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 ($0.08 \le x \le 0.16$) 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-$(Cr_{1-x}Al_x)_2O_3$ ($0.08 \le x \le 0.16$) 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.

Author Index

Bold page numbers indicate presenter