiwan

The effect of hot-dip aluminum (HDA) coating on the hot-corrosion behavior of dissimilar weldment was studied. The dissimilar weldment of low carbon steel and 304 stainless steel (SS 304) was joined by gas tungsten arc welding, using 309L stainless steel (SS 309L) filler. Weldment was coated by hot-dipping into pure molten aluminum for 60 and 120 seconds respectively. Prior to hot corrosion of as-welded and aluminized specimens in static air at 750 °C, specimens were coated with 2 mg/cm^2 of a various portions of NaCl and Na_2SO_4 salt mixtures. The results of as-welded specimens show that the intergranular corrosion took place in both SS 304 and SS 309 L, also especially in the heat-affected zone (HAZ) of SS 304 due to chromium depletion as a results of sensitization. In addition, the interface between low carbon steel and SS 309L was under severe corrosion attributed to difference in chemical composition. The results of HDA for 60 seconds show that there was no intergranular corrosion observed in each zone of stainless steel. Results also show that the low carbon steel/SS 309L interface was protected by aluminide, which eliminate the compositional effect on the surface. Same phenomenon was also observed for HDA 120 seconds, however, more cracks were observed in the aluminide layer on the interface of low carbon steel/SS 309L. It therefore shows that HDA processing on dissimilar weldment performed better hot-corrosion resistance with less difference of chemical composition.

AP-13 Influence of Arc Power and Spray Distance on Mechanical Properties of ZrO_2-10%Y_2O_3-18%TiO_2 Coatings Produced by Plasma Spray, ***Sugehis Liscano***, *L Gil,* Universidad Nacional Politecnica UNEXPO, Venezuela (Bolivarian Republic of)*; A Portoles,* Universidad Politecnica de Madrid, Spain*; K Silva,* Universidad Nacional Central de Venezuela, Venezuela (Bolivarian Republic of)

Torch Power and spraying distance during the deposition have been referred as important factors in the coating microstructure and properties. ZrO_2-10%Y_2O_3-18%TiO_2 coatings were prepared on NiCrAlCoYO bond coat and metal substrate by atmospheric plasma spraying (APS) to evaluate the effect of these parameters on the mechanicals properties. The microstructures of the coatings were characterized using scanning electron microscopy (SEM) technique coupled with X-Ray microanalysis (EDS). The coatings microhardness and adhesion strength were determined using ASTM E384-2010 for Vickers microhardness and ASTM-C633 for adhesion test. The results corroborate that torch power and spraying distance have significant influence on the mechanical properties in the range evaluate. The adhesion strength of the prepared coatings was between 7 - 14 MPa, while the microhardness measurement was more between 251 - 942 $HV_{(0,5)}$. It was concluded that the best coatings properties, for the level of the variables studied in this work, could be obtained if the torch power is maintained at 34 KW and the spraying distance in 100 mm.

AP-14 A Parametric Study for Minimizing Thermal Stress of a Thermal Barrier Coating System, ***JangGyun Lim***, *M Kim,* Sungkyunkwan University, Republic of Korea

1. Introduction

Thermal barrier coating (TBC) is presently used as thermal insulating coating to protect hot component of gas turbines. Commonly, TBC system consists of four layers; a substrate, an aluminum containing metallic bond-coat, a thermally grown oxide (TGO), and a thermally insulating ceramic layer called top-coat. However, its full usage is limited by unexpected pre-failure mainly caused by thermal stress. Temperature change in an operation cycle induces thermal stress on TBC due to mismatch of material properties. Additionally, growth and wavy deformation of TGO, creep, delamination complicate this failure mechanism. Despite of intensive research on pre-failure for several decades, it is difficult to predict the lifetime because of the variety of specifications, operating conditions, and the emergence of new materials. Therefore, it is necessary to understand the influence of the design parameters of the TBC system on the thermal stress, including the properties and specifications, in consideration of interplays.

2. Modeling and conditions

We constructed a 2D rectangular unit cell model in the axis symmetry and periodic conditions. The topological features of TGO and depletion region were figured out by a microstructural analysis so that TGO was represented by sinusoidal wave. In addition, temperature-dependent-properties were assigned to elasto-plastic deformation and the creep behavior was also considered by power-law creep strain rate. Particularly, nano-indentation was conducted on aluminum depletion area in bond-coat to measure elastic modulus. After constructing a model considering interplays, heat transfer analysis and thermal stress analysis are sequentially conducted. Based on the proposed model, an intensive parameter study with 144 different cases was conducted to investigate the effects of various design parameters on thermal stress. They are elastic modulus, thermal expansion coefficient of the top-coat, and thickness of both bond-coat and top-coat.

3. Results and discussion

As a result, it is observed that elastic modulus is the most influential parameter to thermal stress and thermal expansion coefficient, top-coat thickness, and bond-coat thickness follow. Also, the smaller mismatch of thermal expansion coefficient between bond-coat and TGO is in favor of thermal stress reduction. This parametric study will play an important role in an optimal design of TBC system.

AP-15 Investigation of the Influence of Subcoating on Thermal Shock and Corrosion Resistance in the Liquid Zinc of APS ZrO_2 Coating Doped with MgO, ***Aleksander Iwaniak,*** Silesian University of Technology, Poland*; A Moscicki,* Jolanta Mzyk Silesian University of Technology, Poland*; G Wieclaw,* Krzysztof Rosner Certech, Poland

Liquid zinc is an aggressive corrosive medium and poses a considerable problem for steels that come into contact with it. In the paper, the thermal shock and corrosion resistance of APS coating ZrO_2-24MgO to the action of molten zinc was examined. Various types of bond coats were used: Ni-Cr single-layer and layer with different contents of NiCr and ZrO_2-24MgO. The tests of thermal shock and corrosion resistance involved cyclical exposure of coated specimens in a molten zinc bath for one hour and subsequently, their rapid cooling in water. The coatings were subjected to structural examination (SEM, EPMA, XRD, 3D topography of surface) before and after the test. Macroscopic evaluation of the condition of coatings' surfaces after thermal shock test in liquid zinc, in comparison with their original state after spraying, showed the following changes in their image: surface discoloration, spots, and local fractures in case of ground coating. It was noticed that sectional view of all tested samples was reduced after corrosion resistance test (cyclic exposure to liquid zinc). It was connected with coating thickness decrease. Structural tests proved formation of zinc and zinc oxide on samples' surfaces. Coating thickness decrease after the test was caused by dissolution of ZrO2-24MgO coating in liquid zinc. Strong relation between the kind of subcoating and fractures formation in ZrO2-24MgO coating was not noticed. Only in case of a single subcoating sample, a slight flake in the upper section of ZrO2-24MgO coating was noticed after corrosion resistance test.

Hard Coatings and Vapor Deposition Technologies
Room Grand Exhibit Hall - Session BP
Symposium B Poster Session

BP-8 Large Lattice Strain-caused Change in Nanoscale Plastic Deformation Behavior of Multi-component (AlCrTaTiZr)$N_xC_ySi_z$ Nanocomposite Coatings, *Y Lai, Y Hsiao,* National Tsing Hua University, Taiwan*; **Shao-Yi Lin,*** National Chung Hsing University, Taiwan*; S Chang,* National Tsing Hua University, Taiwan

The relationship between the nanostructure and nanoscale deformation behavior of nanocomposite coatings is of importance to their mechanical performance and thus of interest for investigation. In this study, multi-component face-centered cubic (fcc) (AlCrTaTiZr)N_x, (AlCrTaTiZr)NC_y and (AlCrTaTiZr)NSi_z coatings were prepared by sputtering, and their nanostructures and nanoscale plastic deformation behavior were characterized using nanoindentation and transmission electron microscopy. The multi-component (AlCrTaTiZr)N_x coating had a simple fcc solid-solution structure and exhibited a typical full dislocation-mediated plastic deformation. With the addition of C or Si (the incorporation of covalent –C or –Si bonds), an fcc nanocomposite structure (with small-angle domain boundaries) formed in the (AlCrTaTiZr)NC_y and (AlCrTaTiZr)NSi_z coatings. Large lattice strains (severe lattice distortions) in the multi-component nanocomposite coatings caused the change of plastic deformation behavior. Under a large indentation stress, low-energy small-angle dislocation structures (with extended partial dislocations or stacking faults) were formed at the small-angle domain boundaries. When the applied stress (the stored high strain energy) was released, many of the stacking faults were removed, and a near-perfect ordered crystal structure was observed. The activities of stacking fault decahedra consisting of highly reversible 1/6 <112> and 1/9 <222> partial dislocations were expected to dominate the plastic deformation and recovery (W_e ~ 76%) of the multi-component (AlCrTaTiZr)NC_y and (AlCrTaTiZr)NSi_z nanocomposite coatings.

BP-9 Advanced Deposition of Hard a-C:Me Coatings by HPPMS using Ne as Process Gas, *K Bobzin, T Brögelmann, N Kruppe, **Martin Engels,*** Surface Engineering Institute - RWTH Aachen University, Germany

Diamond-like carbon (DLC) coatings are used in numerous tribological applications, for example on highly-loaded components of the automotive powertrain. The hardness and roughness of these coatings contribute to the reduction of the component wear. The hardness correlates with the sp^3/sp^2 bond ratio between the carbon atoms, where sp^3 bonds are similar to the diamond structure. The roughness is strongly influenced by the physical vapor deposition (PVD) technology such as the pulsed laser deposition (PLD) or the high power pulsed/impulse magnetron sputtering (HPPMS/HiPIMS). In a previous work it was shown that hard a-C coatings with a low roughness can be deposited by means of HPPMS in a high volume coating unit using Ne as process gas. Furthermore, the doping of hydrogenated a-C:H coatings by means of plasma-assisted chemical vapor deposition (PACVD) with metals is the subject of current research. Significant changes of the coating properties have been found. The formation of nanocomposite a-C:H:Me coatings was reported, which exhibit an increased hardness or reduced plastic deformation, compared to a-C:H coatings. However, a-C:H coatings generally exhibit lower hardness values, compared to a-C coatings. Therefore, the deposition of metal doped a-C:Me coatings by means of HPPMS might contribute to a performance increase in tribological applications. Hence, in the present work a-C:Me coatings were successfully deposited in a high volume coating unit by means of two HPPMS cathodes with Zr and C targets. Furthermore, a correlation with a hybrid process using one direct current magnetron sputtering (dcMS) cathode and one HPPMS cathode was performed. Based on previous works, Ne was used as process gas to increase the ionization in the carbon plasma. Therefore, a high content of sp^3 bonds in the a-C matrix was expected. The average power of the cathode with the Zr target was varied between P = 600 W and P = 1,200 W in order to obtain coatings with different chemical compositions. The resulting coating properties were analyzed by means of nanoindentation, Raman spectroscopy, scanning electron microscopy, X-ray diffractometry and confocal laserscanning microscopy. In summary, the deposition of a-C:Zr coatings by means of HPPMS was successful, since hard coatings with HU > 25 GPa with a low roughness Ra < 0.05 µm are deposited. Finally, the plasma was analyzed by means of energy resolved mass spectroscopy to correlate the coating properties with the composition of the plasma.

BP-10 Plastic Deformation Behavior of Nanostructured CrN/AlN Multilayer Coatings Deposited by Hybrid dcMS/HPPMS, *K Bobzin, T Brögelmann, **NathanChristopher Kruppe**, M Arghavani,* Surface Engineering Institute - RWTH Aachen University, Germany

The physical vapor deposition (PVD) is a commonly applied technology for deposition of hard coating systems such as chromium (Cr)-based nitride coatings on tools and components in tribological applications. In such applications the tools and components are subjected to complex loads, which can lead to elastic-plastic deformation of coating/substrate compounds or crack formation. One approach to increase the life time of compounds under significant loadings is the deposition of nanostructured coatings such as CrN/AlN-nanolaminates with promising hardness and crack resistance. The understanding of the deformation behavior of such multilayers is, however, a key factor for further coating developments. Implementation of nanoscratch analyses in conjunction with high resolution microscopy techniques is an approach to study the tribological behavior of nanostructured coatings and gain information about their plastic deformation under normal and lateral loads. Nanoscratch analyses on the coating system CrN/AlN-nanolaminate deposited on quenched and tempered AISI 420 steel substrate and investigations on the resulted plastic deformation are the subjects of current research. In the present work, a hybrid technology, consisting of direct current and high power pulse magnetron sputtering dcMS/HPPMS, was used for deposition of the coating. The CrN/AlN-nanolaminate was deposited with a bilayer period (thickness CrN + AlN) of Λ = 10 nm. In order to study the plastic deformation of the coating, nanoscratch analyses were performed applying a Berkovich tip. The deformation of coating system under nanoscratch loads was quantitatively analyzed by means of depth profiling using confocal laser scanning microscopy (CLSM). A comprehensive study of the plastic deformation and crack resistance was furthermore performed using scanning electron microscopy (SEM). The SEM analyses were carried out on surface and cross section fractures of the nanoscratch tracks. Scanning transmission electron microscopy (STEM) was applied to explore the micro-scale cracking underneath the nanoscratch tracks. High resolution transmission electron microscopy (HRTEM) was furthermore applied to explore the mechanism of plastic deformation of the investigated coatings. Based on the results, the CrN/AlN-nanolaminate exhibited a significant resistance against plastic deformation and crack formation. Furthermore, the plastic deformation of the investigated coating was explained by reorientation and sliding of grains imbedded in individual layers CrN and AlN.

BP-13 Control and Characterization of Texture in CVD α-Al_2O_3 Coatings, ***Chen Chen**, P Leicht, R Cooper, Z Liu, D Banerjee,* Kennametal Inc., USA

CVD Alumina coating has been one of the most important components of coated cutting tools for many years. Recently, texture control in α-Al_2O_3 has attracted increasing attention due to the possibility to further improve the anisotropic properties such as thermal conductivity and mechanical properties. The influence of process parameters on textures is complex. In

this study, we have investigated the influence of nucleation surface condition and catalyst (H_2S) on the texture in CVD α-Al_2O_3 coatings. The α-Al_2O_3 coatings were deposited by CVD in a hot wall vacuum deposition reactor on WC substrates, and were characterized by advanced analytical techniques including SEM, XRD and EBSD. It has been shown that without the addition of catalyst, the crystal orientation in the Al_2O_3 coatings is primarily dominated by the surface condition, while the effect of reactant composition on texture is minimal. On the other hand, in the presence of catalyst during growth, reactant composition also plays an important role in affecting the crystal orientation. This effect is likely due to the strong interaction between the surface the catalyst.

BP-14 New Tools and Models for Industrial Surface and Coating Optimization of Composite Structures, ***Nick Bierwisch***, *N Schwarzer,* SIO, Germany

Nowadays the used materials or material combinations in all application fields (e.g. optical, avionic, fun sports or automotive industry) are getting more and more complex. These complex structures are needed in order to increase the performance and lifetime of the components. Such improvements of each part of your complex device, tool or structural element are necessary to reach the performance goals demanded by the desired application. This increased complexity demands extended analyzis and optimization methods. Engineering knowledge and rules of thumb aren't enough anymore.

Proper characterization and optimization of such structures requires invertible mathematical tools of sufficient holistic character. Unfortunately, as such tools are still not available one often finds trial and error or half empirical sensitivity analysis methods in combination with FEM or BEM. Faster tools could help here a lot to save development time and costs [1].

All models (FEM or analytical based) will need exact and generic material parameters for each part of our material system.

A few years ago, SIO developed a model and a dedicated software package called Oliver & Pharr for Coatings (OPfC® [2]) which allows the determination of true generic material parameters (like Young's modulus and Yield strength) for a coating by knowing the parameters of the substrate and all underlying layers.

The software package FilmDoctor® [3] contains analytical models which dramatically speed up the simulation of complex contact situations compared to FEM systems.

The poster will focus on the results of a joint project with Naish international [5] about standup paddling boards and paddles. It will present how the models and software packages are used to improve the performance in critical application conditions dramatically.

References:

[1] N. SCHWARZER, Scale Invariant Mechanical Surface Optimization - Applying Analytical Time Dependent Contact Mechanics for Layered Structures, Proceedings of the 28th International Conference on Surface Modification Technologies, 287-327, SMT 28, June 16th – 18th, 2014, Tampere University of Technology, Tampere, Finland, Publisher: Valardocs, ISBN Number:978-81-926196-1-3

[2] www. [http://siomec.de/OPfC]

[3] www [http://siomec.de/FilmDoctor]

[4] www.naish.com

BP-15 Selection of a Reactive Magnetron Sputtering Method to Produce Films for Biosensors, ***Brenda García***, *L Melo-Máximo, O Salas, D Melo-Maximo, A Murillo,* Tecnológico de Monterrey-CEM, Mexico*; J Lin,* Southwest Research Institute, USA*; J Oseguera,* Tecnológico de Monterrey-CEM, Mexico

Three different reactive sputtering methods were evaluated for the production of Al/AlN/Al thin film architectures for biosensing applications. The methods included were direct current, radiofrequency, and modulated pulse power reactive magnetron sputtering. The films were deposited on Si substrates at equivalent power densities and characterized by optical microscopy, glancing angle x-ray diffraction, and scanning electron microscopy + microanalysis. The comparative analysis of the films was based on the most relevant film features for biosensing, namely control of the type of crystalline phases formed, control of preferred orientations, easiness to produce inclined structures, and adhesion to the substrate. Other features such as surface morphology, and density of the films were also considered, as no systematic studies regarding their effect on biosensing have been published.

BP-20 Preparation of Carbon based Multilayered Coatings by means of Pulsed Laser Deposition: Outstanding Mechanical Properties and Enhanced Film Toughness, ***René Bertram***, University of Applied Sciences Mittweida, Germany*; M Hess,* Fritz Stepper GmbH & Co.KG, Germany*; H Gruettner, D Haldan, S Weißmantel,* University of Applied Sciences Mittweida, Germany

It will be presented how amorphous carbon coatings can be deposited at low temperatures with mechanical characteristics varying in a wide range depending on deposition parameters and that these properties such as hardness and elasticity can easily be assessed by Raman spectroscopy. For this the indentation hardness and indentation modulus of carbon films deposited at various laser pulse fluences were determined by means of nano indentation and brought into correlation with the peak ratio of the disordered (D-) and graphite (G-) peaks. This offers a fast and simple method to assess H_{IT} and E_{IT} for carbon single layers, for the presented coatings in the range of roughly 20 GPa to 60 GPa and 290 GPa to 620 GPa, respectively.

It will also be shown that the architecture of films designed as multilayered stacks of such different carbon compounds strongly affects the toughness of protective coatings when exposed to high mechanical stresses induced in scratch test or indentation at high loads. Nano indentation measurements showed that this multilayered design does not result in a loss in hardness and elasticity if suitable layer structures are built up. The preliminary computation of stress evolution in the film-substrate system and the actual layer behavior for several layer stack designs will be part of the presentation as well. These coating systems combine a very good adhesion on several metal and hard metal substrates, very high hardness and low abrasive wear, very high elasticity up to 80 % elastic recovery in nano indentation and high crack resistivity in scratch tests and indentation experiments. These superior properties indicate the high potential of laser deposited carbon multilayer as wear protective coatings for cutting tools, bearings and engine components to name but a few.

BP-22 Elastic Constants of Epitaxial Cubic Tantalum Nitride: Thin Film Growth and *ab initio* Calculations, ***Gregory Abadias***, Institut P', Université de Poitiers-UPR 3346 CNRS-ENSMA, France*; P Djemia, C Li,* Laboratoire des Sciences des Procédés et des Matériaux (LSPM), France*; Q Hu,* Shenyang National Laboratory for Materials Science, China*; L Belliard,* Université Pierre et Marie Curie-INSP, France*; F Tasnadi,* Linköping University, (IFM), Sweden

Information is still scarce concerning the properties of single-crystal cubic metastable TaN thin films. This work aims at providing some new insights on the elastic and structural properties of TaN epitaxial nitride thin films, especially regarding the influence of defects and nitrogen stoichiometry. 150 nm-thick TaN films were deposited by magnetron sputtering under reactive Ar+N_2 plasma discharges on MgO(001), (110) and (111)- oriented substrates, at a temperature of 650°C. In parallel, *ab initio* calculations were performed in the framework of the density functional theory (DFT) using the VASP software. It has been evaluated how vacancies influence the lattice parameter, the mass density and elastic constants of c-TaN.

The thickness and mass density were determined by x-ray reflectivity measurements, while x-ray diffraction pole figure and reciprocal space maps were employed to study epitaxial orientation and determine the lattice parameters. Elastic constants of thin films can be accurately studied by photoacoustic measurements. The Brillouin light scattering (BLS) technique allows measuring sound velocity of a few kinds of surface acoustic waves (V_{SAW}) in thin films and thus estimating single-crystal elastic constants (ρV^2), in the case of epitaxial films, if the mass density ρ of the film is known. The Rayleigh surface wave is much more dependent on the shear elastic constant C_{44}, thus BLS can provide at least this constant. It is well adapted for thin films and can be conveniently combined with the picosecond ultrasonics technique that measures the sound velocity of longitudinal waves (V_L) that are travelling forth and back within the film along the direction perpendicular to the film plane, i.e. [001], [110] and [111] crystallographic directions.

We used this combination of techniques to measure the elastic constants C_{11}, C_{12} and C_{44} of our epitaxial nitride films. Our results show good agreement between experiments and DFT calculations if defects are taken into account

BP-24 Mechanical and Structural Properties of CrN/AlN Superlattices, ***David Holec***, Montanuniversität Leoben, Austria; *M Friak,* Institute of Physics of Materials, Academy of Sciences of the Czech Republic; *Z Zhang,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria; *M Bartosik, P Mayrhofer,* TU Wien, Austria

Density Functional Theory is a well established tool for predicting structural and mechanical properties of bulk materials. Recent progress facilitated by modern efficient codes and increased computational power has opened doors to studying also extended systems. Examples of such are superlattices, an important design approach of materials with controlled architecture.

In this contribution, we will report on first principles calculations of structural and mechanical properties of CrN/AlN superlattices. The *ab initio* predicted oscillating interplanar distances are corroborated by high-resolution transmission electron microscopy analysis. Further on, we will present fully quantum mechanical calculations of directionally-resolved Young's modulus [1]. We will demonstrate that these yield comparable results with a simple continuum model of Grimsditch and Nizzoli [2]. Also these predictions are in excellent agreement with experimental measurements [1]. Finally, we will discuss the ideal tensile strength of these superlattices.

References:

[1] M. Friak, D. Tytko, D. Holec, P.-P. Choi, P. Eisenlohr, D. Raabe, and J. Neugebauer, New J. Phys. 17, 093004 (2015).

[2] M. Grimsditch and F. Nizzoli, Phys. Rev. B Condens. Matter 33, 5891 (1986).

BP-25 Characterization of the Hard Coating on Gray Cast Iron Under Hydrogen Charging, ***Noe Lopez Perrusquia***, *M Doñu Ruiz, M Reyes Cortes,* Universidad Politecnica Del Valle De Mexico, Mexico; *C Torres San Miguel,* Instituto Politécnico Nacional - ESIME, Mexico; *V Cortes Suarez,* Universidad Autónoma Metropolitana, Mexico

This work enhance the mechanical properties on pearlitic gray cats iron with hard coating under hydrogen charging. The formation of hard coating was carry out by boron paste dehydrated at temperature of 1173 and 1193 K, with 8 hour exposure time. The characterization of hard coating were using: optical microscopy (OM), X-ray diffraction (XRD), energy dispersive spectrometry (EDS) and the mechanical properties: elastic modulus and hardness were obtained nanoindentation and the adhesion by Rockwell C indentation test. All sample boride were subjected to hydrogen charging and evaluate the behavior of hydrogen on gray cast iron with FeB/Fe_2Bcoating using three point bending results. The mechanical properties enhance the surface on gray cast iron due to hard coatings and increase the bending stress value.

BP-27 Characterization and Growth of B-doped Diamond Grown on HPHT Diamond Substrates using Mode Conversion Type Microwave Plasma CVD, ***Tomoya Sakuma***, Chiba Institute of Technology, Ogura Jewell Industry Co., Ltd., Japan; *A Suzuki, Y Sakamoto,* Chiba Institute of Technology, Japan

Diamond has excellent physical and chemical properties such as high hardness, high thermal conductivity, optical transmission from UV to IR and chemical inertness. In addition, diamond is well known an electrical insulator with a resistivity of the order of 10^{16} Ω･cm. However, it was changed to the semiconductor by inclusion of dopants such as boron or phosphorus. Generally, diborane (B_2H_6) or trimethyl-boron {$B(CH_3)_3$} is used as a dopant to synthesize B-doped diamond. Though these dopants are toxic to humans. Trimethyl-borate {$B(OCH_3)_3$} is harmless. Furthermore, accuracy of the machined surface with single crystalline diamond is better than polycrystalline diamond and it is essential for ultra-precision machining and ultra-precision measurement.

In this report, growth and characterization of B-doped diamond on HPHT diamond substrates using mode conversion type microwave plasma CVD were studied.

B-doped diamond was synthesized on single crystalline diamond substrates using mode conversion type microwave plasma CVD apparatus. HPHT diamond substrates were synthesized using high pressure high temperature method and their (1 0 0) facets were crystal orientation. Reaction gases were used CH_4 (15 SCCM) and H_2 (100 SCCM). Trimethyl-borate was used as a boron source. Vapor of trimethyl-borate was carried by H_2 carrier gas into the vacuum chamber with its flow rate of 3 SCCM. Pressure was 20.0 kPa and microwave power was 1.0 kW, respectively. The surface and cross sectional morphologies of deposits were observed by SEM. Qualities of the deposits were estimated by Raman spectroscopy and Laue pattern. Electrical resistivities were measured by the four-point probe method.

In the cross sectional SEM image after laser cutting, epitaxial layer of 0.1 mm thickness was observed.

Raman spectra of B-doped diamond growth layer, the broad peak at around 500, 1230 cm^{-1} and the weak peak at 1333 cm^{-1} were observed in each spectra. These peaks were due to high concentration boron inclusions.

As a result of Laue pattern from deposits, clear Laue pattern and weak halo pattern were confirmed.

As a result of the electrical resistivity measurements by the four-point probe method, the minimum electrical resistivitiy was 4.2×10^{-3} Ω･cm.

As a conclusion, single crystalline B-doped diamond was fabricated on HPHT diamond substrate. In the Raman spectra of the film, the peaks caused high boron inclusion were observed.

BP-28 Effects of the Reaction Gas Flow Rates on the Plasma State during Boron-doped Diamond Synthesis, ***Asuka Suzuki***, *Y Sakamoto,* Chiba Institute of Technology, Japan

Diamond has excellent physical and chemical properties such as high hardness, high thermal conductivity, optical transmission from UV to IR and chemical inertness. In addition, diamond is well known an electrical insulator with a resistivity order of 10^{16} Ω･cm. However it was changed to the semiconductor by inclusion of dopants such as boron or phosphorus. However, the liquid B source in the bubbling tank was evaporated at room temperature, it is difficult to control flow rates because it is introduced using H_2 carrier gas, and control range is so narrow. Towards further industrial applications, it is desirable to extend electrical resistivities range by using a relatively less toxic liquid B source. Application to a variety of electronic components to be able to safely control the volume resistivities of the B-doped diamond can be expected to spread.

The investigation was carried on the effects of the reaction gas flow rates on the plasma state during boron-doped diamond synthesis.

Boron-doped diamond films were synthesized using mode-conversion type microwave plasma CVD apparatus. Si substrate was scratched by diamond powder and then cleaned ultrasonically in acetone solution. Reaction gases were used CH_4 and H_2. Vapor of $B(OCH_3)_3$, the boron source, was introduced by H_2 carrier gas into the vacuum chamber. Their flow rate was $H_2/CH_4/H_2$ carrier=100/15/3, 200/30/6, 300/45/9 sccm , respectively pressure was 20.0 kPa and microwave power was 1.0 kW. Reaction time was fixed to 3h. During synthesis, plasma states were estimated using optical emission spectroscopy (OES) . The surface was observed by SEM. Qualities of the deposits were estimated by Raman spectroscopy. Volume resistivities were measured by the four-point probe method.

As a result of OES, the peaks of B(249nm), BH(433nm), BO(436nm), CH(387nm,431nm), H_α(656nm), H_β(486nm) and C_2(404nm, 406nm, 473nm, 516nm, 563nm, 619nm) were observed for each conditions. In the SEM observation, the grain sizes of deposits were 1 to 3 mm. In the Raman spectra of the deposits, the broad peak at about 500, 1230 cm^{-1} and the weak peak at 1333 cm^{-1} were obtained for each samples . These peaks due to inclusion of high concentration boron in the films. As a result of the electrical resistivity measurements by the four-point probe method, the minimum Volume resistivities of 0.2Ω ・ cm was obtained. With the reducing of B/Hα, BH/Hα and BO/Hα emission intensity ratio in emission spect ra, volume resistivity is reduced.

As a conclusion, relationship between volume resistivit ies of boron doped diamond and intensity ratio of B-system emissions in OES spectra was suggested.

BP-29 Effects of Pluse Frequency and Duty Cycle on Synthesis of Carbon Nitride using Pluse Microwave Plasma CVD, ***Koudai Yarita***, Chiba Institute of Technology, Japan; *I Tanaka,* Gifu University, Japan; *Y Sakamoto,* Chiba Institute of Technology, Japan

Carbon nitride has fascinated properties such as high hardness and high current density of field emission. In addition, if a β-C_3N_4 or c-C_3N_4 structure can be synthesized, it is possible to obtain a hardness higher than that of diamond. Our laboratory had investigated to obtain crystalline carbon nitride, and α-C_3N_4 was obtained from a CH_4 – N_2 reaction gas system by microwave plasma CVD. In addition, pulse plasma is possible to control the state of plasma such as electron temperature. Also, pulse microwave CVD is possible to vary particle size and density.

Investigation was carried out on the effects of pulse frequency and duty cycle on synthesis of carbon nitride using pulse microwave plasma CVD。

Carbon nitride was synthesized using an improved microwave plasma CVD apparatus equipped with a water cooled substrate holder and can be selected microwave radiation mode cw or pulse. Si was used as the substrate. A mixture of CH_4 and N_2 was used as a reaction gas system. CH_4 and N_2 flow rates were 2 and 200 SCCM, pressure was 4.0 kPa. The reaction time was 5h. The reaction time was at 5h and the peak microwave power was 1000W. Pulse frequency was varied from 30, 300 and 3000Hz, duty cycle was varied 30, 50 and 70%. The deposits were estimated by Scanning electron microscopy (SEM), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS). The plasma state was estimated by Optical emission spectroscopy (OES).

As a result of SEM observation, crystalline particles were obtained at pulse frequency of 30Hz, duty cycle of 50 and 70%, at frequency of 300 and 3000Hz, duty cycle of 30, 50 and 70%. However, Ball-like particles were obtained at pulse frequency of 30Hz and duty cycle of 30%. Particle densities were from 6.2×10^7 to 2.3×10^8 numbers/cm^2. Particle density was lowered with decreasing of duty cycle. As a result of Raman spectroscopy, the peak corresponding to Si was observed at pulse frequency of 30 to 3000Hz and duty cycle of 30 to 70%. On the other hand, the peak corresponding to amorphous carbon was observed at pulse frequency of 30Hz and duty cycle of 30%. As a result of XPS, the Si_3N_4 and C-N bond peaks were observed in at all sample. In OES spectra, the peak of CN radical emission was observed for all condition.

Examination result of effect of pulse frequency and duty cycle of microwave plasma on carbon nitride synthesis, crystalline carbon nitride was obtained proper synthesis condition. Also, Particle densities were about 6.2×10^7 to 2.3×10^8 numbers/cm^2. Particle density was lowered with decreasing of duty cycle.

BP-30 Duplex Coating of DLC on High Speed Tool Steel Substrates, *Y Kikuchi,* ***Ryohei Fujita****, Y Sakamoto,* Chiba Institute of Technology, Japan

Diamond-like carbon (DLC) is applied to a wide variety of fields in the industry because of its tribological properties and hardness. However, one of the major issues is the adhesion strength between DLC films and the metal substrate. Many efforts have been made to obtain a higher adhesion strength, such as the formation of an interlayer and the modification of the surface layer. In contrast, radical nitriding is one of the most suitable methods for the pretreatment of duplex coatings, because it possible to increase the surface hardness while maintaining the roughness of the original surface. According to this process, a diffusion layer is formed in the surface region using plasma state control.

High-speed tool steel was used as the substrate. A radical nitridation apparatus was used for the radical nitriding and PNC processes. The conditions for the radical nitriding process were a pressure of 133 Pa, an applied voltage of −380 V, an H_2 flow rate of 50 SCCM, an NH_3 flow rate of 50 SCCM, an external heater temperature of 843 K, and a processing of 60 min. The conditions for the PNC process after radical nitriding were a pressure of 532 Pa, an applied voltage of −380 V, an H_2 flow rate of 50 SCCM, an NH_3 flow rate of 50 SCCM, a CH_4 flow rate of 50 SCCM, an N_2 flow rate of 1 SCCM, an external heater temperature of 843 K, and processing times that were varied from 5 to 10 to 15 min.

After the plasma treatment process, the DLC film was coated onto the substrate using RF magnetron sputtering equipment. The target was graphite, the sputtering gas was Ar, the RF power was 50 W, the pressure was 0.4 Pa, and the processing time was 60 min, respectively. The DLC films were prepared after pre-sputtering under the same conditions for 10 min. The DLC film thickness was 300 nm.

DLC coated on an untreated substrate exhibited extensive delamination and micro-cracks that extended from the vicinity of the crater. High adhesion strength of DLC coatings on high-speed tool steel was accomplished via PNC treatments. In particular, PNC showed the best adhesion strength in this study at 5 min after radical nitriding.

Radical nitriding formed a nitrogen-diffusion layer, followed by the formation of a carbon layer by nitrocarburizing without the formation of a brittle compound layer. It maintained surface roughness compared with the untreated substrate. The resulting DLC films exhibited better adhesion to the treated-steel substrates than to the untreated ones.

BP-33 The Stability of Diamond-Like Coatings under Thermo-Mechanical Conditions, *Q Liu,* ***Xiaoying Li****, H Dong,* The University of Birmingham, UK

Diamond-like carbon (DLC) is an attractive carbon-based coating material for many applications due to their unique combination of low-friction, self-lubrication and high wear resistance in conjunction with good biocompatibility. However, the metastable nature of the amorphous structure restricts the wide application of DLC coatings under harsh conditions. Although there have been many reports on the thermal stability of DLC, limited or no work has been conducted to investigate the stability of DLC coatings under both thermal and pressure conditions.

This work presents a study on the stability of DLC coatings: a-C, a-C:H, a-C:Si and a-C:H:Si thermo-mechanical conditions using a hot isostatic pressure (HIP) furnace to apply both high-temperature and high-pressure. In order to investigate the influence of the applied pressure, thermal stability was also conducted by heating the DLC samples up to 600ºC in air and in argon without pressure. The microstructure of the as-deposited, heat treated and HIPped DLC samples were fully studied using XRD, Raman, FIB/SEM and XTEM; the change of their mechanical and tribological properties were investigated using nano-indentation and tribo-meters.

The experimental results reveal that the high isostatic pressure introduced during HIPping accelerated the graphitization process and hence reduced the stability of these DLC coatings at elevated temperature; the introduced isostatic pressure also reduced the adhesion between the top DLC coatings and the substrates. The mechanisms involved are discussed based on XTEM, XPS and Raman analysis.

BP-38 Growth of DLC Films on the Internal Surface of a Long Metallic Tube Using the PECVD Technique, *E Mitma Pillaca, M Ramirez Ramos, D Lugo González,* ***VladimirJesus Trava-Airoldi****,* National Institute for Spacial Research INPE, Brazil

Plasma Enhanced Chemical Vapor Deposition (PECVD) is a well established method for growing DLC films on substrate with complex shapes, in a fast and efficient way. By this technique, surfaces of mechanical components, for example, are protected from wear and corrosion due to excellent properties that feature this film. However, coating inside tube owns some disadvantages. For example, homogeneous deposition is usually difficult to be achieved in tubes with low aspect ratio. On the other hand, coating in long tubes (some meters) using plasma are not economically feasible due to need for vacuum chambers with greater dimensions than the own tube. In this work, a tube with 0.1 m diameter and 2 m length was prepared to be used as the own vacuum chamber for the growth of DLC film on its internal surface by PECVD technique. Electric tests were performed to study the response of discharge current, as a function of the gas pressure and of the applied voltage in Ar plasma. These results have shown that the plasma inside of the tube is sustained at pressure as low as 5 mTorr and at negative applied voltage as low as -400 V. Different conditions were figuring out for silicon deposition as an interface and also for DLC deposition. Thus, SiH_4 and C_2H_2 has been used as a precursor gas for the silicon and DLC films, respectively. Matching of some parameters in terms of inside pressure, applied bias voltage and gas flow were established in order to get the DLC films with good adhesion, high hardness and good structural quality. A 1500N indentation, nano indentation and Raman spectroscopy analysis has been confirmed the DLC properties deposited on Stainless Steel substrates placed along of the tube. The uniformity along of the tube of DLC films in terms of friction coefficient and growth rate is an important part of this study.

BP-39 Characterization and Tribologic Study in High Vacuum of Hydrogenated DLC Films Deposited using Pulsed DC PECVD System for Space Applications, *D Lugo González,* ***Marco Antonio Ramirez Ramos****, V Trava-Airoldi, P Santana da Silva, E Mitma P., E Corat,* National Institute for Space Research - INPE, Brazil*; C Rodriguez, N Fukumasu,* University of São Paulo, Brazil

DLC is a metastable form of amorphous carbon that has excellent properties such as high hardness, high elastic modulus, chemical inertness, high wear resistance, and low friction coefficient. DLC has been studied as a promising solid lubricant since liquid lubricants are ineffective and undesirable for many space applications. Solid lubricants require performing properly under space environment conditions, such as high vacuum. This paper reports the structure, morphology, adhesion, and high-vacuum tribologcal performance of DLC films with different hydrogen content. The films were deposited by pulsed DC PECVD technique with an additional cathode and using acetylene as a precursor gas. An amorphous silicon interlayer was deposited in order to guarantee the adhesion between coating and substrate. For the films characterization, Raman spectroscopy, Scanning Electron Microscopy (SEM), Rockwell C indentation test, and scratch test were performed. In addition, hydrogen content in the DLC films was determined by Elastic Recoil Detection Analysis (ERDA). Friction coefficient value and wear rate of DLC films in high vacuum

conditions were obtained applying loads of 2N and 5N at different sliding speeds. Results showed that DLC films deposited by pulsed DC PECVD can act as a space solid lubricant due to its low friction coefficient value, high adhesion and keeping its structural quality in high vacuum environment.

BP-40 Numerical Analysis on Gas-Pressure and Input-Power Dependence of Substrate-Incident Hydrocarbon Species in Tetramethylsilane Plasmas for Silicon-Containing Diamond-Like Carbon Thin-Films Coatings, ***Akinori Oda**, K Ohki,* Chiba Institute of Technology, Japan*; S Kawaguchi, K Satoh,* Muroran Institute of Technology, Japan*; H Kousaka,* Gifu University, Japan*; T Ohta,* Meijo University, Japan

Diamond-like carbon (DLC) films are the hydrogenated amorphous carbon films, which is composed of a mixture of sp^2- and sp^3-bonded carbon. Since this films have excellent material properties in high wear resistance, high hardness, low friction, and chemical stability, the films have been widely used for many technological applications such as automotive, semiconductors, medical devices, and so on. Recently, silicon-containing DLC (Si-DLC) films have been investigated, since the Si-DLC films with lower friction coefficient, compared with conventional DLC films, can be obtained. However, the effect of silicon in Si-DLC films on friction properties has not been clarified. Therefore, the understanding of fundamental properties in tetramethylsilane (TMS, $Si(CH_3)_4$) plasma, which are ion and radical source of Si-DLC films deposition, has been strongly required. Previously, our research group have developed a self-consistent one-dimensional fluid model of capacitively-coupled radio-frequency TMS plasmas, composed of the continuity equations for electron and sixteen TMS-derived ion species, the Poisson equation, and the electron energy balance equation, coupled with the Boltzmann equation solver. And then, the influence of process parameters (e.g. gas pressure, input power) on the plasma properties has been discussed. In this paper, in order to simulate the TMS plasma in realistic geometry (i.e. plasma chamber with realistic size), we developed the axially-symmetric three-dimensional fluid model of TMS plasma, and then examined the process parameter dependence of carbon-containing ion and radical fluxes onto substrate. As a result, it was clarified that three hydrocarbon ion species such as $Si(CH_3)_3^+$, $Si(CH_3)_4^+$ and $HSi(CH_3)_3^+$ are important and dominant ion species with higher density magnitude of 10^9 cm^{-3} in TMS plasma. Other simulation results will be presented in this conference. Acknowledgement: This work was partly supported by KAKENHI (No. 26420247).), and the MEXT-Supported Program for the Strategic Research Foundation at Private Universities 2013-2017 (s131104).

BP-41 The Effect of Substrate Bias on the Structure and Mechanical Properties of the a-C:N Films by a 90°-Bend Filtered Cathodic Arc Plasma (FCAP) System, ***Chih-Chiang Wang**,* National Chung Hsing University, Taiwan*; H Shih,* Chinese Culture University, Taiwan

The carbon-related materials have been attracting lots of attention for decades in flat panel display, optoelectronic devices, etc. due to their unique chemical, electronical, mechanical, and thermal properties. In this study, amorphous nitrogenated carbon (a-C:N) films have been prepared on silicon wafer at 800°C with varying substrate bias upto -650V in a 90°-bend filtered cathodic arc plasma (FCAP) system. The magnetic coil removes neutral carbon atoms and macroparticles from the plasma stream and in this case only the carbon arc discharge is available to form nitrogen ions. XRD showed the peak of (111) plane actually from the nanodiamond nucleated in the a-C:N films and agreed well with the result of HRTEM of d-spacing of 1.76 Å. The hardness of the resulting film was found to be 12.2GPa under an optimal bias of -350V.

The ratio of I_D/I_G of the Raman analysis increased to ~3.5 under the bias of -350V, indicating enriched sp^3-bonded carbon of the graphite domain. The FTIR spectra showed that the higher intensity at 1330cm^{-1} of D-band and 709 cm^{-1} of plane bending mode resulting from the graphite-like domains with N ions incorporated; more sp^3 bonds facilitated the completion of the nanodiamond structure. Binding energies of C1s, e.g., 287.6 (sp^3), 285.5 (sp^2), and 284.6 eV (free carbon), and N1s, e.g., 402.0 (N-O), 400.0 (sp^2), and 399.0 (sp^3) eV, have been resolved in the XPS spectra. The ratios of N/C were able to reach as high as 50% at -350V, indicating that higher substrate temperatures together with higher contents of nitrogen promotes the sp^3 clusters in the a-C:N films. These properties and the structure of the a-C:N film are sensitive to the energy of depositing C^+ and strongly dependent on the substrate bias.

BP-42 Stress Optimized Hard Nitride Coatings for High-performance Gear Hobbing, ***Martin Beutner**,* Otto von Guericke University, Germany*; A Lümkemann, M Morstein,* PLATIT AG – Advanced Coating Systems, Switzerland*; B Karpuschewski,* Otto von Guericke University, Germany*; M Jilek, Jr.,* PLATIT AG., Czech Republic*; T Cselle,* PLATIT AG – Advanced Coating Systems, Switzerland

In 2015 the automobile production and therefore also the transmission production exceeds the 90 million. Containing of several gears the manufacturing is of major importance. As the dominating green manufacturing process gear hobbing is applied the most. Here cutting conditions regarding chip thickness and cutting length change continuously within every generating position. Hence, the load at the cutting edge varies critically too and affects abrasive and crater wear on the tool. Nowadays gear hobbing is performed more and more without coolant which intensifies the thermal load and thus the wear phenomena.

To examine the performance of different coatings, cutting trials were carried out using the well-established fly-cutter analogy test. Subsequently the worn out single hob teeth are examined by REM and fringe projection to evaluate the wear phenomena.

To reduce crater wear and to extend the lifetime of gear cutting tools a range of AlCrN-based coatings was deposited in an industrial π411 rotating arc cathodes PVD unit. Significant performance differences between the chemically and structurally modified coatings were found. In this contribution the authors are focusing on the influence of the internal stress of AlCrN-based Hard Nitride Coatings on the wear behavior and tool life for both, high speed steel and solid carbide fly-cutters.

BP-43 Growth of B-Doped Diamond using Hot Filament CVD, ***Mai Imamiya**, Y Sakamoto,* Chiba Institute of Technology, Japan*; Y Takahashi, K Sugiura,* Material Processing Studio Co.,Ltd., Japan

Diamond has excellent physical and chemical properties such as high hardness, high thermal conductivity, optical transmission from UV to IR and chemical inertness. In addition, diamond is well known an electrical insulator with a resistivity of the order of 10^{16} Ω·cm. However it was changed to the semiconductor by inclusion of dopant such as boron or phosphorus.

However it was changed to the semiconductor by inclusion of dopant such as boron or phosphorus. Generally, diborane (B_2H_6) or trimethyl-boron {$B(CH_3)_3$} are used as dopant to synthesize boron-doped diamond. In this report, growth of B-doped diamond using Hot Filament CVD.

Hot Filament CVD was used for preparation of diamond. Reaction gases were used CH_4 and H_2. Boron sourse was trimethyl-boron. The synthesis pressure was 4.0 kPa, reaction time was 5 h and distance between the filament and the substrate was kept 8 mm. The surface morphologies of deposits were observed by SEM. Qualities of the deposits were estimated by Raman spectroscopy. Electrical resistivities were measured by the four-point probe method.

As a result of SEM observation, particle was about 1 μm in diameter. Crystal orientation of the deposits was (1 1 1) facet. In Raman spectra, of all the samples, the broad peaks at around 500cm^{-1}, 1230cm^{-1} and the weak peak at 1333 cm^{-1} were observed. These peaks due to the films includes of boron. As a result of the electrical resistivity measurements by the four-point probe method, the lowest electrical resistivitie was 1.6×10^{-4} Ω·cm.

As a result of investigation, boron-doped diamond films were fabricated using Hot Filament CVD and films were orientated to (1 1 1) facets. In the Raman spectra of the films, the peaks caused high boron concentrations were observed.

BP-44 Formation Of Anti-Reflection Double Layers For Si Lens By Atomic Layer Deposition, ***Jaeyeong Heo**, K Kim,* Chonnam National University, Republic of Korea

Increasing demand for mobile services like SNS and movies requires high-speed optical connectivity. In this regard, silicon (Si) photonics takes the center stage in which data is transferred among computer chips by optical rays. Optical transceiver is an integrated circuit that transmits and receives data using optical fiber. For optical transceiver, silicon has recently been highlighted as a material for optical coupling lens due to its low transmission loss and high refractive index. It is expected to increase the coupling efficiency further by fabricating a proper anti-reflection (AR) coating. First, we used Essential Macleod program to simulate the reflectance of single and double-layer anti-reflection coating. Then, we used atomic layer deposition for fabricating anti-reflection coating on Si substrates such as TiO_2 and Al_2O_3. Single layer and double-layer schemes

were compared. Detailed structural and optical properties of these AR coatings will be presented.

BP-45 Texture, Mechanical and Electrochemical Properties of Magnetron Sputtered $Cr_{1-x}W_xN/Si_3N_4$ Super Hard Nanocomposite Thin Films for Protective Coatings, ***Ravi Prakash***, *D Kaur,* Indian Institute Of Technology Roorkee, India

The effect of tungsten content in $Cr_{1-x}W_xN/Si_3N_4$super hard nanocomposite coatings deposited using reactive DC magnetron sputtering on the silicon substrate (100) has been investigated. The texture, surface morphology, hardness, young modulus and corrosion resistance were studied using X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), atomic force microscopy (AFM), nanoindentation and electrochemical potentiostat respectively. The XRD results show that the $Cr_{1-x}W_xN/Si_3N_4$solid solution formed with preferred orientations of dominant (111) and (200). The crystallite size initially decreased and the increased with the W content. The XRD peaks shifts towards higher angle with the increased as W content increases. Hardness and young modulus of films initially increase and then decrease with increasing tungsten concentration. The maximum values of hardness 42~45 Gpa and young modulus ~500 Gpa were found for tungsten content in the range 4-32 at %. Electrochemical studies of the films indicate that the best corrosion rate (38 nmy) was found at 43% of tungsten content which is excellent compared to other reported value. This study proposed that $Cr_{1-x}W_xN/Si_3N_4$nanocomposite thin films could have future potential as protective coatings.

BP-46 Internal Stress on Adhesion of Hard Coatings Synthesized by Multi-arc Ion Plating, *L Qiu,* ***Xiaodong Zhu***, *K Xu,* Xi'an Jiaotong University, China

Hard coatings have been widely employed in tools, dies and wear-resistant parts. Most commercial coatings are limit in a few microns due to the adhesion problem induced by the stress developed at the film/substrate interface during film deposition and subsequent cooling processes. The residual stress state is considered to be key factor governing the adhesion of thick hard coatings. It is significant to understand the relationship between the residual stress and the bonding strength of hard coatings.

In this work, one group of TiN coatings was prepared by multi-arc ion plating (MAIP). In order to investigate the influence of the residual stress on coating's adhesion, all coatings were synthesized with the same pretreatment and interlayer to obtain an identical interfacial state. During the coating deposition, the working pressure and bias voltage were varied respectively to obtain different residual stress. The average residual stress of the coatings was calculated from the bending deformation of the sliced steel substrate. The bias voltage is shown to have a strong impact on the residual stress of coatings. As the bias voltage increases from -10 V to -200 V, the residual stress increases from -1.8GPa to -3.2 GPa for the coatings with thickness of 10 µm, and the corresponding critical load by scratch test decreases from 60N to 40N. The working pressure is another important parameter that affects the residual stress. The stress level of the coating deposited under 6 Pa is -1.8 GPa in comparison to -2.2 GPa which deposited under 1 Pa, and the critical load by scratch is higher. Higher bias or lower working pressure may cause higher ion energy transferred to deposition ions, and produce fine grain structure.

Another group of TiN coatings with five thicknesses (3.7µm, 5.8µm, 9.7µm, 15.5µm and 25µm) was coated under same parameters and different deposition time. Low critical loads by scratch and indentation tests are obtained for the thick coating indicating the high interfacial stress, yet its average residual stress is lower. Finite element analysis was employed to reveal the stress at the interface. It is found that high residual stress results in a lager shear stress at the interface. This implies that the accumulated residual stress is more appropriate than the average one in characterizing the residual stress effect on coating adhesion for those with different thicknesses.

BP-47 Diamond-like Coatings using High Power Impulse Magnetron Sputtering, ***Tomas Kubart***, *A Aijaz,* Uppsala University, Sweden

Diamond-like carbon (DLC) coatings exhibit excellent mechanical, electrical and optical properties such as high hardness, low friction coefficient, high refractive index which make them attractive for a wide range of applications from cutting tools to engine components. The main limitations of existing DLC solutions stem from its high internal stresses and limited thermal stability. High internal stresses in excess of ~10 GPa limit the maximum achievable thickness due to poor adhesion and limited thermal stability makes DLCs unsuitable for high temperature applications. In order to address these issues, strategies for developing a new generation of DLC coatings exhibiting low-stresses, high hardness, good adhesion and good thermal stability are desired.

This work deals with the development of a deposition process for DLC coatings based on High Power Impulse Magnetron Sputtering (HiPIMS). We synthesize DLC coatings using Ne-based HiPIMS process to enhance the ionization of C. For comparison, plasma and film properties using standard Ar-HiPIMS process are also studied.

The plasma properties investigated by time-resolved Langmuir probe measurement reveal that Ne-based HiPIMS discharge provides high density plasma with higher electron temperature that entails a higher C^+ ion fraction as compared to Ar-HiPIMS discharge. A direct consequence of higher C^+ ion fraction is the higher mass densities (up to 2.7 g/cm^3) obtained using Ne-HiPIMS process. Surprisingly, even the Ar-HiPIMS process led to a pronounced increase in the density (2.5 g/cm^3) albeit lower than in in Ne-HiPIMS. Results from time-resolved behavior of electron temperature and plasma density are discussed with respect to the properties or resulting films for both process gases.

Acknowledgement: The work has been carried out in frame of M-Era.Net project TANDEM supported by VINNOVA.

BP-48 Synergistic Effect of Cu/Cr Co-doping on the Wettability and Mechanical Properties of Diamond-like Carbon Films, ***Lili Sun***, *P Guo, X Li, A Wang,* Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, China

By choosing carbide-forming element Cr and non-carbide-forming element Cu as co-doped metal elements, we firstly fabricated Cu and Cr co-doped diamond-like carbon (Cu/Cr-DLC) films using a facile hybrid ion beam deposition system. The effect of Cu/Cr co-doping on wettability and mechanical properties of DLC films were focused. The resultant Cu/Cr-DLC films were shown to afford good hydrophobicity and superior mechanical performance. In particular, the film with Cu11.88%Cr6.57% (at.%) exhibited a relatively high water contact angle of 103.6°, lower residual stress of 0.89 GPa and high hardness of 13.44 GPa. The combined structural analysis demonstrated that the synergistic Cu/Cr co-doping resulted in the critical and significant relaxation of distorted C-C bond length, which ultimately caused the reduction in residual stress. Due to the formation of hard Cr carbide nano-particles in amorphous carbon matrix, the films maintained the high value of hardness. Noted that the interesting wetting variety from hydrophilic to hydrophobic state was attributed to the enhanced surface graphitization and emergence of copper oxidation phases. The film topographical structure could also promote the hydrophobicity when the maximum height of roughness was in a certain range. These results provide an expected robust method to make DLC film a promising protective coating for long lasting hydrophobic application and related harsh fields.

BP-49 Novel Technology for ta-C Coatings Deposition, ***Jan Kluson***, *M Jilek, Jr.,* PLATIT a.s., Czech Republic

Platit presents a novel patented technology enabling to prepare ta-C coatings with their unique properties in industrial scale. The technology is based on the cathodic vacuum arc burning on the cylindrical rotary cathode. The achieved coatings are designated as DLC^3 and represent the 3rd generation in the Platit DLC family. These coatings are characterized by very high mechanical hardness around 80GPa. Measurements of microhardness were complemented with Raman spectrometry which revealed sp^3 to sp^2 ratio up to 85%. DLC^3 coatings are further characterized by very low friction coefficient and low roughness. The given parameters can be achieved with a new focusing magnetic field source PisCoat (Pi smooth Coating) for particle filtering. Various applications of the technology will be shown.

BP-53 Evaluation of Plant-Extract-Based Metallic Nanoparticles for Corrosion Inhibition of Metallic Component, ***Omotayo Sanni***, *A Popoola, O Fatoba,* Tshwane University of Technology, South Africa

Corrosion of metal is costly material science problems which originate from the day of metal discovery. Corrosion inhibitor usage is an effective way of addressing metallic corrosion in aggressive environments but continued usage of synthetic chemicals for inhibiting corrosion is indefensible as a result of toxicity of the chemicals to the environmental ecosystem. Eco-friendly corrosion inhibiting alternatives, including plant-extract usage, are therefore needed. Characterization of this nanoparticles material will be studied using. Ultra violet analysis, morphology by SEM-EDS and TEM analyses, phase composition by XRD analyses, inorganic element constitute analyses by RAMAN spectroscopy and organic element constituents' analyses by FTIR spectroscopy. Effect of the nanoparticles on metallic samples in different aggressive environment will be studied in the

laboratory using weight loss method. The samples exposed to the inhibitors showed a lower corrosion rate values and excellent polarization resistance as compared with the corrosion rate samples without inhibitor. Grey relational used in this research correspond with the experimental results.

BP-55 Deposition of Crystalline Cr_2O_3 Coatings by Reactive Radio-frequency Magnetron Sputtering, *M Mohammad Taheri, Q Yang,* ***Jesus Corona Gomez,*** University of Saskatchewan, Canada

Reactive radio-frequency magnetron sputtering technique was employed to study the deposition conditions for crystalline chromium oxide films with Cr_2O_3 stoichiometry. Chromium oxide coatings with a thickness of 1-2 micrometers were deposited on Silicon wafers under various oxygen partial pressures and substrate temperatures. The effect of deposition parameters on the chemical composition, crystal structure, microstructure, phase composition, and hardness of coatings were investigated by electron dispersive spectroscopy, X-ray diffraction (XRD), scanning electron microscope, Raman spectroscopy, and nanoindentation, respectively. Crystalline coatings obtained by increasing the oxygen flow rate or the substrate temperature, however vitrification of coatings was triggered again by flowing more oxygen. No coatings could be deposited at temperatures higher than 300 ° C due to volatilization behavior of chromium oxides at high temperatures. The results illustrated that pure crystalline Cr_2O_3 coatings with highest hardness could be obtained at a substrate temperature of 300 ° C and an oxygen content of 6 vol. %.

BP-56 Cerium Doping of Ti-Al-N Coatings for Excellent Thermal Stability and Oxidation Resistance, *H Asanuma,* Mitsubishi Materials Corporation, Japan*; P Polcik, S Kolozsvári,* Plansee Composite Materials GmbH, Germany*; F Klimashin, H Riedl,* ***Paul H. Mayrhofer,*** Institute of Materials Science and Technology, TU Wien, Austria

Ti–Al–N thin films are well established due to their outstanding thermo-mechanical properties. Nevertheless, this system is still a subject of many research activities to further enhance their oxidation resistance and thermal stability. The addition of reactive elements, such as Cerium, can significantly improve especially the oxidation resistance of various materials. Therefore, we study in detail the impact of Ce (2 at% alloyed to powder metallurgically prepared $Ti_{0.50}Al_{0.50}$ targets) on growth processes, structure, mechanical properties, thermal stability, and oxidation resistance of magnetron sputtered $Ti_{1-x-y}Al_xCe_yN$ coatings prepared with DC bias potentials of U_{bias} = -25, -50, -75, and -100 V. The deposition rate is significantly increased by a factor of ~1.75 (U_{bias} = -25 V) to 1.45 (U_{bias} = -100 V) when using $Ti_{0.49}Al_{0.49}Ce_{0.02}$ instead of $Ti_{0.50}Al_{0.50}$ targets. Furthermore, also the hardness of the resulting single phase face centered cubic $Ti_{0.43}Al_{0.55}Ce_{0.02}N$ is with ~35.2 GPa above that of $Ti_{0.42}Al_{0.58}N$ with ~33.7 GPa, for coatings on polycrystalline Al_2O_3 and U_{bias} = -50 V. Coatings on steel substrates typically show ~5 GPa higher values.

All temperature dependent characteristics of $Ti_{0.42}Al_{0.58}N$ are improved significantly by the addition of Cerium. Wurtzite-structured AlN formation within $Ti_{0.43}Al_{0.55}Ce_{0.02}N$ can only be detected at T_a = 1100 °C, about 200 °C higher as for $Ti_{0.42}Al_{0.58}N$. Their peak-hardness, due to spinodal decomposition of the supersaturated cubic phase is ~37.0 GPa with T_a = 900 °C, as compared to 34.6 GPa with T_a =800 °C for $Ti_{0.42}Al_{0.58}N$. Additionally, even after exposure to ambient air at 950 °C for 3 h, still > 50 % of the $Ti_{0.43}Al_{0.55}Ce_{0.02}N$ coating is intact (below the ~1.2 µm thin oxide scale), whereas $Ti_{0.42}Al_{0.58}N$ is already fully oxidized.

Based on our results we can conclude, that Ce-doping improves the deposition characteristics and mechanical properties as well as thermal stabilities (incl. oxidation resistance) of Ti–Al–N, to be used as protective coatings for a wide range of high-demanding applications.

BP-57 Arc Evaporated W-alloyed Ti-Al-N Coatings for Improved Thermal Stability, Mechanical, and Tribological Properties, *S Glatz,* Institute of Materials Science and Technology, TU Wien, Austria*; H Bolvardi,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; S Kolozsvári,* Plansee Composite Materials GmbH, Germany*; C Koller,* ***Helmut Riedl,*** Institute of Materials Science and Technology, TU Wien, Austria*; P Mayrhofer,* Christian Doppler Laboratory for Application Oriented Coating Development at the Institute of Materials Science and Technology, TU Wien, Austria

The protection of various tools and components through wear resistant coatings is imperative in highly efficient and precise industrial manufacturing processes. Especially, physical vapour deposited $Ti_{1-x}Al_xN$ and $Cr_{1-x}Al_xN$ coatings have been commonly used as hard protective coatings due to their outstanding thermal stability and mechanical strength. However, to increase the applicable working temperatures by simultaneously enhancing the wear performance (e.g., to allow for higher cutting speeds) further improvements are required.

Therefore, we studied in detail the impact of tungsten (W)—in combination with the substrate bias potential (U_{bias})—on the thermo-mechanical properties and wear performance of arc evaporated

$Ti_{1-x-y}Al_xW_yN$ thin films. With increasing W content the quality of our coatings significantly increases due to pronounced reduction of growth defects (quantity of macro particles). All coatings studied crystallise in a supersaturated, single-phased face-centred cubic $Ti_{1-x-y}Al_xW_yN$ structure and their hardness (H) increases whereas the indentation modulus (E) decreases with increasing W content. This results in increased H^3/E^2 values, with a maximum of 0.19 GPa for $Ti_{0.50}Al_{0.41}W_{0.09}N$ prepared with U_{bias} = -120 V (H ≈ 35 GPa, E ≈ 483 GPa). All W-alloyed coatings exhibit wear rates below $2 \cdot 10^{-5}$ mm^3/Nm during our dry sliding pin-on-disk tests against alumina balls at room temperature, with a tendency for reduced values if more droplets are present. The highest thermal stability, with respect to the decomposition of the supersaturated $Ti_{1-x-y}Al_xW_yN$ phase towards the stable constituents (at high temperature) TiN, AlN, and W, is obtained for $Ti_{0.53}Al_{0.42}W_{0.05}N$ prepared with U_{bias} = -80 V. Here, the formation of the wurtzite-structured AlN can be delayed to 1000 °C after 60 min lasting isothermal annealings in vacuum.

Fundamentals and Technology of Multifunctional Materials and Devices
Room Grand Exhibit Hall - Session CP
Symposium C Poster Session

CP-1 Reversible Photo-Induced Deformation of Amorphous Carbon Nitride Films and their Potential Application to Light Driven Actuators, *T Harata, M Aono, K Ishii, N Kitazawa,* ***Yoshihisa Watanabe,*** National Defense Academy, Japan

Amorphous carbon nitride (a-CNx) films are known as useful coating materials. Recently, we first observed reversible photo-induced deformation of hydrogen-free a-CNx films under visible light illumination [1]. This phenomenon suggests that the a-CNx films have potential applications to light driven actuators. In this paper, we report fundamental studies for applying a-CNx films to light driven actuators.

The hydrogen free a-CNx films were prepared by reactive radio frequency magnetron sputtering using a graphite target and pure nitrogen gas. The substrate temperature during deposition was kept at 573 K. The substrates used were silicon single crystal plate with the thickness of about 0.5 mm. The self-standing a-CNx film with the thickness of about 1 µm was obtained by peeling the deposited film from the Si substrate in pure water. The diaphragm with the diameter of 4.6 mm was prepared by sandwiching the self-standing a-CNx film between metal rings and the movement of the diaphragm was measured using a laser vibrometer under white light illumination.

The photomechanical response was measured when the light illumination is turned on and off with the interval of 15 s, and the results show that the diaphragm reiterates stably and the typical amount of the displacement was about 120 µm. These results suggest that the a-CNx films have potential for light-driven actuators with good stability.

The authors would like to thank Keyence Corporation for helping the laser vibrometer measurements. This research is supported by JSPS KAKENHI Grant Number 26790054.

[1] M. Aono, T. Harata, N. Kitazawa, Y. Watanabe, Diamond & Related Materials **41** (2014) 20-24.

CP-2 Mechanisms of Grain Growth Enhancement in Sintered-CZTS Nanoparticle Thin Films, ***Edgar Palmes,*** *S Exarhos, R Xu, L Mangolini,* University of California, Riverside, USA

An innovative and scalable synthesis approach to the formation of Cu_2ZnSnS_4 (CZTS) nanocrystals has been developed using aerosol spray pyrolysis. This quaternary-phase material is a potential replacement for currently commercialized semiconductors such as CdTe and CIGS that are currently used in photovoltaic devices. However, sustainability and environmental issues threaten long-term viability of these materials. Based upon earth abundant constituents and low chemical toxicity, CZTS, with a reported band gap of ~1.5 eV, appears to be a superior alternative to these other materials. Additional research and development is necessary to increase the efficiency of CZTS-based cells from the current record (12.6% by Wang *et al.*[1]) to the >18% necessary to be considered commercially

viable. Our work stresses the controllable, cost-effective, and reproducible synthesis of high-quality CZTS nanoparticles and sintered thin films. Specifically, our goal is to demonstrate increased crystal grain growth in CZTS needed for higher efficiency rates of CZTS-based cells. Incorporating alkali dopants, specifically sodium, has been successful in enhancing grain growth in CZTS thin films [2]. However, current methods of sodium doping primarily rely on imprecise external diffusive sources such as sodium halides, sodium hydroxides, or the use of soda lime glass. Based off of work by Tiong *et al*., who experimented with controllably doping sodium into CZTS films via dipping in sodium halide solutions [3], we show further results of attempting to control sodium composition by coating the surface of CZTS nanoparticles with a controlled amount of sodium hydroxide – our group has also shown that the introduction of an oxide to the surface of CZTS nanoparticles can also enhance uniform grain growth. The coated particles are then dispersed into a CZTS nanoparticle ink, coated onto a sodium-free substrate, mechanically compacted, and annealed at 600 ºC for 1 hour in a low pressure sulfur atmosphere. The resulting material is extensively characterized to determine morphology, composition, and structure.

[1] Wang, Wei, Mark T. Winkler, *et al*. "Device Characteristics of CZTSSe Thin-Film Solar Cells with 12.6% Efficiency." Advanced Energy Materials 4, no. 7 (2014).

[2] Johnson, M., S. V. Baryshev, *et al*. "Alkali-Metal-Enhanced Grain Growth in Cu2ZnSnS4 Thin Films." Energy & Environmental Science 7, no. 6 (2014): 1931-38.

[3] V. Tiong, T. Hreid, *et al*. "Morphology evolution and stability of Cu_2ZnSnS_4 nanocrystals in sodium halide salt solution." Thin Solid Films, Vol. 615 (2015).

CP-3 Development of Dual Coating Process for Effective Combination of Sand Mold Process and 3D Printing Technique, ***Hyun-Hee Choi**, H Park, E Tumenbayar, G Cho, E Kim, Y Jung,* Changwon National University, Republic of Korea*; J Zhang,* Purdue University, USA

In a conventional sand casting, the mold is prepared by mixing silica-based starting powders with resin-based organic binders. Therefore, the mold collapses easily by the degradation of the organic binders during casting. Nevertheless, the sand mold has been widely used in the manufacturing industry due to its simplicity and low production cost. In this work, a dual coating process is developed to combine the sand mold process and 3D printing technique. Two types of polyvinyl alcohol (PVA) with the different boiling points were applied. In the dual coating process, the starting powder was coated with PVA with the lower boiling point, and then re-coated with PVA with the higher boiling point, followed by 3D printing process. The sample was heat-treated at 250C for 4h in order to burn out the PVA with the lower boiling point. The heat-treated sample was dipped into an inorganic binder slurry, composed of tetraethyl orthosilicate (TEOS) and sodium methoxide (NaOMe), which are the silica (SiO_2) and sodium oxide (Na_2O) precursors, respectively. After dried at 80C for 1h, the final heat-treatment was conducted at 1000C for 1h for organic-inorganic conversion. The green and firing strengths were much enhanced compared with the conventional converting process, which are due to the increased amount of inorganic precursor causing a sol-gel reaction for the green strength, and the glass phase converted by the inorganic precursor filled in the spaces of the evaporated PVA and coated on the surfaces of particles for the firing strength. Relationship between the coating process and the strength was extensively discussed, including applicability of dual coating process into 3D printing technique.

CP-4 New Converting Process for Fabrication of Ceramic Core through 3D Printing Technique, ***Hye-Yeong Park**, H Choi, E Tumenbayar, G Cho, E Kim, Y Jung,* Changwon National University, Republic of Korea*; J Zhang,* Purdue University, USA

In a conventional converting process, the core green body prepared with starting powder and organic binder, generally called as resin, is directly dipped in the inorganic binder precursor. However, the process reduces the content of inorganic precursor by the organic binder filled on the interface between the starting particles, resulting in reduced mechanical properties of the core. In this work, a new converting process combined with 3D printing technique has been developed to fabricate core samples. The new process allows to provide sufficient amount of inorganic binder on the particle surface and at the interface between particles. Two types of poly vinyl alcohol (PVA), which have the same molecular structure with a large difference in the boiling point, were used as an organic binder. Green body with the two kinds of PVA was 3D printed, and then heat-treated at 250℃ to evaporate the PVA with the lower boiling point. The heat-treated core samples were dipped into the inorganic precursor, and dried and heat-treated at 1000℃ for organic-inorganic converting process. T his series of new processes could enhance the fracture strength of core owing to the increase of the inorganic precursor infiltrated in spaces/sites of the evaporated PVA. In the new converting process, the formability of core sample was induced through the organic compounds remained and inorganic binder penetrated between particles and/or coated on the particle surfaces, and the firing strength is attributed from the glass phase generated by the inorganic precursor. Therefore, the formability and firing strength of core prepared through the new process were favorably improved. This means it would be readily applied to the production of core using 3D printing techniques, without further shrinkage in heat treatment at high temperature.

CP-7 Bias-photo Stability of Hafnium-aluminum-zinc-oxide Thin Film Transistors, ***Ju-Hee Park**, S Lee, H Jun, J Park,* Hanyang University, Republic of Korea

Amorphous oxide semiconductors (AOSs) have demonstrated their advantages as applications for flat panel displays (FPDs) due to their electrical performance, transparency in visible light, and room-temperature deposition. Oxygen vacancies in AOS materials play the role of generating carriers and thus provide a conducting path and at the same time, they are components that may deteriorate the stability of the AOS-based thin film transistors (AOS-TFTs) by forming defects. To improve the stability of AOS-TFTS, the oxygen vacancies have to be reduced. Recently, a number of studies regarding the incorporation of materials with a low standard electrode potential (SEP) into AOS materials, such as yttrium (Y), hafnium (Hf), and zirconium (Zr), have been reported. Particularly, Hf has a lower SEP (- 1.56 eV) than that of Zn (- 0.76 eV) and HfO_2 has a larger bandgap (5.8 eV) than that of ZnO (3.3 eV). Thus, the addition of Hf to the indium-zinc-oxide (IZO) system is expected to control the electrical characteristics of the films and improve the stability of TFTs by controlling oxygen vacancies. Recently, K. Ghaffarzadeh et. al. introduced TFTs using hafnium-indium-zinc-oxide (HIZO) as an active layer. They showed that the stability of the HIZO TFTs due to bias-stress and photo-stress was improved as a result of the reduced interface charge trapping. However, when Hf is used in TFTs, it may decrease the channel mobility due to the reduction of carrier concentration, leading to the significant decrease of the on-current. Furthermore, the In element used in the HIZO TFTs is an earth-rare material. For this reason, some studies without using In in AOS-TFTs have recently been reported to aim at maintaining high channel mobility.

In this study, we have fabricated a TFT using the channel layer with a hafnium-aluminum-zinc-oxide (HAZO) thin film in order to enhance the device performance and stability. The HAZO films were deposited on SiO_2/Si substrates at room-temperature via co-sputtering where separate targets of hafnium-oxide and aluminum-zinc-oxide were used. The structural, optical, and electrical characteristics of HAZO films were evaluated using various methods, such as X-ray diffraction (XRD), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), UV/visible spectrophotometer, Hall measurements, and I-V characteristics analyzer. The electrical characteristics of the HAZO-TFTs as well as the stability of the devices due to bias-photo stress were also analyzed as functions of Hf and Al contents.

CP-11 Electrical and Magnetic Properties of (Al, Co) co-doped ZnO Films Deposited by RF Magnetron Sputtering, ***Yu-Wei Lin**, S Chen,* Ming Chi University of Technology, Taiwan*; H Sun,* Ocean University of China, China*; C Wang,* Ming Chi University of Technology, Taiwan*; C Wen, T Chuang,* National Taiwan University, Taiwan*; X Wang,* Ocean University of China, China

In this work, (Al, Co)-ZnO films were co-sputtered on glass substrate through radio frequency sputtering at 100 °C. The film's structure, electrical and magnetic properties as a function of Al doping content is investigated. The results indicate that (Al, Co)-ZnO films crystallinity can be suppressed by Co doping or (Co, Al) co-doping. With the substitution of Zn by Al , the film's conductivity improves. All the films present ferromagnetic behavior at room temperature. With increasing Al doping amount, the film's saturation magnetization expresses a carrier-concentration dependent behavior. Three different regions can be defined, where BMP model and carrier-mediated exchange mechanisms play a role in the various regions.

CP-13 Development of Low Temperature TiO_2 Mesoporous Scaffold for Perovskite Solar Cells, ***Gwomei Wu**,* Chang Gung University, Taiwan

Perovskite solar cells have become attractive candidates for modern thin-film photovoltaic devices due to their high performance and promising cost-competitiveness. The prevailing fabrication methods involve spin-

coated materials and vapor-deposited thin films. They are much less expensive than the high-vacuum deposition equipments used in the semiconductor industry. The organic-inorganic hybrid solar cells combine a mesoporous scaffold, a perovskite light absorber and an organic hole transporter. However, it requires a high annealing temperature up to 500℃ to sinter the mesoporous layer. Thus, it is interesting to develop lower temperature processing schemes by different chemical sources for the solution spin-coating techniques. The different film-forming characteristics should be investigated. In this report, TiO2 nanoparticles could be coated from a binder-free colloid to form the mesoporous scaffold with low processing temperature. The different chemical formulations were prepared for solution-processed spin-coatings on glass substrates. The low temperature processed multi-layered photovoltaic structures were examined and presented in this study. This work was supported in part by the Ministry of Science and Technology under research grants MOST105-2221-E182-059-MY3 and NERPD2E0481.

CP-15 Atmospheric Plasma Deposition of Oxide Semiconductors, ***Blake Emad***, University of Dayton, USA; *J Ferguson,* Materials and Manufacturing Directorate, Air Force Research Laboratory, USA; *C Muratore,* University of Dayton, USA

Atomic layer deposition (ALD) is unsurpassed as a technique for application of uniform, conformal, and continuous thin films on a broad range of useful substrates, especially those with ultra-high aspect ratios or complex morphologies, as the precursors are in the gas phase and easily fill all spaces with characteristic lengths greater than 0.5 nm. Three principal shortcomings of conventional ALD include: (1) reliance on vacuum pumps to reduce the pressure in the growth chamber and pull gas in resulting in long individual half cycle times—many of which are required to apply films of appreciable thickness (~50 nm), (2) contamination from precursor gas reactions that only proceed to a fraction of total completion, and (3) challenges (high temperature, high vacuum, containment within vacuum reaction vessel, etc.) associated with integration into additive manufacturing which could lead to custom components with integrated antennas and other device functionality especially in components employing conformal nature of the ALD coatings. Novel atmospheric plasma-based processes for synthesis of semiconducting oxides such as ZnO, GaO, IGZO (indium gallium zinc oxide) are presented. Techniques include a rapid ALD process where gas is cycled thru microvolumes adjacent to the substrate, rather than filing and vacating an entire processing chamber with the necessary series of vapor phase precursors to increase the effective growth rate of materials substantially. The precursors are selected so gaseous byproducts after ALD film formation are safe for exposure to open air. Results from optical spectroscopy of the atmospheric plasma processes is presented to demonstrate relationships between process characteristics and the structure and composition of the materials. For example, the degree of ZnO crystallization will play a critical role in its transport properties, and will therefore be thoroughly characterized using Raman spectroscopy and X-ray diffraction. The composition will first be measured with XPS, which has a resolution of approximately 1 atomic percent. Once contaminants are below this level, property measurements will be most useful for understanding atomistic-scale defects such as impurity atoms or vacancies. Nanocrystalline ZnO grown via pulsed laser deposition is a semiconductor material reported to possess high charge mobility (>100 cm^2 V^{-1} s^{-1}), an extremely high on/off ratio (>10^{12}), and be useful for high frequency (500 MHz) device operation. These parameters set the baseline for our comparisons of atmospheric pressure plasma enhanced ALD, where the aim is to match or surpass these values of mobility, on/off ratio, and maximum operating frequency.

CP-18 Structural and Magnetic Properties of Perovskite $SrMnO_3$ Thin Films Grown by Molecular Beam Epitaxy, ***Jiawei Bai,*** East China Normal University, China

In this work, we report the structural and magnetic properties of the ~30 nm epitaxial (001) $SrMnO_3$ thin films grown on (001) $SrTiO_3$ substrate by molecular beam epitaxy (MBE). In situ reflection high energy electron diffraction (RHEED) intensity oscillation is used to precisely adjust the stoichiometry by tuning the shuttered time during the growth. The structural properties of the $SrMnO_3$ thin film is characterized by atomic force microscopy (AFM), X-ray diffraction (XRD) and transmission electron microscopy (TEM). The surface of the thin film with obvious steps is observed to be atomically flat. The epitaxial single crystal $SrMnO_3$ thin film which is grown along the direction of (001) STO substrate is typical cubic crystal structure. The film is confirmed to be four-fold symmetric along the <001> azimuth by X-ray diffraction ϕ scan. The XRD reciprocal space map indicates that the $SrMnO_3$ thin film is fully strained in the present thickness. Due to the tension strain, the $SrMnO_3$ film exhibits ferromagnetic behavior while the bulk $SrMnO_3$ is antiferromagnetic at the same low temperature.

CP-19 Yb-doped Zinc-Tin-Oxide Thin Film and its Application to Solar Cell, ***Youngsang Park,*** *W Kim,* Yeungnam University, Republic of Korea; *G Ferblantier, A Slaoui, A Dinia,* CNRS-Université de Strasbourg, France; *H Jung, S Alhammadi, S Kwon,* Yeungnam University, Republic of Korea

The use of rare earth elements with semiconductor materials has attracted a lot of interest due to its unique properties. In this paper, we investigated ytterbium(Yb)-doped zinc tin oxide (Yb:ZTO) thin film characteristics and its application to a potential down-converter of Cu(InGa)Se2 (CIGS) thin-film solar cells. Yb:ZTO thin films were deposited by reactive sputtering of Zn and Sn metal with an oxygen flow. A few pieces of Yb were embeded in Zn metal target and thus Yb elements were supplied during Zn sputtering process. The relatively composition of Zn and Sn was controlled by changing the sputtering power(10-70W) of Sn with the fixed sputtering power for Zn(70W). Also, the substrate temperature varied from room temperature to 400 degC. It was confirmed that smaller amount of Sn with lower sputtering power led to more incorporation of Yb into ZTO. The X-ray photoelectron spectroscopy analysis confirmed that incorporation of Yb in ZTO, and photoluminescence measurement demonstrated Yb emission. The glazing incidence X-ray diffraction showed the shift of ZTO peaks induced by the difference in composition of Zn and Sn. Finally, CIGS solar cells with a Yb:ZTO layer have been fabricated. The results suggested that cells with the highest Yb PL emission showed the highest short circuit current density and cell efficiency.

CP-20 Mo-patterning on Graphene-coated Glass Substrate for a Bifacial Cu(InGa)Se2 Thin Film Solar Cell, ***Dohyun Park,*** *W Kim,* Yeungnam University, Republic of Korea

The Molybdenum (Mo) has been used as a back-contact electrode for high-performance chalcopyrite Cu(InGa)Se2 (CIGS)-based thin film solar cells, which were recently reported to have the world-record cell efficiency of 22.7 % (ZSW, 2016). The substrate-type typical CIGS cell structure is glass/Mo/CIGS/CdS/ZnO. In this paper, to investigate the feasibility of CIGS cell for the application to bifacial solar cells, Mo layer has been patterned and a few layers of transparent conducting graphene were inserted to glass/Mo interface yielding glass/graphene/Mo(patterned) substrate. The graphene sheets grown on Cu foil by chemical vapor deposition were transferred to glass substrates by a simple wet-based graphene transfer process. Then, Mo was deposited onto glass/graphene by DC sputtering. The diverse design of Mo patterning for light transparency was achieved by using custom-designed masks during Mo deposition. It was confirmed that glass/graphene/Mo thin films showed lower sheet resistance than glass/Mo samples, and the sheet resistance was monotonically decreased with the number of graphene layers inserted. The resulting CIGS device results will be also discussed.

CP-21 Enhanced Stability of Plasmonic Metal-dielectric Thin Films by CVD Grown Graphene Transfer, *T Del Rosso, Q Zaman, E Cardona Romani, F Lazaro Freire Jr., O Pandoli, R Queiroz Aucélio,* ***Marco Cremona,*** Pontifícia Universidade Católica do Rio de Janeiro, Brazil

The major problem to practical application of plasmonic devices is the chemically instability of the metal-dielectric interfaces which easily oxidize and degrade influencing the performances of the thin film plasmonic substrates [1]. Here we use angle interrogation scheme of Surface Plasmon Resonance spectroscopy to study the stability of plasmonic devices constituted by metal-dielectric thin films covered with graphene grown by CVD on copper foil [2]. The gold (Au) and silver (Ag) thin films deposited on glass slides functionalized with (3-ercaptopropyl) trimethoxysilane were monitored by AFM measurements up to 24 hours, in order to observe the morphological changes of the metal surfaces during the interaction with atmosphere.

Taking advantage of the high impermeability property of graphene to gases and liquids [3], we demonstrate that a graphene on metals substrates can be used to prevent it from chemical reactions and degradation of the adhesion of the metal deposition over the glass substrates. Raman spectroscopy has been used to verify the existence and quality of graphene after transfer process over gold and silver thin films.

The stability measurements where performed in atmosphere, and are based on the monitoring of SPR angle and full width half maximum (FWHM) during time.

Our results demonstrate that graphene protected gold (Au) and silver (Ag) depositions exhibit greater stability as compared to unprotected samples (exposed to air), similar to the one associated to samples protected by

typical OLEDs encapsulation technique [4]. We observed a shift in the SPR angle of about 0.005^0 for Ag /graphene and Au/graphene samples after 4 hours of observation. Such a change is comparable to the zero angle determination and limits the time interval useful for the characterization of thin films in air. Similar results were obtained for graphene covered dielectric loaded waveguides (DLWGs).

The presented stability enhancement is very important both for the graphene optical characterization [5] as well as to the use of graphene in biosensing application [6].

1. V. G. Kravets, R. Jalil, Y.-J. Kim et al., Scientific Reports, 4 (2014) 05517.

2. X. Li, L. Colombo, R. S. Ruoff, Adv. Mater. 28 (2016) 6264.

3. Y. Su, V.G. Kravets, S.L. Wong, J. Waters, A.K. Geim, Nature communication 5 (2014) 4843.

4. T. Del Rosso, J. E. H. Sanchez, R. Dos Santos Carvalho, O. Pandoli, M. Cremona, Optics Express 22 (2014) 18915.

5. H. Jussila, H. Yang, N. Granqvist, Z. Sun, Optica 3 (2) (2016) 151–158.

6. O. Salihoglu, S. Balci, C. Kocabas, Appl.Phys. Lett. 100 (2012) 213110.

CP-23 Optical Characterization and Structural of ZnO Thin Film Prepared by Reactive Electron Beam Evaporation with Ion-Assisted Deposition from Metal Zinc, ***Hung-Pin Chen**, W Cho,* Instrument Technology Research Center, National Applied Research Laboratories, Taiwan*; C Lee,* National Central University, Taiwan*; Y Lin,* National Tsing Hua University, Taiwan*; C Hsiao,* Instrument Technology Research Center, National Applied Research Laboratories, Taiwan

Zinc oxide thin films were fabricated by reactive electron beam evaporation with ion assisted deposition using metal zinc as a starting material. The transmittance spectra were measured by a UV/VIS/NIR spectrometer and the optical constants of the Zinc oxide films were calculated from the transmittance spectra using envelope method. The refractive indices were close to bulk value of 2 and the extinction coefficients were lower than $1x10^{-3}$ in the visible light ranges when the substrate temperatures exceeded 200°C. After annealing at 600°C for 2 hours in air, the extinction coefficients of Zinc oxide films prepared at room temperature increased as the annealing temperature increased, especially in short wavelength region. The ZnO films prepared at high temperatures exceeding 200°C were polycrystalline and had a preferred orientation of (100).

CP-24 Opto-electrical Properties of Few-layer $ReSe_2$ FETS for Phototransistors, ***DongJin Lee**, M Yoo, N Kim, G Cho, P Ko,* Chosun University, Republic of Korea

The two-dimensional (2D) materials, including graphene, h-BN, layered transition metal–chalcogenides (TMC) and layered transition metal-dichalcogenides (TMDCs), are the next generation of the opto-electronic devices. Ultra-thin devices based on the 2D materials still under development, and many of the 2D materials remained almost unexplored field. Recently, there have been reports on photodetectors based on multilayered 2D materials such as GaSe, $MoSe_2$, WSe_2 et al. In this research, we fabricated field-effect transistor (FET) based on few–layered $ReSe_2$ on substrate (Ti / p–Si / SiO_2). The electrodes (Ti) deposited by electron-bean (EB) evaporation at room temperature on silicon substrates (doped p+, conductivity: 0.003 – 0.007 Ω cm) covered with 300 nm of thermally oxidized silicon dioxide (SiO_2). The thickness of the $ReSe_2$ flake was measured by atomic force microscopy (AFM) using a Pico plus 5500 AFM (Agilent Technologies, USA). The electrical characterization was carried out using Semiconductor Parameter Analyzer 4155-A (Hewlett Packard, USA). The layered $ReSe_2$ phototransistors were high values, underscoring that $ReSe_2$ is a promising 2D material for phototransistor applications. Acknowledgement: This work was supported by the Korea Institute of Energy Technology Evaluation and Planning(KETEP) and the Ministry of Trade, Industry & Energy(MOTIE) of the Republic of Korea (No. 20164010201020).

CP-28 UV Photosensitivity in Metal-Oxide-Semiconductor Structures based on SiO_x Films containing Si Nanoparticles, *M Curiel, **Oscar Perez**, N Nedev,* Universidad Autónoma de Baja California, Mexico*; D Nesheva,* Institute of Solid State Physics, Mexico*; B Valdez,* Universidad Autónoma de Baja California, Mexico*; E Manolov,* Institute of Solid State Physics, Mexico*; A Arias, D Mateos,* Universidad Autónoma de Baja California, Mexico*; O Contreras,* Universidad Nacional Autonoma de Mexico, Mexico*; V Dzhurkov,* Institute of Solid State Physics, Mexico*; R Nedev,* Universidad Politecnica de Baja California, Mexico*; J Paz,* Universidad Autónoma de Baja California, Mexico

Metal-Oxide-Semiconductor (MOS) structures using SiO_x films as gate insulators are promising for application in different types of optoelectronic devices. In this work we present results for the effect of UV light on the electrical characteristics of MOS structures containing crystalline or amorphous Si nanoparticles in the gate insulator.

SiO_x films with thickness of ~50 nm and various compositions, x varies between 1.15-1.5, were deposited by thermal evaporation in vacuum on n-type crystalline Si. After the deposition the samples were annealed at temperatures in the 250 - 1000 °C range for 30, 60 and 120 min. High temperature annealing at T ≥ 700 °C leads to formation of amorphous and/or crystalline Si nanoparticles in SiO_x layers. The formation of nanocrystals in the samples annealed at 1000 °C was verified by Transmission Electron Microscopy (TEM) and X-ray Photoelectron Spectroscopy (XPS). High resolution TEM images revealed that the nanocrystal size depends on the composition and the annealing time; for example, samples with x = 1.15 and 1.3 annealed at 1000 °C for 60 min exhibit nanocrystals with diameters of approximately 4 and 6 nm, respectively. The XPS results showed that the annealing at 1000 °C leads to complete phase separation and formation of Si in SiO_2.

Lateral currents between two metal contacts on the top of the Si/SiO_x structure were measured in dark and under visible and UV light illumination. The dark and visible light I-V characteristics coincide, while the UV light leads to an increase of the current through the structure. The UV effect is more pronounced with the increase of the annealing temperature. The observed effect may be explained assuming UV light assisted transport between neighbor nanocrystals of electrons injected from the crystalline silicon wafer.

The obtained results indicate that the studied SiO_x layers have a potential for application in UV sensors.

CP-29 Photoresponse and Electrical Properties for Photodiodes from Graphene Oxide (GO), ***Asmaa Hendi**,* King Abdulaziz University, Saudi Arabia

The nanocomposites of zinc oxide/graphene oxide (ZnO-GO) were synthesized to fabricate the photodiodes. The ZnO-GO/p-Si and ZnO-GO/n-Si diodes were prepared for various GO contents. The electrical characteristics of the ZnO-GO/p-Si and ZnO-GO/n-Si diodes were analyzed under dark and light illuminations. The photocurrent of ZnO-GO/p-Si and ZnO-GO/n-Si diodes increases with increasing GO content.

The ZnO-GO/p-Si diode having 0.03 M ratio of GO:ZnO exhibited the highest photoresponsivity with 0.5 A/W under 100 mW/cm2. It is evaluated that ZnO-GO composites can be used in fabrication of high photo sensitivity diodes.

Coatings for Biomedical and Healthcare Applications
Room Grand Exhibit Hall - Session DP
Symposium D Poster Session

DP-2 Bone-like Nano-hydroxyapatite Coating on Low-modulus Ti-5Nb-5Mo Alloy Using Hydrothermal and Post-heat Treatments, *H Hsu, S Wu, S Hsu,* Central Taiwan University of Science and Technology, Taiwan*; C Hsu,* Da-Yeh University, Taiwan*; **Wen-Fu Ho**,* National University of Kaohsiung, Taiwan

Titanium and its alloys have been widely used as biomaterials for orthopedic and dental implants because of their excellent biocompatibility and mechanical properties. However, they are considered to be bioinert, such that when they are inserted into the human body these implants cannot bond directly to the surrounding living bone. This study aimed to improve the bioactivity of a low-modulus Ti-5Nb-5Mo alloy with a hydroxyapatite (HA) surface coating using eggshells as a Ca source through hydrothermal reaction and heat treatment. The results showed that the whole alkali-treated alloy surface was covered with amorphous calcium

phosphate nanoparticles after hydrothermal reaction at 200 °C for 48 h. When subsequently heat-treated at various temperatures (400, 500 or 600 °C) for 48 h, the surface coating of Ti-5Nb-5Mo alloy was transformed into crystalline rod-like HA nanoparticles. Also, heat treatment enhanced the adhesion between the HA coating and the Ti alloy substrate. Additionally, FTIR analysis confirmed the production of HA containing mixed AB-type carbonate substitutions. To evaluate bioactivity of the bone-like HA-coated Ti-5Nb-5Mo alloy, the capability of calcium phosphate apatite formation on the alloy surface was assessed by immersion in a simulated body fluid (SBF). Dune-like apatite layer was observed to densely deposit on the surface of HA-coated Ti alloy after 6 h of immersion in the SBF. Notably, the ability of Ti-5Nb-5Mo alloy subjected to sequential process with alkali, hydrothermal, and heat treatments to form bone-like HA nanoparticle coating was obviously greater than that of its counterpart without HA coating.

DP-3 Niobium Oxide Scaffolds on Nb and on TNZT for use in Bone Implants, ***Madelyn Kramer,*** University of North Texas, USA*; E Leveque,* University of Rouen, France*; J Barclay, S Aouadi, M Young,* University of North Texas, USA

In this study, a TNZT alloy composed of Ti-35Nb-7Zr-5Ta in at.% and pure niobium were comparatively tested for their ability to grow nano-scaffolds on the surface for biomedical applications such as implant devices. The TNZT alloy was made by vacuum arc melting; and then rolled into a plate where it was subsequently sectioned and cut. The TNZT and niobium samples were polished flat, ultrasonically cleaned, and underwent hydrothermal treatments to grow nano-scaffolds of oxides on the surface. The TNZT and niobium produced Nb_2O_5 nano-scaffolds from a hydrothermal reaction in varying alkaline solutions: KOH at 170°C and NaOH at 60°C. Oxide scaffolding was also created when samples were annealed in air at 900°C for 2 hours. The TNZT and niobium nano-scaffolds were characterized by scanning electron microscopy (SEM). The nano-scaffolds will be characterized by X-ray diffraction (XRD) and Raman spectroscopy and will be further examined in simulated body fluid to further assess their biocompatibility.

DP-6 Muti-functional Porous TaOxNy Film Deposited on Ta/TaN-Ag Layers Prepared by Co-sputtering and De-alloying Approach, *J Hsieh,* ***ChungChieh Hsu,*** *Y Lin,* Ming Chi University of Technology, Taiwan

The oxynitride of a transition metal is able to form a new grade of functional thin film. In this study, TaOxNy-Cu films were first prepared using reactive co-sputtering, with the variation of O/N flow ratios. After deposition, the films were annealed, and Cu was etched away to form porous oxynitride structures with various O/N ratio. These porous films were then built on Ta/TaN-Ag layers, in order to induce antibacterial behavior and improve biocompatibility. The films were characterized using nano-indentation, XRD, and SEM. The results showed that the porosity of these films could be varied depending on Cu contents and O/N ratios. The samples were then tested for their biocompatibility and viability using MG-63 cells, and for the antibacterial efficiency against E. coli. According to the results obtained from biocompatibility and MTT assay testing, it was found that the pore size (or roughness) played a major role in terms of biocompatibility and cell viability. The antibacterial efficiency depends on the temperature and time of the second rapid thermal annealing.

DP-7 Increased Ag+ Dissolution Rate of TaN-Ag Nanocomposite Thin Films by Air Atmospheric Pressure Plasma Jet, *J Hsieh,* ***Yi-Zheng Yang,*** *C Lin,* Ming Chi University of Technology, Taiwan

The present study was aimed at activating nano-sized Ag particles emerged on TaN-Ag thin films by air atmospheric pressure plasma jet (APPJ). It was proved that the dissolution rate of Ag NPs could be accelerated, and bactericidal efficiency could be enhanced. In the experiment, TaN-Ag thin films were prepared by reactive co-sputtering, followed by rapid thermal annealing. The annealed films were then treated in either dry or wet (immersed in buffer solution) environments by APPJ. It is found, after activation, the dissolution rate of Ag ions could be increased significantly. Hence the antibacterial efficiency was increased tremendously.

DP-8 Tribocorrosion Behaviour of DLC-Coated Ti-6Al-4V Alloy Deposited by PIID and PEMS+PIID Techniques for Biomedical Applications, ***Andre Hatem,*** Pontifícia Universidade Católica do Paraná, Brazil*; J Lin, R Wei,* Southwest Research Institute, USA*; R Torres, C Laurindo, P Soares,* Pontifícia Universidade Católica do Paraná, Brazil

One of the main drawbacks observed from the usage of titanium alloys implants is premature failure due to excessive wear and corrosion. These often lead to a total revision arthroplasty and also may expose human body to noxious elements if they are present in the implant alloy composition. Recently, new deposition techniques and coating compositions have been emerged targeting higher mechanical, microstructural and tribocorrosion properties on the implant surfaces. Diamond-like carbon (DLC) appears as a considerable coating option in this case, since it has an amorphous structure chemically inert composed by two types of carbon hybridizations (sp^2 and sp^3) that provides an extreme hardness, low friction coefficient, biocompatibility and still is a solid lubricant. The tribocorrosion behaviour of DLC films are influenced by the fraction between sp^2 and sp^3 bonds contained in the coating microstructure. Nonetheless, not only the bonds fraction affects this behaviour, but also the adhesion between coating and substrate to avoid its detachment, which in turn is strongly related to the applied deposition technique. Moreover, carbide and nitride interlayers are often deposited over substrate to favoring the DLC coatings adhesion. Among the advanced DLC deposition techniques are the plasma immersion ion deposition (PIID) and the plasma enhanced magnetron sputtering (PEMS). Both are examples of the plasma enhancement during film vapor depositions that results in coatings with higher density and adhesion when compared to other conventional techniques. This work aims to investigate the tribocorrosion behaviour of DLC coatings with distinct carbide and nitride interlayers, obtained by PIID only and PEMS+PIID hybrid techniques, applied on Ti-6Al-4V alloy samples for biomedical applications. The tribocorrosion tests were performed under phosphate-buffered saline (PBS) solution on the DLC-coated samples and compared to a Ti-6Al-4V bare alloy sample. Besides tribocorrosion tests, it were performed X-ray diffraction (XRD) analysis, Raman spectroscopy, scanning electron microscopy (SEM), nanoindentation hardness and scratch tests to evaluate the microstructure, morphology, mechanical properties and adhesion of the DLC-coated samples. The tribocorrosion tests demonstrated that the applied deposition techniques and interlayers compositions affect not only the adhesion but also the main wear mechanism, which implies in significant wear rate disparities between the DLC-coated samples. Nevertheless, the results show that DLC coatings deposited by the plasma enhanced techniques could be promissory to improve tribocorrosion behaviour in Ti-6Al-4V alloy implants.

DP-9 Fluorine-Incorporated Hydrogen-free Amorphous Carbon Thin Film for Artificial Heart (Ventricular Assist Device), ***Shunto Maegawa,*** Keio University, Japan*; T Hasebe,* Tokai university, Japan*; M Nakayama, K Bito, Y Yamato,* Keio University, Japan*; T Mine, T Matsumoto,* Tokai university, Japan*; A Hotta, T Suzuki,* Keio University, Japan

Advanced blood-contacting medical devices has been more intensive for reducing the mortality rate of cardiovascular diseases. Surface coating is one interesting method of improving the mechanical, physical and biocompatible properties of devices in direct contact with blood and tissue. Fluorine-incorporated hydrogenated amorphous carbon (a-C:H:F) has received much attention as a coating material because of outstanding blood compatible properties which suppress fatal failure of the devices. However, mechanical strength of a-C:H:F film is too low to apply for mechanical medical devices such as blood pump of ventricular assist device (VAD). Thus, fluorine-incorporated hydrogen-free amorphous carbon (a-C:F) films were newly synthesized with vacuum arc deposition method focused on both blood compatibility of a-C:H:F and excellent mechanical properties of hydrogen free tetrahedral amorphous carbon (ta-C). In this study, we evaluated the possible medical applications of new a-C:F films for frictional parts of blood pump in VAD.

The ta-C (control) and a-C:F films were deposited by filtered cathodic vacuum arc (FCVA) method using a graphite target and introducing C_3F_8 gas into the chamber. We synthesized these films by varying the pressure of C_3F_8 gas to control fluorine content in the films. The fluorine content of the film surfaces was measured by X-ray photoelectron spectroscopy. Carbon bonding structure was analyzed with Raman spectroscopy. Blood compatibility was evaluated by human platelets adsorption tests, and ball-on-disc tests were used to measure friction coefficient (f) for evaluating wear resistant properties. Finally, we applied a-C:F film on blood pump of ventricular assist device.

The fluorine content rate increased from 10 to 50 at.% with increase of C_3F_8 gas pressure. The shift of G peak position in the Raman spectra became lower with increase of fluorine content, and no peaks was identified at 50 at.% fluorine content as usual in a polymer-like film. The a-C:F films containing fluorine content reduced platelets adhesion than ta-C films. On the other hands, much fluorine doping in ta-C simultaneously degrade wear resistant ability. However, friction coefficient of a-C:F films with fluorine content of 10 and 30 at.% (f = 0.121, 0.138, respectively) were greater than

or equal to ta-C (f = 0.138). We applied 10 at.% a-C:F on frictional parts of VAD, and consequently improved driving of VAD without frictional wear.

In conclusion, the fluorine-incorporated hydrogen-free amorphous carbon (a-C:F), which we newly developed by using FCVA method, is a promising candidate for frictional parts of blood-contacting medical devices.

DP-10 A Sustainability Investigation on the Hemocompatibility of Heparin/Dopamine and Heparin/Collagen Self-Assembled Multilayers Coated on a Titanium Substrate, *W Cherng,* Chang Gung Memorial Hospital, Taiwan; ***Chau-Chang Chou***, *Y Pan,* National Taiwan Ocean University, Taiwan; *C Yeh,* Chang Gung Memorial Hospital, Taiwan; *T Wu, Z Dong, J Ho,* National Taiwan Ocean University, Taiwan

This work used self-assembly technology to build a heparin/collagen and a heparin/dopamine multilayers on a titanium substrate. Both the coatings' hemocompatibility and adhesion were investigated. The substrate was commercial pure grade 2 titanium which was electropolished for 48h. The oxidation condition of the dopamine interlayer was achieved by being treated treating in a 2 mg/ml dopamine solution under an atmospheric environment for 8 h. After the pretreatment, the samples were immersed in a poly-L-lysine solution for 30 minutes. Then they were alternatively dipped in a heparin and a collagen solutions for 30 minutes . On the other hand, in a heparin and a dopamine solutions to for 30 or 60 minutes until the desired number of layers were achieved. The hydrophilicity, chemical composition, and surface topography of the films were investigated by water contact angle measurement, Fourier transform infrared spectroscopy, and scanning electron microscopy. The film thickness was evaluated by the cross-sectional technique of a focused ion beam microscopy. The amount of the heparin that attached to the samples was measured by toluidine blue O test. The hemocompatibility was verified by the hemolysis ratio, platelet coverage area, and activated partial thromboplastin time (APTT) in vitro. The adhesion of the multilayers was studied by conducting micro-scratch tests. To investigate the performance under dynamic fluid contact, an orbital shaker was implemented. At dynamic environment state, the heparin quantity which was derived by the toluidine blue O test and APTT were assessed after dynamic test. Experiment results show that, the blood compatibility of heparin/dopamine sample is not superior than heparin/collagen one. Moreover, heparin/dopamine multilayers have stronger binding between multilayers and the substrate while not be capable of improving blood compatibility of titanium substrate. However, the extend of coating time are not conducive for the improvement of the related performance. After the dynamic tests, basing on the comparison of residual heparin content, dopamine is capable of resisting physiological fluid shearing stress, but the capability of anticoagulation are no more significantly enhanced from the original Ti substrate, which is worthy of more extensive investigation in the future.

DP-11 Wear Characteristics of Total Ankle Joint Prosthesis with Their Surface Roughness, *Y Jeong,* ***Jae-Woong Yang***, *K Park, S Lee, T Jung,* Osong Medical Innovation Foundation, Republic of Korea

The ankle joint consists of the tibia and fibula above, and the talus below. In the disabling conditions, total ankle replacement (TAR) is becoming an alternative to arthrodesis, i.e. fusion of the tibio-talar articulation, which implies long immobilization, loss of function, and a variable rate of success. This short comings of ankle fusion have led to the development of numerous ankle joint replacements. The conventional type of prosthesis is the three component prosthesis, have a free gliding core and give multi-axial motion, which designs the upper articulation allows for gliding and rotation and the lower articulation allows for flexion/extension. In spite of the increasing interest in TAR, the high failure rate associated with wear of the PE component that has related with their material property and surface roughness. The aim of this study was to verify the wear characteristics of total ankle joint prosthesis with their surface roughness.

The wear specimen of total ankle joint prosthesis was prepared with Ti-6Al-4V alloy and UHMWPE (ultra-high molecular weight polyethylene) for tibia-talus and bearing component, respectively. A wear test was carried out using a Force 5 (AMTI, Massachusetts, US) wear simulator which can be allowed to move in three axis to flexion-extension, internal-external axial rotation, as well as sinusoidal compressive load. All tests were performed following standard ISO 14243, wear rate was calculated with weight loss of UHMWPE bearing while the specimen has tested at certain cycles. The surface roughness by wear simulation cycles was measured using a SJ-411 surface roughness tester (Mitutoyo, Yokohama, Japan).

As based on the preliminary results, wear rate of UHMWPE bearing was 7.9 × 10^{-6} mg/cycles. The surface roughness (Ra) of tibia-talus increased (0.05 to 0.1) with accumulation of simulation cycles while that of bearing component decreased (1.0 to 0.65).

Acknowledgement: This research was supported by a grant of the Korea Health Technology R&D Project through the Korea Health Industry Development Institute (KHIDI), funded by the Ministry of Health & Welfare, Republic of Korea (grant number HI15C2149).

Keywords: Total Ankle Joint Prosthesis, Wear, Simulation, Surface Roughness, Biomaterials

DP-12 2D Materials for Bioelectronic Sensing, *W Lai,* University of Dayton/Sensors Directorate, Air Force Research Laboratory, USA; *A Stroud,* Institute for Micromanufacturing/Physics Program, Louisiana Tech University, USA; *R Berry,* Materials and Manufacturing Directorate, Air Force Research Laboratory, USA; *P DeRosa,* Institute for Micromanufacturing/Physics Program, Louisiana Tech University, USA; *R Naik,* Human Effectiveness Directorate, Air Force Research Laboratory, USA; ***Christopher Muratore***, University of Dayton, USA

Detection of compounds in liquids (such as sweat or saliva) and vapors (such as air in a workplace, a packaged food container, or the cockpit of a fighter jet) has broad reaching applications in industry, home, and battlefield. Analytical devices such as mass spectrometers or gas chromatographs can be used in these applications but they lack portability and the ability to operate continuously yet unobtrusively. Flexible sensor materials could be wearable or otherwise easily integrated into any of the environments suggested above. Mono- and few-layer TMDs are known to demonstrate extreme mechanical flexibility, accommodating up to 10% strain prior to rupture. In addition to convenient form factors afforded by their flexible nature, the high surface to volume ratio of ultrathin semiconducting materials allows detection of very low concentrations of adsorbed molecules via a measurable alteration of their electrical response (e.g., their current-voltage (IV) curve) as if they are "doped" by the presence of surface adsorbates. While the effects on adsorbate-surface relationships in graphene could be understood in context of decades of studies of p-based interactions dictating nanomaterial behavior, 2D TMD interactions are based on d-electron interactions and therefore respond much differently than carbon-based low-dimensional structures to adsorption events and other interactions with molecules. Non-covalent bonding on 2D TMD is only understood qualitatively. Measuring the response in materials with controlled densities of defects introducing localized metallic-like regions of exposed Mo plane-edge atoms and changing the 2D MoS_2 electronic band diagram systematically as predicted by simulations.will provide insight on charge transfer or redistribution in analyte-functional molecule-2D semiconductor interactions. We have demonstrated attachment of a binding peptide to a functional MoS_2 transistor, and observe a significant response in the I-V characteristic curve. Sensitivity to adsorbed molecules for semiconducting 2D TMDs such as MoS_2 is approximately two orders of magnitude higher than graphene based on the predicted minimum subthreshold swing (SS), defined as the inverse of the slope of a transistor IV curve in its steepest part (for a field effect transistor (FET), $SS=d(V_{gate\text{-}source})/d(I_{drain})$. Smaller values of SS suggest higher sensitivity as a small change in surface potential gives rise to a significant change in current, thus enhancing sensitivity. For 2D MoS_2, the SS is around 60 mV/decade in contrast to 1000-5000 mV/decade minimum for graphene, suggesting >100 X higher sensitivity for TMD-based 2D sensors in comparison to graphene.

DP-13 Study of TiO_2-MgO Composites to Improve the Corrosion Resistance of Mg for Development of Biodegradable Orthopedic Implants, ***EricNoé Hernández-Rodríguez***, *C Vicencio-Acosta, C Íñiguez-Contreras, A Balvantín-García, J Diosdado-de la Peña,* DICIS, University of Guanajuato, Mexico; *R Mis-Fernández, J Peña-Chapa,* CINVESTAV-IPN Mérida, Mexico; *M Zapata-Torres,* CICATA-IPN Legaria, Mexico; *A Márquez-Herrera,* DICIVA, University of Guanajuato, Mexico

In this work we report the study of TiO_2-MgO composites as anticorrosive coatings on Mg substrates. Mg has been extensively studied in order to develop biodegradable implants, however, the fast degradation in the physiological fluid is its main disadvantage. Here, we propose the use of the biocompatible TiO2-MgO composite as a protective coating in order to modulate the corrosion resistance of Mg pieces. TiO_2-MgO composites were deposited on Mg substrates by the RF-sputtering technique, and the TiO_2/MgO ratio was changed through the sputtering power. XRD analysis showed that coatings with a high content of MgO present a cubic crystalline structure, while a decrease on the crystallinity was found as the TiO2 content is increased; finally, coatings with the highest content of TiO_2 are amorphous. XPS analysis showed the formation of Ti-O, Mg-O and Ti-

Mg-O bonds; the rate between this bonds is related to the resistance against corrosion of the samples. Corrosion experiments were conducted by using the Hank´s solution as the corrosive media and Tafel curves were obtained by employing a potentiostat in the three electrode configuration. Values of corrosion current (i_{corr}) demonstrate that it is possible to improve the corrosion resistance of Mg by employing the TiO_2-MgO composite; even more, the TiO_2/MgO rate on the coatings permits to modulate the corrosion resistance, with the lowest resistance when the coating is only composed by MgO, and the highest resistance when only the TiO_2 is present.

This work is supported by PRODEP-SEP under project number UGTO-PTC-540.

DP-15 Fabrication and Characterization of Magnesium Incorporated Hydroxyapatite on the Titanium Substrates via Electrochemical Deposition, *Y Chor,* National Taipei University of Technology, Taiwan*;* ***Chien-Ming Lei,*** Chinese Culture University, Taiwan*; S Chen, K Huang, P Chen,* National Taipei University of Technology, Taiwan

Titanium and its alloys have been widely used for biomedical implant due to their desirable mechanical properties, corrosion resistance, and excellent biocompatibility. However, titanium and its alloys have an issue of their insufficient bioactivity. Recently, studies have shown that hydroxyapatite coated metal surface can improve both biocompatibility and bioactivity.

Hydroxyapatite is the major composition in tooth and bone. Compared to synthetic hydroxyapatite, natural bones have various trace elements which play important roles for cell growth. Magnesium incorporated hydroxyapatite stimulate the proliferation of osteoblast during the early stage of implantation. It has a significant effect in bone metabolism. In this study, magnesium ion was added into the electrolyte which composed of P and Ca ions, and then MHA coatings on titanium substrate were prepared by electrochemical deposition. We carried out characterizations to identify the phase composition, the changes of surface morphology, surface roughness and corrosion resistance of coatings in the simulating body fluid. Results show that magnesium incorporated hydroxyapatite has higher surface roughness and corrosion current density. Moreover, the magnesium incorporated hydroxyapatite can induce nucleation and growth of the new apatite on the surface where $Ca_3(PO_4)_2$ precipitates can be found after immersion test. As a result, the magnesium incorporated hydroxyapatite shows better biocompatibility and bioactivity.

DP-16 Electrochemical Characteristics of RF-sputtered Zn and Si Coatings on HA Coated Ti-6Al-4V by PEO Treatment, ***InJo Hwang,*** *H Choe,* Chosun University, Republic of Korea

Commercially pure titanium (cp-Ti) and Ti alloys (typically Ti-6Al-4V) display excellent corrosion resistance and biocompatibility. Ti and its alloys are not bioactive. Therefore, they do not chemically bond to the bone, whereas they physically bond with bone tissue. Their poor surface biocompatibility, the surface of Ti alloys has to be modified to improve the surface osteoinductivity. Among various surface modification methods, the electrochemical deposition process provides an effective surface for biocompatibility because large surface area can be served to cell proliferation. Plasma electrolyte oxidation (PEO) enables control in the chemical composition, porous structure, and thickness of the TiO_2 layer on Ti surface. In addition, previous studies have concluded that the presence of Ca^{+2} and PO_4^{3-} ion coating on porous TiO_2 surface induced adhesion strength between Hap and Ti surface during electrochemical deposition.

Radio frequency(RF) magnetron sputtering in the various PVD methods has high deposition rates, high-purity films, extremely high adhesion of films, and excellent uniform layers for depositing a wide range of materials, including metals, alloys and ceramics like a hydroxyapatite. The aim of this study is to research the Zn and Si ions coatings on the micro-pore formed Ti-6Al-4V alloys by RF-magnetron sputtering for dental applications.

Silicon (Si) in particular has been found to be essential for normal bone and cartilage growth and development. Zinc (Zn) plays very important roles in bone formation and immune system regulation, and is also the most abundant trace element in bone. The objective of this work was to study electrochemical characteristics of RF-sputtered Zn and Si coatings on HA coated Ti-6Al-4V by PEO treatment.

The coating process involves two steps: 1) formation of porous TiO_2 on Ti-6Al-4V at high potential. A pulsed DC power supply was employed. The sparking energy also will affect the size of micro pores and the ions concentrations. 2) Electrochemical tests were carried out using potentiodynamic and AC impedance methoeds. The morphology, the chemical composition, and the micro-structure analysis of the sample were examined using FESEM, EDS, and XRD. The enhancements of the Hap forming ability arise from Si/Zn-TiO_2 surface, which has formed the reduction of the Si/Zn ions. The promising results successfully demonstrate the immense potential of Si/Zn-TiO_2 coatings in dental and biomaterials applications (Supported by NRF: 2015H1C1A1035241 & NRF: No.2008-0062283 ; hcchoe@chosun.ac.kr).

DP-18 Nucleation and Growth of Bone-like Apatite Formation on Ti-6Al-4V in Solution Containing Mn, Mg, and Si Ions after Plasma Electrolytic Oxidation, ***SangGyu Lim,*** *H Choe,* Chosun University, Republic of Korea

Titanium and its alloys that have a good biocompatibility, corrosion resistance, and mechanical properties such as hardness and wear resistance are widely used in dental and orthopedic implant applications. They can directly connect to bone. However, they do not form a chemical bond with bone tissue . Plasma electrolytic oxidation (PEO) that combines the high voltage spark and electrochemical oxidation is a novel method to form ceramic coatings on light metals such as titanium and its alloys . This is an excellent reproducibility and economical, because the size and shape control of the nano-structure is relatively easy.Silicon (Si), m anganese (Mn), and magnesium (Mg) has a useful to bone. Particularly, Si has been found to be essential for normal bone, cartilage growth and development. Manganese influences regulation of bone remodeling because its low content in body is connected with the rise of the concentration of calcium, phosphates and phosphatase out of cells. Insufficience of Mn in human body is probably contributing cause of osteoporosis. Pre-studies have shown that Mg plays very important roles in essential for normal growth and metabolism of skeletal tissue in vertebrates and can be detected as minor constituents in teeth and bone.

The objective of this work was to study nucleation and growth of bone-like apatite formation on Ti-6Al-4V in solution containing Mn, Mg, and Si ions after plasma electrolytic oxidation. Anodized alloys was prepared at 270V~300V voltages. And bone-like apatite formation was carried out in SBF solution for 1, 3, 5, and 7 days. The morphologies of PEO-treated Ti-6Al-4V alloy in containing Mn, Mg, and Si ions were examined by FE-SEM, EDS, and XRD (Supported by NRF: 2015H1C1A1035241 & NRF: No.2008-0062283 ; hcchoe@chosun.ac.kr).

DP-19 Ion Release of Zn, Si, Mn-doped Hydroxyapatite Films Formed on the Ti-6Al-4V Alloy by Plasma Electrolytic Oxidation, ***MinGyu Park,*** *H Choe,* Chosun University, Republic of Korea

Titanium and its alloys have been used in the fields of orthopedics and dentistry due to their abilities to exhibit high specific strength, high corrosion resistance, and chemical inertness particularly in biological circumstances. Despite these attractive properties, their passive films were somewhat bioinert in nature so that sufficient adhesion of bone cells to implant surface was delayed after surgical treatment. Recently, the Plasma electrolyte oxidation (PEO) of titanium metal has attracted a great deal of attention.

Silicon (Si) in particular has been found to be essential for normal bone and cartilage growth and development. Zinc (Zn) plays very important roles in bone formation and immune system regulation, and is also the most abundant trace element in bone. Manganese(Mn) is important in terms of protein synthesis, the manganese is insufficient, the generation of cartilage synthesis of the organic matrix is low is delayed, thickness and length decreased abnormal bone generation is performed. Si, Zn, and Mn has a beneficial effect on bone.

The objective of this work was research on i on r elease of Zn, Si, Mn-doped h ydroxyapatite f ilms f ormed on the Ti-6Al-4V a lloy by p lasma e lectrolytic o xidation. Anodized alloys was prepared at 270V~300V voltage in the solution containig Zn, Si, and Mn i ons. Ion release test was carried out using potentidynamic and AC impedance method in 0.9% NaCl solution. The surface characteristics of PEO treated Ti-6Al-4V alloy were investigated using XRD, FE-SEM, AFM and EDS(Supported by NRF: 2015H1C1A1035241 & NRF: No.2008-0062283 ; hcchoe@chosun.ac.kr [mailto:hcchoe@chosun.ac.kr]).

DP-20 Nanotube Shape Changes on Ti-30Nb-xTa Alloys with Continuously Changed Potentials, ***Han-Cheol Choe,*** Chosun University, Republic of Korea

CP-Ti and its alloys have over the past few decades become the premier choice as biocompatible dental and hip replacement implant materials. Although the Ti-6Al-4V alloy is an acceptable prosthetic biomaterial, recent studies indicated that the release and accumulation of Al and V ions could have harmful effects on the human body. In order to overcome these disadvantages of Ti-6Al-4V alloy, new β type Ti alloy made of non-toxic

alloying elements such as Nb, Ta and Zr have been developed. Surface modification is generally essential to improve the chemical bonding between Ti implant and bone tissues. Thus, it has been shown that nano-scale porous as well as tubular oxide layers on titanium alloys can increase the bioactivity of an implant material. Also, it should be possible to control the nanotube size and morphology for biomedical implant use by controlling the applied voltage, alloying element, current density, anodization time and electrolyte. The aim of this study was surface modification of nanotube formed Ti-30Nb-xTa alloys with changes in anodization factors. The Ti-30Nb-xTa alloys with Ta contents of 0, 15 wt. % were melted by using a vacuum arc-melting furnace and, homogenized for 12h at 1000℃. The anodization was performed by changing of applied voltage from high to low (30 V to 10 V) and, from low to high (10 V to 30 V) for 1h. The electrolyte was composed of 1 M H_3PO_4 + 0.8 wt.% NaF. This study was evaluated the phase of Ti-30Nb-xTa alloys using an x-ray diffractometer (XRD), and the microstructure of the samples was investigated with field emission scanning electron microscopy (FE-SEM) and optical microscope (OM). For biocompatibility, fibroblast cell was cultured and contact angle was measured. (NRF: No.2008-0062283; hcchoe@chosun.ac.kr).

DP-21 Shapes of Bone-like Apatite Formation on Sr and Si-doped Hydroxyapatite Surface of Ti-6Al-4V Alloy after Plasma Electrolytic Oxidation, ***Ji-Min Yu***, *H Choe,* Chosun University, Republic of Korea

Metallic biomaterials have been mainly used for the fabrication of medical devices for the replacement of hard tissue such as artificial hip joints, bone plates, and dental implants. Because they are very reliable on the viewpoint of mechanical performance. This trend is expected to continue. Especially, Ti and Ti alloys are bio- inert. So, they do not chemically bond to the bone, whereas they physically bond with bone tissue. For t heir poor surface biocompatibility, the surface of Ti alloys has to be modified to improve the surface osteoinductivity. Recently, ceramic-like coatings on titanium, produced by plasma electrolytic oxidation (PEO), have been developed with calcium- and phosphorus-enriched surfaces. A lso included the influences of coatings, which can accelerate healing and cell integration, as well as improve tribological properties. However, the adhesions of these coatings to the Ti surface need to be improved for clinical use.

Particularly Silicon (Si) has been found to be essential for normal bone, cartilage growth and development. This hydroxyapatite, modified with the inclusion of small concentrations of silicon has been demonstrating to improve the osteoblast proliferation and the bone extracellular matrix production. Strontium-containing hydroxyapatite (Sr-HA) was designed as a filling material to improve the biocompatibility of bone cement. In vitro, the presence of strontium in the coating enhances osteoblast activity and differentiation, whereas it inhibits osteoclast production and proliferation.

The objective of this work was to study shapes of bone-like apatite formation on Sr and Si-doped hydroxyapatite surface of Ti-6Al-4V alloy after plasma electrolytic oxidation. Anodized alloys was prepared at 270V~300V voltages with various concentrations of Si and Sr ions. Bone-like apatite formation was carried out in SBF solution. The morphology of PEO, phase and composition of oxide surface of Ti-6Al-4V alloys were examined by FE-SEM, EDS, and XRD(Supported by NRF: 2015H1C1A1035241 & NRF: No.2008-0062283 ; hcchoe@chosun.ac.kr [mailto:hcchoe@chosun.ac.kr]).

[1] A. K. Mishra, J. A. Davidson, R. A. Poggie, P. Kovacs, T. J. FitzGerald, Mechanical and tribological properties and biocompatibility of diffusion hardened Ti-13Nb-13Zr a new titanium alloy for surgical Implants, ASTM Spec Tech Publication 1272 (1996) 96-112.

DP-22 Chemical Bonding Characteristics of Biocompatible TiO2 Oxide Multilayer by the XPS Depth Analysis, ***Jae-Myung Jang***, GwangJu Nambu University, Republic of Korea*; T Park,* Eco-Tech Korea, Republic of Korea*; H Choe,* Chosun University, Republic of Korea

Most recently, to improve the biocompatibility, various processes that aim at coating an implant material with a bioactive nanoparticles such as synthetic hydroxyapatite have been proposed[1]. For this purpose, barrier and porous/tubular type of anodic oxide films could be formed by electrochemical anodization using a set of specific conditions including optimized potential, electrolyte composition, and temperature. Also, the chemical component of the electrolyte is essential in determining the type of morphology that is eventually formed, and the geometric morphology of TiO_2 oxide film is mutually important in direct contact with biological tissue in dental or surgical implants. In addition, the specific ions in the contact surface with the bone site plays a critical role in terms of adhesion and stability for long periods in the living body.

Thus, in this work, the manufacture of the TiO_2 barrier-type multilayerwas accurately performed in a mixed electrolyte containing HAp, Pd, and Ag nanoparticles. The temperature of the solution was kept at approximatively 32℃and was regularly rotated by a magnetic stirring rod in order to increase the ionic diffusion rate. The manufactured specimens were carefully analyzed by XPS depth profile to investigate the result ofchemical bonding behaviors. From the analysis of chemical states of the TiO_2 oxide multilayer using XPS, the peaks are showed with the typical signal of Ti oxide at 459.1 eV and 464.8 eV, due to Ti 2p(3/2) and Ti 2p(1/2), respectively. The Pd-3d peak was split into Pd-3d(5/2) and Pd-3d(3/2)peaks, and shows two bands at 334.7 and 339.9 eV for Pd-3d3 and Pd-3d5, respectively. Also, the peaks of Ag-3d have been investigated. The chemical states consisted of the O-*1s*, P-*2p,* and Ti-*2p* were identified in the forms of PO_4^{2-} andPO_4^{3-}. Based on the results of the chemical states, the chemical elements into the TiO_2 oxide multilayer were also inferred to be penetrated from the electrolyte during anodic process. The structure characterization of the modified surface were performed by using FE-SEM, and from the result of biological evaluation in simulated body fluid(SBF), the biocompatibility of TiO_2 oxide multilayer was effective for bioactive property(Supported by NRF: 2016R1D1A1B01016542 & NRF: No.2008-0062283 ; hcchoe@chosun.ac.kr)

DP-25 Corrosion and Antibacterial Properties of Micro-Arc Oxidized Biodegradable Mg-Sr Alloys for Biomedical Applications, ***Mehmet Yazici***, Ondokuz Mayis University, Turkey*; E Gulec,* Gebze Technical University, Turkey*; M Gurbuz,* Ondokuz Mayis University, Turkey*; Y Gencer, M Tarakci,* Gebze Technical University, Turkey

Despite magnesium has some advantages over the present biomaterials it has some handicaps for orthopedic applications, such as high corrosion rate, mechanical properties [1, 2]. To improve the corrosion resistance of magnesium a ceramic layer was produced on the Mg alloys by micro-arc oxidation (MAO) method. To provide a better corrosion resistance Ag ions added antibacterial HA nano particles were added to the electrolyte in the range of 1-15 g/lt. The coated alloys were characterized by using scanning electron microscopy and X-ray diffractometer. Also immersion tests, corrosion tests and anti-bacterial tests were done to compare the coatings.

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces
Room Grand Exhibit Hall - Session EP
Symposium E Poster Session

EP-2 Clarification of the Relationship between Friction Behavior and Tribo-electrical Performance of Triboelectric Nanogenerator, *W Zhang,* Key Laboratory of Education Ministry for Modern Design and Rotor-Bearing System, Xi'an Jiaotong University, China*; **Pengfei Wang**, D Diao,* Institute of Nanosurface Science and Engineering, Shenzhen University, China

Ever since the concept of triboelectric nanogenerator (TENG) was proposed in 2012, the TENG attracted much attention from researchers for its unprecedented advantages of simple fabrication, low weight, low cost and abundant choices of materials and so on. When the in-plane sliding mode TENG working, one of the friction pair sliding on the other one, sliding friction is introduced to the sliding surface and the friction behavior between two surfaces have great influence on the tribo-electrical performance (including output current, voltage and power) of TENG. However, until now the law between friction behavior and tribo-electrical performance is unclear and it limits the journey of TENG's widely practical utilization. Moreover, the research about the relationship between friction behavior and tribo-electrical performance of TENG isn't receiving enough attention . The target of this research is to clarify the relationship between friction behavior and tribo-electrical performance of TENG.

In this work, graphene sheets embedded carbon (GSEC) films were fabricated by mirror confinement electron cyclotron resonance (MCECR) plasma sputtering method under low-energy electron irradiation and Polydimethylsiloxane (PDMS) are selected as the friction pair materials of in-plane sliding mode TENG. The electrometer and independently designed reciprocating tribometer was used to obtain the output current, voltage and the friction behavior of GSEC film based TENG, respectively. Moreover, the dependence of the short-circuit current and open-circuit voltage on the external loading resistance and the output power as a function of variety resistance of the GSEC film based TENG was obtained with connecting

different resistance during measurements. It believed that with the friction coefficient increasing, so did the output current and voltage of GSEC film based TENG, but the energy conversion efficiency decrease. On the contrary, when the friction coefficient decreases, the tribo-electrical performance of GSEC film based TENG decrease slightly but the energy conversion efficiency increase dramatically. The clarification of the relationship between the friction behavior and tribo-electrical performance of TENG is beneficial to improve the tribo-electrical performance as well as optimize the design of TENG.

EP-4 Effect of Cr Content and Various Interlayers on Mechanical Properties of CrAlN Coatings Synthesized by UBMS, ***HoeKun Kim***, *J La, M Song, S Lee, Y Hong,* Korea Aerospace University, Republic of Korea

Transition metal nitride coatings are very attractive materials because of their excellent mechanical properties. Especially, the CrAlN coatings have been paid much attention to cutting tool's film due to their high hardness, low surface roughness and excellent thermal stability.In this work the influence of Cr content and various interlayers on mechanical properties of CrAlN coating was investigated. In order to control the Cr content the pulsed DC current was adjusted between 0.4 and 2.0 A, and various interlayers such as CrN, CrZrN, CrN/CrZrSiN were synthesized between the CrAlN coating and the WC substrate. The microstructure, residual stress, hardness and elastic modulus, and friction coefficient were evaluated by field-emission scanning electron microscopy (FE-SEM), laser reflectance system, nano-indentation, and ball-on-disc type wear tester, respectively.

When the Cr content in the CrAlN coatings increased from 0.11 to 0.24 at.%, the hardness and compressive residual stress were measured to be in a range from 31 to 41 GPa, and from 4.3 to 5.7 GPa, respectively. Hardness enhancement could be attributed to the solid solution hardening, in that with Cr insertion. The lattice distortion in the coating developed, and this leads a compressive residual stress enhancement. Therefore, the dislocations became more and more difficult to move, and the hardness of coatings gradually increased. After the scratch test, the critical load of the CrAlN coatings gradually decreased from 48 to 41 N. Generally, the high residual stress causes the low adhesion, and the compressive residual stress could be considered as a factor on the adhesion decreasement. During the wear test, the friction coefficient of the CrAlN coatings with the CrN and CrN/CrZrN interlayer exhibited improved values of 0.34 compared to that of the CrAlN coating with the CrZrN interlayer (COF 0.41). These improved friction coefficient could be attributed to the H/E ratio of the interlayer between the CrAlN coating and the WC substrate. In view of the coating structure, there exists a gradual increase in the H/E ratio from the WC substrate (H/E, 0.040), to the CrN interlayer (H/E, 0.076), and CrZrSiN interlayer (H/E, 0.083), and the CrAlN coating (H/E, 0.089). The CrN and CrZrSiN interlayers induced a smooth transition of the stress effectively under loading conditions, and wear properties could be improved significantly by structuring the coating with an optimal gradient of the H/E ratio of the coating/interlayer/substrate.

EP-5 Effect of Boride Coating on Hydrogen Embrittlement of AISI 8620 Steels, ***MarcoAntonio Doñu Ruiz***, *N Lopez Perrusquia,* Universidad Politecnica Del Valle De Mexico, Mexico; *V Cortes Suarez, J Romero Serrano,* Univerisdad Autónoma Metropolitana, Mexico; *M Reyes Cortes,* Universidad Politecnica Del Valle De Mexico, Mexico

The present work studied the effect of boriding coatings on hydrogen embrittlement on AISI 8620 by means the mechanical behavior. The formation of boride were carry out at three different temperatures (1173, 1223, and 1273K) for 6 hours of exposure time by dehydrated paste pack method. After boronizing, the presence of the boride coatings were observed scanning electron microscopy (SEM), X-ray diffractometer and energy dispersive spectroscopy (EDS) analysis.

Hydrogen was introduce into samples with boride coating through cathodic charging applying a current density of 50 mA/cm^2 by 0.5 M sulphuric acid solution kept at a room temperature.

The mechanical behavior of boride coating with hydrogen diffusion were used the following experimental techniques: Vickers micro-hardness, Daimler-Benz Rockwell-C indentation and three-point bend test. As a result of the hydrogen diffusion on sample boride, the borided layer thickness decrease and microhardness tests showed a significant increase in the surface hardness caused by the increased boronizing temperature, moreover the adhesion strength in all condition obtained sufficient cohesion. Finally, three point bend tested show a drastic reduction in ductility and increase the fracture stress value.

EP-6 Characterization and Wear of Co-Cr-Mo-Si Alloy Coatings at High Temperatures, *L Amaral,* Universidade Federal do Paraná, Brazil; *E Nascimento,* Universidade Técnológica Federal do Paraná, Brazil; ***AnaSofia D'Oliveira***, Universidade Federal do Paraná, Brazil

CoCrMoSi alloys were developed for high temperature applications particularly to resist liquid metal corrosion, due to the distribution of the Laves phase. However, the range of properties of this alloy system allows for uses well beyond the original scope. The metallurgical stability of CoCrMoSi coatings exposed to temperature has been shown to be associated with the stability of Laves phase. The successful use of coatings for high temperature applications requires the understanding of oxidation behavior and influence of the oxide layer on wear. This research focuses on the study of the abrasive wear behavior of CoCrMoSi coatings exposed at 450C and 750C for 6h in an air furnace. The aim is to characterize the oxides formed at the surface of coatings and their role on wear. The CoCrMoSi alloy was deposited by Plasma Transferred arc on AISI304 stainless steel plates (120mmx100mmx12mm). Abrasive wear tests were carried out on a rotating ball apparatus with applied loads ranging from 0.2N to 0,45N. The low loads intended to magnify the impact of surface oxides on wear behavior. For each surface a set of wear tests was carried out with small increments on the applied load until the oxide film was broken and the CoCrMoSi coating started to worn. Raman spectroscopy and X-ray diffraction identified oxides at the surface. Confocal microscopy and scanning electron microscopy analysis characterized the wear scar. At the oxidation temperature used of 450ºC Co and Fe oxides form. The kinects of Co_3O_4, Fe_3O_4 and Fe_2O_3 allow for the fast oxidation of Co and Fe even at low temperatures. Under these conditions scratches were identified on the wear scar associated with the removal of oxide particles, suggesting a low adherence to the coating surface. Exposure at 750ºC resulted on a continuous oxide film of Cr_2O_3 , analysis of the wear scar reveals rolling to be the predominant mechanism. Correlation with non-oxidized CoCrMoSi coatings shows that oxides formed at 450ºC do not impact on the wear performance of coatings. Oxidation at 750ºC resulted on a reduction of friction coefficient, leading to an increase on wear resistance.

EP-7 Influence of Nitrogen Content on the Properties of CNx Coatings Deposited onto AISI H13 Steel by DC Magnetron Sputtering, ***Elbert Contreras***, *F Bolívar, M Gómez,* Universidad de Antioquia, Colombia

The increasing interest for new coatings with higher properties, opened the doors to research of carbon nitrides (CNx); these coatings are attractive for industrial applications due to their its high recovery rates, low friction coefficients and wear rates, in addition to their self-lubricating properties. In this research, CNx coatings were deposited by DC magnetron sputtering, using a Graphite target and a power density of 2,4W/cm^2, deposition temperature was 250°C, working pressure of 6-7x10^{-3} mbar and a BIAS voltage of -70V, prior to the deposition an ionic cleaning was carried out to clean the surface of the substrates, the percentage of nitrogen was varied between 10% and 50% (N_2/(Ar+N_2)) in the gas mixture, in order to evaluate the effect of nitrogen incorporation on microstructure, composition, mechanical and tribological properties. The thicknesses around 2.0 µm were obtained for all coatings; SEM images revealed homogeneous, compact and columnar coatings; the XRD analysis showed that all coatings are completely amorphous. The micro-Raman spectra are characteristic of carbon-rich sample; these clearly show D band (*disordered aromatic rings)* and G band *(graphite).* It was also possible to identify the band associated to C-N triple bonds. The mechanical and tribological properties are affected by the incorporation of nitrogen, by increasing the nitrogen in the gas mixture, increasing the compressive residual stress and hardness; all coatings show similar tribological behavior, with smooth friction records, their low friction coefficients and wear rates are significantly low compared to others self-lubricating coatings like, VN, VSiN, CrVN, etc.

EP-9 Modelling of IN 738 LC Alloy Mechanical Properties based on Microstructural Evolution Simulations for Different Heat Treatment Conditions, *M Boyraz,* ***Bilge Imer***, Middle East Technical University, Turkey

Conventionally cast nickel-based super alloys, such as commercial alloy IN 738 LC, are widely used in manufacturing of industrial gas turbine blades. With carefully designed microstructure and the existence of alloying elements, the blades show improved mechanical properties at high operating temperatures and corrosive environment. The aim of this work is to model and estimate these mechanical properties of IN 738 LC alloy solely based on simulations for projected heat treatment conditions or service conditions. The microstructure (size, fraction and frequency of gamma prime- γ′ and carbide phases in gamma- γ matrix, and grain size) of IN 738 LC needs to be optimized to improve the high temperature

mechanical properties by heat treatment process. This process can be performed at different soaking temperature, time and cooling rates. In this work, micro-structural evolution studies were performed experimentally at various heat treatment process conditions, and these findings were used as input for further simulation studies. The operation time, soaking temperature and cooling rate provided by experimental heat treatment procedures were used as micro-structural simulation input. The results of this simulation were compared with the size, fraction and frequency of γ' and carbide phases, and grain size provided by SEM (EDS module and mapping), EPMA (WDS module) and optical microscope for before and after heat treatment. After iterative comparison of experimental findings and simulations, an offset was determined to fit the real time and theoretical findings. Thereby, it was possible to estimate the final micro-structure without any necessity to carry out the heat treatment experiment. The output of this microstructure simulation based on heat treatment was used as input to estimate yield stress and creep properties. Yield stress was calculated mainly as a function of precipitation, solid solution and grain boundary strengthening contributors in microstructure. Creep rate was calculated as a function of stress, temperature and microstructural factors such as dislocation density, precipitate size, inter-particle spacing of precipitates. The estimated yield stress values were compared with the corresponding experimental hardness and tensile test values. The ability to determine best heat treatment conditions that achieve the desired microstructural and mechanical properties was developed for IN 738 LC based completely on simulations.

EP-10 Influence of EP Additive Containing Lubricants on the in-situ Formation of Low Friction Tribofilms on Tungsten Based Coatings, ***Bernhard Kohlhauser***, *H Riedl,* Institute of Materials Science and Technology, TU Wien, Austria*; M Ripoll,* AC2T Research GmbH, Austria*; P Mayrhofer,* Institute of Materials Science and Technology, TU Wien, Austria

The reduction of the coefficient of friction combined with reduced wear rates is a major topic in many different industrial applications. Extreme-pressure (EP) and anti-wear (AW) additives as well as low friction coatings have been intensively investigated for several years to achieve this behavior. Lately, the addition of WS_2 or MoS_2 nanoparticles has been proven to be beneficial to the reduction of friction in various tribological contacts. Investigations into the application of sulphur containing lubricants in combination with tungsten functionalized or doped surfaces like W-DLC coatings revealed an additional decrease in the coefficient of friction and wear rates compared to base oils. This effect was proposed to be related to the in-situ formation of a WS_2 carrying low friction tribofilm.

To obtain more information about the suggested formation of WS_2, tungsten based carbide coatings have been deposited applying physical vapour deposition (PVD) and were tested in a linear oscillation SRV testing system. The influence of the applied normal load and EP additive concentration was investigated. Energy dispersive X-ray spectroscopy (EDXS), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and transmission electron microscopy (TEM) analyses were carried out to investigate the interface near regions within the tribocontact. An emphasis was placed on the distinction whether the reduction of friction and wear is contributed by the in-situ formation of WS_2 rather than by the generation of Magnéli phase oxides.

EP-13 Laser Cladding Ni-based Alloy/nano-Ni Encapsulated h-BN Self-lubricating Composite Coatings, ***Hua Yan***, *P Zhang, Q Gao, Y Qin,* Shanghai University of Engineering Science, China*; R Li,* Central South University, China

Nano-Ni encapsulated h-BN/Ni-based alloy (Ni60A) self-lubricating composite coatings on a medium carbon steel were fabricated by laser cladding using two types of lasers: a 5kW continuous wave (CW) CO_2 laser and a 400W pulsed Nd:YAG laser, respectively. A high-energy ball milling method was adopted to clad nano-Ni onto nano-h-BN with an aim to enhance the compatibility between the h-BN and the metal matrix during laser cladding process. The microstructure, phase structure and wear properties of the the self-lubricating composite coatings were investigated by means of scanning electron microscopy (SEM) and X-ray diffraction (XRD), as well as dry sliding wear testing. The research indicated that laser cladding of the self-lubricating composite coatings demonstrates sound cladding layers free of cracks and porosities. It was found that a reaction between h-BN and Ni-based alloy was occurred, which generated hard phase CrB and Ni_3B leading to the increasing of the microhardness of the coatings by CO_2 laser cladding, and laser molten pool suppressed h-BN floating up to upper regions of coating for lower temperature and quickly solidification by YAG laser cladding.The high energy ball milling of nano-Ni onto nano-h-BN significantly improved the interfacial compatibility between h-BN and Ni60A matrix. The friction coefficient of the laser-clad Ni60A/nano-Ni encapsulated h-BN coating was reduced obviously.

EP-14 Leather Treated with Ag/TiO_2 Nanoparticles for Footwear Industry: Tribological and Antimicrobial Activity, *I Carvalho,* University of Coimbra, Portugal*; S Ferdov,* ***CristianaFilipa Almeida Alves***, University of Minho, Portugal*; M Cerqueira,* INL-International Iberian Nanotechnology Laboratory, Portugal*; R Franz,* Montanuniversität Leoben, Austria*; C Gaidau,* INCDTP-Leather and Footwear Research Institute Division, Romania*; S Carvalho,* University of Minho, Portugal

The proposed work aims to functionalize leathers for footwear industry with antimicrobial properties based on Ag-TiO_2 nanoparticles. The synthesis of nanoparticles was carried out through an innovative and optimized method. The structural characteristics were evaluated by X-ray powder diffraction and the results showed that the TiO_2 nanoparticles are in the anatase phase, with dimensions below 10 nm.

Leather samples were functionalized with TiO_2 and Ag-TiO_2 NP's; these nanomaterials did not change the surface chemical composition of the leathers. Fourier transform infrared spectroscopy showed that the characteristic chemical bands of leathers (-CH_3 stretching vibration) were maintained.

The antimicrobial activity was evaluated by agar diffusion tests against two bacteria species – a Gram negative and a Gram positive, Pseudomonas aeruginosa and Staphylococcus aureus, respectively, and a fungus specie – Candida albicans. The results revealed that the leathers covered with Ag-TiO_2 nanoparticles have antimicrobial activity. The cytotoxicity of nanoparticles was also assessed by MTS test using fibroblast 3T3 which shows the cell's viability. This test was performed to test if these nanoparticles easily penetrated inside the human body. The results showed that the nanoparticles are non-cytotoxic. In order to test the adhesion of the deposited Ag/TiO_2 nanoparticles to the leather substrates, a series of tribological tests in ball-on-disc configuration has been performed using different counterpart materials ranging from rubber (e.g. nitrile rubber) to polymers (e.g. PTFE, PUR or POM). The analysis of the coating wear by light optical and scanning electron microscopy, as well as Raman spectroscopy, revealed details regarding the adhesion of the Ag/TiO_2 nanoparticles depending on the deposition method and parameters applied. The conducted experiments represent a first step towards a systematic study of the mechanical performance of leathers treated with nanoparticles in order to evaluate their suitability for future applications in the footwear industry.

EP-17 An Oliver&Pharr Method for Lateral-Force Nanoindenters, ***Norbert Schwarzer***, SIO, Germany

It will be shown how the classical Oliver and Pharr method [1] has to be extended in order to make it fit for the performance and analysis of mixed loading nanoindentation tests. While the classical Oliver and Pharr method can only deal with pure normal loads and allows the extraction of hardness and Young's modulus for a given Poisson's ratio [1, 2, 3], the extended method principally allows for the simultaneous parameter identification of hardness, yields strength in two directions, Young's modulus and Poisson's ration. Under proper experimental conditions, also the extraction of intrinsic stresses seems to be possible. The author will present the method, the theoretical background and a few experimental examples (data from T. Chudoba, ASMEC GmbH, with thanks).

[1] W.C. Oliver and G.M. Pharr, J. Mater. Res. 7, 1564 (1992)

[2] N. Schwarzer, G. M. Pharr, Thin Solid Films, Vol. 469-470C pp. 194-200

[3] N. Schwarzer, T. Chudoba, F. Richter: „Investigation of ultra thin coatings using Nanoindentation", Surface and Coatings Technology, Vol 200/18-19 pp 5566-5580

EP-18 Investigation of Tribological Properties of Aluminium-Titanium Diboride (Al/TiB_2) MMC under Dry Sliding Condition, *A Sheelwant, S Narala,* BITS Pilani Hyderabad Campus, India*;* ***Palaparty Shailesh***, Methodist College of Engineering and Technology, India

Aluminium Metal Matrix Composites are a special class of metal matrix composites with immense potential which open up countless possibilities to enhance properties of materials that are needed in aerospace, military and automotive applications. The potential of these materials lies into their ability to be tailored to fulfil the expectations of the designer. In this study, microstructure and wear properties of aluminium metal matrix composite (AMMC) reinforced with titanium diboride (TiB_2)were investigated. The composite was fabricated through liquid state processing by incorporating 3, 6, 9, 12 and 15 wt% of titanium diboride into aluminium matrix. Uniform

distribution of the reinforcement particles into the metal matrix was observed by the microscopic examination of the composite. To determine the friction and wear properties of the composite, experiments were conducted on a pin-on-disc tribometer, under dry condition, by varying applied load and sliding velocity while keeping the sliding distance constant. Loads of 10N, 30N, 50N and velocities of 100 m/min, 200 m/min, 300 m/min were employed over a constant sliding distance. Results obtained from the test revealed that the friction coefficient and overall wear rate increase with the increasing load and sliding velocity. However, the Al/TiB_2 composite shows lower wear rate in contrast to the unreinforced aluminium. Analysis of the worn out surface of the composite under scanning electronic microscope reveals the domination of abrasive wear. The details presented in the current paper form a basis for materials engineers to switch over to AMMCs from monolithic metals and alloys which offer superior wear properties.

Keywords: Aluminium metal matrix composite, Al-TiB_2, Friction, Wear, Dry sliding

EP-20 Tribological Characterization of Thin Films based on Residual Stress, Volume of Wear, Micro-abrasive Wear Modes and Coefficient of Friction, ***Ronaldo Cozza**, J Wilcken, S Delijaicov, G Donato,* University Center of FEI – Educational Foundation of Ignatius "Padre Sabóia de Medeiros", Brazil

The purpose of this work is to conduct a tribological characterization of thin films based on residual stresses, micro-abrasive wear modes, volume of wear (V) and coefficient of friction (μ). Initially, the residual stresses of thin films of TiN, CrN, TiAlN, ZrN, TiZrN, TiHfC and TiHfCN were analysed by X-ray diffraction; after ball-cratering wear experiments were performed using a ball of AISI 52100 steel and abrasive slurries prepared with black silicon carbide (SiC) particles and glycerine. The normal force (N) and the tangential force (T) were monitored throughout the tests and the coefficient of friction was calculated as $\mu = T/N$. The results showed that the abrasive slurry concentration affected the volume of wear, the occurrence of micro-abrasive wear modes (grooving abrasion or rolling abrasion) and, consequently, the magnitude of the coefficient of friction: *i*) a low abrasive slurry concentration was related with low volume of wear, action of grooving abrasion and a relatively high coefficient of friction; *ii*) a high abrasive slurry concentration was related with high volume of wear, action of rolling abrasion and a relatively low coefficient of friction. In general, the compressive residual stresses measured were relatively low (< 1 GPa).

Keywords: Micro-scale abrasion, residual stress, two-body abrasion, three-body abrasion, PVD coatings.

EP-22 Frictional Behavior of Bismuth-based Soft Coatings, *B Pilotti, G Prieto,* Universidad Nacional del Sur, Argentina; ***Esteban Broitman**,* Esteban Broitman Engineering Consulting, Sweden; *W Tuckart,* Universidad Naciona del Sur, Argentina

The aim of this study was to analyze the frictional behavior of a bismuth-based soft coating, developed using a novel, eco-friendly and economically competitive synthesis. Bismuth has a non-toxic nature, making it attractive for the development of new tribological applications such as coatings or as oil additives.

Bismuth sulfide (Bi_2S_3) nanoparticles were synthesized in-house by means of an eco-friendly reaction in an aqueous medium under mild reaction conditions, in presence of a surfactant. The obtained particles were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The Bi_2S_3 nanoparticles were mixed with a commercial organic varnish in order to generate a soft coating. The coating had a weight fraction of nanoparticles of 17.4 wt% and was manually applied on a SAE 4140 steel disk . The frictional response of the soft coating was evaluated using a pin on disc test (v_I=0.02 m/s; p_0=1100 MPa; 6 m of sliding speed), using an AISI 52100 steel ball with a diameter of 6 mm as the counterpart. The same test procedure was employed using a commercially available molybdenum disulfide varnish to serve as a reference.

Both coatings exhibited similar friction coefficients during the test, with an initial low value (<0.1) that increased slightly towards the end of the test. The bismuth based soft coating showed an average friction coefficient ~30% higher than the molybdenum disulfide coating used as reference.

Note: B. Pilotti, G. Prieto, and W. R. Tuckart are also affiliated to CONICET, Argentina.

EP-24 Compositional and Mechanical Characterization of Ti-Ta Coatings Prepared by Confocal Dual Magnetron Co-Sputtering, *A Bahrami,* Universidad Nacional Autónoma de México, Universidad Nacional Autónoma de México, Mexico; *J Pérez Alvarez, R Mirabal-Rojas,* Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Mexico; ***Osmary Depablos-Rivera**,* Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Ciudad Universitaria, Mexico; *A Ruiz-Ramirez, A Valencia-Velazco,* Universidad Nacional Autónoma de México, Ciudad Universitaria, Mexico; *S Rodil,* Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Mexico

Toughness and hardness are two important characteristics for coating applications in manufacturing industry. In this study, Titanium-Tantalum coating were deposited by magnetron co-sputtering technique, using titanium and tantalum as targets, on steel and silicon substrate. The power applied to the Ti target was fixed at 200 W, while the Ta power was varied from 10 to 60 W. The effects of the Ti- to- Ta ratio on the chemical composition, mechanical and wear properties of Ti-Ta films were investigated. X-ray photoelectron spectroscopy (XPS), Scanning electron microscopy and X-ray diffraction (XRD) were used to evaluate the composition and oxidation state of the films, morphology and structure of obtained thin films, respectively. The hardness was evaluated by nano-indentation test. The XPS results showed that the Ti in the films without Ta is presented only in the metallic state. Also it was found that the percentage of the added Ta varies from 2 to 14 at% by increasing the applied power to the Ta target. The XRD results showed that the coatings were crystalline, and there is no evidence of the formation of intermetallic phases. The results show that increasing the Ta content cause a significant improvement in scratch resistance of the coatings. The crack propagation analysis was evaluated using the data obtained from micro-indentation and the residual stress from XRD and hardness results.

New Horizons in Coatings and Thin Films
Room Grand Exhibit Hall - Session FP
Symposium F Poster Session

FP-3 Monolayer Controlled Deposition of ZnO Thin Films by Catalytic Reaction-assisted Chemical Vapor Deposition, *S Ono, T Saitou, R Tajima, Y Tamayama, **Kanji Yasui**,* Nagaoka University of Technology, Japan

The large bandgap (3.37 eV at RT) and exciton binding energy (60 meV) of ZnO [1] have recently stimulated intensive research into optoelectronic device applications, such as light-emitting diodes and laser diodes that operate in the ultraviolet region [2-6]. We have previously developed a new CVD method for ZnO film growth based on the reaction between alkylzinc (DMZn) and high-temperature H_2O generated by a Pt-catalyzed exothermic H_2-O_2 reaction. The resulting ZnO films grown on a-plane (11-20) sapphire (a-Al_2O_3) substrates exhibited excellent optical and electronic properties [7]. Superlattices are often used to enhance the efficiency of optical emission devices. Such structures involve alternating layers with different compositions, with each layer often being just a few molecules thick. It is therefore necessary to be able to control the growth process at the monolayer level. Therefore, in the present study, the applicability of catalytic reaction–assisted CVD using a pulsed gas supply was investigated for monolayer controlled growth of ZnO on a-Al_2O_3 substrates.

Except for the gas supply mode, the CVD apparatus and growth procedure were the same as those previously reported [7]. DMZn gas was supplied to the reaction zone in pulses with durations of 4 and 8 ms, and was reacted with a catalytically generated high-energy H_2O beam effused from a de Laval nozzle. The growth rate per pulse was evaluated based on the final film thickness and the total number of DMZn pulses. Pulse rates of 2 and 4 Hz were used, with the gas being supplied for 30 and 15 min, respectively. For a pulse duration of 8 ms, based on the final ZnO film thicknesses of 1300 and 1400 nm, the deposition rate was 0.36 and 0.39 nm per pulse for a pulse rate of 2 and 4 Hz, respectively. For a pulse duration of 4 ms, based on the final film thickness of 1400 nm, the deposition rate was 0.19 nm per pulse. Since the c-lattice constant of ZnO is 0.52 nm, the thickness of a single molecular layer is 0.26 nm. Therefore, from the above results, the thickness of the deposited layer could be controlled to less than the thickness of a single molecular layer using catalytic reaction-assisted CVD with a 4 ms pulsed gas supply.

References

[1] B. K. Meyer et al., Phys. Stat. Sol. B., 241 (2004) 231. [2] M. Sano et al., Jpn. J. Appl. Phys., 42 (2003) L1050. [3] H. Tampo et al., Appl. Phys. Lett., 84 (2004) 4412. [4] A. Tsukazaki et al., Nat. Mater., 4 (2005) 42. [5] E. M. Kaidashev et al., Appl. Phys. Lett., 82 (2003) 3901. [6] J. Dai et al., Appl. Phys. A, 89 (2007) 645. [7] K. Yasui et al., MRS Symp. Proc., 1315 (2011) 21.

FP-6 Optical and Electronic Properties of MoS2: Joint Theoretical/Experimental Study, ***Miller Eaton**, H Sirikumara, H Samassekou, D Mazumdar,* Southern Illinois University, USA*; L Liyanage, M Nardelli,* University of North Texas, USA*; T Jayasekera,* Southern Illinois University, USA

First-principles calculations of the optoelectronic properties of semiconductors using density function theory (DFT) have suffered from slight inaccuracies due to the exchange energy interaction approximations used. The inclusion of the Hubbard parameter U allows for more accurate predictions with a negligible increase in computational time. We use the DFT + *U* approach to perform *ab initio* calculations of the optical and electronic properties of thin film MoS2. We then fabricate pristine MoS2 thin films on BN-buffered silicon substrates via magnetron sputtering. Few-layer films are first confirmed with X-ray reflectivity and diffraction measurements, and then further characterized using variable angle spectroscopic ellipsometry (VASE). Agreement of DFT + *U* predictions with layer specific modeling of VASE data demonstrates the viability of sputtering for large-area growth. This study paves the way for the controlled introduction of chemical dopants to further improve electronic and optoelectronic properties of MoS2 for nanoscale device application.

FP-7 Possibility of Selective and Morphology-Controlled Growth of CuO and Cu_2O Films, ***Tomoaki Terasako**, K Ohnishi, H Okada, S Obara,* Ehime University, Japan*; M Yagi,* National Institute of Technology, Kagawa College, Japan

Both CuO (Eg=~1.35 eV) and Cu_2O (Eg=~2.1 eV) exhibit *p*-type conduction. These materials have attracted much attention because of their promising applications, such as photocatalytic water splitting, solar cells, electrode materials for lithium-ion batteries, gas-sensing devices and so on. Chemical bath deposition (CBD) is performed at temperatures typically lower than 100 °C, which allows us to use polymers as substrate materials. In this paper, we will discuss the possibility of the selective and morphology-controlled growth of CuO and Cu_2O films on Au/SiO_2/Si(100) substrates by CBD from the same precursor, *i.e.* $Cu(NO_3)_2{\cdot}3H_2O$ (CuNit).

The CuO films grown from the aqueous solutions of CuNit with the different pH values adjusted by the use of NH_3(aq) were composed of the needle-like grains whose average length increased with increasing pH value. At pH≥10.5, the needle-like grains were organized in the caddis clew-like shapes. The most probable mechanism for assembling the needle-like grains is the "oriented attachment" in which the rotations of the needle-like grains can be driven by torques introduced by the misalignment of the neighboring grains [1, 2]. The appearance of the caddis clew-like shapes is probably due to the imperfect rotation of the needle-like grains caused by the increase in the average length.

The Cu_2O films were grown from the mixed aqueous solutions of CuNit and $C_6H_{12}N_4$ (HMT) with the assistance of a piece of Fe plate immersed in the solution, denoted by "Fe-assisted CBD". No Cu_2O film could be obtained without the immersion of the Fe plate [3]. The reduction from the Cu^{2+} ions to the Cu^{+} ions is required for the formation of Cu_2O from CuNit. Oxidation-reduction potential (ORP) measurement during the Fe-assisted CBD process revealed that the ORP exhibited a sudden decrease just after immersing the Fe plate. Moreover, the ORP values during the Fe-assisted CBD were overall low in comparison with those during the usual CBD process. Taking into account the fact that *α*- and *δ*-FeOOH were formed on the surface of the Fe plate during the CBD process, the CBD solution in which the Fe plate was immersed had high concentration of electrons contributing to the reduction of Cu^{2+} ions. The preferential growth direction of the Cu_2O film changed from [111] to [100] with increasing CuNit (or HMT) concentration, accompanied with the change from the triangular-plate grains to the four-sided pyramidal grains.

This work was supported by JSPS KAKENHI Grant Number JP26390029.

[1] J. Liu *et al*., Cryst. Growth Des. 6 (2006) 1690.

[2] E. J. H. Lee *et al*., J. Phys. Chem. B 109 (2005) 20842.

[3] T. Terasako *et al*., 43rd ICMCTF, FP-1 (2016).

FP-8 Thermal Stability of Arc Evaporated Oxide, Nitride, Oxinitride, and Oxide/Nitride Coatings within the Systems Al-Cr-N and Al-Cr-O, ***Robert Raab**,* CDL-AOS TU Wien, Austria*; C Koller,* TU Wien, Austria*; S Kolozsvári,* Plansee Composite Materials GmbH, Germany*; J Ramm,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P Mayrhofer,* TU Wien, Austria

The most common materials systems synthesised by cathodic arc evaporation for industrial applications are nitrides or oxides (e.g., TiAlN, CrAlN,Al_2O_3,…). Among these, Al-Cr-based films find application in multitude of applications, such as forming or cutting tools, which not only required a consistent performance over a temperature range up to 1000°C and beyond, but also the capability to withstand oxidising environments.

In this regard, we have studied the thermal stability of $Al_xCr_{1-x}N/(Al_xCr_{1-x})_2O_3$ multilayer coatings and compared them with the homogenously grown counterparts $Al_xCr_{1-x}N$, $(Al_xCr_{1-x})_2O_3$, as well as its combination in terms of quaternary Al-Cr-O-N.

We used a combination of differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), X-ray powder diffraction (XRD), and hardness investigations after annealing the samples up to 1500 °C in vacuum for one hour to investigate the decomposition of the Al-Cr-based oxide, nitride, oxinitride, and oxide/nitride coatings.

Based on our results we can conclude that a multi-layer arrangement with optimized bilayer period is superior to the monolithically grown $Al_xCr_{1-x}N$, $(Al_xCr_{1-x})_2O_3$, and quaternary Al-Cr-O-N.

FP-9 Parametric Study of TiN Thin Films Deposited on 316 L Substrates by HiPIMS, *L Melo-Máximo,* ITESM-CEM, Mexico*; F Estrada-Martinez,* Termoinnova S.A. de C.V., Mexico*; D Melo-Maximo,* TRAMES S.A. de C.V., Mexico*; **Joaquin Oseguera**,* ITESM-CEM, Mexico

Thin films of TiN were prepared by High-power impulse magnetron sputtering (HiPIMS) on 316L substrates. The main objective of this work was to evaluate the thin film growth under various conditions, in order to show the effect that process parameters have on the properties of the films. The microstructure and the adhesion of the coatings were studied by the characterization with scanning electron microscopy, optical microscopy, x-ray diffraction and scratch test.

FP-11 Transition Metal Dichalcogenides for Next Generation Semiconductor Devices, *B Sirota,* University of North Texas, USA, U*; A Waite, N Glavin,* Air Force Research Laboratory, USA*; C Muratore,* University of Dayton, USA*; S Krylyuk, A Davydov,* National Institute of Standards and Technology, USA*; **Andrey Voevodin**,* University of North Texas, USA

New advances in technology encourage the proliferation of next generation electronic devices. Two dimensional semiconductor materials such as MoS_2, WS_2, $MoTe_2$, $MoSe_2$ and similar compounds have gained significant interest for their capabilities due to their size, flexibility, optical transparency, and tunable electronic bandgap. In addition, ultra-thin amorphous BN has gained recent interest as a dielectric material due to its large band gap, flexibility, optical transparency, and low temperature processing compatible with polymer substrates. Herein, we present a study on 2D transition metal dichalcogenides prepared by physical vapor deposition (MoS_2) and mechanical exfoliation ($MoTe_2$). We also examine their heterostructures with pulsed laser deposited ultra-thin amorphous BN layer, and integrated into electronic devices. Proof-of-concept field effect transistors with 2D semiconductors serving as the channel material are made using conventional electronic beam lithography and lift off. Microstructure, electronic and optical properties are determined and compared to devices made from traditional techniques in the recent literature. These results demonstrate the functionality of 2D transition metal dichalcogenide layers and their heterostructures with amorphous ultra-thin BN as a use for electronic devices with advanced functionality.

FP-13 Microscopic Barrier Mechanisms and Interface Damage Behavior of Two-dimensional Nanomaterials, ***Pu Jibin**, L Wang, J Xue,* Key Laboratory of Marine New Materials and Related Technology, Ningbo Institute of Material Technology and Engineering, Chinese Academy of Sciences, China

The serious surface damage of high-tech facilities in the marine and spatial environment has become a key problem that restrains the reliability and life span of marine engineering facilities and spacecrafts. The common mechanism of material damage in the marine and spatial environment is infiltrated and eroded by the medium of external environment. Two-dimensional nanomaterials (graphene, hexagonal boron nitride, disulfide, etc.) have a wide coverage of surface area and excellent mechanical, electrical, thermal and obstructing properties. So they have natural

advantages as materials of resisting ion penetration and atomic oxygen erosion in the marine and spatial environment. By studying the influence of the electronic structure, electric conductivity, thermal conductivity, layer number, surface functional group and defect degree of two-dimensional nanomaterials on obstructing marine medium and atomic oxygen and the influence of the controllable dispersion, ratio, distribution pattern and multi-scale interface of two-dimensional nanomaterials on the damage of composite coatings, this paper expounds the obstructing regulation mechanism of two-dimensional nanomaterials so as to provide theoretical guidance for developing new-type long-life materials of marine protection and spatial anti-atomic oxygen.

FP-14 Corrosion Performance of Waterborne Epoxy Coating using Non-covalent Dispersion of Graphene as Inhibitor, ***Shuan Liu,*** *H Zhao,* Key Laboratory of Marine Materials and Related Technologies, Zhejiang Key Laboratory of Marine Materials and Protective Technologies, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, China*; P Jibin,* Key Laboratory of Marine Materials and Related Technologies, Zhejiang Key Laboratory of Marine Materials and Protective Technologies, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, P. R. China, China*; L Wang,* Key Laboratory of Marine Materials and Related Technologies, Zhejiang Key Laboratory of Marine Materials and Protective Technologies, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, China

To improve the anticorrosion performance of waterborne epoxy coating and expand its practical applications, Graphene was initially stabilized by sulfonated polyaniline in aqueous solution, and its structure and dispersant performance were investigated by SEM.TEM Raman and AFM respectively. Then the corrosion behaviour of different composite coatings in 3.5% NaCl solution was studied based on a series of electrochemical measurements. Results indicated that graphene could be dispersed uniformly in water. Sulfonated polyaniline was not only a graphene dispersant but also an corrosion inhibitor. The addition of well-dispersed graphene into waterborne epoxy coating improved corrosion protection significantly compared with neat waterborne epoxy coating.

FP-16 Production and Testing of Enhanced Photocatalytic Coatings onto Nanoparticles by Magnetron Sputtering, *P Kelly,* ***Marina Ratova****, G West,* Manchester Metropolitan University, UK

Magnetron sputtering is a well-established technique for the deposition of high quality metallic and ceramic coatings onto a wide range of substrate materials and forms. It is not generally suitable, though, for the coating of fine particulates (particle sizes from 10s of nm to 100s of μ m). This paper, however, describes the use of an oscillating mechanism to manipulate particulates under two co-planar magnetrons, such that uniform coverage of the particles is achieved.

This technique has been used to deposit a range of coatings onto photocatalytic anatase titania nanoparticles (PC500), with the aim of overcoming some of the limitations of this material, specifically rapid charge carrier recombination and low visible light activity. The materials selected include bismuth tungstate, a visible light active photocatalyst, which can increase charge carrier numbers and lifetimes through semiconductor coupling with titania; and carbon, which can be used as a dopant to increase overall activity. The bismuth tungstate coatings were deposited by reactive magnetron co-sputtering from two targets. Two strategies were used for carbon doping; direct sputtering from a carbon target and reactive sputtering using CO_2 as a process gas.

The nanoparticles were characterised by SEM, EDX, TEM, XRD and BET surface area measurements. Photocatalytic activity was assessed using an acetone degradation test under visible light irradiation, in which the rate of CO_2 evolution was measured as a function of the surface area of the sample. Preliminary results indicate that the bismuth tungstate coatings, where the Bi/W content is in the ratio of 2:1 can significantly increase the visible light activity of the titania product. The mechanism through which this enhancement occurs is discussed in terms of more efficient separation of the charge carriers and the inherent activity of the coating.

FP-17 3D Printing of Metal Oxide Semiconductor?, ***Chuong Nguyen,*** University of Auckland, New Zealand*; J Leveneur,* GNS Science, New Zealand*; M Taylor, J Metson,* University of Auckland, New Zealand

Ion-induced reduction can potentially provide two important features for metal oxide semiconductors: amorphous state and tuneable contact resistance. It is well known that ion bombardment causes amorphitization of target materials. Ion fluence can also be controlled to reduce oxide to metallic state in various proportions, tuning the metal – semiconductor contacts from Schottky to Ohmic.

This study involved argon ion bombardment on multi-valent iron oxides. The reduction extents, in terms of oxidation state and effective depths, as a function of ion fluence is characterized by energy-resolved x-ray photoelectron spectroscopy (ERXPS), complemented by x-ray absorption of near-edge structure (XANES). The correlation is assessed against the transport of ions (TRIM) simulation. Our early results indicate a possible method to build up a functionally graded thin-film transistor layer by layer using physical vapor deposition (PVD) coupled with a supplementary ion gun.

FP-18 A Proposal for Laser Annealing Process with Continuous Wave Nd:YAG Laser (λ_o = 532 nm) for Photovoltaic CIGS Thin Films: Effect of Laser Annealing Time on Optical and Electrical Properties, ***MyoungHan Yoo,*** *D Lee,* Chosun University, Republic of Korea*; Y Jun,* Hyobjin Jeongbo Co., Inc., Republic of Korea*; P Ko, N Kim,* Chosun University, Republic of Korea

$CuIn_{1-x}Ga_xSe_2$ (CIGS) thin-film solar cells are strongly considered as an absorber layer in light-weight and flexible thin-film solar cells . For preparing CIGS thin film at low cost, critical problems still remained in the selenization process of the sputtered Cu-In-Ga precursors by using H_2Se vapor, such as highly toxic H_2Se, poor adhesion to the back contact and the slow rate of reaction. A non-selenization process was proposed to be developed for fabricating CIGS thin film by these authors; however, the annealing temperature was over the decomposition temperature of the typical flexible polymer substrates. A novel method by using a rapid laser annealing process has also been proposed and investigated to demonstrate the feasibility of crystallization and grain growth for CIGS thin film. In our prior study, a continuous wave (CW) second harmonic wavelength of Nd:YAG (λ_o = 532 nm) laser was selected to improve the microstructure of CIGS thin film with a change of the laser optical power from 2.25 to 3.00 W for 200 sec. CIGS chalcopyrite (112), (220/204) and (312/116) phases were formed in the laser-annealed CIGS thin films, but the weak diffraction peaks of Cu-Se related phases were also observed due to the insufficient energy for the grain growth. In this study, the laser annealing time was controlled to accomplish long-range atomic diffusion, chemical reactions and grain growth with a considering mass-production manufacturing. The crystal structures and chemical compositions of the laser-annealed thin films were analyzed by X-ray diffraction and energy-dispersive X-ray spectroscopy as a function of laser annealing time. The effects of them on the optical properties and electrical characteristics of CIGS thin films were examined by using an UV-Visible spectrophotometer and a Hall Effect measurement system. Not only sufficient crystal structure but also excellent optical and electrical properties were obtained by this rapid laser annealing process for CIGS thin film. Acknowledgement: This work (Grants No. C0267866) was supported by Business for Academic-industrial Cooperative establishments funded Korea Small and Medium Business Administration in 2015.

FP-20 Production of Ag Clusters by Plasma Gas Condensation and their Incorporation in an a:C Sputtered Matrix, *I Carvalho,* University of Coimbra, Portugal*;* ***Sandra Carvalho****,* University of Minho, Portugal*; A Cavaleiro,* University of Coimbra, Portugal

Ureteral stents are essential tools in contemporary urologic practice. However, urethral stents present complications at the level of microbial colonization leading to recurrent infections, being of extreme importance the development of new materials. In this way, the main propose of this study is to develop a new material aiming to improve biocompatibility, corrosion resistance, elasticity and, most especially, to reduce or eliminate adverse reactions in the body due to microbial colonization. A silver delivery device composed of a DLC coating embedded with Ag clusters, covering the existing stent material, is proposed.

Firstly, it is necessary evaluate the Ag clusters formation with respect to their size and shape since these parameters will controls the silver ion release and consequently the antimicrobial performance. In this sense, Ag clusters were produced by plasma gas condensation process consisting in a gas aggregation cluster source connected to a main deposition chamber. The work pressure in the main chamber and gun was 4 $x10^{-3}$ Pa and 100 Pa, respectively to produce Ag clusters, which will be incorporated in a:C matrixes with a current density applied of 2.4 up to 9.2 mA cm^{-2}.

The clusters growth was evaluated in static and rotation mode. Current density applied to Ag target was kept constant at 7.6 mA cm^{-2}. TEM results show that the deposition in rotation mode (2 rpm) leads to a decrease in the clusters mean size, 25 nm to the static mode to 15 nm to the rotate

mode. In both modes, the clusters shape is spherical, however in the rotate mode the clusters appear to aggregate. The crystalline structure of Ag clusters was evaluated by the selected area diffraction patterns and the results show the formation of fcc crystalline Ag.

FP-22 Biocompatible Thin Film Intermetalic $Ti_{3-x}AuO_x$, ***Vladimir Vishnyakov,*** University of Huddersfield, UK*; B Beake,* Micro Materials Ltd, UK*; J Devitt,* University of Huddersfield, UK

Titanium-gold intermetallics (both materials being biocompatible) are well suited as a replacement for hard tissue, and represents an opportunity to develop new medical applications in the field of arthritis, rheumatic and musculoskeletal diseases. It has been reported by other groups that intermetallics have the additional advantage, in right composition and crystallinity, of having a hardness value as high as 8 GPa. This high degree of hardness makes material exceptionally valuable for load-bearing body implants, for example. It is also know that the incorporation of relatively small amounts of oxygen, at the level of few atomic percent, can lead to titanium hardening. On the other hand, a small percentage of oxygen is almost inevitably incorporated in the titanium thin films during Physical Vapour Deposition (PVD). Ion sputtering of elemental titanium and gold targets with argon has been used to deposit $Ti_{3-x}AuO_x$ (where $0.03<x<0.1$) onto various substrates in pure Ar or Ar/O atmosphere. Energy Dispersive X-Ray Spectroscopy (EDX) and X-Ray Diffraction (XRD) have been used to assess the film composition and crystalline structure. Even at the highest level of investigation, the oxygen content in the films remain crystalline and its hardness can increase to almost 10 GPa. In addition, nanoscratching reveals certain loss of ductility as oxygen content increases.

FP-24 Features of Incident Particle Flux determining Growth Rates and Electrical Properties of Indium Tin Oxide Films Deposited by Ion-plating with dc Arc Discharge, ***Hisashi Kitami,*** *T Sakemi, Y Aoki,* Sumitomo Heavy Industries, Ltd., Japan

We have investigated the factors limiting growth rates and electrical properties of indium tin oxide (ITO) films on glass substrates (@ 200 °C) deposited by ion-plating with dc arc discharge. We clarified the incident particle fluxes during film growth under the deposition conditions; the pressure in the deposition chamber of 0.18 – 0.71 Pa and the discharge current of 150 A. The resulting thickness of the ITO films was 150 (±3 %) nm. The carrier concentration of the ITO films was 1.0×10^{21} (±3 %) cm^{-3}.

We measured the incident particle fluxes of the neutral atoms and ions for each species at the substrate level using a mass-energy analyzer (Hiden, EQP300), a Langumuir probe and a diaphragm gauge during the deposition. To clarify the factors limiting the growth rate and Hall mobility (μ_{-H}) of ITO films, we analyzed the relationship between the growth rates, μ_{-H}, and the incident fluxes of In species and O species.

As the pressure increased, the fluxes of In^+ (>10 eV) ions and O^+ (> 10eV) ions decreased and the fluxes of In^+ (<10 eV) ions and O^+ (< 10eV) ions increased. We found that the fluxes of In^+ (>10 eV) ions were dominant factor to limit the growth rate. The sticking coefficient of In species should be dependent on the incident energy into the substrate. As the fluxes of In^+ (> 10eV) ions and/or O^+ (> 10eV) ions increased, μ_{-H} increased. The μ_{-H} was governed by the microstructure and carrier concentration of the films, which originated in the incident energy fluxes (> 10eV) of In^+ ions and/or O^+ ions under the current deposition conditions. We will discuss it in more detail.

FP-25 Development and Microstructure Characterization of Single and Duplex Nitriding of UNS S31803 Duplex Stainless Steel, *L Varela,* University of São Paulo, Brazil*; C Pinedo,* Heat Tech & University of Mogi das Cruzes, Brazil*; H Dong, X Li,* University of Birmingham, UK*;* ***André Tschiptschin,*** University of São Paulo, Brazil

The microstructural changes involved in single Low Temperature Plasma Nitriding - (LTPN) and Duplex Nitriding (DN): High Temperature Gas Nitriding (HTGN) + Low Temperature Plasma Nitriding (LTPN), surface treatments of UNS S31803 were studied. Specimens of UNS S31803 duplex stainless steel (DSS) were (i) single low temperature plasma nitrided (LTPN) and (ii) duplex nitrided (DN) using high temperature gas nitriding (HTGN), followed by low temperature plasma nitriding (LTPN). In both cases, LTPN was carried out at 400°C for 20 h, in a $75\%N_2+25\%H_2$ atmosphere. HTGN was carried out at 1200ºC, under a 0.1 MPa high purity N_2 gas atmosphere, during 8 hours. The microstructure of the as received material was composed by ferrite and austenitic stringers, aligned in the rolling direction. The results showed that LTPN of the UNS S31803 duplex stainless steel promotes the formation of a duplex modulated structure composed by 2.5 µm thick, 1509 HV hard, expanded ferrite (α_N) regions, and 3.0 µm thick, 1362 HV hard, expanded austenite (γ_N) regions on ferrite and austenite grains, respectively. Intense coherent ε-Fe_3N nitride precipitation inside expanded ferrite was observed. ε-Fe_3N nitrides precipitated with an orientation relationship [111] α_N // [120] ε-Fe_3N, leading to increased microhardness of the expanded ferrite regions. After the first step of the duplex nitriding treatment (HTGN) a 550 µm thick, 330 HV hard, nitrogen rich, fully austenitic layer formed at the surface of the specimens, by transformation of ferrite stringers into austenite. The second nitriding step (LTPN) led to the formation of a homogeneous expanded austenite layer, 1144 HV on top of the thick fully austenitic layer, formed during the first step. The duplex treatment resulted in a more homogeneous, precipitate-free, microstructure and a better transition between the mechanical properties of the hardened outermost layer and the softer substrate.

Surface Engineering - Applied Research and Industrial Applications

Room Grand Exhibit Hall - Session GP

Symposium G Poster Session

GP-2 Oxidation Resistance of Cr_2N and Cr_2WN Coatings Deposited on Ferritic Stainless Steel, *S Yang,* ***Yung-Ting Huang,*** National University of Kaohsiung, Taiwan*; Y Chang,* National Formosa University, Taiwan*; D Lin,* National University of Kaohsiung, Taiwan

Bipolar plate is a key component of solid oxide electrolysis cells, which increases the power density and decreases the costs of the stacks. In general, high operating temperature cause a severe oxidation to decline electrical conductivity. Although Crofer 22 APU (ferritic stainless steel) was developed specifically for SOFC interconnect applications, the oxidation rate is not sufficiently low to enable uncoated Crofer22 APU interconnects to meet the current 40,000 h SOFC lifetime requirement. Therefore, Crofer 22 APU also requires a protective coating both to retard the oxidation rate and to prevent the volatile chromium species.

In this study, Cr_2N and Cr_2WN coatings were selected as the protective coatings deposited on Crofer 22 APU ferritic stainless steel by cathodic arc evaporation. Oxidation kinetics of the Cr_2N- and Cr_2WN-coated samples was evaluated via isothermal tests in atmospheric furnace at 800°C for 1,000 h. Morphology and cross sections of scales were examined under a field-emission scanning electron microscope in both backscattered and secondary electron modes. Coating phase assemblies were assessed using X-ray diffraction. High resolution transmission electron microscopy was utilized for a close examination of the coating/alloy interfacial chemistry. The results showed Cr_2N and Cr_2WN-coatings on Crofer 22 APU possessed denser structure and excellent adhesion between coating/alloy. The top scale of Cr_2N and Cr_2WN-coatings belong to spinel structure, but Cr_2WN-coating had higher manganese content than Cr_2N-coating after 1,000 h oxidation. In addition, Cr_2WN-coating possessed smooth surface of scale due to W-doping to decrease surface roughness. After 1,000 h oxidation, both Cr_2N and Cr_2WN-coatings had bilayer scales were Cr_2O_3 and $(Mn,Cr)_3O_4$. Both Cr_2N and Cr_2WN-coatings had excellent anti-oxidation performance; moreover, Cr_2WN-coating had the lower oxidation rate constant than Cr_2N-coating.

GP-4 Synergetic Effect Improved Deposition of Titanium Nitride Films, *C Chang,* Ming Chi University of Technology, Taiwan*; C Ho,* MingDao University, Taiwan*; P Chen,* Da-Yeh University, Taiwan*; W Chen, D Wang,* MingDao University, Taiwan*;* ***Wan-Yu Wu,*** Da-Yeh University, Taiwan

Cathodic arc deposition (CAD) has been widely used in industry for high quality thin film coatings. However, the CAD also produces macro particles or droplets during the deposition process. leading to the degradation of the film properties. Lately, a newly developed physical vapor deposition process known as high power magnetron sputtering (HiPIMS) was found to have the capability of yielding highly ionized flux of both gas and sputtered materials by applying a high power in short pulses to the target. As a result, a smoother and denser thin film with better adhesion to the substrate can be obtained, leading to enhanced mechanical, electrical, and optical properties. However, it was also found the deposition rate of the HiPIMS process was much slower than conventional dc magnetron sputter deposition and CAD. Therefore, a hybrid deposition system combining CAD and HiPIMS was studied in this paper to gain synergetic effect. The two processes were used alternatively in different sequences. Titanium nitride (TiN) film was deposited in such hybrid system to investigate their microstructure and the mechanical properties, including surface roughness, hardness and friction coefficient. We demonstrate that the hybrid

deposition system provides a synergetic effect of combining the advantages and compensates the diadvantages of these two deposition techniques. It was found that the macro particles are suppressed. Enhanced hardness was observed in CAD based TiN thin film.

GP-5 Fuel Cell Hot Runner-layer Composite Carbon Bipolar Plates, *S Wu,* MingDao University, Taiwan*;* ***Ai-Huei Chiou,*** National Formosa University, Taiwan*; Y Huang,* Fujian University Of Technology, China

Bipolar plate is one of the important components of proton exchange membrane fuel cell (PEMFC), which in addition to the fuel and the gasifying agent supplied to the reaction zone may be external, and has removed the product, collect current, and as a mechanical support structure of the cell stack . Weight and cost of the proportion of the bipolar plates accounted for 60% and 30% of the battery. Therefore, by using cheap materials and lightweight design to improve the flow channel, will greatly reduce the weight, size and cost of the battery. Therefore, the present study used a lightweight inexpensive PMMA sheet as a bipolar plate body molding material, the use of hot pressing technology has been formed on the upper layer of the PMMA sheet of conductive graphite carbon powder , made of composite bipolar plate. And by hot pressing temperature, time and pressure control, work out the optimum parameters. At the same time, also made out of composite bipolar plate corrosion resistance, electrical conductivity and surface material graphite adhesion effect analysis.

GP-6 Oxinitride Coatings for Milling Tools, ***Joern Kohlscheen,*** Kennametal GmbH, Germany*; V Derflinger,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein

Industrial manufacturing has to adapt to an increasing share of difficult-to-cut materials like stainless steels and nickel based alloys. Well-established nitride coatings like TiAlN have limitations in friction behavior and high temperature stability. To overcome some of these limitations, oxide and oxinitride thin films are becoming more popular in PVD coating research and application. The Al-O system is generally considered as first choice and has been studied intensively. In the present work, a well proven AlTiN base layer was modified by adding one or more AlON and AlCrON layers with a thickness of up to 1 micron. Deposition was done by cathodic arc PVD using a commercial system on carbide samples (WC/Co). Al cathode material was evaporated in a plasma of pure oxygen or an oxygen/nitrogen gas mixture. Basic mechanical properties of the resulting multi-layers were determined by universal hardness testing. Structural analysis was done by SEM and XRD. It will be shown that oxidic top layers have quantifiable effects on friction and wear behavior. AlTiN/AlON multi-layers seem to be more resistant against abrasive wear than mono or bi-layer (nitride/oxide) coatings of comparable thickness. The main effect of the oxidic top layer(s) seems to be reduction of the friction in the cutting process. Milling of mild steel (dry and wet) was performed to test the wear behavior of the coated carbide inserts (ISO P). Thermal cracking at the cutting edge could be significantly reduced when oxide top layers were added.

GP-8 Phase Composition, Microstructure Evolution and Wear Behavior of Ni-Mn-Si Coatings on Copper by Laser Cladding, ***Peilei Zhang,*** *X Liu, H Yan,* Shanghai University of Engineering Science, China

Three Ni–Mn–Si coatings were synthesized on copper plate by laser cladding. There are Mn_5Si_2, Mn_5Si_3, Mn_3Si, Ni_3Si, Ni_2Si, Cu_3Si, Mn_3Ni_2Si and $Mn_6Ni_{16}Si_7$ in three coatings. Ni_2Si and Ni_3Si were found in Coating 1# and 2# and there is not any $MnSi_{1.75-x}$ phase in three coatings. Mn_3Ni_2Si phase was found in Coating 1# and $Mn_6Ni_{16}Si_7$ phase was found in Coating 2# and 3#. Phases in Coating 1# should be MnSi + MnNiSi. $Mn_{15}Ni_{50}Si_{35}$ and $Mn_3Ni_3Si_2$ were found in Coating 2#. $Mn_3Ni_3Si_2$ and Mn_3Ni_2Si were found in Coating 3#. Cu_3Si was found in all three coatings. The highest hardness which is about 1100 HV occurs in the clad layer of Coating 1#. Metal silicates (Ni-Si and Mn-Si) are the major factor in increasing the hardness of coatings. There are mainly Ni-Si metal silicates in Coating 1#, Mn-Si metal silicates in Coating 2# and 3#. Hardness of Ni-Mn-Si coatings depends on Ni-Si phases especially Ni_3Si in laser processing. The average friction coefficient for Coating 1#, Coating 2# and Coating 3# is 0.1964, 0.2393 and 0.2582, respectively. Ni-Si phase plays a more important role than Mn-Si in increasing the hardness and decreasing the friction coefficient of coatings.

GP-9 Assessment of Surface Integrity During Machining of Superduplex Stainless Steel Obtained With Three Different PVD Hard Coatings, ***Edinei Locks Junior,*** Católica SC, Brazil*; P Stolf, M Martins,* Centro Universitário Cátolica de Santa Catarina - CATÓLICA -SC, Brazil*; F Amorim, R Diego Torres,* Pontifícia Universidade Católica do Paraná - PUCPR, Brazil*; J Paiva,* Centro Universitário Católica de Santa Catarina - CATÓLICA -SC, Brazil

The Superduplex stainless steel (SDSS) are biphasic materials compound portion of ferrite and austenite with equal parts approximately as well as high levels of chromium and nickel in its chemical composition. This materials are usually employed as pipeline for offshore oil and gas industry. During the cutting process this material presents the follow combination: (i) It shows a tendency to work hardening the surface reflecting in microstructural modifications and residual stress on surface machined; and (ii) It presents high temperatures in the cutting region, resulting in a reduction of tool life. The goal of this work is to evaluate the surface integrity (work hardening and stress corrosion behavior) of the SDSS obtained after machining process (finish turning) with cemented carbide tools coated with three different PVD coatings. The cemented carbide inserts were coated by Physical Vapor Deposition (PVD) with $Al_{50}Cr_{50}N/Ti_{95}Si_5N$, $Al_{50}Cr_{50}N$ and $Al_{67}Ti_{33}N$. The responses analyzed were tool wear, microstructural characterization, machined surface and stress corrosion analysis. The results indicate that aluminum-rich ($Al_{67}Ti_{33}N$) coatings improve the wear resistance of inserts in this type of machining as well as reduce the surface hardening levels of machined part, reflecting in a better stress corrosion resistance.

GP-11 Surface and Interface Characterstics of CeO_2 doped Al_2O_3 Coating on Solution Treated and Peak Aged AZ91 Mg Alloy, ***Sanjeet Kumar,*** *D Kumar, J Jain,* Indian Institute of Technology Delhi, India

Mg alloy, being lightest among the engineering materials, has limited use in automotive, biomedical and structural industries due to poor surface mechanical properties. Protection against wear and corrosion may increase the use of Mg-alloys in various engineering applications. Wear and corrosion being the surface related phenomenon, surface modification by various techniques can be sought for improved performance. This paper investigates the deposition and estimation of surface and interface properties of thermally sprayed alumina based coatings. Effect of CeO_2 doping into Al_2O_3 based coatings is also explored. The elastic modulus and hardness at surface and interface both were measured using nanoindentation. In order to investigate the role of substrate microstructure on coating characteristics, the solution treated and peak aged samples of AZ91 Mg alloy have been used as a substrate material. The coatings were characterized using scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD). The results indicate that peak aged substrate microstructure results in coating with better interfacial properties as compared to solution treated case. The role of ceria doping in manipulating the microstructure is discussed in detail.

GP-14 Vacancies in MONTAN – a Mechanism for Tuning the Hardness–toughness Relationship, ***Fedor F. Klimashin,*** CDL-AOS TU Wien, Austria*; M Arndt,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P Polcik,* Plansee Composite Materials GmbH, Germany*; L Lobmaier, N Koutná,* TU Wien, Austria*; D Holec,* Montanuniversität Leoben, Austria*; P Mayrhofer,* TU Wien, Austria

The cubic-structured nitrides of Mo and Ta exhibit excellent tribo-mechanical and electrical properties and are often used as alloying components for improving e.g. materials resistance against wear and oxidation. The outstanding properties both materials owe to their inherent driving force to form vacancies, which are commonly disregarded for any material.

Fusing Mo–N[1,2] with Ta–N[2] – experimentally and theoretically – we have investigated a novel quasi-binary materials system Mo–N–Ta–N. Its natural preference for point defects inherited from relative binaries can furthermore be significantly influenced e.g. by altering the chemical potentials. When dealing with the point defects, the *ab initio* studies are of a great significance: particularly to distinguish between the structures developing “without” point defects and with Schottky defects is anything but trivial experimental issue. Varying the type and volume density of vacancies we present the evolution of structure and mechanical properties of “MoNTaN” coatings. The insights into the origin of the observed phenomena allow us to tune the hardness–toughness relationship and hence design materials for applications requiring tailor-made properties.

References:

1 Klimashin, F., Koutná, N., Euchner, H., Holec, D. & Mayrhofer, P. The impact of nitrogen content and vacancies on structure and mechanical

properties of Mo–N thin films. *Journal of Applied Physics* **120**, 185301 (2016).

2 Koutná, N., Holec, D., Svoboda, O., Klimashin, F. F. & Mayrhofer, P. H. Point defects stabilise cubic Mo-N and Ta-N. *Journal of Physics D: Applied Physics* **49**, 375303 (2016).

GP-15 Effects of Solidification Behaviour on the Microstructure, Hardness and Corrosion Resistance Properties of Laser Alloyed Al-Fe-Si Coatings, *E Akinlabi,* ***Olawale Fatoba****, E Makhatha,* University of Johannesburg, South Africa

Aluminum and its alloys have been a successful metal materials used for many applications like commodity roles, automotive and vital structural components in aircrafts. A substantial portion of Al-Fe-Si alloy is also used for manufacturing the packaging foils and sheets for common heat exchanger applications. The present research was aimed at studying the morphology and distribution of the iron-containing intermetallics in the Al-Fe-Si alloy. These Fe-intermetallic compounds influence the material properties during rapid cooling by laser alloying technique and play a crucial role for the material quality. Thus, it is of considerable technological interest to control the morphology and distribution of these phases in order to eliminate the negative effects on microstructure. A 3 kW continuous wave ytterbium laser system (YLS) attached to a KUKA robot which controls the movement of the alloying process was utilized for the fabrication of the coatings at optimum laser parameters. The fabricated coatings were investigated for its hardness and corrosion properties. The corrosion performance was investigated in 0.5M H_2SO_4 and 0.5M NaCl solutions at 30^oC via Open Circuit Potential (OCP) and Linear Polarization techniques. The field emission scanning electron microscope equipped with energy dispersive spectroscopy (SEM/EDS) were used to study the morphology of the fabricated coatings and X-ray diffractometer (XRD) for the identification of the phases present in the coatings . The coatings were free of cracks and pores with homogeneous and refined microstructures. The enhanced hardness and anti-corrosion performances were attributed to metastable intermetallic compounds αAlFeMnSi, $Fe_2Si_2Al_2$, Fe_3SiAl_{12}, Al_5Fe_2, Fe_5Si_3, $Al_4Fe_5Si_6$ formed. Computational model used in this research authenticates reasonably with the experimental results.

Advanced Characterization Techniques for Coatings and Thin Films
Room Grand Exhibit Hall - Session HP
Symposium H Poster Session

HP-2 How Can the Icephobicity of an Engineered Surface be Screened by Means of Simple Laboratory Testing and Characterization?, *G de la Fuente, L Angurel,* CSIC-Universidad de Zaragoza, Spain*; C López-Santos, V Rico, A Borrás, A González-Elipe,* Instituto de Ciencia de Materiales de Sevilla (CSIC), Spain*; J Mora, P García,* ***Alina Agüero****,* Instituto Nacional de Técnica Aeroespacial (INTA), Spain

Ice formation and accretion present serious safety issues for aircraft, the automotive industry, signalling devices, railway systems, buildings, wind energy conversion plants, terrestrial power lines and many others. Considerable effort has been devoted to tackle this crucial yet challenging issue, mainly by developing anti-icing coatings that, based on the idea that a non-wetting material would diminish the water-surface contact and avoid the ice formation, link the hydrophobic properties of the materials with a supposed anti-icing function. However, it has been demonstrated that this rule is not always true, as in very humid environments ice can form on superhydrophobic materials.

The Canadian-European project"Super-IcePhobic Surfaces to Prevent Ice Formation on Aircraft" (PHOBIC2ICE) aims at producing durable icephobic surfaces by means of surface engineering and/or coatings. One of the main challenges faced by this project is to achieve screening laboratory tests capable of establishing if a given coating or engineered surface shows promising anti-icing properties, before having to run complex and expensive icing wind tunnel (IWT) or flying tests. Most published work in this domain use the measurement of the wetting angle and on the superhydrophobicity level of the surfaces as a pass or not pass criterion for further testing, despite that hydrophobicity and icephobicity are not necessarily correlated. The present work evaluates a simple test developed within the project, for measuring ice accretion, and compares it with a series of other simple laboratory tests and characterization techniques such as wetting angle, contact angle hysteresis, freezing delay, and roughness. Various surface treatments have been investigated in an attempt to correlate the results of these test results and the icephobicity of said materials. On the second stage of PHOBIC2ICE, the results will be compared with those obtained in an icing wind tunnel and flight tests.

HP-3 Pushing the Envelope in Variable Temperature Nanoindentation: High and Cryogenic Temperature Measurements, *N Randall, M Conte,* Anton Paar TriTec, Switzerland*; J Schwiedrzik, J Michler,* EMPA, Switzerland*;* ***Pierre Morel****,* Anton Paar, USA

One of the primary motivations for development of instrumented indentation was to measure the mechanical properties of thin films. Characterization of thin film mechanical properties as a function of temperature is of immense industrial and scientific interest. The major bottlenecks in variable temperature measurements have been thermal drift, signal stability (noise) and oxidation of/condensation on the surfaces. Thermal drift is a measurement artifact that arises due to thermal expansion/contraction of indenter tip and loading column. This gets superimposed on the mechanical behavior data precluding accurate extraction of mechanical properties of the sample at elevated/cryogenic temperatures. Vacuum is essential to prevent sample/tip oxidation at elevated temperatures and condensation at cryogenic temperatures.

In this poster, the design and development of a novel nanoindentation system that can perform reliable load-displacement measurements over a wide temperature ranges (from -150 to 800 °C) will be presented emphasizing the procedures and techniques for carrying out accurate nanomechanical measurements. This system is based on the Ultra Nanoindentation Tester (UNHT) that utilizes an active surface referencing technique comprising of two independent axes, one for surface referencing and another for indentation. The differential depth measurement technology results in negligible compliance of the system and very low thermal drift rates at high temperatures. The sample, indenter and reference tip are heated/cooled separately and the surface temperatures matched to obtain drift rates as low as 1nm/min at 800 °C without correction. Instrumentation development, system characterization, experimental protocol, operational refinements and thermal drift characteristics over the temperature range will be presented, together with a range of results on different materials.

HP-4 Surface and Sub-Surface Damage in Si and Ge Crystals after Nano-Machining, ***Jozef Keckes****,* Montanuniversität Leoben, Austria*; Z Zaprazny, D Korytar, M Jergel, Y Halahovets, P Siffalovic,* Slovak Academy of Sciences, Slovakia*; C Ferrari, C Frigeri,* CNR-IMEM Institute Parma, Italy*; I Matko, J Drga,* Slovak Academy of Sciences, Slovakia*; P Vagovič,* DESY, Center for Free-Electron Laser Science, Germany

Nano-machining methods like single point diamond turning (SPDT) and fly cutting (FC) are used to fabricate high-quality active surfaces of X-ray crystal optics. In this contribution, experimental results from Ge and Si surfaces will be used to demonstrate sub-surface damage (SSD) of the crystal lattices after various machining steps. The machined surfaces are characterized using atom probe microscopy, transmission electron microscopy (TEM), focused ion beam milling, scanning electron microscopy and Raman spectroscopy. The results reveal that the SSD and residual stresses correlate with the machining conditions. The morphology of surface ripples as well as a periodic variation of Raman peak shift are observed and correlated. TEM results are used to demonstrate the influence of the machining on the cross-sectional lattice damage.

This work was supported by projects APVV-14-0745 and VEGA 2/0004/15 and FFG M-ERA.net project 841930 XOPTICS.

HP-6 Influence of Post-deposition Annealing on the Electrical Properties of Thin SiO2/a-Si:H/SiO2 Structures Obtained by Electron Cyclotron Resonance, ***David Mateos****,* Universidad Autónoma de Baja California, Mexico*; J Diniz,* University of Campinas, Brazil*; N Nedev, B Valdez, M Curiel,* Universidad Autónoma de Baja California, Mexico*; M Mederos,* Renato Archer Center for Information Technology, Brazil*; O Pérez, A Arias,* Universidad Autónoma de Baja California, Mexico

In this work results are presented for the deposition of thin multilayer structures, SiO2/a-Si:H/SiO2, by electron cyclotron resonance-chemical vapor deposition (ECR-CVD) technique. The ECR remote plasma systems present excellent characteristics that allow deposition of high quality uniform films at room temperature suitable for application in CMOS technology.

The depositions were carried out at an applied microwave power of 250 W under a gas pressure of 2.0 mTorr and a substrate temperature of 20°C. SiO2 film with thickness of ~6-8 nm were deposited using O2 and 2% SiH4 diluted in Ar as precursor gases. Hydrogenated amorphous silicon (a-Si:H)

films with thickness of ~3-4 nm were deposited using the same flows of SiH_4 and Ar as in the case of SiO_2 but without O_2 flow. The films were deposited on p-type (100) c-Si substrates.

The film thicknesses in the multilayer structures were evaluated using the deposition rates of the a-Si:H and SiO_2. Individual layers of SiO_2 and a-Si:H were deposited on c-Si wafer and their thicknesses were determined ellipsometrically. As-deposited films were annealed at 800°C and 1100°C in N_2 atmosphere for 60 minutes.

Three-layer MOS structures were patterned by lithography and sintered in forming gas for 20 min. The influence of high temperature post-deposition annealing on the electrical properties of the structures was studied by current-voltage (I-V) and capacitance-voltage (C-V) measurements.

I-V measurements indicated that the high temperature annealing improves the gate dielectric properties. The C-V dependencies showed a correlation between the annealing temperature and the memory window of the structures. A possible explanation is that the high temperature annealing leads to structural modifications and formation of traps suitable to trap carriers. In addition, a strong improvement of the insulating properties of the SiO2 films was observed. Both changes may contribute to the observed memory effect. The obtained results show that the studied structures have a potential for application as gate insulators in non-volatile memory devices.

HP-7 Comparison of Three Methods for Ellipsometry Characterization of Thin Absorbing Films, ***Frank Urban,*** Florida International University, USA; *D Barton,* Retired, USA

Ellipsometry is a surface and film analytical technique which takes advantage of the fact that light reflecting from a surface undergoes a change in polarization state. The change in state results from the geometric structure and materials making up the reflecting surface. The predicted change in state can be determined through appropriate application of Maxwell's equations resulting in a mathematical model containing the surface descriptive parameters. In the common measurement scenario some of these parameters may be known and some, unknown, for example film thickness. Thus the method first requires fabrication of reflecting surfaces which result in tractable models. Next, measurements are made, at times spectroscopic, at multiple incidence angles, and on films of increasing thickness. Finally adjustments in the model and parameters are performed to put measurement and theory into agreement. It is well understood that these steps will depend upon the materials and thicknesses and other aspects of the reflecting surface. The purpose of the work to be presented is to make a direct comparison between different methods for determining the model and achieving agreement using the exact same films and measurements. The relative advantages and disadvantages of each method will be described. The three methods are that of Yamamoto which solves for pairs of measurements on growing films, the method in common use which seeks statistical agreement using the Levenberg-Marquardt algorithm to minimize mean square error, and the methods of the authors in the n-k plane which cast the problem into a deterministic mathematical expression which is solved numerically, typically by Newton-Raphson. Three different materials systems are explored; NiOx/Si, Cr/Si, and Ni/BK7. In each case the film is absorbing and ranges from a few nanometers up to approximately 30 nm in thickness. Differences in resolution, accuracy, model specificity, and difficulty of application will be presented.

Topical Symposia
Room Grand Exhibit Hall - Session TSP
Symposium TS Poster Session

TSP-1 Improved Electron Field Emission Characteristics of Amorphous Carbon Film Embedded with Graphene Nanocrystallites, *K Sun, L Yang,* Xi'an Jiaotong University, China; ***Dongfeng Diao,*** Shenzhen University, China

With excellent mechanical, chemical, and electronic properties, carbon-based thin films have drawn much attention as field emitter candidates in the past few years. Since amorphous carbon (a-C) films don't have outstanding characteristics on s and emission currents, metals are often doped in a-C films to improve the field emission characteristics . Graphene exhibits lower s and larger emission currents, but the emitters are easy to be destroyed under high voltages. Therefore, embedding graphene nanocrystallites in the surfaces and interior structures of a-C film s could be a potential method to improve field emission characteristics of a-C films.

In this study, a-C films and graphene sheet embedded carbon (GSEC) films ware prepared in electron cyclotron resonance (ECR) electron irradiation with different electron irradiation energy. Then the surface morphologies and structures of films were characterized by scanning electron microscope (SEM) and transmission electron microscope(TEM). The field emission currents were measured with a parallel plate capacitor setup. The results showed that GSEC films had a better field emission property than a-C films. The formation of graphene nanocrystallite lowered the work function and increased the local field enhancement factor on the surfaces, and enhanced the conductivity in the interior structures. The research highlighted that graphene nanocrystallite structures embedded in amorphous carbon films have an important role in electron field emission.

TSP-2 Zirconium Carbide Based Self-Healing Ceramics, ***Angela Yang,*** University of North Texas, USA; *P Petry,* University of Rouen, France; *I Hammood, R Reidy, S Aouadi,* University of North Texas, USA

Self-healing ceramics are novel materials that have the ability to restore mechanical properties of cracked materials through annealing. This research focuses on the self-healing ability of zirconium carbide based nano-composites. Zirconium carbide is a stable compound and is commonly used in harsh environments, such as those encountered in space and aerospace applications. A Vickers Hardness Tester was used to inflict small diamond shaped cracks in the sample. The sample was then self-healed through heating at 1100°C for four hours and analyzed using scanning electron microcopy and x-ray diffraction to determine the chemical and structural changes that occurred at the crack site. Three sample compositions were tested for their self-healing ability in this study, namely $ZrC/SiC/Y_2O_3$, $ZrC/Al_2O_3/Y_2O_3$, and $ZrC/Si_3N_4/Y_2O_3$. Sintered and unsintered samples of the same composition were compared to each other. The sintered samples were heated to 1000°C for three hours. The introduction of Fe_2O_3 to $ZrC/SiC/Y_2O_3$ interestingly was found to yield tubular whiskers when sintered.

Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B7

Plasma Diagnostics and Growth Processes

Moderators: Ante Hecimovic, Ruhr-Universität Bochum, Peter Bruggeman, University of Minnesota, USA

8:00am **B7-1 Plasma Surface Interaction Model for Titanium Nitride Thin Film Growth**, ***Tobias Gergs***, *J Trieschmann,* Ruhr University Bochum, Germany*; M Hans, D Music, J Schneider,* RWTH Aachen University, Germany*; T Mussenbrock,* Ruhr University Bochum, Germany

Reliable correlations between a set of plasma parameters and corresponding surface phenomena on the atomistic scale are scarce. The main reason being the complex physics of the two different states of matter, where at least one of which - the plasma - is far from an equilibrium state. In this contribution, we provide an initial step towards a consistent plasma surface interaction model, which covers the combination of generic materials as well as plasma discharges. As a proof of concept, we present a model which couples a direct current magnetron sputtering discharge with the resulting deposition of a titanium nitride thin film. In particular, the nucleation of cubic titanium nitride is studied at various substrate temperatures and fluxes starting from the amorphous state. Initially, the desired plasma parameter range is found by the extrapolation of classical molecular dynamics findings, validated by density functional theory calculations. This *a priori* knowledge is employed as a starting point for test particle simulations taking consistently into account the plasma and its global parameters. The resulting heavy particle fluxes and corresponding distribution functions are then again input to molecular dynamics simulations. Finally, the outcome of these simulations are compared to experimental results for the respective plasma discharge. In conclusion, it is argued that the proposed plasma surface interaction model is applicable to various plasma and material systems as well as surface modification phenomena.

Financial support provided be the German Research Foundation (DFG) in the frame of the collaborative research centre SFB-TR 87 is gratefully acknowledged.

8:20am **B7-2 Correlation of the Debye Sheath Thickness and (Cr,Al)N Coating Properties for HPPMS, dcMS and PCAE Processes**, *K Bobzin, T Brögelmann, N Kruppe, M Arghavani,* ***Martin Engels***, Surface Engineering Institute - RWTH Aachen University, Germany

Physical vapor deposited (PVD) coatings are widely-used in tool applications such as the plastics processing. Predominant aims of the PVD coating application on the tools are the enhancement of the tool lifetime and an improvement of economic efficiency. The achievement of these aims amongst others strongly depends on a homogeneous distribution of the coating properties with respect to the entire functional surface, in particular on complex shaped tools. In many cases, due to the line-of-sight characteristics in PVD processes this homogeneity is hard to achieve. Besides the commonly used rotation of the tools or extensive mounting concepts, another possibility to overcome this issue is the choice of a suitable PVD technology such as the high power pulsed/impulse magnetron sputtering (HPPMS/HiPIMS), or the pulsed cathodic arc evaporation (PCAE). In order to characterize the influence of the different technologies on the coating homogeneity, the corresponding plasma properties, especially the Debye sheath thickness, can be used. Due to the positive charge in this area, the transport of positive charged ions of the coating material to the tool surface is strongly influenced. Therefore, it can be expected that a decreasing thickness increases the homogeneity of the coating, especially on complex surfaces with sharp edges, since the shielding of the surface is reduced. In the present work measurements on plasma properties as well as on coating properties using the high performance plasma processes HPPMS and PCEA with varying process parameters average power P, pulse length t_{on} and frequency f were carried out. In addition, the investigations were carried out as reference with a direct current magnetron sputtering (dcMS) process. In order to determine the Debye sheath thickness and the correlating homogeneity of coatings, the coating system (Cr,Al)N was chosen, as it is widely used as protective coating for plastics processing tools. In a first step, the plasma was analyzed using a Langmuir probe system. From the results of the U-I curves the plasma properties, especially the Debye sheath thickness, were determined. In a second step, (Cr,Al)N coatings were deposited with selected promising process parameters on structured substrates to determine the coating homogeneity. The coatings were analyzed regarding the morphology by scanning electron microscopy, the chemical composition by means of glow discharge optical emission spectroscopy as well as the universal hardness and the indentation modulus by nanoindentation. In summary, significant correlations between the processes and parameters, the Debye sheath thickness and the coating homogeneity were identified.

8:40am **B7-3 The Study of Spoke Merging and Splitting in HiPIMS Plasma**, ***Jaroslav Hnilica***, *P Klein,* Masaryk University, Czech Republic*; F Lockwood-Estrin,* University of Liverpool, UK*; P Vašina,* Masaryk University, Czech Republic*; J Bradley,* University of Liverpool, UK

High power impulse magnetron sputtering (HiPIMS) discharges demonstrate plasma self-organization, in which distinct ionization zones (often called spokes) can be seen to rotate in the ExB direction. Recently, a phenomena of spoke splitting and merging was observed in HiPIMS plasma using an array of phase correlated azimuthally arranged Langmuir probes around the discharge perimeter.

In our experiments, to gain more information on the temporal and spatial behaviour of self-organized spoke structures in HiPIMS plasmas, a correlation between the broadband 2-D optical image of an individual spoke and the current it delivers to the target has been made for a wide range of magnetron operating conditions. As a spoke passes over a set of embedded and isolated strip probes in the niobium cathode target, a distinct modulation in the local current density is observed, typically up to twice the average value associated with the spoke, as it delivers more current that the background plasma between spokes. It matching very well the radially integrated optical emission intensities obtained using 200 nanosecond time-resolved remote ICCD camera imaging. This allows us to relate the shape of spokes seen optically to their "electrical" footprint on the target.

The dual diagnostic system allows us to study the merging and splitting of a set of rotating spokes. It is found that during the merging process the trailing spoke retains its velocity. However, it is unclear whether during the merging process the leading spoke has decreased its velocity or the merging spokes have increased their azimuthal lengths. In the merged spoke both the plasma emission intensity and current collected by the embedded probes is redistributed to have their maximum at a trailing edge. In the spoke splitting process, the total charge collected by an embedded probe is conserved. Merged or split spokes are not always stable in time. Often the spoke system reverses to its former state a short time later.

A simple phenomenological model is developed to describe a stable spoke configuration. Assuming that argon presence is essential for spoke sustainment and based on spoke dimensions, spoke velocity and background gas atom velocity a stable amount of spokes can be predicted. The model provides realistic estimates for particular spoke and plasma conditions.

9:00am **B7-4 Al_2O_3- ZrO_2 Composite Coatings on Aluminum through a Hybrid Plasma Electrolytic- Electrophoretic Process**, ***Nastaran Barati***, *E Meletis,* University of Texas at Arlington, USA

Alumina-zirconia nanostructured layers were coated on 7075 Al alloy through a Plasma Electrolytic based technique in DC potentiostatic mode in the range of 540- 600 V. The layers were coated in an electrolyte containing nano ZrO_2 powder as the zirconia source. The microstructure and phase composition of the coatings were studied along with their tribological properties as a function of processing voltage.

The results showed formation of alumina- zirconia composites with different properties for the layers treated at different voltages. It was found that at higher processing voltage, the composite layers consist of high temperature phases (tetragonal zirconia and a-alumina) in addition to monoclinic zirconia. Also higher voltages introduced larger amounts of zirconia to the coated layers due to higher applied energies to the nanoparticles in electrolyte. The layers coated at 540 V and 580 V showed the lowest friction coefficient (0.14) compared to untreated Al alloy (0.69) in addition to better wear resistance (about 100 times higher in comparison to bare Al alloy). These improvements can be attributed to the formation of hard phases at high processing voltage. Furthermore, formation of tetragonal zirconia with better toughness and mechanical properties can result in improved wear resistance. The results revealed a hybrid of plasma electrolytic oxidation (PEO) and electrophoretic process as an effective coating method. In this regard, PEO was responsible for the formation of transformed tetragonal zirconia, while deposition of unchanged monoclinic zirconia from the electrolyte resulted from the electrophoretic process.

9:20am **B7-5 Low-temperature Atmospheric Pressure Plasma Processing and its Diagnostics for a Healthcare Device**, ***Masaru Hori,*** Institute of Innovation for Future Society, Nagoya University, Japan **INVITED**

The healthcare has attracted much attentions from viewpoints of the innovation of industries and medicine. Technologies for the healthcare which is available everywhere and anytime has made a rapid progress by integrating various kinds of cutting edge multidisciplinary technologies in semiconductor manufacturing, plasma processing and bio fields. In recent years, microfluidic devices have received significant attention for a healthcare devices involving single cell trapping and analysis. We have been developing the non-equilibrium atmospheric pressure plasma for the fabrication of healthcare devices. The plasma is excited by a high-voltage alternating current (AC) power supply that provides a half peak voltage of 7 $kV_{0\text{-}P}$ for a sinusoidal waveform with a frequency of 60 Hz. Argon (Ar) gas was supplied. The electron density and gas temperature were measured by the laser Thomson scattering method and optical emission spectroscopy.

The spatial distribution of absolute densities of O and N atoms were measured by the vacuum ultraviolet absorption spectroscopy (VUVAS). NO and OH were measured by laser induced fluorescence (LIF). Based these diagnostics results, the spatial distribution of radicals was systematically discussed.

The atmospheric pressure plasma was applied to the surface modification and the deposition of SiCHx films on the glass substrate. The surface wettability of micro-sized holes in glass substrates that are similar to those used as flow channels in glass microfiltration devices was drastically changed by the plasma treatment. As a result, the liquid transport flows were driven by internal Laplace pressure differences based on the surface tensions of droplets placed on the front and back sides of the tested substrates and thus cells were successfully trapped in the holes. The non-equilibrium atmospheric pressure plasma was also applied for the direct and indirect treatment of cells.

Using the multiplex coherent anti-Stokes Raman scattering (CARS) microscope, the dynamics of living cells during plasma treatments was observed. The multiplex CARS microscope enabled to obtain label-free information of the plasma-induced effects on the nature of chemical vibrations by probing signals of lipids and mitochondria from living cells

On the basis of these results of plasma diagnostics and plasma processing, plasma processes for the future healthcare are introduced.

10:00am **B7-7 Effects of Incident Particle Fluxes on the Growth and Properties of Ga-doped ZnO Films Deposited by Ion-plating with dc Arc Discharge**, ***Hisashi Kitami,*** Sumitomo Heavy Industries, Ltd., Japan*; J Nomoto,* Kochi University of Technology, Japan*; T Sakemi,* Sumitomo Heavy Industries, Ltd., Japan*; H Makino,* Kochi University of Technology, Japan*; Y Aoki,* Sumitomo Heavy Industries, Ltd., Japan*; T Yamamoto,* Kochi University of Technology, Japan

We have investigated the influences of incident particle fluxes during film growth on the growth and properties of gallium-doped zinc oxide (GZO) films on glass substrates (@200 °C) deposited by ion-plating with dc arc discharge. The Ga_2O_3 contents in the pellets was 4.0 wt.%. Deposition conditions were as follows: the oxygen (O_2) gas flow rates (OFRs) and discharge current (I_D) were varied from 0 to 20 sccm and from 100 to 140 A, respectively.

We measured the incident particle flux of the neutral atoms and ions for each species quantitatively at the substrate level using a mass-energy analyzer (Hiden, EQP300), a Langumuir probe and a diaphragm gauge during the deposition. To clarify the factors limiting the growth rate, carrier density (N), hall mobility (μ_H) and optical mobility (μ_{opt}) of GZO films, we investigated the relationship between the growth rates, N, μ_H, μ_{opt} and incident flux (IF) properties of Zn species such as neutral Zn atoms and Zn^+ ions and O species such as neutral O atoms, O^+ and O_2^+ ions.

We found that an increase in the sum of IFs of O, O^+ and O_2^+ during the film growth increased the growth rates of GZO films. For lower OFR values of 0 to 10 sccm, we found that N slowly decreased and μ_H rapidly increased with increasing the neutral O ratio (= $O/(O+O^+ +2O_2^+)$), regardless of I_D. With further increasing OFR up to 20 sccm, N decreases rapidly and μ_H increases slowly, regardless of I_D. On the other hand, we found that μ_{opt} increased linearly with increasing the neutral O ratio. The above findings imply the strong relationships among growth rates, a microstructure with point defects associated with O species and electrical properties of GZO films. We will discuss it in more detail.

10:20am **B7-8 Mapping Potential of an Ionization Zone in Magnetron Plasma**, ***Matjaz Panjan,*** Jozef Stefan Institute, Slovenia*; A Anders,* Lawrence Berkeley National Laboratory, USA

Investigations over the last few years have shown that plasma in continuous and pulsed magnetron discharges is not azimuthally uniform rather it is organized in dense structures called ionization zones or spokes [1-2]. In this work we present measurements of the plasma potential of moving ionization zone in a direct current magnetron sputtering [3]. Measurements were recorded in a space and time resolved manner using movable emissive and floating probes. This allowed us to make a three-dimensional representations of the plasma potential and derive the related electric field, space charge and electron heating distributions. The data reveal the existence of strong electric fields parallel and perpendicular to the target surface. The largest **E**-fields result from a double layer structure at the leading edge of the ionization zone. Measurements imply that the double layer plays a crucial role in the energization of electrons since electrons can gain several tens of electronvolts from azimuthal **E**-field. As electrons drift over the magnetron there is a sustained coupling between the potential structure, electron heating, and ionization processes. The ionization zone moves in the $-\mathbf{E}_z \times \mathbf{B}$ direction from which the to-be-heated electrons arrive and into which the heating region expands. The motion of the zone is dictated by the force of the local electric field on the ions at the leading edge of the ionization zone. We postulate that electron heating caused by the potential jump and physical processes associated with the double layer also apply to high power impulse magnetron sputtering.

[1] A. Anders *et al.*, *J. Appl. Phys.***111** (2012) 053304

[2] M. Panjan *et al.*, *Plasma Sources Sci. Technol.***24** (2015) 065010

[3] M. Panjan and A. Anders, *J. Appl. Phys.***121**, 063302 (2017)

Fundamentals and Technology of Multifunctional Materials and Devices
Room Royal Palm 1-3 - Session C4
Energetic Materials and Microstructures for Nanomanufacturing

Moderators: Karsten Woll, Karlsruhe Institute of Technology (KIT), Ibrahim Gunduz, Purdue University, USA

8:00am **C4-1 Investigation of Dynamic Processes in Energetic Materials by Ultrafast Transmission Electron Microscopy at the Nanoscale**, ***Volkan Ortalan,*** Purdue University, USA **INVITED**

The ignition of exothermic chemical reaction in energetic materials has long been known to occur after locally heated regions of the material called "hot spots" are formed by various mechanical processes. Once formed, these hot spots either fail to react chemically due to thermal diffusion or react exothermically creating an ignition site. These ignition sites then grow in temperature, size, and pressure, rapidly consuming the energetic material. Despite of its significance, direct experimental evidence of such hot spots, however, is exceptionally limited; mechanisms for their generation are poorly understood and methods to control their locations remain elusive. A complete fundamental understanding of the mechanisms and dynamics of thermo-mechanical processes of energy localization at nanoscale, and the role of the microstructure in the complex energetic materials can only be obtained by directly observing their response to different stimuli at the relevant time and spatial scales. However, although the recent progresses in picosecond spectroscopy are promising, there is currently no single technique alone satisfying the required resolutions (spatial, temporal and energy) relevant to the energetic reaction events to visualize the dynamic processes occurring in energetic materials. However, recently developed ultrafast transmission electron microscopy (UTEM) opens up new possibilities for visualization of these complicated ultrafast processes.

The high time resolution of a UTEM is achieved by creating short electron pulses that are used to illuminate the specimen. A UV laser pulse stimulates photoemission of electrons from a photocathode. The resultant bunch of electrons is then accelerated and sent into the electron-optical column. It is then focused onto the specimen and magnified to produce the image. The response to be studied (chemical reactions in energetic materials, a phase transformation, shock propagation, structural change, chemical reaction, etc.) in the experiment is stimulated by a second laser pulse and the delay between the two laser pulses sets the timing of the observation. The realization of UTEM is a revolutionary step for the *in-situ* investigation of dynamic processes in materials with high spatiotemporal

resolution and the capabilities of UTEM provide an ideal platform to probe dynamic phenomena through a combination of imaging, spectroscopy, and diffraction on their natural length and time scales. Here, the results of dynamic UTEM experiments performed on energetic materials, such as HMX and composite metal-organohalide materials (mixture of aluminum nanoparticles dispersed in a fluoropolymer oxidizer matrix), will be presented.

8:40am **C4-3 A Closer Look at Determining Flame Speeds w ith Imaging Diagnostics**, *R Bratton, M Pantoya,* ***Connor Woodruff***, Texas Tech University, USA

A comparison of flame speed measurements of reacting powders utilizing various filtering and illumination techniques is presented. Reactive energetic composites are often highly luminescent and quantifying reaction propagation can often be difficult because of sensor saturation. To explore the influence of image saturation on flame speed measurements, experiments were designed using micron-sized aluminum (Al) and micron-sized molybdenum trioxide (MoO_3) mixtures and further studied with nano powders of Al +MoO_3. The micron powder mixtures were loaded into tubes at a constant bulk density of 43% of Theoretical Maximum Density (TMD), approximately an average sample mass of 1260mg. The nano powder mixture samples were loaded into tubes at a constant bulk density of 12.5% of TMD. These respective bulk densities were selected in order to maintain sample consistency and prevent density gradients. Regulating the mass and bulk density per sample is of great importance because of the significant effect of variance in bulk density in observed flame speeds. The flame speeds for each powder mixture were determined using a high speed camera and applying a series of neutral density filters to the camera's lens. This technique reduces the oversaturation effect on the camera and allows flame speed to be determined through better tracking of the reaction front. For ultimate oversaturation removal, use of a Copper Vapor Laser (CVL) and coupled 511 nm notch filter was employed to illuminate the reaction and filter the majority (i.e., >99.9%) of reaction illumination. This technique provides a perspective of the solid material and its transition from reactant to product without the interference of light emission from the reaction. The results show that the flame speeds measured through the filtering techniques were not affected by the various levels of filtration. This conclusion is evidenced by the greatest percent difference in average flame speeds in the micron powder mixtures was 15% and in the nano powder mixtures 4.2%. With this conclusion we can say that the filtration applied to the front of the camera for deflagration reactions will not impact the observed flame speed. Also with extreme filtering techniques such as a single bandwidth filter and single wavelength illumination, a more detailed view of thermite powder reaction can be observed. This advanced filtration technique can be used to analyze and characterize combustion phenomena.

9:00am **C4-4 Modeling and Experimental Study of Propagating Exothermic Reactions in Al/Pt Multilayers**, ***David Adams***, *M Abere,* Sandia National Laboratories, USA*; R Reeves,* Sandia National Laboratories, USA, US*; C Sobczak,* Sandia National Laboratories, USA

The propensity of sputter-deposited Al/Pt multilayers to undergo rapid, self-propagating formation reactions is evaluated across a broad range of stoichiometry (nAl:mPt) and layer periodicity. Experiments demonstrate self-propagating reactions in ~1.6 micron-thick Al/Pt multilayers when the molar ratio of reactants is in the range 4Al:1Pt to 1Al:4Pt. This rather large compositional range is characterized by different heats of reaction, reaction rates and reaction modes. High-speed photography shows that equimolar Al/Pt multilayers undergo the most rapid reactions with wavefront speeds as large as 80 m/s. Al- and Pt-rich multilayers react at reduced rates with speeds as low as 1 m/s. A previously developed, analytical method by Mann et al. (J. Appl. Phys. 1997) is utilized to reveal additional details of reactions in the various Al/Pt multilayers. Models that account for the reactant layer thicknesses, composition, the adiabatic temperatures, the flame temperatures, and the measured heats of reaction are used to predict wavefront speeds that closely match measured values. These results are further analyzed to extract information regarding the mass transport characteristics of reactant species.

9:20am **C4-5 Sub-critical Hotspots to Quench Reactions in Ni-Al Nanofoils**, *I Gunduz,* ***Matthew Beason***, Purdue University, USA

Identification of intermediate reactions in reactive nickel aluminum nanofoils is challenging due to the rapid thermal front velocities up to 13 m/s and very thin reaction zones estimated to be on the order of 5-20 micrometers. We present a novel method to quench reactions at rates beyond 10^8 K/s, which are comparable to the self-heating rates in these foils. A thin aluminum wire is used to produce a microscale spark-heated spot on the surface of the foil with an energy below the self-propagation threshold. Upon the application of the spark that lasts approximately 50 ns, the reactions that are initiated are rapidly quenched due to the conductive heat losses to the rest of the foil and stop the conversion of intermediate species. SEM micrographs and TEM analysis using selected area diffraction show a transition zone of 3 micrometers, where amorphous Al solid solution, $NiAl_3$, Ni_2Al_3 and NiAl are sequentially formed at bilayer interfaces. The reactions appear to propagate faster along smoother bilayers compared to the kinked sections that form during the sputtering process, forming a fingered reaction front in the thickness direction starting from the ignited spot.

9:40am **C4-6 Laser Pulse Duration Dependence on Ignition of Al/Pt Reactive Multilayers**, ***Michael Abere***, *C Yarrington, D Adams,* Sandia National Laboratories, USA

Sputter deposited Al/Pt nano-laminates with bilayer thicknesses of 328 nm, 164 nm and 65 nm were ignited via laser irradiation resulting in rapid, self-propagating reactions. Laser ignition of these foils was characterized over eleven decades (10 ms to 150 fs) of pulse duration. For laser ignition with milli- and microsecond pulses, the go/no go threshold is equivalent to the laser intensity at which the heating time required for ignition equals the pulse duration. The heating time required for ignition at a given laser intensity was determined experimentally with high-speed photography and calculated with finite element simulations. Reducing the pulse duration to 150 fs leads to a breakdown of this Joule heating based mechanism as the ignition threshold becomes spot size invariant. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the US Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

10:00am **C4-7 Microstructural Evolution during Thermal Ignition of Self-Propagating Reactions in Ru/Al Multilayers**, ***Karsten Woll***, Karlsruhe Institute of Technology (KIT), (IAM-WBM), Germany*; C Pauly, F Muecklich,* Saarland University, Germany

The ignition of the self-propagating reaction represents one of the crucial processes for reactive materials. Whereas the characterization of reaction initiation often uses macroscopic parameters, such as ignition temperatures or ignition energies, the characterization lacks the knowledge about the underlying microstructural transitions, such as the phase transformations. We take this as motivation and analyze the ignition in sputter deposited Ru/Al multilayers. In greater detail, we thermally ignite free standing Ru/Al foils as well as samples on a substrate. In our experiments we use ignition temperatures and energies just below the ignition threshold. This approach enables us to arrest the reaction immediately after ignition. Eventually, we create characteristic microstructures that help us to infer the phase transformations and microstructural changes during thermal ignition. To analyze the microstructures after igntion we use the transmission electron microscope in combination with chemical analysis, such as atom probe tomography. Finally, based on the experimental observations we suggest a mechanism for thermal ignition in Ru/Al multilayers and deduce characteristics of the ignition process in reactive multilayers in general.

10:20am **C4-8 Waves of Crystallization in Amorphous Metallic Glass Films obtained by Spinning of Melts**, ***Alexander Rogachev***, National University of Science and Technology "MISIS", Russian Federation*; S Vadchenko, A Aronin,* Russian Academy of Sciences, Russian Federation*; A Mukasyan,* University of Notre Dame, USA

Metallic and semiconducting amorphous materials and films possess unique combination of properties that cannot be obtained in the crystalline materials, such as high mechanical strength, corrosion and radiative resistance, specific electrical and magnetic properties. It promotes applications of the amorphous films in contemporary industrial technologies and growing interest in scientific research of the amorphous structures formation and its transition into crystalline state. Despite of significant amount of scientific research, mechanisms and dynamics of amorphous-crystalline transition has not been studied adequately yet, especially, as related to self-propagating waves of crystallization. Propagating waves of crystallization in the vacuum-deposited films of Si, Ge, Sb and other metal or semiconductor material, have been studied for decades ("explosive crystallization") and found some prospective applications, e.g., as a new method of fine-grained polycrystalline silicon films production for solar cells. In this work, we report existence of the self-propagating waves of crystallization in the amorphous metal allows films

produced by spinning of the melts. It is shown that self-propagating waves of amorphous-crystalline transformation can be initiated in the foils CuTi, $Fe_{84}B_{16}$, $Fe_{76}Si_{13}B_{11}$ and other compositions. Using thermal vision (up to 200 fps) and high-speed video (up to 20000 fps) cameras, we have measures propagating velocities, temperature-time profiles and other characteristics of the waves. Crystal structure and microstructure transformations have been studied. Characteristics of a new class of self-propagating thermal waves are compared with those of explosion crystallization in deposited films and reactive waves in multilayer bimetal nanofilms. Promising routes of utilization of this phenomenon for production sub-micron and nanocrystalline metal films are discussed.

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces
Room San Diego - Session E1-3

Friction, Wear, Lubrication Effects, and Modeling

Moderators: Albano Cavaleiro, University of Coimbra, Carsten Gachot, Vienna University of Technology, Giovanni Ramirez, Argonne National Laboratory, USA

8:00am **E1-3-1 Comparing of Adhesion Properties of TiNbVN Coatings Deposited on Different Substrates**, ***Ihsan Efeoglu***, *Y Totik,* Atatürk University, Turkey*; O Baran,* Erzincan University, Turkey*; H Cicek,* Erzurum Technical University, Turkey*; A Keles,* Ataturk University, Turkey

Adhesion properties of hard thin coatings were strong l y affected from used substra t e material. In this study, TiNbVN coa t ings were d e posited on 2024 A l -alloy, M2 and H13 steels substrates using react iv e magnetron sputtering method. Structural and m e chanical properties of the coat i ngs were anal y zed by SEM, EDS, XRD, and nanohardness. Adhesion properties of the coatings were deter m ined via scratch test under progressive load. It was observed that critical load (Lc) values of TiNbVN coa t ings varied in each substra t e. The coati n g m icrostruc tu re is dense a nd the fi l m thickness is about 440n m . The nanohardness values were taken under 1mN load and affec t ed by the substr a tes hardness due to l o ad c arr y ing capacit y . While the softest Al- alloy substrate hardness 1.25GPa, the coating hardness was measu re d 12GPa. On the other hand, the highest coa t ing hardness (39 G Pa) value taken fr o m the hardest M 2 substrate h a rdness (5.7GPa). The results of all the adh e sion tests s h ow a linear relationship between the hardness of th e base mater i al and the adhesion values. While adhesion value fr o m the co ated M2 w a s Lc≈65N, as function of the substrate eff e ct, the measured adhesion values are Lc≈15N and Lc≈50N from 20 2 4 Al-alloy and H13 st e el respectively.

8:20am **E1-3-2 Buckling of Ductile Thin Films on Rigid Substrate**, ***Nadia Ben Dahmane***, *G Parry, R Estevez,* SIMaP, University of Grenoble Alpes, CNRS, France*; C Coupeau,* Institut P', Université de Poitiers-UPR 3346 CNRS-ENSMA, France

The process of deposition of thin films can induce large compressive stresses (up to a few GPa) that combined with the low adhesion of the film to the substrate may result in simultaneous buckling and delamination of the film, leading experimentally to a large variety of buckled structures including straight-sided buckles, telephone cords or circular blisters. The mechanism of nucleation and propagation of elastic blisters has been widely investigated and described, either with analytical [1,2] or numerical methods [3]. In particular, the relationship between the mode mixity dependent interfacial toughness on the morphology of the wavy buckles has been highlighted [3]. The response of ductile thin films deposited on rigid substrates remains an open issue. For instance, it has been evidenced experimentally [4] that circular blisters exhibit folding angles at their base larger to that estimated from an elastic model (figure s1). In addition, recent experimental observations of 400nm gold films deposited on silicon wafers showed straight buckles with higher deflections compared to elastic predictions (figure 2). These differences in morphology are thought to originate from the elastic-plastic response of the film but the governing features need to be clarified. This is the purpose of the present study.

In this context, we carry out Finite Element simulations with a model that accounts for isotropic yielding and the non-linearity of the film. This approach aims at identifying the elastic-plastic constitutive model that is able to capture the experimental observations. A mode mixity dependent cohesive zone model is used to describe the thin film/substrate interface, that enables us to study the effect of plasticity on the stability and growth of straight and circular blisters.

[1] Hutchinson et al., Adv. in Appl. Mech. 29 (1992) 63.

[2] Hutchinson et al. Acta Metallurgica Materialia, 40 (1992) 295

[3] Faou et al., J. Mech. Phys. Sol., 75 (2015) 93.

[4] Coupeau et al., Thin Solid Films 469 (2004) 221.

8:40am **E1-3-3 Study of Multi-cracking of Brittle Thin Films and Brittle/ductile Multilayers on Compliant Substrate**, ***Ilhem Ben Cheikh***, CNRS, Université de Grenoble-Alpes, France*; G Parry,* Laboratoire de Science et Ingénierie des Matériaux et Procédés (SIMaP), Université de Grenoble-Alpes, France*; D Dalmas,* CNRS, Laboratoire de Tribologie et Dynamique des Système (LTDS), Ecole centrale de Lyon, France*; R Estevez,* Laboratoire de Science et Ingénierie des Matériaux et Procédés (SIMaP), Université de Grenoble Alpes, France

Thin films coatings are used in many high technology applications particularly in microelectronics devices. Using flexible polymers as a substrate on which thin films (metal, oxides or organic) are bonded can give rise to new industrial applications such as OLED, flexible electronics or flexible photovoltaics devices. The mechanical stability and failure behavior of multilayer structures deposited on flexible substrate has been extensively studied both experimentally and theoretically [1-3]. Several relaxation mechanisms in thin films have been identified such as channel cracks, debonding or buckle delamination.

The objective of this study is to understand the multi-cracking of the silver and/or zinc oxide layers of various thicknesses coated on elastoplastic substrates (ETFE). In the process of cracking many parameters should be taken into account such as the elastic modulus mismatch between the film and the substrate, the plasticity of the substrate and the ductile or brittle nature of the film.

In the literature several experimental and analytical studies can be found. In [4], after experimental investigations, the existence of three different fracture stages was confirmed, the third one being a saturation stage of the cracks density at high strain with large opening of the existing cracks. Conventional models in literature such as Xia & Hutchinson model [3] and the "Shear lag" formalism [1,2] do not account for those experimental observations. We show that taking into account the plasticity in the substrate allows for capturing the crack density at the saturation regime.

To further validate this new model and the experimental observations, we present a numerical study which uses a cohesive zone model for the interface and to simulate the cracking of the film. This model also takes into account the plastic behavior of the substrate (Fig1). The different stages of cracking observed experimentally, including the nucleation stage were simulated (Fig2). A relationship between the properties of the film toughness, the saturation stress level in the film and the saturation distance between the cracks under deformation has been evidenced.

9:00am **E1-3-4 Tribological Behaviors of UHMWPE Composites with Different Counter Surface Morphologies**, ***Yanzhen Wang***, *Z Yin, H Li, G Gao,* Shanghai Jiaotong University, China

The influence of counter surface morphologies on hybrid glass fiber (GF) and carbon fiber (GF) filled ultrahigh molecular weight polyethylene (UHMWPE) were studied under various contact pressure and sliding speed against GCr15 steel in dry condition. The goals were to investigate the tribological behavior of GF/GF/UHMWPE composite as a kind of water lubricated journal bearing material. The friction and wear behavior of composites were examined using a pin-on-disc tribometer. The morphologies of the worn surface were examined by scanning electron microscopy (SEM) and laser 3D micro-imaging and profile measurement. The results demonstrated that the counter surface morphologies have significant influence on the tribological behavior of GF/GF/UHMWPE composite. Generally, the wear rate and friction coefficient of composites increase as the increment of counter surface roughness. Also, the sliding speed and contact pressure have important effect on the tribological behavior of GF/GF/UHMWPE composite. The friction coefficient increases as the increment of sliding speed, while decrease as the increment of contact pressure.

9:20am **E1-3-5 Evaluation of Friction and Wear Characteristics of Electrostatic Solid Lubricant at Different Sliding Conditions**, ***Rakesh Kumar Gunda***, BITS Pilani Hyderabad campus, India*; S Narala,* BITS Pilani Hyderabad Campus, India

In modern industry, mechanical parts are subjected to friction and wear, leading to heat generation, which effect the reliability, life and power consumption of machinery. Solid lubricant additives have demonstrated better tribological performance in terms of reducing the machining zone temperature by creating friction without polluting the environment. With an appropriate application of solid lubricant additives in the sliding

interface, the friction reduction and wear resistance properties of the lubricant have been successfully improved. Therefore, an attempt has been made in this research work with an investigation of using molybdenum disulphide suspension to reduce the friction at machining zone. To achieve this, in the present work, Electrostatic charged spray lubricant (ECSL) system has been envisaged for effective supply of solid lubricant mixture at an extreme low flow rate to the sliding interface of WC pin and Ti-6Al-4V alloy as disk materials. Excessive tribological measurements with SAE 40 oil concentrated with 20wt% of MoS_2 with micron size particles showed friction coefficient as low as 0.001 and negligible wear. It is proposed that negatively charged sprayed MoS_2 solid lubricant mixture at nozzle tip has found remarkable influence on their tribological behavior.

9:40am **E1-3-6 Evaluation of Friction and Wear Properties of Al-TiC_p Metal Matrix Composite under Cryogenic Condition***, **Sravan Josyula,*** BITS-Pilani, Hyderabad Campus, India*; S Narala,* BITS Pilani Hyderabad Campus, India

Aluminium reinforced titanium carbide particulate (Al-TiCp) composites has gained attention for several engineering and structural applications due to its unrivaled properties, such as high specific strength to weight ratio, high thermal conductivity and excellent wear resistance. However application of Al-TiCp composites in sliding components creates larger friction and wear due to high abrasive nature of reinforcement particles in the soft matrix. It is well known that friction generates increase in contact temperatures can have an imperative impact on the tribological behaviour and failure of sliding components. Further, controlling of friction and wear behaviour enhances the wide application of Al-TiC metal matrix composites in various industrial applications. In this connection current research work try to improve the performance of Al-TiCp composite using cryogenic coolant. Sliding wear tests are performed in order to ascertain friction and wear properties of Al-TiCp metal matrix composites under cryogenic condition. To supply cryogenic coolant effectively to the sliding interface zone, a customized cryo-tribo setup has been developed by fastening cryogenic setup to pin-on-disc tribometer. Comparative studies have been carried out under cryogenic liquid (Liquid Nitrogen (LN_2)) and dry environment under different applied loading and sliding velocities The present analysis reveals that the weight loss of composite sample increases linearly with increase in normal load and sliding distance whereas decreases with increase in sliding velocity. Auxiliary observations revels that presence of cryogenic liquid in sliding contact offers significant reduction in friction and wear values when compared to dry condition through reduction in contact zone temperature and favorable change in pin and disc interface. Microscopic analysis has been carried out to understand the wear behavior of developed under cryogenic condition. The developed technology helps to improve the tribological properties (reduction in friction and wear) there by improving service life and durability of the component in various industrial applications.

10:00am **E1-3-7 Wear Mechanisms and Tribological Characterisation of Novel Nanocomposite Coated Cutting Tool Material for High Temperature Applications***, **Pavandatta Jadhav**, S Narala,* BITS Pilani Hyderabad campus, India

The parts which undergo dry sliding encounter high friction and wear which affects the durability. In recent years, there is a growing interest in the application of Nano-composite coating on the cutting tools to increase the wear resistance, high thermal stability, hardness and durability of the tool. The Nano-composite coatings have been found to have better practical performance capabilities. To reduce the friction and enhance the wear resistance, the hard Nano composites (ZrO_2 Y_2O_3, Ti, Si) N show high performance capabilities. This article attributes a specific study of the application of Nano-composite coating on the cutting tools which shows an impact on the increase in wear resistance, low friction, and increase durability of the tool. In this study, the (ZrO_2 Y_2O_3, Ti, Si) N hard nanocomposite coatings have been deposited on a carbide tool by electrostatic spray coating (ESC) technique. The coatings have been tested for wear and friction behaviour by using a pin-on-disc tribological tester designed according to ASTM G99 standards. The dry sliding wear test was performed on Titanium alloy (Ti6Al4V) disc and (ZrO_2 Y_2O_3, Ti, Si) N hard nanocomposite coated carbide tool (pin) at various speeds and loads at ambient atmosphere. The results revealed that electrostatic Nano-composite coated tools performed much better as compared with those uncoated tools.

Surface Engineering - Applied Research and Industrial Applications

Room Sunrise - Session G1

Advances in Industrial PVD, CVD and PCVD Processes and Equipment

Moderators: Emmanuelle Gothelid, Sandvik Coromant R&D Materials and Processes, Ladislav Bardos, Uppsala University, Sweden

8:00am **G1-1 Industrialized HiPIMS***, **Siegfried Krassnitzer**, D Kurapov, M Arndt, W Kalss, H Rudigier,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein **INVITED**

High power impulse magnetron sputtering (HIPIMS) offers significant advantages over conventional magnetron sputtering because of a much higher degree of ionized species of the sputtered materials. In principle, for hard coating applications, this allows to combine the advantages of arc evaporation – dense hard coatings with excellent adhesion - with smooth surfaces and low defect densities of magnetron sputtered coatings.

HIPIMS includes high power and current density pulses, applied in a reproducible and accurate way. In a classical HIPIMS process, sputter pulses are generated by applying voltage pulses, at different pulse length, followed by a current pulse response. Nevertheless, due to runaway effects at high power density levels, the current response is not very predictable and depends very much on target age, magnetron type or process parameters like reactive gas pressure. To overcome such problems very short voltage pulses are used and current response is mainly given by the current rise time, keeping the current low before reaching a threshold value. It is clear that the discharge properties are always in a transient-like behavior with respect to deposition rate, gas rarefaction and degree of ionization.

A new, different approach, is to apply power-controlled pulses recently described as S3p –technology.

S3p - Scalable Pulsed Power Plasma- overcomes the problem of discharge instabilities by providing a power pulse to establish voltage and current accordingly to the magnetron characteristics.

Key features of recent hardware and process development efforts enable independent adjustment of pulse power density up to 2kW/cm^2 and pulse length in a wide range from 0.05msec up to 100msec at a near perfect rectangular pulse shape for voltage and current. In this presentation examples of S3p-pulses will be presented and the effect on deposition rate and the stability of a reactive sputtering process will be discussed.

A new coating system family was designed around this promising technology. Characteristic data of a small and medium size coating system, together with performance and property data of coatings, produced with S3p-technology like AlTiN, AlCrN, TiSiN, TiN, TiCN also Al2O3 and DLC will be presented.

8:40am **G1-3 Pure HiPIMS Coatings with 2 µm/hour for Cutting Tool Coatings***, **Christoph Schiffers**, T Leyendecker, O Lemmer, W Kölker,* CemeCon AG, Germany

Key feature of this new hardware concept is a deposition rate as high as 2 µm/hour for pure HiPIMS coatings. The paper will present how this equipment does a AlTiN FerroCon® coating in 4 hours 20 mins and a TiAlSiN InoCon® film within 5 hours 20 mins. This data are achieved for 100% HiPIMS mode – not hybrid or mixed set-up – and threefold rotation. An integrated concept of an optimized magnetic set-up of the magnetrons together with the door assembly design of the cathodes – HiPIMS without cable, the pulse unit is right on the chamber door – and a full synchronization between the HiPIMS sources and a dedicated table Bias makes this so far unachieved rate possible.

A scratch load of 120 N for a TiAlSiN coating on a sintered carbide surface indicates enormously high plasma ionization. The dense nature of the films is revealed by nano indentation results showing so far not reachable H^3/E^2 values. SEM images of the fine grain morphology underline this. Machining tests in TiAl6V and in stainless steel show that pure HiPIMS takes the performance of cutting tools to a premium level.

A case study on TiB_2 coatings illustrates the benefit of pure HiPIMS coatings: this technology adds to the advantages of sputtering – smooth, droplet free coatings and an unlimited choice of the chemical composition – a tremendously high ionization and hence best adhesion of a dense and uniform coating. The pure HiPIMS technology broadens the application range of TiB_2 to cutting tools for highly abrasive workpiece materials.

9:00am **G1-4 Deposition of Acrylic Acid on Argon or Air Atmospheric Pressure Plasma Treated Silicon using a Novel Chamber Design**, ***Wei-Yu Chen,*** University of Sheffield, UK*; A Matthews,* University of Manchester, UK*; F Jones,* University of Sheffield, UK

Plasma technologies are of great industrial interest due to their non-polluting nature and possibility to provide rapid treatment times. Whilst vacuum plasma processes have received intense attention over recent years, we are now also seeing increased interest in atmospheric plasmas. For example, peroxide groups formed via atmospheric pressure plasma (APP) activation are favorable for free-radical surface graft polymerization of acrylic acid (AAc). AAc grafting on a material offers carboxylic acid functional groups on its surface, which opens possibilities to find wider uses in different applications, such as biosensors, biocompatibility improvement and enhancement of the interface adhesion in composite materials. In this study, APP treatment with different carrier gases, air and argon, and vapour phase grafting were applied in a bespoke Pyrex glass chamber to deposit of AAc on silicon wafers. To limit the effect of atmospheric gas on the process and prevent AAc monomer from fragmenting during APP, a plasma activating zone and a grafting zone were designed and located separately inside the bespoke chamber. Silicon specimens were first activated using air- or argon-APP, then shifted to the grafting zone downstream of the AAc vapour inlet. The surface wettability was evaluated by water contact angle analysis and chemical composition was identified by X-ray Photoelectron Spectroscopy (XPS). Contact angles with water were initially 56.1±0.8° and after APP treatment with air and argon were 10.2±0.8° and 4.6±0.2° respectively, and increased to between 10.0° to 16.0° after AAc vapour grafting. The binding energy peak at 289 eV from XPS also indicated the presence of carboxylic acid groups on the surfaces. A higher intensity of the peak at 289 eV was also detected, compared with the surface treated by APP with AAc vapour injecting to the activating zone during the treatment.

Keywords: Atmospheric pressure plasma treatment, Acrylic acid, Carboxylic acid groups, Surface grafting.

9:20am **G1-5 Reactive Deposition in the Magnetized Hollow Cathode Activated Magnetron**, ***Hana Barankova,*** *L Bardos,* Uppsala University, Angstrom Laboratory, Sweden

Recently, a new type of the magnetron, Magnetized Hollow Cathode Activated Magnetron has been developed, where the target is coupled with the hollow cathode magnetized by the magnetic field of the magnetron. This configuration, producing intense and stable plasma in a wide interval of pressures brings about enhanced magnetron performance and increases the deposition rate. The results of the TiN reactive deposition are presented and discussed. Increased deposition rate compared to the metal deposition rate is indicated for TiN. This is consistent with previous results obtained for the hollow cathodes.

9:40am **G1-6 Ionisation Enhancement Control for Magnetron Sputtering Processes**, *V Bellido-Gonzalez, F Meyer, T Sgrilli, H Li,* ***Frank Papa,*** Gencoa Ltd., USA*; J Housden, L Espitalier, S Banfield,* Wallwork Cambridge Ltd, UK

Hot Filament technology has been used for a long time for the ionisation enhancement of different PVD technologies such as Electron Beam Evaporation (eBE) and Magnetron Sputtering (MS). These applications already form part of standard industrial production processes in varied coatings such as eBE TiN and Magnetron Sputtered DLC.

In terms of large area scalability, Magnetron Sputtering is one of the most attractive PVD technologies. However, the basic MS process, with no assisted filament, would generally be lacking in ionisation. When a higher degree of ionisation is needed, an additional technology needs to be coupled, such as inductively coupled RF or HIPIMS which offer the possibility of higher plasma density. Both methods however present challenges when it comes to large area. RF discharges become difficult to handle and control over large areas. In a similar way, HIPIMS discharges on large area cathodes present some challenges, such as the levels of peak power delivery ability from commercial power supplies, arcing control, tuning and cabling.

An alternative method to achieve enhanced ionisation for large area systems would be to add a hot filament based technology for enhanced electron emission. Although this method could offer a simpler and more economic route to large area industrialisation, further control of the ionisation enhancement is needed. Design of the deposition system, integration and control of the ionisation enhancement is necessary in order to achieve the consistency in the results demanded in industrial production. Steering and confinement of the electrons emitted from the filament are critical for process enhancement.

Improvements in coating properties for AlNOx and AlCrN will be shown as well as the possibilities to “tune” the plasma density.

10:00am **G1-7 Bipolar Sputtering - Waveform Adaptability in Plasma Applications**, ***Wojciech Gajewski,*** *K Ruda, J Swiatnicki, P Ozimek,* TRUMPF Huettinger Sp. z o.o., Poland

New applications and increasing requirements on cost effective processing stimulates the use of innovative solutions for the precise control of the plasma. Increasingly important in determining the optimal plasma parameters are the functionalities of the power supply The flexibility in output current and voltage shape modification, tunable pulsing frequency, advanced arc and power delivery management are the driving factors for successful usage of bipolar technology in a variety of industrial applications. Furthermore, the flexible design enables an easy up-scaling form single kilowatt up to 180 kW in the biggest industrial sputtering systems.

The flexibility and modifiability of bipolar power supplies are the key factors making them an interesting alternative for the classical MF units with sinusoidal output. This contribution summarizes author’s many years of industrial experience with the application of bipolar technology to summarize the advantages and challenges associated with its exploitation.

First, the dependence of TiN coating properties on different output frequency will be discussed in details. The discussion will be followed by the impact assessment of the output signal shape on plasma and coating properties. Furthermore, functionalities distinctive for bipolar power supplies will be briefly described in comparison with competitive power delivery technologies. As next, deposition from a ceramic target will be used to discuss the relationship between the available arc detection and suppression algorithms and plasma stability. It will be shown how a combination of novel arc management algorithms together with applicability of different pulsing frequencies can be used for process stabilization by reduction of arcing probability. As a summary, cost and benefit statement of industrial implementation of bipolar technology will be emphasized based on latest process results.

10:20am **G1-8 New Hauzer CARC$^+$ Technology Dedicated to Nitriding, Etching and Coating Process**, *J Zhu, G Negrea, M Eerden, D Doerwald,* ***Roel Tietema,*** IHI Hauzer Techno Coating, Netherlands

CARC$^+$, Hauzer lately developed circular arc technology, marked the birth of a new generation of hard coatings, opening up new dimensions of coating performance in various application fields. Thanks to the advanced source architecture of CARC$^+$ technology, the energy and charge status of the species in the generated plasma can be tuned in a wide range by combined configuration of coil magnets and permanent magnets such that, the most advantageous nitride and carbide hard coatings, controlled by its microstructure and composition, are obtained. In addition, the CARC$^+$ source is also able to act as an anode, obtaining much homogeneous and enhanced nitriding and/or etching effect on the to-be-coated parts.

In this work, we will show the microstructure and cutting performance of TiN and TiCN coated HSS tools, processed with CARC$^+$ anode etching and nitriding. Meanwhile, microstructure evolution and cutting performance of AlCrN (64/36 at.%) coating using various cathode magnetic fields will be addressed.

10:40am **G1-9 Characterization of Advanced Coating Architectures Deposited by the HI3 Process**, ***Joerg Vetter,*** Oerlikon Balzers Coating Germany GmbH, Germany*; K Kubota, M Isaka,* Mitsubishi Hitachi Tool Engineering, Japan*; J Mueller, T Krienke,* Oerlikon Balzers Coating Germany GmbH, Germany*; H Rudigier,* Oerlikon Surface Solutions AG, Liechtenstein

The tailoring of coating architectures of vacuum arc deposited coatings is limited to specific cathode material properties which are evaporable by the arc process. The HIPAC magnetron sputtering process (a classical HiPIMS process) can be used to atomize and ionize materials which are difficult to evaporate or not evaporable by cathodic arc . Both deposition methods are running as individual process steps, but also in a hybrid mode. This HI3 process opens a process window to generate advanced coating architectures. Selected advanced coating architectures are highlighted. Multilayer coatings containing sophisticated nano multilayer structures are presented. Both basic coating characteristics like macroscopic stress, x-ray diffraction and mechanical properties and TEM and SEM investigations. are presented.

11:00am **G1-10 Mechanical Property and Thermal Stability of Multicomponent AlTiSiN and AlTiBN Hard Coatings using Ternary Alloy Arc Sources**, ***Meng-Chun Cai***, *Y Chang,* National Formosa University, Taiwan

Ternary transition metal nitride, such as TiSiN and TiBN, have been attracting great interest for industrial application as hard protective coatings due to their high hardness, wear resistance, tribological properties, and chemical stability. In this study, AlTiSiN and AlTiBN coatings were synthesized by cathodic-arc evaporation. During the coating process of AlTiSiN and AlTiBN, TiN was deposited as an interlayer to enhance adhesion strength between the coatings and substrates. The AlTiSiN and AlTiBN coatings were annealing by rapid thermal annealing at high temperature. The microstructure of the synthesized coatings were investigated by field emission scanning electron microscope (FE-SEM) and field emission gun high resolution transmission electron microscope (FEG-HRTEM), equipped with an energy- dispersive x-ray analysis spectrometer (EDS). Glancing angle x-ray diffraction was used to characterize the microstructure and phase identification of the coatings. Mechanical properties, such as the hardness and elastic modulus, were measured by means of nanoindention and Vickers hardness measurement. Ball-on-disc wear tests at room temperature and high temperature (500℃) were conducted to evaluate the tribological properties of the coatings. To evaluate the correlation between impact fracture resistance and hardness/elastic modulus ratio of the deposited coatings, an impact test was performed using a cyclic loading device with a tungsten carbide indenter as an impact probe. The AlTiSiN coating is anticipated to increase the hardness and wear resistance, which were expected to increase film thermal stability and abrasion resistance. The AlTiBN coating is anticipated to increase the adhesion, hardness, toughness and tribological resistance.

Advanced Characterization Techniques for Coatings and Thin Films

Room Royal Palm 4-6 - Session H1

Advanced Microstructural Characterization of Thin Films and Engineered Surfaces

Moderators: Xavier Maeder, Empa, Swiss Federal Laboratories for Materials Science and Technology, Michael Tkadletz, Montanuniversität Leoben

8:00am **H1-1 Imaging Cross-sectional Structure-property Relationship in Thin Films**, ***Jozef Keckes***, Montanuniversität Leoben, Austria **INVITED**

Peculiarity of physical properties of nanocrystalline thin films resides in (i) the small crystalline size typically below 100 nm resulting in a variety of size effects, (ii) a high volume fraction of grain boundaries and (iii) a presence of gradients of microstructure and residual stresses. Those gradients may originate (i) from self-organized film growth far from the thermodynamic equilibrium, (ii) from the intentionally varying deposition conditions and/or (iii) from the inhomogeneous thermal and/or mechanical loads induced during the film service. In order to understand and optimize the functional behavior of the thin films, it is necessary (i) to analyze the properties of thin film distinct regions, like nucleation layers, interfaces and grain boundaries, and (ii) to reveal cross-sectional structure-property relationships.

In this contribution, experimental results from gradient hard and metallic thin films (e.g. TiAlN, CrN, Diamond, W, TiN/SiO_x) are discussed. The films are analyzed using a variety of novel analytical techniques developed by the group in last 5 years. Primarily, cross-sectional X-ray nanodiffraction using monochromatic point and pencil X-ray beams with a diameter or a thickness down to 30 nm was used (at ID13 of ESRF and at P03 of PETRA III) to resolve depth-resolved evolution of phases, texture, crystallite sizes and the first-order stresses across thin film cross-sections. The observed gradients are correlated with the varying film deposition conditions, providing an opportunity to optimize deposition processes. Additionally, results from strain and microstructure characterization (i) in in-situ indented TiN and (ii) in multilayered CrN-Cr thin films after wedge indentation are presented to demonstrate the correlation between the present (i) microstructure, (ii) recorded load-displacement curves as well as (iii) stress concentrations. Additionally, for a graded nanocrystalline TiAlN thin film, the comprehensive characterization of cross-sectional structure-property relationships will be used to analyze the correlation between sub-micron depth variations of fracture stresses, hardness and elastic moduli on one side, and phases, crystallite sizes, crystallographic texture, Ti/Al ratio and residual strain on the other side. Finally, the cross-sectional approach will be used to indicate the possibility of functional optimization of thin films through cross-sectional design.

8:40am **H1-3 Synchrotron and Transmission Kikuchi Diffraction Characterization of Deformed Multilayer Thin Films on Polyimide**, ***Mikhail Polyakov***, *X Maeder,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland; *P Gruber,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM-AWP), Germany; *J Michler,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Nano metallic multilayers (NMMs) are materials which consist of multiple nanometer-thick layers of different metals. NMMs are present in a variety of applications, from protective coatings to electronics to x-ray mirrors. However, the deformation mechanics of such materials, which are especially relevant for protective coatings and electronics on flexible substrates, are difficult to determine for several reasons. Firstly, the small grain sizes and layer thicknesses (<50 nm) limit the use of techniques with larger resolution limits, most notably Electron Backscatter Diffraction (EBSD). In addition, the small layer thicknesses translate to small scattering volumes for X-ray diffraction techniques, which can result in prohibitively long data collection times.

To address these specific limitations, additional characterization techniques were used. The first is Transmission Kikuchi Diffraction (TKD, also referred to as transmission-EBSD or t-EBSD). The technique is similar to EBSD in that one can map grain orientations over a large area, but it utilizes the transmitted diffraction patterns rather than the backscattered diffraction patterns. This results in an improved spatial resolution of less than 10 nm, allowing for the characterization of layers and grains with characteristic lengths below 50 nm, before and after deformation.

The second technique used was in-situ synchrotron XRD of tensile tested films. The brilliance of the synchrotron X-ray source allows for much shorter recording times than for a standard X-ray source. Therefore, a series of diffraction patterns can be collected in a reasonable amount of time during the tensile testing of thin multilayered films. Since the diffraction rings for the different materials can be distinguished, the stress for the different materials can be determined individually. In this way, the deformation of the layers can be decoupled and the contributions of the individual materials to the overall deformation behavior can be calculated.

We have demonstrated the differing load sharing contributions from varying layer thicknesses for Cu/Nb nano multilayers on polyimide [1], and the results will be compared with the deformation of Cu/Zr and Cu/CuZr multilayer samples. With Cu/Nb, Cu/Zr, and Cu/CuZr multilayers, a variety of crystal structures are present, resulting in differing deformation mechanisms.

[1] Polyakov, Mikhail N., Jochen Lohmiller, Patric A. Gruber, and Andrea M. Hodge. Advanced Engineering Materials Adv. Eng. Mater. 17.6 (2014): 810-14

9:00am **H1-4 Advanced EBSD and *in-situ* EBSD Techniques for Microstructure, Crack, Fatigue, and Plastic Deformation Characterization in Metals and Thin Films**, *J Ast, Y Guo, M Polyakov, J Schwiedrzik, G Mohanty, J Michler,* ***Xavier Maeder***, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

The measurement of characteristics such as crystal structure, crystallographic orientation, grain dimension, and residual stress is fundamental for evaluating thin films and coatings and correlating their structures with their mechanical, chemical, or thermal properties. For such analyses in small volume materials, X-ray diffraction techniques and transmission electron microscopy are generally considered to be the tools of choice. Electron backscatter diffraction (EBSD), which can be combined with cross correlation techniques (HR-EBSD), offers the advantage of providing crystal orientation maps from which phase, grain size, grain shape, grain boundary type, texture, residual stress, and crystal defects can be determined with a resolution of 50nm. In addition, Keller and Geiss have recently demonstrated that EBSD patterns can be acquired from a thin film specimen using transmitted electrons in the SEM [1] (Transmission Kikuchi-Diffraction [TKD] or transmission-EBSD), thus improving the lateral resolution of the technique by an order of magnitude, reaching sub-10nm resolution, making it suitable for nano-crystalline materials. We applied transmission-EBSD to characterize the microstructure of PVD and electrodeposited materials. Crystallization and twinning processes have been studied for several materials, such as nanocrystalline Ni, CuNi, CuAl, and pure Cu, and the observed structures have been linked to their mechanical proprieties. We have also applied EBSD and HR-EBSD techniques together with *in-situ* micro-mechanical testing to better assess

the deformation mechanisms in metals and coatings. The detailed microstructure, plastic zone size, dislocation mobility, strain, and stress can be mapped at successive deformation steps in the materials. Examples will be given for micro-cantilever bending and micro-pillar compression.

References:

[1] R.R. Keller, R.H. Geiss, *Journal of Microscopy* 2012, 245, 245–251.

9:20am **H1-5 Characterization of the Porosity of Silicon Nitride Thin Layers**, ***Thomas Barrès***, *H Montigaud,* Saint-Gobain Recherche, France*; O Stephan,* Université Paris-Sud, France*; B Tribollet,* Université Pierre et Marie Curie, France*; Y Cohin,* Saint-Gobain Recherche, France*; M Boinet,* Saint-Gobain, USA

Silicon nitride (SiN_x) is commonly used as a dielectric thin film (10 to 100 nm) within stacks deposited by magnetron sputtering in the glass industry. The porosity of such thin films can be detrimental to the product durability and performances upon ageing [1].

The nanostructural characterization of silicon nitride thin films has been previously carried out by Transmission Electronic Microscopy (TEM) [2]. Thanks to several microscopy techniques such as TEM, Scanning Transmission Electronic Microscopy in High Angle Annular Dark Field mode (STEM HAADF), and Electron Energy Loss Spectroscopy (EELS), we are able to give a quantitative description of the porosity in SiN_x layers at the nanometre scale. In addition to purely topographic characteristics, EELS and HAADF measurements give access to the local composition and atomic density in the thin film. The 3D morphology of the pores was determined by observing the sample from different incidences (plane-view and cross sections obtained by means of FIB lamella).

In parallel to the microscopic approach, we estimated the porosity at a larger scale as well as the through-porosity total fraction, by using Electrochemical Impedance Spectroscopy (EIS) measurements. Impedance measurements have a high sensitivity to the pore distribution in the layer [3], providing a complementary point of view on the layer morphological characteristics to the one offered by TEM.

Finally, the evolution of the layer nanostructure is studied as a function of the SiN_x deposition parameters allowed by reactive magnetron sputtering (deposition pressure, sputtering rate, and plasma composition) as well as final characteristics (density, thickness or intrinsic stress).

References :

[1] J. Kulszyk-malecka, Diffusion studies in toughenable Low-E coatings, PHD thesis, (2012).

[2] C. Colliex, A. Gloter, M. Kociak, K. March, O. Stephan and M. Tencé, Microscopy and Analysis 26(6) (2012), 33-40.

[3] A. Perrotta, S. J. García, J. J. Michels, A-M. Andringa, M. Creatore, ACS Appl. Mater. Interfaces, (2015), 7 (29), pp 15968–15977.

9:40am **H1-6 Microsecond-Scale Chemical Reactions at Interfaces in Thermal Spray Coatings**, ***Anh Tran***, *M Hyland,* The University of Auckland, New Zealand

The possibility of extremely rapid chemical reactions at interfaces between molten metal droplets and metal substrates in thermal spray coatings is reported in this study. Nickel single molten droplet was deposited on different substrates including stainless steel, chromium and titanium at either room temperature or 300 °C by plasma spray. The splat morphology and splat-substrate interfaces were characterised using FIB and TEM. Substrate's element was found to diffuse into the nickel splat, but not vice versa. Thin layers of mixed oxides were detected at the interface of nickel droplet deposited on either chromium or stainless steel substrate, but not on titanium substrate. Instead, a relatively thick intermetallic layer with the thickness up to 1 µm composing of three different phases of $TiNi_3$, TiNi, and Ti_2Ni was found along the entire Ni-Ti interface. We also found that the chemical reactions to form interfacial layers occurred after the splat solidified, thus it is not involved in the way droplet spread on the solid surface and subsequent splat-substrate bonding.

10:00am **H1-7 Thermal Stability of Expanded Austenite formed on a DC Plasma Nitrided 316L Austenitic Stainless Steel**, ***André Tschiptschin***, *A Nishikawa, L Varela,* University of São Paulo, Brazil*; C Pinedo,* Heat Tech & University of Mogi das Cruzes, Brazil

Expanded austenite formed during low temperature plasma nitriding of austenitic stainless steels is known for its excellent wear and corrosion resistance especially when working in systems where galling, erosion-corrosion, cavitation-erosion and pitting corrosion resistance are a major concern. These wear and corrosion properties may degrade by exposure of the surface hardened steel to high temperatures, between 400 °C and 700 °C. In the present work, DC low temperature plasma nitrided 316L austenitic stainless steel (400 °C for 20 hours) was heated up to investigate the stability of the expanded austenite layer in the range 400 °C < T < 700 °C. Time-resolved X-ray diffraction experiments were undertaken in a thermomechanical simulator coupled to the Brazilian National Synchrotron Light Source. Two series of experiments were carried out: a) isothermal treatments conducted at temperatures between 400 and 600 °C for 4h and b) a continuous heating experiments from room temperature up to 700 °C, with a heating rate varying from of 6 °C/min to 60 °C/min. Results show that during the isothermal heat treatments, expanded austenite remains approximately stable up to 400 °C, without losing nitrogen and maintaining its lattice parameter. For isothermal holding temperatures higher than 450 °C a continuous decrease in expanded austenite in the time span of the experiments is observed, presumably due to diffusion of nitrogen to the matrix. This phenomenon is followed by formation of ferrite and chromium nitrides precipitation. In the continuous heating experiments expanded austenite decomposition into three products is observed: ferrite, austenite, and nitrides. As expected from thermal an activated reaction, the critical temperature of this transformation is dependent on the heating rate. At the heating rate of 12 °C/s the initial 0.385 nm expanded austenite lattice parameter increased up to 0.3875 nm at 425 °C due to thermal expansion, indicating an average thermal expansion, over the analyzed expanded austenite layer, of 5×10^{-5} K^{-1}. This value is much lesser than the values reported for the thermal expansion coefficients of the fcc austenitic phase in austenitic stainless steel $K = 15 \times 10^{-5}$ K^{-1}, indicating that expanded austenite is also losing compressive residual stresses during heating.

Topical Symposia
Room California - Session TS1
Biointerfaces

Moderators: Jinju Chen, Newcastle University, Tianyu Zhang, Montana State University, USA

8:00am **TS1-1 The Investigation of Mechanisms about Bacteria-Hydrogels Interactions**, ***Nehir Kandemir***, *W Vollmer, N Jakubovics, J Chen,* Newcastle University, UK

The structure and function of eukaryotic cells, like mammalian cells, can be regulated by altering their micromechanical environment such as alteration of their microenvironment stiffness. However, little work has been done for prokaryotic cells, like bacteria, which may be affected by similar interactions. In addition to this, bacterial cells are exposed to large forces from osmotic pressure differences and their microenvironment, but quantitative measurements of their mechanical properties have been limited. In this study, the aim is to investigate how physical factors (e.g. mechanical properties of the microenvironment), and chemical factors (e.g. chemical composition) would affect bacteria-material interactions and the bacteria cell mechanics. For this purpose, different mechanical characterisation techniques were adopted to extract the mechanical properties of *Escherichia coli* (Gram negative) and *Staphylococcus epidermidis* (Gram positive) encapsulated in agarose hydrogels made with different media. In addition, finite element simulations and theoretical models were employed to reveal more physical insights. Our study has demonstrated that the structure and properties of the microenvironment considerably affect the extraction of mechanical properties of the encapsulated cells. Such findings will help the further understanding of bacterial cell-materials interactions, which would have great potential impact in various healthcare industries.

8:20am **TS1-2 How Nanostructure on Ti Alloy Surface would Affect Bacterial Adhesion and Biofilm Formation?**, ***Yunyi Cao***, Newcastle University, UK*; B Su,* University of Bristol, UK*; S Chinnaraj, N Jakubovics, J Chen,* Newcastle University, UK

Titanium and its alloys have been widely used in biomedical devices and surgical implants due to their excellent mechanical properties and good biocompatibilities. One of big issues for these Ti-based medical devices is bacteria induced infection and inflammation because biomaterial implant surface is also favorable for bacterial adhesion and biofilm formation. This would result in device retrieval and additional surgery, which will significantly affect the patients and increase the financial burden of national health services. To eliminate bacterial adhesion and biofilm formation, different nanostructures such as nanotexture and nanospikes were created on the titanium alloy implant surfaces. In order to understand how these nanostructures would affect bacterial adhesion and biofilm

formation, a typical clinical relevant bacteria *Staphylococcus epidermidis* was cultured on these two nanostructured surfaces and the polished titanium surface (control sample). Both the initial bacterial adhesion and the biofilms grown on these surfaces for 3 days were analyzed. We found that both nanotexture and nanospikes enable to kill the bacteria and significantly inhibit biofilm formation compared to the control sample. Such an effect is even more significant for nanospike surfaces. This is possibly due to the high aspect ratio of the nanospike structures. To further reveal the mechanisms of this, some preliminary computational simulations based on interaction energy between bacteria and material surfaces were adopted.

8:40am **TS1-3 First Contact: Surface Sensing, Motility Appendages, and Hydrodynamics in Bacterial Interactions with Surfaces***, **Gerard Wong,*** California NanoSystems Institute, UCLA, USA **INVITED**

Bacterial biofilms are integrated communities of cells that adhere to surfaces and are fundamental to the ecology and biology of bacteria. The accommodation of a free-swimming cell to a solid surface is more complex than simply modulation of cell adhesion. We investigate the interplay between motility appendages, molecular motors, hydrodynamics, and exopolysaccharide production near the surface environment using state of the art tools from different fields that are not usually combined, including theoretical physics, community tracking with single cell resolution, genetics, and microbiology. Themes such as *surface sensing*, multi-generational signaling via secondary messengers, subsequent downstream motility consequences, and the subsequent *onset of microcolony organization* via interactions between appendages and exopolysaccharides will be discussed.

9:20am **TS1-5 How Surface Physical Properties of Polymer Carrier Materials would Affect Wastewater Biofilm Formation?***, **Sam Charlton,** M Brown, R Davenport, J Chen,* Newcastle University, UK

Biofilms are ubiquitous naturally occurring biological populations encased within an extracellular polymeric substance (EPS) matrix which adhere to substrates within aqueous environments. It was reported that various surface properties and features (e.g. roughness, surface energy, topography, surface chemistry and surface charge) would affect biofilm formation. However, most of these studies are focused on single species biofilms with lack of studies on wildtype multispecies biofilms. Therefore, in this study we investigated how the physical properties of various polymer materials (such as HDPE and PVC) would affect wildtype wastewater biofilm formation. It demonstrated that surface roughness, surface topography and hydrophobicity would affect biofilm growth rate, biofilm microstructure and bacteria community as well as biofilm mechanics. Such finding is important for understanding the interactions between mixed species and material surfaces. It will also potentially have significant impact on nitrification efficiency for wastewater treatment industries.

9:40am **TS1-6 Evaluating the Electrochemical Corrosion and Immune Cell Activation Behaviour of Nano-crystalline Thin Films of Chromium Nitride Prepared by Reactive Magnetron Sputtering***, **SaeedUr Rahman,** A Ogwu, A Crilly,* University of the West of Scotland, UK

We investigated the potential of nano-crystalline chromium nitride thin film implant coatings to reduce the corrosion process and minimise the immune cell response in-vivo faced by patients with osteoarthritis. The films are prepared by reactive magnetron sputtering and characterised for grain growth by scanning electron microscopy. The chemical structure of the prepared films are characterised by X-ray photoelectron spectroscopy and Raman spectroscopy. The nano crystalline structure of the coatings which contributes to their phagocyte activation was probed by x-ray diffraction and radial distribution function analysis. We investigated the presence of surface chemical constituent entities on the coatings with XDLVO surface energy analysis and Kelvin probe contact potential difference/ work function measurements to establish the presence of hydrophobic surface chemical entities on the prepared films. The corrosion susceptibility of the films was investigated in saline solution. Our initial investigation includes open circuit potential measurements (OCP) over several hours, Tafel plots and Potentiodynamic polarization. The coatings show good corrosion resistance against pitting corrosion but could be improved further through a microstructural growth mode switch to eliminate potential pin-holes due to a columnar growth mode. The columnar Volmer-Weber growth mode observed by scanning electron microscopy is suspected to underlie the corrosion behaviour of the coating. The initial in vitro immune cell activation was investigated using peripheral blood mononuclear cells (PBMC) cultured on coated and uncoated control surfaces. Supernatants were collected at various time points and simulation conditions. There was a statistical significance ($P<0.01$) in the secretion of the inflammatory cytokine, interleukin 6 (IL-6), between the chromium nitride coated and the uncoated control surface. The results of our current in-vitro investigation based on corrosion and cellular response tests confirm the potential promise for the application of chromium nitride coatings prepared by reactive magnetron sputtering in orthopaedic implant applications.

10:00am **TS1-7 The Graphene Oxide Biopolymers (Polystyrene Sulfonate, PSS and Heparin), and PEDOT were Electrochemically Polymerized in the SUS316L Stainless Steel***, **HuiMing Tsou,** T Liu,* Ming Chi University of Technology, Taiwan

In this study, the graphene oxide (GO), biopolymers (polystyrene sulfonate, PSS and heparin), and PEDOT were electrochemically polymerized in the SUS316L stainless steel, which could produce an anti-fouling surface to avoid the restenosis of the blood vessels. The negative charge of GO, PSS and heparin would exclude the negative charge of protein and platelets to achieve the purpose of anti-fouling and anti-clotting. Furthermore, we also add the surfactant (SDS) in the electrochemically polymerization process. The result shows that the surface energy would decrease with the SDS addition to form the hydrophobic surface. The lower surface energy surface would enhance the ability of anti-fouling and anti-clotting. In conclusion, we have developed an excellent anti-fouling surface by using GO, PSS, heparin and SDS, which could be applied in the eluting stent. The hemocompatibility, biocompatibility, and drug controlled release would be studied detail in the future.

Author Index

Bold page numbers indicate presenter

Author Index

Author Index

Author Index

Author Index

Author Index

Author Index

Author Index