Protective and High-temperature Coatings
Room Town & Country A - Session MA2-2-WeM

Hard and Nanostructured Coatings II

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

8:00am **MA2-2-WeM-1 Dual-Phase Crystalline-Amorphous Coatings Based on Thin-Film Metallic Glasses: Synthesis and Properties***, Petr Zeman* ***[zemanp@kfy.zcu.cz]***, University of West Bohemia, Czechia **INVITED**

Magnetron sputter deposition has been demonstrated to be a suitable technique for synthesizing metallic glasses as thin films (TFMGs). Thanks to the non-equilibrium conditions of low-temperature plasma and extremely high cooling rates at the atomic scale on the substrate, TFMGs can be prepared with a much wider composition variety and solubility than bulk metallic glasses (BMGs). Moreover, TFMGs exhibit properties and characteristics that surpass those of BMGs as well as conventional metallic and ceramic coatings, particularly in achieving an optimized balance between ductility and strength.

The amorphous structure of TFMGs, characterized by short- and medium-range atomic ordering, combined with their exceptional properties, offers opportunities to create dual-phase architectures incorporating both TFMGs and crystalline materials. These architectures have the potential to overcome the limitations inherent to each constituent phase while enhancing existing properties or even enabling novel functionalities through synergistic phase interactions.

Dual-phase crystalline-amorphous coatings based on TFMGs can be relatively easily prepared in multilayer architectures comprising alternating crystalline and TFMG sublayers. We demonstrated this concept with multilayer Zr-Cu-N coatings consisting of hard ceramic ZrN and ductile glassy ZrCu sublayers. The coatings exhibited enhanced damage tolerance due to effective crack deflection at sublayer interfaces, yielding superior fracture stress and toughness values. Incorporating ZrN-Cu nanocomposite surface sublayers further imparted antibacterial functionality, expanding their potential applications.

The formation of dual-phase crystalline-amorphous coatings based on TFMGs in a nanocomposite architecture presents significant challenges. However, we successfully synthesized such coatings in the Zr-Cu-N and Zr-Cu-B systems using a one-step process of reactive and non-reactive magnetron co-sputtering, respectively. The coatings prepared under optimized conditions were nanocomposites comprising nanocrystalline ZrN or ZrB_2 and glassy ZrCu phases, representing a novel class of nanocomposite coatings combining ceramic and TFMG phases.

The talk will detail the compositional design, synthesis, microstructural evolution, and structure-property relationships of these coatings. Results from ab initio simulations that complement the experimental findings will also be presented, and key differences between the two coating systems will be discussed. It will be shown that these coatings offer promising potential for applications requiring a balance of hardness, toughness, and durability.

8:40am **MA2-2-WeM-3 Multi-Scale Investigation of Superior Mechanical Properties in Nitride Ceramics with Negative Stacking Fault Energy***, Yong Huang* ***[yong.huang@oeaw.ac.at]***, *Zhuo Chen, Zaoli Zhang,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria

Introduction: Ceramics are widely used in various structural and functional applications; however, their intrinsic brittleness at room temperature remains a critical challenge, often leading to early-stage catastrophic failures. This brittleness arises primarily due to the high critical-resolved shear stress required to initiate dislocation movement and the limited number of operational slip systems. Addressing this limitation is crucial for the development of ceramics with improved mechanical properties.This study aims to develop a novel strategy for enhancing the deformability of ceramics by leveraging negative stacking fault energy (SFE). The approach seeks to reduce the energetic barriers to dislocation motion and expand the number of available slip systems, ultimately improving room-temperature plasticity while maintaining high strength and toughness. In this work,a TiN/TaN superlattice was fabricated and subjected to in-situ micro-mechanical testing to evaluate its mechanical response. Post-mortem transmission electron microscopy (TEM) was employed to analyze deformation mechanisms at the atomic scale, providing insights into the role of negative SFE in promoting dislocation activity, atomic plane faulting, and twinning.The TiN/TaN superlattice exhibited remarkable room-temperature compressive plasticity (~43%), attributed to extensive atomic plane faulting and twinning facilitated by negative SFE. This behavior enabled an exceptional combination of plasticity, strength, and toughness, demonstrating the feasibility of overcoming the brittleness barrier in ceramics.

References: Huang, Y., et al. (2025). "Harvesting superior intrinsic plasticity in nitride ceramics with negative stacking fault energy." Acta Materialia: 120774.

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9:00am **MA2-2-WeM-4 Hardness and Fracture Toughness Enhancement in Non-Stoichiometric Diboride Superlattices***, Marek Vidiš* ***[marek.vidis@fmph.uniba.sk]***, *Tomáš Fiantok, Martin Truchlý, Vitalii Izai, Leonid Satrapinskyy, Tomáš Roch,* Comenius University Bratislava, Slovakia*; Rainer Hahn, Helmut Riedl,* TU Wien, Austria*; Peter Švec,* Slovak Academy of Sciences, Slovakia*; Viktor Šroba, Marián Mikula,* Comenius University Bratislava, Slovakia

Superlattice architecture presents a promising strategy for the simultaneous enhancement of hardness and fracture toughness in hard ceramic films. We demonstrate the success of this approach in transition metal diboride films and report the structural and mechanical properties of films composed of nanocrystalline $ZrB_{2+x}$and disordered TaB_{2-y} layers. Superlattice films with a wide range of bilayer periods (Λ = 1.8–31.5 nm) were prepared by magnetron sputtering. Deposition was performed at 300 °C with a floating bias to minimize interdiffusion. The formation of sharp interfaces for all Λ values is confirmed by X-ray reflectivity. The films consist of strongly understoichiometric $TaB_{1.4}$ layers, which lack long-range ordering, and overstochiometric $ZrB_{2.6}$ layers with a preferential (001) crystalline orientation. With decreasing Λ, we observe a change in preferential orientation and the formation of a true superlattice structure, evidenced by satellite peaks. This indicates crystallization of the $TaB_{1.4}$ layers, as confirmed by STEM data which shows both layers exhibiting a (001)-oriented hexagonal structure. This is a result of two effects: locally induced stabilization by the underlying ZrB_{2+x}layer and boron diffusion at the interface, enhanced by the boron concentration gradient and the bombardment of Ar neutrals reflected from the targets. This transition is accompanied by a remarkable increase in hardness from 34.1 ± 1.9 to 47.2 ± 2.3 GPa as Λ decreases to 3.4 nm. The observed hardening exceeds estimations based on Koehler's strengthening mechanism for two layers with a shear modulus difference of only 39 GPa. Improved mechanical properties are observed also from DFT calculations for defect-free ZrB_2/TaB_2 cells (Λ = 1.4–8.2 nm), which reveal a stabilizing effect with decreasing Λ and a significant increase in stiffness, peaking at Λ = 2.7 nm. At the same time, the fracture toughness K_{IC}, obtained from notched cantilever bending tests, increases from 3.3 ± 0.2 MPa·m$^{1/2}$ (average of both monolithic films) to 4.6 ± 0.3 MPa·m$^{1/2}$ for the superlattice film with Λ = 1.8 nm. This improvement is attributed to coherent stresses at the interfaces due to lattice mismatch. The suppression of brittle response under mechanical load is also confirmed by cube-corner indents, which show shorter radial cracks with decreasing Λ. This work demonstrates that the superlattice approach is highly effective in transition-metal diborides and highlights the crucial role of stoichiometry. It was supported by the Slovak Research and Development Agency (Grant No. APVV-21-0042 and APVV-24-0038), Scientific Grant Agency (Grant No. VEGA 1/0473/24) and COLOSSE project (No. 101158464).

9:20am **MA2-2-WeM-5 Effects of Nitrogen Flow Rate and Deposition Temperature on the Structure and Properties of VMoN Thin Films Deposited by High Power Impulse Magnetron Sputtering**, ***Jia-Hong Huang* [jhhuang@ess.nthu.edu.tw]**, *Pei-Fen Peng,* National Tsing Hua University, Taiwan

In this study, vanadium molybdenum nitride (VMoN) thin films were deposited on Si substrate using high power impulse magnetron sputtering (HiPIMS). The purpose of this research was to investigate the effects of process parameters including nitrogen flow rate (N-series) and deposition temperature (T-series) on the structure and properties of VMoN thin films. The results showed that for the coatings deposited at 400 °C, the lattice parameters linearly increased with increasing N/metal ratio, while those deposited at temperatures ranging from 200 to 350 °C, did not follow the Vegard's law. The texture of the VMoN films also significantly affected by the two process parameters. VMoN thin films deposited at 400 °C exhibited a (200) texture, and the texture coefficient of (200) increased with nitrogen flow rate, which could be explained by the steering effect and competitive growth theory. As the deposition temperature decreased, insufficient energy was delivered to the adatoms and promoted the growth of (111)-orientated grains. For the coatings deposited at 400 °C, the ion peening effect became intense with increasing nitrogen flow rate and thereby increasing electrical resistivity from 141.4 to 178.8 μΩ·cm. Furthermore, with increasing N/metal ratio, the hardness of N-series specimens decreased from 25.9 to 17.9 GPa, and compressive residual stress decreased from -3.66 to -1.43 GPa due to the decrease of nitrogen-vacancy hardening effect. In contrast, coatings deposited at temperature ranging from 200 to 350 °C showed no significant variation in N/metal ratio, indicating that nitrogen-vacancy hardening effect was not the primary factor that affected hardness and residual stress of T-series specimens. The results of X-ray diffraction confirmed the presence of a second phase at 350 °C and below, where the resistivity of the specimens substantially increased. The fraction of the second phase increased as deposition temperature decreased, which was correlated with increasing hardness and residual stress. The second phase may play a major role in influencing the properties of T-series specimens.

9:40am **MA2-2-WeM-6 Solubility Limit of Al in Cubic Transition-Metal Nitrides: Case Study of (Al,Cr)N**, ***Fedor F. KLIMASHIN* [fedor.klimashin@empa.ch]**, Empa - Swiss Federal Laboratories for Materials Science and Technology, Switzerland; *M. Učík,* PLATIT a.s., Czechia; *D. Casari,* Empa - Swiss Federal Laboratories for Materials Science and Technology, Switzerland; *S. Lellig,* RWTH Aachen, Germany; *T.J.E. Edwards,* NIMS, Japan; *H. Bolvardi, A. Lümkemann,* PLATIT AG, Switzerland; *J.M. Schneider,* RWTH Aachen, Germany; *J. Michler,* Empa - Swiss Federal Laboratories for Materials Science and Technology, Switzerland

The addition of Al to cubic transition-metal nitrides (TMNs) has been a cornerstone in the development of hard, protective coatings for high-performance applications. Increasing the Al content in cubic TMNs typically enhances hardness, oxidation resistance, and thermal stability. However, under thermodynamic equilibrium, AlN and cubic TMNs are immiscible, as AlN favours the wurtzite (w-) structure. The formation of hexagonal w-AlN, in turn, is generally detrimental to mechanical performance and abrasive-wear resistance.

Theoretical and experimental studies have shown that high compressive residual stresses, high deposition rates, and low substrate temperatures can extend the metastable cubic solubility limit (along with Al subplantation or coherency-strain-stabilised multilayer architectures, which, however, are outside the scope of this study). This behaviour is well captured by metastable phase-diagram calculations for magnetron-sputtered (Ti,Al)N and (V,Al)N films [1,2].

High reported Al solubility levels in cubic TMNs are often inferred solely from the absence of w-AlN reflections in X-ray diffractograms. We investigated a series of sputter-deposited (Al,Cr)N films with Al metal fractions up to 0.72, which exhibited only fcc reflections in X-ray diffractograms. However, selected-area electron diffraction revealed the presence of w-AlN, indicating that the true solubility limit is lower. We discuss the influence of residual stress, substrate temperature, and deposition kinetics on the stabilisation of metastable cubic solid solutions, and propose indirect, experimentally accessible indicators for the onset of wurtzite-phase formation. These findings refine the understanding of Al solubility in (Al,Cr)N and, more broadly, in cubic TMNs.

References:

[1] S. Liu et al., *Acta Mater.* 165 (2019) 615–625.

[2] S. Liu et al., *Acta Mater.* 196 (2020) 313–324.

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