

Advanced Surface Engineering Room 125 - Session SE-MoM

Plasma-Assisted Surface Modification and Deposition Processes/Nanostructured and Multifunctional Coatings

Moderators: Diana Berman, University of North Texas, Filippo Mangolini, The University of Texas at Austin

8:15am SE-MoM-1 Materials Design in Surface Engineering, Johanna Rosen, Linköping University, IFM, Sweden **INVITED**

MAX phases are a family of atomically laminated ceramics where M is a transition metal, A is a group A element, and X is C or N. These materials are a playground for design of both three- and two-dimensional (3D/2D) phases, for diverse applications. MAX phases are to date primarily synthesized in powder form, but we present epitaxial thin films of Ti_3AlC_2 and Ti_3SiC_2 on sapphire through magnetron sputtering from three elemental targets. We show that Ti_3AlC_2 can be converted to 2D Ti_3C_2 MXene through selective etching of Al in hydrofluoric acid (HF), while Ti_3SiC_2 can be transformed into 3D Ti_3AuC_2 , $Ti_3Au_2C_2$ and Ti_3IrC_2 by noble metal substitution reaction, the latter forming high-temperature-stable Ohmic contacts to SiC. Evidence is also presented for synthesis of single-atom thick layers of gold by selective removal of Ti_3C_2 from Ti_3AuC_2 by Murakami's reagent. Insight into these 3D and 2D materials and the methods by which they are formed is given through a combination of first principles simulations and electron microscopy, which suggest additional pathways for design of new phases.

8:45am SE-MoM-3 Development of Texture in Ta_2C Thin Films Sputter-Deposited on Free-Standing Graphene, Suneel Kodambaka, Virginia Tech; K. Tanaka, University of Chicago

Thin crystalline films are commonly deposited on bulk solids and the development of texture (preferred orientation) in such thin films is reasonably well understood.¹ Efforts to grow highly crystalline thin films have included, for example, the use of low-energy ion irradiation² and van der Waals (vdW) epitaxy.³ Exciting developments based on vdW epitaxy include the use of vdW buffer layers (e.g., graphene, and hBN) on crystalline substrates to grow highly oriented MoS_2 and $(VNbTaMoW)_2S_2$ thin films.^{4, 5} Recently, Koichi *et al.*⁶ reported that Ta_2C thin films sputter-deposited on hBN/ Ta_2C surfaces are more highly oriented than those grown using the same deposition parameters on bare Ta_2C . These results led us to question the need for a bulk substrate and if crystalline thin films can be directly deposited on *free-standing* vdW layers instead.

Here, we present results obtained from sputter-deposition of Ta_2C films on monolayer-thick graphene substrates and on relatively thicker (~8 nm) amorphous silicon nitride (a-SiN_x) membranes supported by transmission electron microscopy (TEM) grids. Using plan-view TEM and selected area electron diffraction, we compare and contrast the microstructures of the Ta_2C films on graphene and a-SiN_x. We find that the Ta_2C layers deposited on a-SiN_x are composed of a mixture of nanoscale crystallites and non-crystalline phases, while the Ta_2C film on graphene is polycrystalline with grains that are oriented in-plane as $[2-1-10]_{film} || [10-10]_{graphene}$. These results indicate that even a single-atom-thick crystal can promote crystalline and oriented growth.

References

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9:00am SE-MoM-4 Manufacture and Microstructure of Tantalum Nitride Films by Radio Frequency and High Power Impulse Magnetron Sputtering Techniques, Y. Chiang, Y. Chang, F. Wu, National United University, Taiwan; Jyh-Wei Lee, Ming Chi University of Technology, Taiwan

Tantalum nitride, TaN, film attracted attention for decades due to its merits in thermal, mechanical, tribological, electrical properties and had been employed in versatile applications, including microelectronics, semiconductor, protective layer and so on. However, the TaN films frequently deposited through sputtering process in vacuum possessed various microstructural features according to deposition conditions, leading to the evolution in characteristics. A comparative study focused on the control on fabrication parameters of inlet gas ratio, input power types, including radio frequency, and high power impulse magnetron sputtering, i.e. RFMS and HiPIMS, respectively, and the duty cycle modulation of the HiPIMS technique was conducted. An amorphous/nanocrystalline microstructure feature could be deduced under a low RF power, while a higher level of RF power enhanced the crystallization of the TaN films. The even higher power density upto 0.5 kW by the HiPIMS technique triggered a multiphase microstructure comprised of TaN, Ta₂N, and TaN₂ phases. Under such high power density, a strong columnar feature was obtained regardless of the duty cycle. In addition, under a higher Ar/N₂ gas ratio of 18/2 with limited nitrogen the TaN showed a stoichiometry of Ta₂N, while an elemental ratio Ta:N=1:1 was achieved with a ratio of Ar/N₂=15/5. Recent findings on microstructure evolution and related characteristics of the TaN coatings were discussed.

9:15am SE-MoM-5 In-Situ Laser Diagnostics of Plasma Surface Interactions by Fs-TALIF, Mruthunjaya Uddi, Advanced Cooling Technologies; G. Urdaneta, A. Dogariu, Texas A&M University

Plasma surface interaction has been a critical area of research for many applications such as Plasma-Enhanced Atomic Layer Etching (PEALE). To meet the demanding needs of more advanced atomically controlled microfabrication methods, the physics of PEALE needs to be better understood to enable high quality, repeatable and controllable deposition process. Several challenges that need to be addressed regarding PEALE include damage to the substrate from highly energetic species and UV radiation, need for precise amorphous/crystalline modulated selective layer deposition, conformality in coating non-uniform substrates, achieving an aspect ratio of >100, repeatability and controllability of the finish. To address these challenges, we are developing laser diagnostics methods to measure species over substrates by advanced laser diagnostics such as femtosecond- Two-Photon Absorption Laser Induced Fluorescence (fs-TALIF) to image atomic species over substrates. Here we present measurements of N, O atom densities over a substrate with high spatial (< 10 microns) and temporal resolution (<1 ns) using fs-TALIF at pressures of 5-150 mTorr. Temperature was measured over a substrate surface using NO 2-line LIF using femtosecond laser excitation.

9:30am SE-MoM-6 Interlayer Optimization for Nitrogen-Incorporated Tetrahedral Amorphous Carbon Thin Film Optically Transparent Electrode, Nina Baule, D. Galstyan, L. Haubold, Fraunhofer USA Center Midwest

While several studies around the usage of nitrogen-incorporated tetrahedral amorphous carbon (ta-C:N) in electroanalysis have been published, they mainly focus on ta-C:N films deposited on conductive substrates. This is due to the relatively high resistivity of ta-C:N compared to other carbon and metal-based electrodes: without the electrically conducting substrate, there are high ohmic losses in the ta-C:N when subjected to an electrical current. This limits the use of ta-C:N in optically transparent electrodes (OTEs), which must be deposited on optically transparent (typically electrically insulating) substrates such as quartz. In this study we deposited 50 nm of ta-C:N by laser controlled pulsed cathodic vacuum arc (Laser-Arc) onto insulating quartz substrates to investigate the electrochemical response compared to the same film deposited on conductive silicon. To test the responses of the films, we performed electrochemical oxidation/reduction of potassium ferrocyanide during cyclic voltammetry (CV). Here we find that no oxidation or reduction during CV could be observed at the ta-C:N electrode deposited on quartz. To address this and to maintain optical transparency over the visible wavelength range, we then introduced a 5 nm chromium (Cr) interlayer deposited by magnetron sputtering between the ta-C:N and quartz. While this electrode configuration led to clear cathodic and anodic CV peaks of potassium ferrocyanide, the peak separation compared to the ta-C:N deposited on conductive silicon was increased. That finding indicates that the electrode has a higher resistance. However, we further improved ta-C:N's electrode functionality on quartz by optimizing the Cr sputtering

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conditions and introducing a plasma pretreatment by a single-beam ion source. Atomic force microscopy revealed that these changes caused an improved Cr growth homogeneity, which led to the enhanced electrical conductivity. These results show that ta-C:N's potential as an OTE is not precluded by its high ohmic losses on insulating substrates. In fact, the promise of mechanically stable and electrochemically active ta-C:N requires only that a conductive interlayer be used, and these films could impact the realms of optical materials, flexible electronics, sensors, and more.

9:45am **SE-MoM-7 Highly-Ordered Metallic Nanostructure Arrays: Strategies, Status, and Challenges**, *Jinn P. Chu*, National Taiwan University of Science and Technology, Taiwan

This presentation reports on the wafer-scale fabrication of metallic nanostructure arrays with highly ordered periodicity. With the semiconductor-based lithography and sputter deposition, various metallic arrays including metallic nanotube array, metal mesh, and metallic pillar array are fabricated. The array structure is manufactured by sputtering metals onto a contact-hole array template created in the photoresist by photolithography. Following sputter deposition, the photoresist and any excess top-layer coating were removed using acetone, leaving behind the nanotube array on the substrate. The efforts were recognized with the American Chemical Society (ACS) Award at the nano tech 2018 International Nanotechnology Exhibition & Conference in Tokyo, Japan. We utilized both ferrous (stainless steel) and nonferrous alloys (Cu-, Ni-, Al-, and Ti-based), elemental metals (Cu, Ag, and Au), as well as various oxides to form these array structures. The proposed arrays can be fabricated over a wide range of heights and diameters (from a few hundred nm to 20 μm) and in various shapes, including tall cylinders, dishes, triangles and rhombuses. Furthermore, when combined with other nanomaterials (e.g., ZnO nanowires, graphene oxide, or Au nanoparticles), arrays become nanohybrids suitable for many applications. These applications include thermal emitters, triboelectric nanogenerators, SERS-active biosensors, and anti-icing devices.

10:00am **SE-MoM-8 Refining Deposition and Thermal Processes for High-Quality Bi-Mo-O Thin Films**, *R. Gonzalez-Campuzano, A. Hernandez-Gordillo, Sandra Elizabeth Rodil*, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México

Bismuth molybdates, a family of Bi-Mo-O materials with diverse elemental compositions and crystalline structures, have been extensively investigated for their excellent catalytic properties in the oxidation of lower olefins. These properties facilitate the synthesis of organic chemicals widely used in the plastic industry. Their photocatalytic activity under visible light has recently been demonstrated in micro and nano powder samples. However, there has been limited research on the deposition and characterization of Bi-Mo-O materials as thin films. Since 2016, Matova et al. have shown that sputtering deposition using Bi and Mo targets in an Ar+O₂ atmosphere is feasible, demonstrating the visible-light photocatalytic degradation of dyes in water. Despite these promising results, the broader application of this bismuth-based photocatalyst has seen limited advancement. To address this gap, our research group has renewed the investigation of Bi-Mo-O semiconductors for photocatalytic degradation of recalcitrant pollutants, leveraging their active response to visible light. In this study, we report on the thin-film deposition of Bi-Mo-O samples using a co-sputtering system with Bi₂O₃ and Mo targets. The direct current power applied to the Mo target varied from 20 to 60 W, while the RF power applied to the Bi₂O₃ target was fixed at 30 W, allowing us to achieve films with different Bi/Mo ratios. The substrate was pre-heated to 420 K and rotated at approximately 10 RPM to ensure film uniformity. Our results indicated that the films transitioned from crystalline to amorphous as the Mo content increased. Annealing experiments using rapid thermal processing equipment, introducing air into the chamber, performed at 773.15, 873.15, and 973.15 K for 20 minutes for each sample, aiming to obtain various Bi-Mo-O crystalline structures. The structure variations, optical band gap, and bonding-composition analysis are presented. Mo-rich samples presented high optical absorption with band gaps below 0.5 eV, but most samples presented band gaps in the visible-range. Pure phase Bi-Mo-O films and heterostructures containing MoO_x phases were obtained and tested for the degradation of the indigo carmine dye under visible light.

10:30am **SE-MoM-10 Low-Temperature Synthesis of Stress-Free, Ceramics Thin Films Using Metal-Ion Irradiation**, *Ivan Petrov*, University of Illinois at Urbana-Champaign; *L. Hultman, G. Greczynski*, Linköping University, IFM, Sweden

Ion irradiation is a key tool for controlling epitaxy-to-nanostructure, phase content, and physical properties of refractory ceramic thin films grown by

magnetron sputtering. Until recently, thin film growth relied on enhancing adatom mobility in the surface region by inert and/or reactive gas ion irradiation to obtain dense layers at low deposition temperatures. Development of high-power pulsed magnetron sputtering (HiPIMS), which provides metal-ion plasmas with tunable degree of ionization, enabled systematic studies of the effects of metal-ion irradiation on properties of refractory ceramic thin films. A motivation for the use of metal-ions stems is that they are film constituents, hence they can provide the benefits of ion-mixing without causing the high compressive stresses associated with trapping of gas ions at interstitial sites.

This presentation reviews growth experiments of transition metal nitride model systems including TiAlN, TiSiN, VAlN, TiTaN, TiAlTaN, and TiAlWN. Film synthesis is carried out in a hybrid configuration with one target powered by HiPIMS and other operated in direct current magnetron sputtering (DCMS) mode. A substrate bias potential V_s is synchronized with the metal-ion-rich portion of the HiPIMS pulses to control the metal-ion energy. The time-resolved mass spectrometry analyses performed at the substrate position enables us to suppress the role of gas ion irradiation and select intense

Irradiation with lower-mass metal-ions (Al⁺ or Si⁺) results in near-surface implantation with the depth controlled by V_s amplitude. This enables synthesis of *metastable* ternary cubic Me₁Me₂N solid solutions far above the Me₁N concentration range achieved by DCMS. At the other end, bombardment of the growing film surface with pulsed high-mass metal ion fluxes (W⁺ or Ta⁺) during hybrid HiPIMS/DCMS high-rate deposition of dilute Ti_{1-x}Ta_xN, Ti_{1-x-y}Al_yTa_yN, and Ti_{1-x-y}Al_xW_yN alloys provides high fluxes of low energy recoils and results in fully-dense, low-stress, hard and superhard coatings without external substrate heating (temperature ≤ 130 °C).

10:45am **SE-MoM-11 ASED Young Investigator Award Finalist Talk: Understanding Ceramics Under Extreme Mechanical Loads via Machine-Learning Potential Molecular Dynamics**, *Nikola Koutna¹, S. Lin*, TU Wien, Austria; *L. Hultman, D. Sangiovanni*, Linköping Univ., IFM, Thin Film Physics Div., Sweden; *P. Mayrhofer*, TU Wien, Austria

Inherent brittleness and easy crack formation are serious challenges for applications of hard ceramic films. Prior to the development and targeted testing of a specific material, data-driven ab initio and machine-learning techniques can facilitate efficient and relatively inexpensive screening of the relevant chemical space with desired structure-property constraints. Furthermore, theoretical approaches can aid experiment in providing atomic-to-nanoscale understanding of deformation and crack initiation processes under well-defined loading conditions. In this talk I will discuss the exciting and rapidly growing field of machine-learning interatomic potentials (MLIPs) for molecular dynamics and how these can be used to study boron-based ceramics under extreme mechanical loads, highly relevant for applications of these materials. Transition metal diborides (TiB₂, TaB₂, WB₂) and MAB phases (nanolaminates alternating ceramic-like, Ti-B, Ta-B, W-B, and metallic-like, Al, layers) will be used to exemplify a possible MLIP training strategy as well as to discuss challenges upon up-scaling beyond ab initio length scales. Uniaxial tensile tests as well as compression tests with a surface pre-crack will be simulated for supercells with up to 10⁶ atoms, previously inaccessible to both ab initio as well as molecular dynamics calculations due to the size limitations (ab initio) and due to the fact that only few interatomic potentials for ceramics exist (molecular dynamics) and basically none has been properly tested for large-scale simulations including severe mechanical loads. Equipped with the newly developed machine-learning interatomic potentials, I will further discuss strain-induced nucleation of extended defects MAB phases and relate them to relevant experimental observations.

11:00am **SE-MoM-12 ASED Rising Star Talk: Coupling CdS/g-C₃N₄ Heterojunctions with Remarkably Transfers Process: Impact of Stacking Grade of g-C₃N₄ Micro-flakes**, *Karen Valencia García², A. Henández Gordillo, S. Rodil Posada*, National Autonomous University of Mexico

In this work, heterojunction materials of cadmium sulfide (CdS) with carbon nitride (g-C₃N₄) were prepared and the photocatalytic activity in hydrogen (H₂) production was studied using an ethanol-water solution. The influence of ammonia (NH₃) on the physicochemical and photocatalytic properties of g-C₃N₄ was investigated. It was evaluated in the photocatalytic H₂ production, obtaining a null response, but the g-C₃N₄ exhibit activity in the photodegradation of the indigo carmine dye (IC) solution using blue LED light. From the analysis of the results, a parameter defined as

¹ ASED Young Investigator Award Finalist

² AVS Rising Star

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SA/(WCA*gap) (surface area (SA); water contact angle (WCA) and photon absorption (band gap)) is proposed to show how the different surface parameters in the photocatalytic response. Subsequently, the effect of the amount of g-C₃N₄ on the heterojunction formed with the CdS nanofibers, which were synthesized in the solvent mixture of ethylenediamine and butanol, was studied. The heterojunction of CdS/g-C₃N₄ was carried out using the g-C₃N₄ synthesized by polymerization with 1 mL of hydrazine (UH1, the g-C₃N₄ with the maximum value of SA/(WCA*gap) and with the g-C₃N₄ synthesized with 2 mL of hydrazine (UH2, the g-C₃N₄ that presented the greatest physical-chemical and optoelectronic modification). The CdS heterojunctions with the modified g-C₃N₄ exhibited a high H₂ production rate of (5258 μmol h⁻¹g⁻¹) ~2.0 times higher than the unmodified CdS nanofibers. The increase in H₂ production rates of the heterojunctions was related to the coupling of the CdS nanofibers on the surface of g-C₃N₄ lamellar plate: (1) result of a better capacity to absorb visible light; (2) the lower resistance to charge transfer, decreasing the recombination of the e⁻/h⁺ pairs. For the heterojunctions, the increase in photocatalytic activity suggests that the coupling of the CdS materials with g-C₃N₄ was satisfactorily achieved, observing a synergy of CdS with g-C₃N₄. Physical mixtures equivalent to heterounions were made, and they presented a low rate in the evolution of H₂, the low activity is due to the fact that there is no coupling between the CdS nanofibers and g-C₃N₄.

Keywords: heterojunctions, hydrogen production, photocatalysis.

11:15am **SE-MoM-13 ASED Young Investigator Award Finalist Talk: Advanced EMI Shielding with Quantum Dots and 2D Nanomaterial Enhanced Dual-Polymer Fiber Films**, *Lihua Lou*¹, Florida International University; *G. Al-Duhni*, Florida International University, Jordan; *O. Cruz*, Florida International University, Nicaragua; *J. Volakis*, *M. Pulugurtha*, *A. Agarwal*, Florida International University

An ultra-thin, lightweight, and highly flexible nanocomposite film is developed by synergistically integrating iron oxide quantum dots (FeQDs) and graphene nanoplatelets (GNPs), specifically targeting electromagnetic interference (EMI) shielding applications. To enhance the electrical conductivity of the resulting thin film, a dual-faceted strategy is employed: utilizing a hybrid polymer system as the matrix and constructing a QDs/2D nanomaterial-integrated multilayer network within the film's architecture. This intricate design approach facilitates a robust investigation into the fiber-based thin films' structural, chemical properties, electrical conductivity, and EMI shielding capabilities, including characterization and simulation methodologies. Findings reveal that the electrospun fibers of 10GNP-1QDs exhibit an average diameter of $\sim 613 \pm 192$ nm, presenting a significantly higher surface roughness than the pristine PAN fibers. This morphological variance is attributed to the intricate particle-polymer interactions. Raman spectroscopy analysis confirms the successful incorporation of GNPs and FeQDs into the fiber matrix, as evidenced by slight shifts in peak positions, indicative of atomic and molecular interactions between the composite's organic and inorganic constituents. Electrical conductivity measurements underscore a remarkable figure of 350,000 S/m, a characteristic partially ascribed to GNPs and FeQDs' facilitative role in enhancing the polymer matrix's conductive pathways. The magnetic SE within the frequency range of 250 to 1000 MHz spans between 30 to 35 dB, surpassing the performance of all other thin films, including control samples fabricated through coating and casting methodologies. This enhanced performance is linked to the improved electron mobility afforded by FeQDs. Additionally, within the low-frequency range of 0 to 1 MHz, the film exhibits an SE ranging from 40 to 50 dB, markedly outperforming Al and Cu films of equivalent thickness. Notably, within the high-frequency X-band spectrum of 8 to 12 GHz, the SE reaches levels up to 170 dB, ~ 30 dB higher than that of Al and Cu films. Furthermore, across the far-field frequency range of 100 MHz to 12 GHz, the film demonstrates an SE between 65 to 100 dB. The predominant shielding mechanisms contributing to these outcomes include absorption, multi-reflection, reflection, hysteresis loss, and polarization loss, collectively ensuring the nanocomposite's superior performance in EMI shielding applications. This exploration significantly advances the field by demonstrating the exceptional capabilities of 1D/2D nanomaterial-integrated thin films across a wide frequency spectrum.

11:30am **SE-MoM-14 Microstructural, Nanomechanical, and Tribological Properties of Thin Dense Chromium Coatings**, *Esteban Broitman*, *A. Jahagirdar*, SKF Research and Technology Development, Netherlands; *E. Rahimi*, Delft University of Technology, Netherlands; *R. Meeuwenoord*, SKF Research and Technology Development, Netherlands; *A. Mol*, Delft University of Technology, Netherlands

Nowadays, Thin Dense Chromium (TDC) coatings are being industrially used in rolling bearings applications due to their claimed advantages such as high hardness, low wear, and good corrosion resistance. However, despite their broad commercial use, very little has been published in the open scientific literature regarding their microstructure, nanomechanical and tribological properties.

In this presentation, TDC coatings with a thickness of about 5 μm were deposited by a customized electrochemical process on 100Cr6 bearing steel substrates. Surface microstructure and chemical composition analysis of the TDC coatings was carried out by X-ray Diffraction, Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy, and Atomic Force Microscopy. The results revealed a coating with a dense, nodular, and polycrystalline microstructure. Unlike standard electrodeposited "Hard Chromium" coatings, TDC coatings show no presence of micro/nano-cracks, likely contributing to their superior corrosion resistance. The nanomechanical behavior, studied by nanoindentation as a function of penetration depths exhibits a pronounced size effect near the coating surface, that can be linked to the nodular microstructure. A hard surface with hardness $H_{IT} \sim 25$ GPa and reduced Young's modulus $E_{IT} \sim 300$ GPa at 150 nm depth from the surface was observed. Tribological characterization was performed by two single-contact tribometers using coated and uncoated steel balls against flat steel substrates. An in-house fretting wear rig was used to measure the lubricated friction coefficient in pure sliding conditions, whilst the friction performance in rolling/sliding lubricated conditions was evaluated using a WAM test rig. In pure sliding, both steel/steel and TDC/TDC show similar friction coefficients. However, under rolling/sliding conditions with 5% sliding, the traction coefficient of TDC/TDC coating contact was 22% lower than that for steel/steel contact. The tribological results obtained in various contact conditions demonstrate the benefits of applying TDC coatings to reduce bearing friction.

¹ ASED Young Investigator Award Finalist

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Surface Engineering Solutions for Sustainable Development

Moderators: **Jyh-Wei Lee**, Ming Chi University of Technology, **Ivan Petrov**, University of Illinois at Urbana-Champaign

1:30pm **SE-MoA-1 Towards Responsible Surface Engineering Based on PVD Technology**, **Marcus Hans**, J. Schneider, RWTH Aachen University, Germany; **A. Matthews**, The University of Manchester, UK; **C. Mitterer**, Montanuniversität Leoben, Austria

INVITED

The sustainable development goal (SDG) 12 'Responsible Consumption and Production' of the United Nations deals with the necessary change of consumption and production patterns towards a more sustainable future. Plasma-assisted physical vapor deposition (PVD) is increasingly employed to address global challenges, such as energy efficiency and reduction of CO₂ emissions. Two important questions are critically evaluated in this context:

- 1) How sustainable are state-of-the-art PVD processes and materials?
- 2) Which pathways are needed for future responsible surface engineering?

While our modern world and human life benefit from surface engineering, the consideration of energy and mass balances demonstrates that state-of-the-art PVD processes and products are not necessarily sustainable, leaving space for innovation. Responsible surface engineering comprises pathways to enhance the sustainability of processes as well as materials. Impurities will be discussed with respect to tolerable levels and even exploitation of 'impurities', which can be beneficial for the performance of a coating. Moreover, the microstructural design of chemically simple coatings offers opportunities to avoid economically and ecologically expensive elements. Prospective product cycles of emerging technologies and future products will enable the evaluation of ecological, economical as well as societal costs and benefits. Finally, responsible surface engineering involves a change in mindset of materials scientists, process engineers and of all stakeholders involved in garnering innovation.

2:00pm **SE-MoA-3 ASER Rising Star Talk: Unprecedented B Solubility in Cubic (Hf,Ta,Ti,V,Zr)B-C-N Coatings**, **Andreas Kretschmer**¹, TU Wien, Austria; **A. Kirnbauer**, TU Wien, Institute of Materials Science and Technology, Austria; **R. Frost**, D. Primetzhofer, Uppsala University, Sweden; **M. Hans**, J. Schneider, RWTH Aachen University, Germany; **P. Mayrhofer**, TU Wien, Institute of Materials Science and Technology, Austria

In the past, we have studied the system (Hf,Ta,Ti,V,Zr)B-N with exceptional hardness and thermal stability, but the coatings contained a significant amount of C impurities, which may have influenced the properties [1]. To investigate the impact of C in this system, we have deposited new coatings with a TiN target, on which we placed diboride and/or carbide pieces of the metals Hf, Ta, V, and Zr. We have varied the composition by using either only diborides, only carbides, or different mixtures of the two material types to make 5 coatings containing either N and B, N and C, or all three. The B concentration varies between 42 and 0 at%, the C content between 25 and 0 at%, and the N content is stable at around 30 at% in all coatings. The Ti makes up roughly 20 at%, while the other metals are in the range between 2 and 5 at%. X-ray diffraction (XRD) shows a weakly textured single-phase fcc solid solution in all coatings. The FWHM of the 200 reflex ranges from 2 ° in the C-free coating down to 0.5 ° in the B-free coating, indicating different grain sizes. This is confirmed by transmission electron microscopy, revealing fine columnar growth in the 2.3 to 3.2 µm thick coatings, with especially fine grains in the B-richer coatings. Electron diffraction confirms that no secondary phases are present. We annealed the coatings in a vacuum furnace at 1000, 1200, and 1400 °C for 10 min, followed by XRD and nanoindentation. The coatings stay stable up to 1200 °C and start decomposing at 1400 °C. The as-deposited hardness of all coatings lies between 36 and 38 GPa, and is maintained after annealing at 1000 °C. After annealing at 1200 °C, the coatings containing only C or only B both soften to ~34 GPa, while the coatings with both C and B do not lose any hardness at this temperature. Only after annealing at 1400 °C does the hardness of all coatings drop below 30 GPa. We confirmed the thermal stability by atom probe tomography on the most promising sample, hereby we show that despite the high B content of 22 at%, decomposition into a diboride phase initiates only after annealing at 1400 °C. We further investigated the fracture-toughness by in-situ micromechanical cantilever bending. The best performing coating yields 4.0±0.5 MPa·m^{1/2}, thus

surpassing other similar coatings not only in hardness and thermal stability, but also fracture toughness.

[1] Kretschmer, A., et al. (2022). *Materials & Design*, 218, 110695. <https://doi.org/10.1016/j.matdes.2022.110695>

2:15pm **SE-MoA-4 ASER Rising Star Talk: High Temperature Behavior of Ti_{0.12}Al_{0.21}B_{0.67} Coatings Investigated by High-Resolution Transmission Electron Microscopy and DFT Calculations**, **Sebastian Lellig**², RWTH Aachen University, Germany, Switzerland; **A. Navidi Kashani**, RWTH Aachen University, Germany; **P. Schweizer**, Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland; **M. Hans**, **G. Nayak**, RWTH Aachen University, Germany; **J. Michler**, Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland; **J. Schneider**, RWTH Aachen University, Germany

The oxidation behavior of stoichiometric Ti_{0.12}Al_{0.21}B_{0.67} coatings is investigated by high resolution Transmission Electron Microscopy (TEM) after oxidizing for 1, 4 and 8 h at 700 °C and at 800 and 900 °C.

In the as deposited state, a ~ 4 nm thick, native, amorphous oxide layer covers the surface of the coating while the magnitude of incorporated O along the column boundaries decreases with depth. During oxidation, the formation of scale layers consisting predominantly of Al, O and B is observed that appear to be amorphous at 700 °C in which, after oxidation at 900 °C for 8h, nanocrystalline Al₅(BO₃)O₆ regions form. Concurrently, underneath the scale, the formation of Al- and Ti-rich boride regions, consistent with spinodal decomposition, is observed. Chemical environment dependent DFT predictions of the energies required for mass transport on the metal sublattice indicate that Al diffusion is initiated before Ti. Hence, as the temperature is increased, the migration of Al is initiated first, leading to the formation of the oxide scale observed already after oxidation at 700 °C after 1 h. Below the oxidized region, the formation of Al-rich and Ti-rich regions by spinodal decomposition require the concurrent migration of Al and Ti. The fact that decomposition takes place at 900 °C and hence at larger temperatures than the Al diffusion mediate scale formation is consistent with DFT predictions as the averages of the predicted energies required for both, vacancy formation and migration for Ti are larger than for Al.

2:30pm **SE-MoA-5 ASER Rising Star Talk: Friction and Wear of MXene/MoS₂ Nanocomposite Coating Under Dry and Hydrocarbon-Lubricated Conditions**, **Ali Zayaan Macknoja**³, **A. Voevodin**, **S. Aouadi**, University of North Texas; **S. Berkebile**, Army Research Laboratory; **D. Berman**, University of North Texas

Friction and wear-related failures remain the greatest problems in moving mechanical assemblies operating under various conditions. This study demonstrate lubricity achieved by spray-coating solution-processed multilayer Ti₃C₂T_x-MoS₂ blends onto rough 52100-grade steel surfaces. Blends exhibited lower frictional performance for individual pristine materials, MoS₂ and Ti₃C₂T_x, under high pressure, sliding speed. Study investigated the processing, structure, and property correlation to gain a deeper understanding of the underlying phenomena. Raman spectroscopy, scanning electron microscopy, and transmission electron microscopy results revealed the formation of an in-situ robust tribolayer responsible for the outstanding performance observed at high contact pressures and sliding speeds. This study has broad implications for the development of solid lubricants that can operate under extreme conditions and low viscosity fuel environment, inspiring further research and development in this field.

2:45pm **SE-MoA-6 ASER Rising Star Talk: Tunable Tribochemical Behavior of Pt-Au Thin Film Alloys Using High-Throughput Testing**, **Tomas Babuska**⁴, **F. DelRio**, **J. Hall**, **B. Boyce**, **D. Adams**, **J. Custer**, **M. Jain**, Sandia National Laboratories; **J. Killgore**, NIST-Boulder; **F. Mangolini**, **C. Edwards**, University of Texas at Austin; **J. Curry**, Sandia National Laboratories

Binary alloy systems such as Pt-Au have been shown to exhibit ultra-low wear and high hardness enabled by its intrinsically thermally stable nanocrystalline microstructure making them suitable candidates for electrical contact materials. When the unique mechanical properties are combined with the catalytic behavior of platinum under cyclic shearing in inert environments, adventitious carbon can be mechano-chemically transformed into lubricious surface films (µ < 0.05). While ideal for solid lubrication applications, carbon deposits can inhibit electrified interfaces

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and compromise end-use performance. By balancing the catalytic and mechanical properties of Pt-Au thin films, the friction behavior and surface film morphology can be controlled to either promote/prevent lubricious carbon film formation. In this work, we explore 448 compositions of sputter deposited Pt and Au thin films spanning 0-100 at% and the intertwined role of hardness and composition on the resulting friction and wear behavior. We highlight the use of custom high-throughput tribological platforms with robotic automation to rapidly test large material spaces and for the creation of in-depth structure-property relationships that will play a crucial role in the development of next-generation tribological coatings. SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525.

3:00pm SE-MoA-7 ASED Rising Star Talk: Advanced Hipims Nanocrystalline and Metallic-Glass High Z Coatings for Interaction with Liquid Metals, Davide Vavassori¹, L. Bana, M. Bugatti, M. Galli De Magistris, Politecnico di Milano, Italy; M. Iafrazi, Department of Fusion and Technology for Nuclear Safety and Security, ENEA, Italy; D. Dellasega, M. Passoni, Politecnico di Milano, Italy

Liquid metals (LMs) are of interest for the development of several applications related to the energy sector. However, the presence of LMs creates concerns about the compatibility with standard structural materials since, generally, LMs affects their integrity and mechanical properties through different phenomena [1]. Therefore, the mitigation of LM corrosion emerges as a crucial step. This especially applies if the aim is the integration of LMs in a nuclear energy system which, being characterized by high temperatures and strong radiation fields, introduces constraints on the choice of possible structural materials.

The deposition of nanocrystalline or metallic-glass protective coating is an appealing approach to engineer the structural material surface and, consequently, to control the interaction with LMs. In this respect, the fine tailoring of the coating properties at the nanoscale represents a key aspect to optimize its performances in the harsh LM environment. To this end, the use of an advanced Physical Vapor Deposition methods such as High Power Impulse Magnetron Sputtering (HiPIMS) [2] can play a key role to produce films with controlled properties.

In this framework, a notable example is represented by the magnetic confinement fusion research area where innovative divertor designs based on liquid tin (Sn) are under investigation [3,4]. Nevertheless, the action of liquid Sn is detrimental for many structural materials typically used in fusion systems. Specifically, liquid Sn heavily corrodes the heat-sink components which are constituted by CuCrZr alloy to satisfy the thermomechanical and cooling requirements imposed by the fusion power flux.

This work aims at investigating the corrosion resistance of tungsten (W)-based coatings produced by HiPIMS when in contact with liquid Sn. To this end, two different strategies have been studied to grow the metallic coating on CuCrZr substrates. On the one hand, the application of different pulsed substrate bias voltages synchronized with the HiPIMS pulse were considered to produce pure W coatings. On the other hand, the co-sputtering from a W target and an aluminium (Al) target, both working in HiPIMS mode, was examined to realize a multilayer coating. The produced samples were tested in corrosion experiments carried out at 400 °C for relatively short periods of time (150 or 600 minutes). The characterization of the samples before and after the exposure allowed to evaluate how coatings properties determined their effectiveness as protective layer and, thus, to retrieve preliminary information about their ability to withstand the typical operation condition expected in a LM-based divertor.

3:15pm SE-MoA-8 Eliminating Surface Charging in X-Ray Photoelectron Spectroscopy of Insulators for Reliable Bonding Assignments, Grzegorz (Greg) Greczynski, Linköping University, Sweden

Sample charging during X-ray photoelectron spectroscopy (XPS) analyses of electrically insulating samples is a widely recognized challenge of this essential technique. If the electron loss caused by the photoelectric effect is not compensated due to specimens' poor electrical conductivity, the positive charge building up in the surface region results in an uncontrolled shift of detected core level peaks to higher binding energy (BE). This seriously complicates chemical bonding assignment, which is based on measured peak positions, and accounts for a large spread in reported core level BE values. Here, we show that peaks from several industry-relevant oxides, serving as model insulators, typically displaced by several eV due to charging, shift back to positions characteristic of electrically-neutral samples following *ex-situ* capping with a few nm thick metallic layer with

low affinity to oxygen. The effect is present only if the capping layers contain sufficiently large non-oxidized volume that provides long-range conduction paths to grounded Cu clamps, while being thin enough to allow for recording high quality spectra from the underlying insulators. The versatility of the charging elimination is demonstrated for different oxides/cap combinations and air exposure times. The method is robust and easy to apply.

4:00pm SE-MoA-11 Strengthening Mechanisms for High Entropy Alloy Coatings Fabricated by Magnetron Sputtering, Jyh-Wei Lee, Ming Chi University of Technology, Taiwan, Republic of China; B. Lou, Chang Gung University, Taiwan

Prof. Yeh has been developing high entropy alloys (HEAs) for twenty years. The research on bulk HEA materials has attracted much attention due to their unique properties being better than those of traditional alloys. On the other hand, the HEA coatings fabricated by magnetron sputtering methods have been ensured for improving substrate materials' mechanical properties, corrosion resistance, oxidation resistance, and wear resistance. In this work, several strengthening mechanisms, including nitridation, carburization, solid solution hardening, and grain refinement, were adopted to study their effects on the mechanical properties improvements of VNbMoTaW, VNbMoTaWAl, VNbMoTaWCr, TiZrNbTaFe, TiZrNbTaFeB, and ZrTiNbSiFe high entropy alloy coatings grown by magnetron sputtering technique. The chemical compositions, phase structures, microstructures, and surface roughness of these HEA coatings were examined. The nanohardness, reduced elastic modulus, and wear resistance of HEA coatings were measured by nanoindenter and pin-on-disk wear tester, respectively.

We can conclude that good mechanical properties, including higher hardness and lower wear rate, can be obtained for those HEA coatings through the proper selection of strengthening mechanisms and the addition of several constituents, such as nitrogen, carbon, TiB₂, and Cr elements. This work evaluated some strengthening mechanisms and promising results of HEA coatings that can be used as protective coatings in harsh environments.

4:15pm SE-MoA-12 ASED Rising Star Talk: Multifunctional Optical Surfaces for Displays: From Antireflective to Self-Cleaning and Antimicrobial Functionalities, Iliyan Karadzhov², C. Graham, A. Mezzadrelli, ICFO-Institut de Ciències Fòtoniques, Spain; W. Senaratne, K. Koch, P. Mazumder, Corning Research and Development Corporation; V. Pruneri, ICFO-Institut de Ciències Fòtoniques, Spain

Glass is an indispensable part of display technologies, and knowing how to incorporate multiple useful properties into a single optical surface will enhance their performance. For example, nature-inspired designs can deliver high transparency and clarity, broadband and omnidirectional optical response, self-cleaning capabilities, and mechanical resistance. However, fabricating these surfaces with the desired properties can be complex, often requiring multistep lithography methods, which are costly and not easy to scale. In this talk, we discuss our team's recent developments in utilizing thermal dewetting of ultrathin metal films (Cu, Ag, Ni) as a lithography-free method to create durable, nanostructured optical surfaces with tailored multifunctional features.

In the first part, we demonstrate a transparent anti-microbial coating on glass surface based on dewetted copper (Cu) nanoparticles encapsulated by conformal SiO₂ and fluorosilane functional layers. The coatings kill more than 99.9% of *Staphylococcus aureus* within 2 hours due to the released Cu ions and can maintain their anti-microbial properties after wiping tests. The relatively flat transmission of 70-80% in the 380-750 nm range along with color neutrality and non-conductivity make them suitable for high-touch surfaces in medical and public settings where hygiene is important.

The second part focuses on a simplified method to create abrasion-resistant antireflective glass surfaces by creating randomly arranged subwavelength nanoholes. The fabrication process involves three main steps. First, silver nanoparticles are obtained by quickly thermally annealing an ultra-thin silver film on the glass substrate. These particles then serve as a base for a secondary etch mask, created by depositing a thin nickel layer over the silver nanoparticles and performing selective chemical wet etching. Finally, this mask is used in a dry etching process to carve nanoholes of varying depths into the glass surfaces. We achieve a transmission above 99% across a broad wavelength range with minimal scattering, where maximum spectral performance can be tuned to either the visible or near-infrared range by adjusting the lateral arrangement of the silver nanoparticles and

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the depths of the nanoholes. After undergoing an abrasion test of 10,000 passes with cheesecloth under constant load, the nanoholes remain structurally intact due to the redistribution of shearing mechanical forces.

4:30pm SE-MoA-13 Effect of Europium and Gadolinium Alloying Elements on the Tribological Response of Low Hydrogen Content Amorphous Carbon, C. Edwards, H. Lien, N. Molina, **Filippo Mangolini**, The University of Texas at Austin

Dopants and alloying elements are commonly introduced in amorphous carbon (a-C) materials to tailor their mechanical and tribological properties. While most published studies have focused on doping and/or alloying a-C coatings with metals or metalloids, doping a-C films with rare-earth elements has only recently been explored. Notably, our understanding of the shear-induced structural changes occurring in rare-earth element-containing a-C films is still elusive, even in the absence of any liquid lubricants. Here, the friction response of Eu- and Gd-containing a-C films with low hydrogen content deposited by high-power impulse magnetron sputtering (HIPIMS) on silicon was evaluated in open air and at room temperature. The load-dependent friction measurements indicated that the introduction of Gd (2.3 ± 0.1 at.%) and Eu (2.4 ± 0.1 at.%) into the a-C matrix results in a significant reduction of the shear strength of the sliding interfaces (41 ± 2 MPa for a-C, 16 ± 1 MPa for a-C:Gd2.3 at.%, and 11 ± 2 MPa for a-C:Eu2.4 at.%). Near-edge X-ray absorption fine structure (NEXAFS) spectromicroscopy experiments provided evidence that no stress-assisted sp³-to-sp² rehybridization of carbon atoms was induced by the sliding process in the near-surface region of undoped a-C, while the amount of sp²-bonded carbon progressively increased in a-C:Gd2.3 at.% and a-C:Eu2.4 at.% upon increasing the applied normal load in tribological tests. The formation of an sp²-bonded carbon-rich surface layer in a-C:Gd2.3 at.% and a-C:Eu2.4 at.% films was not only proposed to be the origin for the reduced duration of the running-in period in tribological tests, but was also postulated to induce shear localization within the sp²-carbon rich layer and the transfer film formed on the countersurface, thus decreasing the interfacial shear strength. These findings open the path for the use of Gd- and Eu-containing a-C even under critical conditions for nearly hydrogen-free a-C films (i.e., humid air).

4:45pm SE-MoA-14 Importance of the Near-Infrared Optical Properties of Thermal Barrier Coatings, F. Blanchard, M. Bruzzese, B. Baloukas, J. Klemberg-Sapieha, **Ludvik Martinu**, Polytechnique Montreal, Canada

As aircraft engine operating temperatures increase, so must the thermal insulation capabilities of the thermal barrier coatings (TBCs) used to shield metallic components in the combustion chamber and high-temperature turbine areas. Heat transfer from the hot gases to the engine components occurs through two main mechanisms: conduction and radiation. Considerable efforts have been deployed over the years to ensure TBCs have low thermal conductivity, thanks to a porous microstructure generally achieved by thermal spray or EB-PVD techniques. The radiative component of heat transfer, however, has been largely ignored in TBC design. This aspect is however very important due to an exponential increase in radiative heat transfer for higher gas temperature. While TBCs are naturally reflective of radiative heat due to light scattering, this property is very vulnerable to degradation.

Degradation of TBCs over their lifetime is related to microstructural change mainly due to high temperature exposure and CMAS (Calcium-Magnesium-Alumino-Silicate) attack. Basic understanding of the underlying mechanism is an important aspect of the design and development of high performance TBCs. In this work, the effects of high temperature cycling and CMAS infiltration on the optical performance of Ytria-stabilized zirconia (YSZ) coatings prepared by atmospheric plasma spray (APS) were systematically investigated. Optical absorption and scattering coefficients have been extracted from spectrophotometry using integrating sphere measurements in a novel way via the inverse adding-doubling (IAD) method. The microstructure was analyzed using scanning electron microscopy (SEM) and mercury infiltration porosimetry (MIP) in an attempt to establish a relationship between the evolving microstructure and the optical properties. Both were found to have a significant impact on performance, with CMAS infiltration having the biggest effect. To further study the evolution of their performance as the pores are filled, atomic layer deposition (ALD) is used to mimic CMAS infiltration in a controllable fashion. The results show that most of the performance loss occurs with very little material inserted into the pores and that a saturation point is quickly reached. In addition, a finite-difference time-domain (FDTD) model was developed to predict the optical performance of TBCs before and after

degradation with good agreement with experimental data. This model can now be applied to investigate ways to mitigate the degradation processes.

5:00pm SE-MoA-15 Assessing the Feasibility of Laser Ablation Coating Removal (LACR) on Legacy Bridge Steel: Coating Removal and Adhesion, and Effects on Mechanical Properties, W.P. Moffat, University of Virginia; S. Sharp, J. Provinces, Virginia Transportation Research Council; S. Agnew, J. Fitz-Gerald, University of Virginia

The application of protective organic coatings is one of the most effective and commonly used corrosion mitigation strategies. To maintain the protective nature of coatings on long-term-exposed surfaces such as steel bridge components, coatings must be periodically removed and reapplied. A relatively new method called laser ablation coating removal (LACR), which incorporates a high energy nanosecond pulsed laser beam (1 kW, 1064 nm, Nd:YAG) in combination with a high efficiency filtration system, allows for safe and effective removal of coatings and contamination from metal surfaces and provides excellent re-coating adhesion.

LACR cleaning has been applied to legacy bridge steel components to investigate its effect on substrate cleanliness, adhesion, and steel mechanical properties. Legacy bridges were never grit blasted and contain a 20–100 μm thick mill-scale layer (Fe_3O_4 , Fe_2O_3 , FeO) below several coating layers (including lead-rich coatings). The surface oxide layer thermally insulates the underlying steel, preventing melting of the metallic substrate. Characterization of the LACR surfaces with electron microscopy, hardness, tensile, and fatigue testing has shown that LACR does not cause any measurable detrimental effects to the bulk mechanical properties of the bridge steel.

Re-coating LACR surfaces was found to have the same or higher adhesion values in comparison with the state of the art grit blasted surfaces, despite a three-fold decrease in surface roughness. Detailed analysis and adhesion testing of both zinc rich organic and inorganic (OZ and IOZ respectively) coating systems show that LACR cleaning provides excellent adhesion. OZ coatings show exclusively cohesive failures during adhesion testing, whereas IOZ coatings show a mix of both cohesive and adhesive failures.

Advanced Surface Engineering Room Central Hall - Session SE-ThP

Advanced Surface Engineering Poster Session

SE-ThP-1 High-Temperature Oxidation Resistance of Sputtered (Al,Cr,Nb,Ta,Ti,Si)N Coatings, *Andreas Kretschmer*, TU Wien, Austria; *P. Mayrhofer*, TU Wien, Institute of Materials Science and Technology, Austria

High-entropy metal-sublattice (Al,Cr,Nb,Ta,Ti)N coatings, with up to 15.0 at.% additional Si content were developed and investigated for their oxidation resistance by exposing them for 3, 30, and 100 h to ambient air at 900, 950, and 1000 °C, which represents the harshest oxidation experiment for crystalline nitrides reported so far. The Si-free coating is rapidly oxidized, but all of the Si-alloyed coatings survive even the harshest oxidation test. The oxides crystallize mostly in the rutile structure with some Ta₂O₅-type phase fractions at higher Si contents. Detailed TEM investigations reveal a varied microstructure across the oxide scales with a succession of Cr-, Al, and Ti-rich top oxide layers, which agrees with a reported thermodynamical calculation of oxide stabilities.

SE-ThP-2 ASED Rising Star Talk: The Influence of Deposition Parameters on the Structure and Properties of TiZrNbTaMo High Entropy Alloy Films Fabricated by High Power Impulse Magnetron Sputtering, *Chia-Lin Li¹*, Center for Plasma and Thin Film Technologies, Ming Chi University of Technology; *S. Hou*, Department of Materials Science and Engineering, National Tsing Hua University; *B. Lou*, Chemistry Division, Center for General Education, Chang Gung University; *J. Lee*, Department of Materials Engineering, Ming Chi University of Technology; *P. Chen*, Department of Materials Science and Engineering, National Tsing Hua University, Taiwan

TiZrNbTaMo high-entropy alloys (HEAs) with a body-centered cubic (BCC) structure are known for their excellent compressive yield strength and significant compressive plasticity. These advantageous properties are retained even in their thin film forms, making them highly promising for a variety of applications. In this study, we prepared TiZrNbTaMo high entropy alloy films (HEAFs) grown by high power impulse magnetron sputtering and investigated the influence of deposition parameters on their structure and properties. It is well known that several deposition parameters affect the density and microstructure of thin films, influencing the hardness, wear resistance, toughness, and corrosion resistance. The cross-sectional morphology and crystal structure of TiZrNbTaMo HEAFs were characterized using field emission scanning electron microscope (FE-SEM) and X-ray diffractometry (XRD), respectively. Mechanical properties of the HEAFs, including hardness, elastic modulus, adhesion, and wear resistance, were evaluated by nanoindentation, scratch tester, and pin-on-disk wear tester. This study systematically investigated the effects of critical processing parameters, including pulse frequency, duty cycle, substrate bias, and working pressure for TiZrNbTaMo HEAFs for achieving outstanding properties.

SE-ThP-5 Magnetron Sputtering Deposition of Metallic-Based Nanostructured Coatings for Nuclear Energy Applications, *Maria Sole Galli De Magistris*, *D. Vavassori*, *V. Russo*, *D. Dellasega*, Politecnico di Milano, Italy; *M. Gentile*, *F. Garcia Ferré*, newcleo Srl, Italy; *M. Passoni*, Politecnico di Milano, Italy

Lead-cooled Fast Reactors (LFRs) are considered among the most promising Generation IV nuclear reactors owing to their inherent safety and high power density [1]. Nevertheless, conventional structural and cladding materials suffer from severe corrosion issues when in contact with liquid lead [2]. Surface coating technology is a valuable technique to improve materials performance in harsh environments without modifying the properties of the bulk [3]. Nonetheless, coatings must also withstand the high temperature and radiation fields characterizing LFRs. Therefore, realizing coatings with improved adhesion and precisely controlled properties is of fundamental importance. In this respect, in recent years, metallic coatings have gained increasing interest thanks to their enhanced compatibility with steel substrates and the possibility of triggering a self-passivation mechanism when strong oxide formers, such as Al and Cr, are present in the optimal amount. Physical Vapor Deposition techniques, particularly Magnetron Sputtering (MS) [4], have proven their effectiveness in realizing films with controlled and tunable properties. Magnetron Sputtering includes different deposition regimes: Direct Current (DCMS), Radio-Frequency (RFMS), and High Power Impulse Magnetron Sputtering

(HiPIMS). Compared to DCMS and RFMS, the HiPIMS process generates a higher fraction of ionized species, with energies further adjustable through substrate biasing or Bipolar HiPIMS. Additionally, according to the working regime, a plethora of process parameters can be adjusted, including sputtering power, duty cycle, pulse width, and bias voltage amplitude, enabling film optimization for the specific application.

This contribution reports the development and characterization of advanced nanostructured mono and multi-elemental metallic coatings produced via magnetron sputtering. In particular, the attention is focused on two types of coatings. The first set consists in steel films, enriched in other elements such as aluminum and tungsten to improve the oxidation and the high-temperature behavior. The other set consists of chromium films; widely investigated for claddings in light water reactors, they might be of interest for LFRs owing to their excellent oxidation behavior. Different deposition conditions were exploited and relevant working parameters were adjusted to tune coatings properties. Morphological and crystallographic studies were performed, together with preliminary tests in LFR relevant conditions. The obtained results provide an insight into the interconnection between process parameters and coatings properties and behavior.

SE-ThP-6 UV-Vis-NIR Optical Analysis to Understand the Electrical Properties of Nitrogen-Incorporated Tetrahedral Amorphous Carbon Thin Films, *Nina Baule*, Fraunhofer USA Center Midwest; *D. Tsu*, The Mackinac Technology Company; *L. Haubold*, Fraunhofer USA Center Midwest; *T. Schuelke*, Fraunhofer USA

Tetrahedral amorphous carbon (ta-C) thin films have received significant attention due to their diamond-like mechanical properties, achieved via low-temperature synthesis. More recently, the electrochemical behavior of nitrogen-incorporated ta-C:N has attracted interest, as it exhibits electrical conductivity as well as chemical inertness. The modified electrical properties of ta-C:N have been mainly attributed to the conjugation of sp² carbon-carbon and/or carbon-nitrogen bonds. Commonly, with an increase in nitrogen incorporation into the growing film, the electrical resistivity decreases proportionally. Here, however, we find that the electrical properties plateau at higher nitrogen content for ta-C:N thin films (100 nm) deposited by laser controlled pulsed cathodic vacuum arc (Laser-Arc), despite the fact that mechanical and structural properties indicate an increase in sp² fraction. Hence, to gain a better understanding of the electronic properties, the dielectric constants [ϵ_1] and [ϵ_2] were obtained from the optical constants, the refractive index [n] and extinction coefficient [k], which were numerically determined from reflectance [R] and transmittance [T] measurements in the wavelength range from 190 to 2500 nm (0.5 to 6.5 eV). The dielectric constant [ϵ_1] was used to calculate the dielectric volume of the atom, which is interpreted as a measure of the conjugated electron system. Furthermore, modeling of the dielectric constants yielded the number of conjugated electrons per atom. The ta-C:N samples with the highest values of electrical conductivity, were either characterized by the largest occupied volume or the highest number of conjugated electrons. Through the dielectric volume and number of conjugated electrons, it was discovered that the electrical conductivity does not only depend on the sp² content and cluster size, but on how many electrons are conjugated and how much space these electrons occupy.

SE-ThP-7 A Critical Issue in Coatings Nanoindentation: Validity of the 10% Bückle's Rule of Thumb, *Esteban Broitman*, SKF Research and Technology Development, Netherlands

When an indenter penetrates the surface of a film deposited onto a substrate, the mechanical response of the coating will be influenced by the mechanical properties of the substrate, according to its penetration depth *h* and the film thickness *t*. As the depth of penetration *h* increases, more of the mechanical contribution will come from the substrate.

The first who tried to separate the contribution of the substrate from the total measured hardness at the microscale was Bückle, who suggested a 10% rule of thumb: to indent no more than 1/10 of the film thickness to avoid the influence from the substrate. The rule has been adopted later by many researchers for nanoindentation experiments and extended also as valid for the elastic modulus. However, there are many experimental studies and numerical simulations showing that this rule is too strict for a hard coating on a very soft substrate and too loose for a soft coating on a hard substrate [1].

In this presentation, we will review the issue, and will discuss all factors that affect the maximum penetration depth for independent coating measurements. We will also present a simple experimental methodology

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that, in most of cases, gives the correct values for hardness and elastic modulus, independently of the coating/substrate system.

[1] E. Broitman, Indentation Hardness Measurements at Macro-, Micro-, and Nanoscale: A Critical Overview. *Tribol Lett* **65**, 23 (2017)

SE-ThP-8 Optimizing Laser Surface Melting Parameters to Enhance Corrosion Resistance of AA5083 Aluminum Alloy, *Md Sojib Hossain*, University of Virginia, USA, Bangladesh; *W. P. Moffat*, University of Virginia, USA; *J. Skelton*, University of Virginia, USA, United States Virgin Islands; *J. Fitz-Gerald*, University of Virginia, USA

AA5083 is a solution-strengthened Al-Mg alloy widely used in marine environments and other harsh, corrosive settings due to its excellent corrosion resistance. However, this alloy is susceptible to a deleterious process known as sensitization, where Mg-rich intermetallic particles, primarily the β -phase, precipitate at grain boundaries under prolonged exposure to moderately elevated temperatures. This anodic β -phase forms a galvanic couple with the cathodic aluminum matrix, leading to intergranular corrosion (IGC). Although several heat treatment processes have been developed to dissolve the β -phase within the matrix, these methods are not feasible for service components, and processed samples can easily be re-sensitized. Laser surface melting (LSM) offers a promising solution to this issue. In this study, a nano-second pulsed laser with varying power was used to investigate LSM's effects on minimizing intergranular corrosion. A low-power excimer laser with 50% overlap was applied to a 1200-grit polished surface, while a high-power ADAPT laser was used on as-received samples with different overlaps. Electrochemical polarization scans of the base and LSM samples in a 0.6 ml NaCl solution showed notable improvements in corrosion properties for all laser-processed samples, as evidenced by low open circuit potential and nearly a two-order-of-magnitude decrease in exchange current density. Backscattered scanning electron micrographs and energy dispersive spectroscopy (EDS) scans confirmed that the improved corrosion resistance was due to a homogenized LSM surface, ranging from only 3 to 7 μm in depth. Electron backscattered diffraction (EBSD) analysis of the excimer LSM samples' cross-sections identified very small sub-grains with different grain boundary characteristics compared to the sensitized base metal. These sub-grains are highly inert to re-sensitization, and create significant interruptions to intergranular corrosion, thereby enhancing IGC resistance.

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Kirnbauer, Alexander: SE-MoA-3, 4
Klemborg-Sapieha, Jolanta: SE-MoA-14, 6
Koch, Karl W.: SE-MoA-12, 5
Kodambaka, Suneel: SE-MoM-3, 1
Koutna, Nikola: SE-MoM-11, 2
Kretschmer, Andreas: SE-MoA-3, 4; SE-ThP-1, 7
— L —
Lee, Jyh-Wei: SE-MoA-11, 5; SE-MoM-4, 1; SE-ThP-2, 7
Lellig, Sebastian: SE-MoA-4, 4
Li, Chia-Lin: SE-ThP-2, 7
Lien, Hsu-Ming: SE-MoA-13, 6
Lin, Shuyao: SE-MoM-11, 2
Lou, Bih-Show: SE-MoA-11, 5; SE-ThP-2, 7
Lou, Lihua: SE-MoM-13, 3
— M —
Macknojia, Ali Zayaan: SE-MoA-5, 4
Mangolini, Filippo: SE-MoA-13, 6; SE-MoA-6, 4
Martinu, Ludvik: SE-MoA-14, 6
Matthews, Allan: SE-MoA-1, 4
Mayrhofer, Paul: SE-MoA-3, 4; SE-MoM-11, 2; SE-ThP-1, 7
Mazumder, Prantik: SE-MoA-12, 5
Meeuwenoord, Ralph: SE-MoM-14, 3
Mezzadrelli, Alessia: SE-MoA-12, 5
Michler, Johann: SE-MoA-4, 4

Mitterer, Christian: SE-MoA-1, 4
Moffat, W.P.: SE-MoA-15, 6
Mol, Arjan: SE-MoM-14, 3
Molina, Nicolás: SE-MoA-13, 6
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Navidi Kashani, Amir Hossein: SE-MoA-4, 4
Nayak, Ganesh: SE-MoA-4, 4
— P —
P. Moffat, William: SE-ThP-8, 8
Passoni, Matteo: SE-MoA-7, 5; SE-ThP-5, 7
Petrov, Ivan: SE-MoM-10, 2
Primetzhofer, Daniel: SE-MoA-3, 4
Provines, J.: SE-MoA-15, 6
Pruner, Valerio: SE-MoA-12, 5
Pulugurtha, Markondayaraj: SE-MoM-13, 3
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Rahimi, Ehsam: SE-MoM-14, 3
Rodil Posada, Sandra Elizabeth: SE-MoM-12, 2
Rodil, Sandra Elizabeth: SE-MoM-8, 2
Rosen, Johanna: SE-MoM-1, 1
Russo, Valeria: SE-ThP-5, 7
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Sangiovanni, Davide: SE-MoM-11, 2
Schneider, Jochen: SE-MoA-1, 4; SE-MoA-3, 4
Schneider, Jochen M.: SE-MoA-4, 4
Schuelke, Thomas: SE-ThP-6, 7
Schweizer, Peter: SE-MoA-4, 4
Senaratne, Wageesha: SE-MoA-12, 5
Sharp, S.: SE-MoA-15, 6
Skelton, Jonathan: SE-ThP-8, 8
— T —
Tanaka, Koichi: SE-MoM-3, 1
Tsu, David V.: SE-ThP-6, 7
— U —
Uddi, Mruthunjaya: SE-MoM-5, 1
Urdaneta, Gerardo: SE-MoM-5, 1
— V —
Valencia García, Karen: SE-MoM-12, 2
Vavassori, Davide: SE-MoA-7, 5; SE-ThP-5, 7
Voevodin, Andrey: SE-MoA-5, 4
Volakis, John: SE-MoM-13, 3
— W —
Wu, Fan-Bear: SE-MoM-4, 1