Advanced Surface Engineering
Room 125 - Session SE-MoA

Surface Engineering Solutions for Sustainable Development

Moderators: Ivan Petrov, University of Illinois at Urbana-Champaign, **Fan-Bean Wu**, National United University, Taiwan

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 CO_2 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 ASED 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 ASED 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 $Al_5(BO_3)O_6$ 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 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 Surface Engineering for New Highly Graphitized Carbon with High Pyrrolic-N as a Robust Support for Pt Electrocatalysts**, *H. Lee, D. Lee,* ***Jong-Sung Yu***, DGIST, Republic of Korea

For polymer electrolyte membrane fuel cells (PEMFCs), the state-of-the-art electrocatalysts are based on carbon-supported Pt group metals. However, current carbon supports suffer from carbon corrosion during repeated start-stop operations, causing performance degradation. We report a new strategy to produce highly graphitized carbon with controllable N-doping that uses extremely low-temperature synthesis (650 ℃) from g-C_3N_4 carbon-nitrogen precursor with novel surface engineering pyrolysis using Mg. The high graphiticity is confirmed by high-intensity 2D Raman peak with low I_D/I_G (0.57), pronounced graphitic XRD planes, and excellent conductivity. Without further post-treatment, this robust highly graphitized N-doped carbon (HGNC) material combines high pyrrolic-N content with high porosity.

Supporting Pt on HGNC exhibits excellent oxygen reduction activity for PEMFC with greatly improved durability as proved by real-time loss measurements of Pt and carbon, the first to surpass the DOE 2025 durability targets for both catalyst and support. The Pt/HGNC prepared at 650 ºC shows 32 and 24% drops in mass activity after accelerated durability tests of both electrocatalyst and support, respectively, which are less than DOE target of 40% loss. These values represent extremely small drop compared to those of commercial Pt/C, underscoring the merits of the novel low-temperature surface engineering pyrolysis with Mg. The atomistic basis for this durability is explained via quantum mechanics-based molecular dynamics simulations. Interestingly, it is found that pyrrolic-N strongly interacts with Pt, making the Pt catalyst more stable during fuel cell reaction. We expect that high porosity robust graphitized materials will lead to many other novel applications for electrocatalysis with durable carbon frameworks.

[1] **Rising Star**

[2] **Rising Star**

2:45pm **SE-MoA-6 ASED Rising Star Talk: Tunable Tribochemical Behavior of Pt-Au Thin Film Alloys Using High-Throughput Testing**, ***Tomas Babuska***[1], *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 ($\mu < 0.05$). While ideal for solid lubrication applications, carbon deposits can inhibit electrified interfaces 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 Vavassori***[2], *L. Bana, M. Bugatti, M. Galli De Magistris,* Politecnico di Milano, Italy*; M. Iafrati,* 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 of 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 in detrimental for many structural materials typically used in fusion systems. Specifically, liquid Sn heavily corrodes the heath-sink components which are constituted by CuCrZr alloy to satisfy the thermomechanical and cooling requirements imposed by the fusion power flux.

This works 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***, Linkoping 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.

3:30pm **SE-MoA-9 ASED Rising Star Talk: Friction and Wear of MXene/MoS2 Nanocomposite Coating Under Dry and Hydrocarbon-Lubricated Conditions**, ***Ali Zayaan Macknojia***[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 Ti3C2Tx-MoS2 blends onto rough 52100-grade steel surfaces. Blends exhibited lower frictional performance for individual pristine materials, MoS_2 and $Ti_3C_2T_x$, 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.

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, TiB_2, 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.

[1] **Rising Star**

[2] **Rising Star**

[3] **Rising Star**

4:15pm **SE-MoA-12 ASED Rising Star Talk: Multifunctional Optical Surfaces for Displays: From Antireflective to Self-Cleaning and Antimicrobial Functionalities**, ***Iliyan Karadzhov***[1], *C. Graham, A. Mezzadrelli,* ICFO-Institut de Ciencies Fotoniques, Spain*; W. Senaratne, K. Koch, P. Mazumder,* Corning Research and Development Corporation*; V. Pruneri,* ICFO-Institut de Ciencies Fotoniques, 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 SiO_2 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 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).

[1] **Rising Star**

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