Advanced Surface Engineering Division
Room 317 - Session SE+AS+BI+SS+TF-ThM

Nanostructured and Multifunctional Thin Films and Coatings I

Moderators: Suneel Kodambaka, University of California Los Angeles, **Jianliang Lin**, Southwest Research Institute

8:00am **SE+AS+BI+SS+TF-ThM-1 Nanostructured Optical Thin Films for Energy Applications and More**, ***Bill Baloukas,*** Polytechnique Montréal, Canada **INVITED**

The range of applications of optical coatings is ever expanding, and the list of requirements they must fulfil, be it in terms of performance and in terms of functionality, is also increasing. This has stimulated the need for thin film materials with novel nanostructures often based on unconventional materials. The present talk will focus on various coating systems for applications ranging from antireflective (AR) coatings to plasmonic nanocomposites to passive and active materials for anticounterfeiting, smart windows and micro/nanosatellites.

AR coatings are the most widely implemented optical coating solution as they can be found on ophthalmic and camera lenses, displays, solar cells, etc. Most often based on dielectric materials, their mechanical performance can often be problematic when implemented onto polymer substrates, the latter possessing much higher thermal expansion coefficients. As a means of improving their elastoplastic properties, hybrid films consisting of a combination of organic and inorganic materials were explored. We will also show how this concept was pushed further by producing ultralow refractive index hybrid films by glancing angle deposition (GLAD).

GLAD films have also found application in angular selective coatings, which display anisotropic optical properties. Typically based on metals, we show how the angular selectivity (AS) can be tuned independently from the thickness of the film by conformally overcoating dielectric GLAD films with an absorbing film (e.g.: TiN) deposited by atomic layer deposition (ALD).

While the previous examples are based on passive materials, we have also extensively studied active materials, mainly electrochromic (EC) WO_3 and thermochromic (TC) VO_2. We will discuss how by tuning the deposition conditions, one can deposit, for instance, electrochromic interference filters and highly durable EC films when in the presence of significant ion bombardment. In the case of TC VO_2 films, we will show how, by incorporating them into judiciously designed optical filters, one can enhance their overall optical performance (e.g.: luminous transmittance, solar transmission variation, emissivity change, etc.).

Finally, we will conclude this talk by discussing our most recent implementation of a gas aggregation cluster source to produce various nanoparticles of interest for the above-mentioned optical applications.

8:40am **SE+AS+BI+SS+TF-ThM-3 Constitution, Microstructure and Mechanical Properties of Magnetron Sputtered RuAl Thin Films**, ***Vincent Ott,*** Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany; *T. Wojcik,* TU Wien, Austria; *S. Ulrich,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany; *S. Kolozsvári,* Plansee Composite Materials GmbH , Germany; *P. Polcik,* Plansee Composite Materials GmbH, Germany; *P. Mayrhofer, H. Riedl,* TU Wien, Austria; *M. Stueber,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany

Considering high temperature applications, aluminide intermetallics arrived increasing importance over the last decades. They are well known for their mechanical properties, such as high melting point, strength and good oxidation resistance. In Ni-superalloys, for example, aluminide precipitations are widely used as toughening phase, increasing the high temperature strength and durability of the construction material. Although they are commonly used as an additive in composite materials, their usage as a bulk material is hindered by their poor manufacturing due to its brittle behavior at room temperature.

A relatively new candidate material of B2 structured aluminides is the RuAl intermetallic phase. Compared to other candidates of its class, such as NiAl or TiAl, RuAl exhibits a ductile-brittle-transition below room temperature, which may considerably expand the range of its potential applications.

Thin film synthesis can enable the exploitation of their full potential for example as a protective coating in aircraft and aerospace applications. To elucidate this potential, RuAl single layer thin films were synthesized by magnetron sputtering, utilizing a powder manufactured sputtering target with a composition of 50 at. % Ru and 50 at. % Al. Thin film deposition was done for a variation of the process parameters such as the mode of the power supply, gas pressure and substrate bias voltage to investigate their impact on the thin films constitution and microstructure. Major structural thin film characterization was done by X-ray diffraction and transmission electron microscopy methods. These data are subsequently used to discuss the mechanical properties of the thin films, determined by microindentation.

9:00am **SE+AS+BI+SS+TF-ThM-4 Microstructure, Thermal Stability and Oxidation Resistance of an arc-evaporated $Cr_{0.74}Ta_{0.26}N$ Coating**, ***Christina Kainz,*** Christian Doppler Laboratory for Advanced Coated Cutting Tools at the Department of Materials Science, Montanuniversität Leoben, Austria; *M. Tkadletz, M. Burtscher,* Department of Materials Science, Montanuniversität Leoben, Austria; *C. Saringer,* Christian Doppler Laboratory for Advanced Coated Cutting Tools at the Department of Materials Science, Montanuniversität Leoben, Austria; *A. Stark, N. Schell,* Institute of Materials Physics, Helmholtz-Zentrum Hereon, Germany; *C. Czettl, M. Pohler,* CERATIZIT Austria GmbH, Austria; *D. Kiener,* Department of Materials Science, Montanuniversität Leoben, Austria; *N. Schalk,* Christian Doppler Laboratory for Advanced Coated Cutting Tools at the Department of Materials Science, Montanuniversität Leoben, Austria

CrTaN coatings have recently received increasing industrial interest due to their combination of high hardness, beneficial fracture toughness and promising performance in cutting tests. However, up to now, no thorough investigation on the thermal stability and oxidation resistance of this coating system is available. Thus, this work aims to elucidate the evolution of the microstructure and phase composition of an arc evaporated $Cr_{0.74}Ta_{0.26}N$ coating in protective atmosphere and air up to 1400 °C. The as–deposited coating crystallizes in an fcc–$Cr_{0.74}Ta_{0.26}N$ solid solution with a preferred <311> orientation. Alternating Cr–enriched and Ta–enriched nano–layers are identified in the cross–section, which arise from the three–fold rotation during deposition. $Cr_{0.74}Ta_{0.26}N$ powder is stable in protective atmosphere up to temperatures of ~1200 °C, where a transformation into fcc-$Cr_{0.74}Ta_{0.26}N$ to t–$Cr_{1.2}Ta_{0.8}N$ sets in. Vacuum annealing of $Cr_{0.74}Ta_{0.26}N$ on sapphire substrate results in the loss of the nano-layers at 1000 °C, a texture change to <200> at 1270 °C and the transformation to t-$Cr_{1.2}Ta_{0.8}N$ at 1300 °C. When exposed to ambient atmosphere, powdered CrTaN starts to oxidize to t–$CrTaO_4$ and r–Cr_2O_3 at 1050 °C. A partly oxidized CrTaN coating on sapphire was found to consist of intact fcc-$Cr_{0.74}Ta_{0.26}N$ grains close to the substrate interface, a porous transition layer of r-Cr_2O_3 and t-$CrTaO_4$ and a dense r-Cr_2O_3 layer at the surface. The present study confirms the exceptional thermal stability and oxidation resistance of CrTaN coatings, making them promising candidates for use in demanding machining applications.

9:20am **SE+AS+BI+SS+TF-ThM-5 Microstructural Characterization and Tribological Evaluation of TiN, CrN, TiSiCN, and CrSiCN Coatings for Applications in Cold Regions**, ***Nicholas D'Attilio,*** *F. Thompson, G. Crawford,* South Dakota School of Mines and Technology; *E. Asenath-Smith,* US Army Corps of Engineers Cold Regions Research and Engineering Laboratory

Transition metal nitride and nanocomposite coatings have the potential to improve the efficiency, service lifetime, and durability of equipment operating in the extremely cold and dry environments found in Earth's polar regions. Ceramic coatings are sensitive to their operating conditions, and development efforts have been focused on ambient and high temperature environments. Thus, there is a need to understand the influence of arctic conditions on the performance of these materials. To investigate the influence of coating phase content on cold environment performance, TiN, CrN, TiSiCN, and CrSiCN coatings were deposited by plasma enhanced reactive magnetron sputtering. The structure and composition of the coatings was characterized by scanning electron microscopy, energy dispersive X-ray spectroscopy, atomic force microscopy, and X-ray diffraction. Tilting base contact angle goniometry was used to determine the surface energy using the Owens-Wendt-Rabel-Kaelble method. Coating hardness and apparent elastic modulus were measured by nanoindentation. Sliding wear tests were conducted under simulated arctic conditions with a ball-on-flat tribometer equipped with an active cooling stage. Coating microstructure, surface properties, and their relationships to the wear mechanisms identified at low temperatures are discussed.

9:40am **SE+AS+BI+SS+TF-ThM-6 Development and Evaluation of TiAlNb/YSZ Protective Coatings for Titanium Alloys**, ***Jianliang Lin,*** Southwest Research Institute, San Antonio Texas*; T. Stinnett,* Lockheed Martin Missiles and Fire Control

There are increasing demands in the development of advanced thermal protection coatings for aerospace components made by titanium alloys for hypersonic applications. A conventional thermal barrier coating based on MCrAlY/YSZ produced by thermal spray or EB-PVD (Electron Beam Physical Vapor Deposition) provided thermal protection, but was found insufficient in thermal stain tolerance and mechanical strength match for titanium alloys. In this study, TiAlNb alloy with specific chemistry was selected as the bond coat for Ti-6Al-4V alloys. The TiAlNb bond coats were prepared by different magnetron sputtering techniques, including plasma enhanced magnetron sputtering (PEMS), high power impulse magnetron sputtering (HiPIMS), and a combination of PEMS and HiPIMS. The structure, adhesion, oxidation resistance, and thermal fatigue resistance of the TiAlNb coatings was studied by different means. Then an yttrium stabilized zirconium oxide (YSZ) top coat was applied on the top of the optimized TiAlNb by thermal spray. The thermal strain resistance and phase stability of the overall coating system were evaluated using high energy laser irradiation and compared to a thermal spray MCrAlY/YSZ coating in ambient air. It is found that TiAlNb/YSZ outperform MCrAlY/YSZ in high energy laser irradiation, and exhibited no structure and integrity degradation.

11:00am **SE+AS+BI+SS+TF-ThM-10 Imperfections in Metal Diborides – from Ab-Inito Calculations to Transmission Electron Microscopy**, ***Martin Dahlqvist,*** IFM, Linköping University, Sweden*; M. Dahlqvist,* Linköping University, Sweden **INVITED**

Transition metal diborides (MB_2) are considered as an extremely hard ceramics owing to their outstanding chemical, mechanical, corrosion, thermal and electrical properties. This makes MB_2 coatings attractive for applications in erosive, abrasive, corrosive, and high-temperature environments [1]. Typical coatings are overstoichiometric in boron ($B/M>2$) [2] but the recent addition of understoichometic MB_2 coatings ($B/M<2$) have widened their compositional range [3-8]. However, when comparing calculated and measured lattice parameters of MB_2, perfect match is found for M from Group 3 (Sc, Y) and 4 (Ti, Zr, Hf) while deviations are found for M from Group 5 (V, Nb, Ta) and 6 (Cr, Mo, W). Reason for this have been discussed to be attributed to non-stoichiometric MB_2. In our quest for improving the properties of MB_2 we must thus not only master their composition but also related defects. Reliable theoretical studies thus require detailed information about type of defects and their distribution in MB_2. It will be shown how theory can be used to identify possible defects in MB_2 and explain the discrepancy between theory and experiment. It will be demonstrated that vacancies in MB_2 have a significant impact for M from Group 5 (Nb, Ta) and 6 (Mo, W) with improved thermodynamical and dynamical stability as well as mechanical properties. Moreover, extended planar defects have also been identified for multiple MB_2 where atomically resolved aberration-corrected scanning transmission electron microscopy imaging, electron energy loss spectroscopy elemental mapping and first principles calculations have been applied to decode the atomic arrangements of the observed planar defects in non-stoichiometric MB_2 coatings.

[1] M. Magnuson, et al, Vacuum. **196**, 110567 (2021).
[2] P.H. Mayrhofer, et al, Appl. Phys. Lett. **86**, 3 (2005).
[3] I. Petrov, et al,J. Vac. Sci. Technol. A. **35**, 050601 (2017).
[4] N. Hellgren, et al, Vacuum. **169**, 108884 (2019).
[5] J. Thörnberg, et al, Surf. Coat. Technol. **404**, 126537 (2020).
[6] M.M. Dorri, et al, Scripta Mater. **200**, 113915 (2021).
[7] B. Paul, et al., Acta Mater., **211**, 116857 (2021).
[8] J. Palisaitis, et al, Acta Mater. **204**, 116510 (2021).

11:40am **SE+AS+BI+SS+TF-ThM-12 Mechanical Property and Corrosion Resistance Evaluation of $Ti_xZrNbTaFeB_y$ High Entropy Alloy Thin Films**, *B. Lou,* Chang Gung University, Taiwan*; F. Kan,* Ming Chi University of Technology, Taiwan*;* ***Jyh-Wei Lee,*** Ming Chi University of Technology, Taiwan

High entropy alloy (HEA) thin films have been widely explored due to their unique properties as compared with conventional alloy coatings. In this work, an equimolar TiZrNbTaFe HEA target and a TiB2 target were used to fabricate five TixZrNbTaFeBy HEA thin films with different Ti and B contents using a hybrid high power impulse magnetron sputtering and radio frequency power deposition system. The Ti and B contents were increased by decreasing the input power of TiZrNbTaFe HEA target. The (Ti+B)/(Zr+Ta+Nb+Fe) ratio of the thin films increased from 2.70 to 19.44 as the ZrTiNbTaFe HEA target input power decreased from 200 to 50 W. The TixZrNbTaFeBy thin film kept its amorphous structure while the (Ti+B)/(Zr+Ta+Nb+Fe) ratio was less than 19.44. A nanocomposite microstructure consisting of TiB_2 nanocrystallites embedded in an amorphous TiZrNbTaFe matrix was obtained for the $Ti_{26.4}Zr_{1.1}Nb_{1.0}Ta_{1.3}Fe_{1.1}B_{61.1}$ thin film. The hardness of TixZrNbTaFeBy thin films increased with increasing Ti and B contents. Good adhesion properties were found for five thin films. Each amorphous TixZrNbTaFeBy thin film enhanced the corrosion resistance of bare 304 stainless steel substrate because of the dense microstructures to block the attack of corrosive electrolytes. The amorphous structured $Ti_{26.9}Zr_{3.5}Nb_{3.4}Ta_{3.8}Fe_{3.7}B_{54.6}$ thin film coating exhibited a potential application as a protective coating in harsh environments due to its high hardness of 18.8 GPa, excellent adhesion, good wear resistance, and adequate anticorrosion property.

12:00pm **SE+AS+BI+SS+TF-ThM-13 Tuning the Properties of Thin Films via Disorder**, ***Alessandro Troglia****, M. van de Poll,* Advanced Research Center for Nanolithography (ARCNL), Netherlands*; J. van de Groep, A. de Visser,* Van der Waals-Zeeman Institute, University of Amsterdam, Netherlands*; R. Bliem,* Advanced Research Center for Nanolithography (ARCNL), Netherlands

Structural disorder in thin films is often considered detrimental compared to the well-defined nature of epitaxial layers. However, some examples of amorphous thin films show superior properties such as better corrosion resistance, mechanical strength and catalytic performance. Structural disorder can thus serve as an ideal parameter to tune the properties of thin films to specific applications. In this work, we investigate how structural disorder affects the properties of metallic thin films for two selected alloys: CuZr and HfMoNbTiZr. Due to its excellent glass-forming ability, CuZr is an ideal model system for metallic glasses, while the refractory high-entropy alloy (HEA) HfMoNbTiZr has shown a strong preference towards crystallinity. For both materials, amorphous and crystalline alloy thin films of identical composition were achieved by varying the substrate temperature during deposition onto sapphire substrates via pulsed laser deposition (PLD). Grazing-incidence x-ray diffraction (GI-XRD) demonstrate that CuZr thin films grown at room temperature are fully amorphous, while signs of polycrystallinity are observed at 500°C. The effect of disorder is clearly visible in the optical, transport and corrosion properties. The amorphous films are optically transparent in the visible, while polycrystalline films are dark and reflective. The temperature-dependent electronic transport changes its mode from a bad metal to a charge-hopping conductor with an increase in structural disorder. Moreover, the surface chemical properties measured with x-ray photoelectron spectroscopy (XPS) show a clear preference in the surface oxidation of the Cu species. Cu is fully metallic in the disordered film after air-exposure, whereas both oxide and hydroxide species are detected in the polycrystalline film. On the other hand, HfMoNbTiZr thin films grown with PLD are amorphous according to GI-XRD and display a remarkable thermal stability. In contrast with literature, no sign of crystallinity is detected with GI-XRD from room temperature up to 700°C. A further increase of the growth temperature reveals the onset of directed crystallization at 900°C. These results pave the way to the synthesis of metallic thin films with superior and tunable properties via disorder for a wide variety of technological applications.

Author Index

Bold page numbers indicate presenter