Protective and High-temperature Coatings
Room Town & Country A - Session MA2-1-TuA

Hard and Nanostructured Coatings I

Moderators: Stanislav Haviar, University of West Bohemia, Czechia, **Kuan-Che Lan**, National Tsing Hua University, Taiwan , **Norma Salvadores Farran**, TU Wien, Austria

1:40pm **MA2-1-TuA-1 The Fabrication, Microstructure, and Characterization of Functional Electroless Ni-P Composite Surface Coatings on Dried Luffa as Bio-Plate***, Tzu-Hsiu Hung* ***[andybenny2012@gmail.com]****, Kai-Tse Tsai, Fan-Bean Wu,* National United University, Taiwan

This study employed luffa sponge as a natural substrate for the electroless deposition of nickel-phosphorus, Ni-P, alloy to enhance its structural performance. The phosphorus contented the Ni-P coating was controlled by adding sulfuric acid to adjusting the pH value of the plating bath, allowing analysis of compositional and property variations. The luffa sponge was first sensitized and activated using $SnCl_2$ and $PdCl_2$, followed by deposition in a solution containing $NiSO_4$, NaH_2PO_2, and $Na_2C_4H_4O_4$, with sulfuric acid used to adjust pH. Sodium hypophosphite acted as the reducing agent, promoting the co-deposition of Ni and P. Since the electroless plating rate was approximately 0.1–0.3 μm/min, electroplating was subsequently applied to increase film thickness and investigate its microstructure and mechanical behavior. This technique demonstrates a promising route for the functional surface modification of natural porous materials, enabling the fabrication of lightweight, high-strength composites with potential applications in electronic, structural, and environmental fields.

2:00pm **MA2-1-TuA-2 Erosion-Corrosion Analysis of Cr2N/Ni3N Multi-Layer Coating System Deposited on Nickel Aluminium Bronze (Nab) Using the Dc Magnetron Sputtering***, Aakanksha Jain* ***[aakanksha_j@me.iitr.ac.in]****, Ramesh Chandra, Rahul S Mulik,* Indian Institute of Technology Roorkee, India

Nickel–aluminium bronze (NAB) alloys are extensively used in marine environments owing to their strength and corrosion resistance, yet they remain highly susceptible to erosion–corrosion during long-term service. In this work, multilayer Cr_2N/Ni_3N coatings were deposited on NAB substrates using DC magnetron sputtering to address these limitations. The multilayer design combines the chemical stability of Cr_2N with the mechanical robustness of Ni_3N, thereby enhancing hardness, corrosion protection, and erosion resistance, while also modifying surface wettability. Microstructural and chemical characterisation was performed using FE-SEM, EDX, XRD, XPS, AFM, and TEM. Mechanical and functional properties were evaluated through nanoindentation, contact angle measurements, electrochemical corrosion tests, and solid particle erosion studies. The multilayer coating exhibited a hardness of 26.29 GPa and a hydrophobic contact angle of ~134.7°. Electrochemical testing confirmed a drastic reduction in corrosion rate, from 0.184 mm/y for bare NAB to 0.117×10^{-3} mm/y for the coated sample. Erosion resistance was also significantly improved, with material loss reduced to 4.59 mm^3/kg. These results demonstrate the synergistic benefits of Cr_2N/Ni_3N multilayers in enhancing the durability of NAB alloys, highlighting their potential application in marine turbine blades and related components.

2:20pm **MA2-1-TuA-3 Characteristics of TiBCN-based Thin Film with Different Mo Content by Direct Current Plasma Chemical Vapor Deposition***, Takeyasu Saito* ***[t21165j@omu.ac.jp]****, Rizu Kurogi, Noki Okamoto,* Osaka Metropolitan University, Japan

Recently, the concept of high-entropy alloys (HEAs) has been extended from metallic systems to ceramic compounds such as nitrides, carbides, and borides, offering a promising strategy to develop next-generation protective thin films with superior hardness, thermal stability, and oxidation resistance. Ti-based thin film such as TiN, TiC, and TiCN was widely used as conventional protective thin films. Further improvements in hardness and oxidation resistance were carried out by incorporating elements such as B, to from TiBCN thin films composed of Ti(C,N) nanocrystals in an amorphous TiBCN matrix. Incorporating refractory metals such as Mo into Ti-based systems is also expected to enhance solid-solution strengthening and oxidation resistance due to their high melting points and in oxide formation resistance. However, the effects of Mo addition in multi-component hard thin films remain unclear. Most previous studies employed physical vapor deposition (PVD) methods such as magnetron sputtering or arc evaporation, while plasma enhanced chemical vapor deposition (CVD) provides potential advantage on higher conformality, stronger interfacial adhesion strength and low temperature fabrication for complex-shaped tools and components fabrication. The objective of this study is to investigate the role of Mo addition in TiBCN thin film containing Ti(C,N) nanocrystals and amorphous TiBCN, as well as the role of Mo addition on solid-solution hardening and oxidation resistance.

TiBCN thin films with different Mo contents were deposited on Si and cemented carbide (WC–Co) substrates using direct current (DC) plasma CVD at around 600℃ where WC–Co substrates were pretreated with aqua regia to improve interfacial adhesion. The precursor gases were $TiCl_4$, CH_4, N_2, BBr_3, and $MoCl_5$. It was confirmed that, B content in TiBCN films increased with increasing BBr_3 flow rate. The effects of Mo incorporation on phase formation, microstructure, and mechanical properties were systematically evaluated using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and nanoindentation. The results from the TiBCN film with Mo will be discussed in order to demonstrate the HEA design concept thin film by DC plasma CVD, which provides a promising method for low temperature next generation hard thin film procedures to enhance mechanical and chemical durability.

2:40pm **MA2-1-TuA-4 CrAlN-based Protective Nanostructured Coatings: Process–Structure–Property Correlations and Performance in Energy-Related Applications***, Juan Carlos Sanchez-Lopez* ***[jcslopez@icmse.csic.es]****, Teresa Cristina Rojas,* Institute of Materials Science of Seville (ICMS), Spanish National Research Council (CSIC), Spain*; Ramón Escobar-Galindo,* Universidad de Sevilla (US), Spain*; Santiago Dominguez-Meister, Marta Brizuela,* TECNALIA, Basque Research and Technology Alliance (BRTA), Spain*; Sonia Mato, Francisco Javier Pérez,* Universidad Complutense de Madrid (UCM), Spain **INVITED**

Chromium aluminum nitride (CrAlN)-based coatings represent a model system for understanding and engineering protective nanostructured materials operating under extreme environments. Over the past decade, our research has focused on correlating deposition parameters, microstructure, and functional performance of magnetron-sputtered CrAlN coatings. Particular attention has been paid to the influence of multiple factors, such as film architecture (single- or multilayered), aluminum and dopant concentrations and distributions (Y, Zr, Si, and O), the nature of the substrate, and the type of surrounding atmosphere (air or steam), on oxidation mechanisms, thermal stability, and functional behavior at high temperatures. These studies reveal how nanoscale architecture and compositional design govern mechanical integrity and resistance to degradation at high temperature. Complementary investigations have addressed tribological behavior and oxidation resistance in steam atmospheres, representative of demanding industrial and energy-generation conditions.

Building on this knowledge, recent developments have extended CrAlN-based coatings toward advanced energy technologies, including concentrated solar power systems, where coatings must combine optical functionality with long-term durability above 550 °C. This invited talk will review the evolution of CrAlN-based protective coatings from model hard systems to multifunctional materials for energy-related applications, emphasizing the process–structure–property relationships and degradation mechanisms that underpin their outstanding performance in harsh and sustainable operating environments.

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[5] Synthesis and Characterization of Multilayered CrAlN/Al_2O_3 Tandem Coating Using HiPIMS for Solar Selective Applications at High Temperature, *ACS Appl. Ene. Mater.* 7 (2024) 438-449 [tel:7 (2024) 438-449] .

4:00pm **MA2-1-TuA-8 Enhancement of Thermal Stability of Sputtered Nanotwinned Ag Thin Films by Cu Doping for Reliable Electronic Applications**, ***Jun-Hui Qiu [junhui-qiu@gapp.nthu.edu.tw]***, Department of Engineering and System Science, National Tsing Hua University, Taiwan; *Yu-Lin Liao,* College of Semiconductor Research, National Tsing Hua University, Taiwan; *Fan-Yi Ouyang,* Department of Engineering and System Science, National Tsing Hua University, Taiwan

The rapid expansion of artificial intelligence, data centers, and electric vehicles has intensified the demand for reliable interconnect materials capable of withstanding high-temperature and high-current operating conditions. Silver (Ag) is a promising candidate for electronic applications due to its exceptional electrical conductivity; however, its poor thermal stability often leads to reliability concerns. To address this issue, this study investigates the effect of copper (Cu) doping on the thermal stability of sputtered nanotwinned Ag thin films.

Nanotwinned Ag and co-sputtered 6 at% Cu-doped Ag thin films were fabricated via magnetron sputtering and subsequently annealed at 200 °C, 300 °C, 400 °C, and 500 °C under a vacuum of 5.5 mTorr. In pure Ag films, the nanotwinned structure remained stable up to 400 °C for 1 hour but progressively transformed into large grains with increasing annealing time. After 48 hours at 400 °C, nanotwins disappeared completely due to abnormal grain growth, resulting in a (200)-oriented microstructure. In contrast, the 6 at% Cu-doped Ag films exhibited significantly slower grain coarsening and superior structural stability even after prolonged annealing. At 400 °C, nanotwins were still observed after both 1 hour and 24 hours of annealing. Cu doping also suppressed the orientation transition from (111) to (200), indicating enhanced thermal stability. Furthermore, Cu addition increased hardness from 1.29 GPa to 3.33 GPa through solid-solution strengthening, while causing only a slight rise in electrical resistivity from 2.03 μΩ·cm to 2.90 μΩ·cm. These findings demonstrate that Cu doping effectively improves the thermal and mechanical stability of nanotwinned Ag thin films, providing a promising pathway toward reliable metallic interconnects for next-generation electronic devices.

4:20pm **MA2-1-TuA-9 Backscattered Argon Neutrals: Hidden Architects of Hf–Al–N Nanostructure Evolution**, ***Naureen Ghafoor [naureen.ghafoor@liu.se]***, *Marcus Lorentzon,* Linköping Univ., IFM, Thin Film Physics Div., Sweden; *Rainer Hahn,* TU Wien, Austria; *Diederik Depla,* Ghent University, Belgium; *Justinas Palisaitis, Jens Birch,* Linköping Univ., IFM, Thin Film Physics Div., Sweden

Transition metal aluminum nitrides (TM–Al–N) are multifunctional ceramics whose nanostructure can be tailored for extreme mechanical performance. However, the Hf–Al–N system remains largely unexplored. Here, we demonstrate that energetic backscattered argon neutrals, inherently produced during magnetron sputtering of heavy targets, dominate the structure formation in $Hf_{1-x}Al_xN_Y$ thin films—surpassing the influence of both ion assistance and substrate temperature.

Single-crystal cubic (c) $Hf_{1-x}Al_xN_Y$ films with x < 0.30 deposited on MgO(001) exhibit a unique three-dimensional checkerboard superstructure composed of HfN- and AlN-rich nanodomains aligned along the <001> directions. This periodic modulation, detected via XRD satellites and high-resolution STEM, originates from sub-surface spinodal decomposition triggered by backscattered Ar neutrals with energies exceeding the displacement threshold (~40–50 eV). SDTrimSP and SIMTRA simulations reveal that ~40 % of the neutrals impinging on the film surface possess sufficient energy to induce bulk atomic displacements, leading to compositional modulations even at low growth temperatures (300 °C). In contrast, varying ion flux (up to 15 ions per atom at 20 eV) or substrate temperature (300–900 °C) produced negligible structural changes, underscoring the primary role of energetic neutrals.

The superstructure period increases linearly with Al content (9–13 Å), correlating with hardness enhancements from 26 GPa for HfN_Y to ~38 GPa for c-$Hf_{1-x}Al_xN_Y$ due to dislocation pinning by strain fields. For Al-rich compositions (x > 0.41), a nanocrystalline wurtzite phase with 0001 texture forms, yielding ~22 GPa hardness. Micropillar compression of c-$Hf_{0.93}Al_{0.07}N_{1.15}$ confirmed brittle fracture along {110}<011> slip systems, reflecting superstructure-induced dislocation confinement.

These findings reveal a previously unrecognized mechanism of film nanostructuring in heavy-element sputtering: backscattered neutral atoms act as energetic sculptors, promoting coherent superstructure formation and enhanced mechanical performance. This insight extends beyond Hf–Al–N, providing a general framework for controlling nanostructure evolution in metastable nitrides through energetic neutral engineering.

4:40pm **MA2-1-TuA-10 From Grain Refinement to Precipitation Hardening: Si-Driven Microstructural Control in (Al,Mo,Ta,v,W)C Coatings**, *M.A. Altaf, Balint Hajas,* TU Wien, Austria; *Szilard Kolozsvári,* Plansee Composite Materials GmbH, Germany; *Tomasz Wojcik, Alexander Kirnbauer,* ***Paul Mayrhofer [paul.mayrhofer@tuwien.ac.at]***, TU Wien, Austria

High-entropy carbides (HECs) are emerging as promising candidates for extreme-environment applications due to their exceptional hardness and thermal resistance. This work investigates the influence of Si incorporation (0, 1, and 7 at%) on the microstructure, mechanical properties, and thermal stability of reactively sputtered $(Al,Mo,Ta,V,W)C_y$ coatings. X-ray diffraction and transmission electron microscopy (TEM) confirm single-phase face-centered cubic structures for all compositions. Increasing Si content strongly refines the columnar grain morphology—from ~500 nm in the Si-free coating to ~20 nm in the 7 at% Si variant—and induces a pronounced (200) texture.

Upon annealing at elevated temperature, Si segregates to column boundaries and forms coherent nanoscale SiC precipitates, as evidenced by HAADF-STEM and EDS mapping. These precipitates act as effective barriers to boundary motion and dislocation activity, stabilizing the microstructure against coarsening. Mechanical testing shows very high as-deposited hardness values of 41 GPa (Si-free), 39 GPa (1 at% Si), and 41 GPa (7 at% Si). After annealing, all coatings retain excellent mechanical performance, with the Si-rich variants exhibiting minimal hardness reduction.

These results demonstrate that controlled Si addition enables precipitation-driven microstructural stabilization in HECs through strong carbide-forming enthalpies and multi-element chemical/size mismatch—rather than configurational-entropy effects. This mechanism provides a robust pathway for designing thermally stable, ultrahard ceramic coatings for demanding applications such as aerospace, energy, and high-temperature manufacturing environments.

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