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^{o}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.

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