Tuesday Morning, May 13, 2025

Protective and High-temperature Coatings
Room Palm 3-4 - Session MA3-1-TuM

Hard and Nanostructured Coatings I

Moderators: Rainer Hahn, TU Wien, Institute of Materials Science and Technology, Stanislav Haviar, University of West Bohemia, Fan-Yi Ouyang, National Tsing Hua University

8:00am **MA3-1-TuM-1 Hard TiAlTaN Coating by HIPIMS Deposition for Cutting Tools: Experiments, Simulations and Cutting Tests*, Emile Haye,*** University of Namur, Belgium*; Jérôme Muller, Pavel Moskovin,* University of Namur, Innovative Coating Solutions, Belgium*; Loris Chavee,* University of Namur, Belgium*; Szilard Kolozsvari,* Plansee Composite Materials GmbH, Germany*; Stéphane Lucas,* University of Namur, Innovative Coating Solutions, Belgium **INVITED**

The quaternary $Ti_{1-x-y}Al_xTa_yN$ system has been shown to possess superior thin film properties compared to $Ti_{1-x}Al_xN$. In addition to the impact of Ta content, the sputtering technique significantly influences the structural and mechanical characteristics of these films. In this study, high power impulse magnetron sputtering (HiPIMS) was employed to deposit dense, tough, and hard $Ti_{1-x-y}Al_xTa_yN$ thin films from composite targets, which were then compared to TiAlN thin films. The effects of Ta addition were explored both experimentally and through simulations. VirtualCoater® was used to simulate thin film growth and properties, providing insight into the role of Ta in the densification process and the relationship between target composition and film composition. Subsequently, the mechanical, structural, and thermal properties of the films were experimentally examined, highlighting the significant benefits of Ta addition.

The observed enhancements are attributed to: (1) increased hardness due to film densification facilitated by intense Ta bombardment, (2) stabilization of the cubic structure at elevated temperatures, and (3) superior thermal resistance resulting from the formation of a mixed ($Ti_xAl_yTa_z$) oxide monolayer, as opposed to the Al_2O_3/TiO_2 bilayer observed in TiAlN-based coatings, as confirmed by XPS depth profiling.

Finally, dry cutting tool tests demonstrated a substantial increase in tool life and improved surface finish of the machined parts.

8:40am **MA3-1-TuM-3 Development and Comparison of AlTiN-Based HiPIMS Coatings for Microtool Machining Applications*, Ivan Fernández-Martínez,*** Nano4Energy S.I.N.E, Spain

Currently, the coating of microtools plays a critical role in precision manufacturing, as tool performance and longevity are heavily influenced by the properties and quality of the coating employed. In this context, HiPIMS technology provides hard coatings with a smooth finishing, a low defect density, and homogeneous coverage of 3D intricate parts – an essential advantage when coating tools with diameters smaller than a millimeter – thus representing an ideal choice for these applications.

AlTiN-based coatings doped with silicon (AlTiSiN) and boron (AlTiBN) have been developed to meet the specific demands of micro-tool applications, such as enhanced wear resistance, high thermal stability, and low friction in extreme operating environments. Properties such as hardness, adhesion, and residual stress were tailored and correlated to HiPIMS process parameters. In addition to mechanical properties analysis, tool performance was evaluated through machining tests, selecting Hardened Steel (HRC60) and Ti6AlV4 alloy as case materials. Both the finishing of the machined parts, and the wear suffered by the tool were analyzed.

The results highlight the potential of HiPIMS-deposited AlTiN-based coatings to significantly extend tool life and improve machining quality in precision manufacturing. Furthermore, this study provides insights into the trade-offs between boron and silicon doping, offering practical guidelines for selecting the most appropriate coating for specific micro-tool applications.

Our findings underline the versatility of HiPIMS technology in tailoring thin-film properties for high-performance applications, demonstrating its growing relevance in the field of advanced microtools.

Keywords: hard coatings, nitrides, sputtering, HiPIMS.

9:00am **MA3-1-TuM-4 Micro-Fracture Toughness and Durability of HiPIMS-Deposited Hard Coatings used for Micro-Machining of $TiAl_6V_4$ Alloys*, Arley Garcia,*** Nano4Energy SL, IMDEA Materiales, Spain*; Jose Antonio Santiago,* Nano4Energy SL, Spain*; Christoph Kirchlechner,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany*; Pablo Diaz Rodriguez,* Nano4Energy SL, Spain*; Miguel Monclús,* IMDEA Materiales, Spain*; Iván Fernández Martínez,* Nano4Energy SL, Spain*; Alvaro Guzmán,* Universidad Politécnica de Madrid, Spain*; Subin Lee,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany*; Jon Molina Aldareguia,* Universidad Politécnica de Madrid, Spain

The High-Power Impulse Magnetron Sputtering (HiPIMS) technique enables the deposition of coatings with high hardness, low defect densities, and uniform, conformal coverage over complex 3D geometries, meeting the strict tolerances required in micromachining applications. High-speed machining (HSM) applications demand not only high hardness but also sufficient fracture toughness K_{IC}, which is critical for maintaining the structural integrity of both bulk and coated engineering components [1]. However, these mechanical properties are often antagonistic, particularly in materials capable of plastic deformation, where high hardness typically correlates with lower fracture toughness [2].

This study aims to systematically evaluate the fracture toughness and machining performance of AlTiN- and TiN-based coatings doped with Si, deposited by HiPIMS using different process parameters. Micro-fracture toughness was assessed on freestanding films using single cantilever bending tests, effectively minimizing residual stress and substrate interactions to obtain precise K_{IC} values. Crack formation at the cutting edge of a 0.4 mm diameter microdrill was observed using FIB, while the composition of the coatings was determined by GDOES. Additionally, XRD was employed to analyze grain growth texture and peak shifts, enabling the evaluation of biaxial stresses. The AlTiSiN coatings exhibited a hardness of 35 GPa, while TiSiN coatings reached 40 GPa. Fracture toughness ranged from 1.78 MPa·√m to 2.2 MPa·√m, depending on the HiPIMS parameters used. In micromachining tests on the TiAl6V4 alloy, the coatings allowed continuous micro-milling to be extended from 40 minutes to over one hour. These findings link toughness values, stress reduction, and crack formation at the cutting edges with tool durability in machining applications.

[1]. BARTOSIK, M., et al. Fracture toughness of Ti-Si-N thin films. *International Journal of Refractory Metals and Hard Materials*, 2018, vol. 72, p. 78-82.

[2]. HAHN, Rainer, et al. Superlattice effect for enhanced fracture toughness of hard coatings. *Scripta Materialia*, 2016, vol. 124, p. 67-70.

9:20am **MA3-1-TuM-5 Effect of Process Parameters on the Structure and Mechanical Properties of TiZrN Thin Films Prepared by Co-Sputtering HPPMS/UBMS*, Chun Lin Yang,**** Jia-Hong Huang,* National Tsing Hua University, Taiwan

Transition metal nitrides (TMeNs) are widely used in protective hard coatings for cutting tools due to their superior mechanical and tribological properties, and high thermal stability. Among the TMeNs, TiZrN possesses higher hardness, better thermal stability, and greater corrosion resistance, compared with their counterpart binary TMeNs, and therefore TiZrN becomes a promising hard coating material and attracts attention from both academia and industry. The purposes of this study is to investigate the effects of duty cycle (D-series) and working pressure (P-series) on the structure and mechanical properties of TiZrN thin films. TiZrN coatings were deposited on Si substrate using high-power pulsed magnetron and unbalanced magnetron co-sputtering techniques (HPPMS/UBMS). The dc-UBMS was for sputtering zirconium, while HPPMS was for sputtering titanium. The duty cycle of HPPMS was adjusted from 100% to 5%, and at a duty cycle of 5%, the working pressure was varied from 3 to 10 mTorr. The results of X-ray diffraction (XRD) showed that the film structure varied with the two process parameters. As the duty cycle decreased, the preferred orientation of the TiZrN thin films changed from random to (200), with increasing peak power density finally reaching 0.3 kW/cm^2, indicating that the increase in energy facilitated the formation of the (200) texture. Residual stress increased with decreasing duty cycle, except in the D5 sample. However, the hardness, resistivity, and roughness of D-series samples remained unaffected by changing duty cycle. With increasing working pressure, the preferred orientation of the TiZrN coatings switched from (200) to (111). The cross-sectional observation of P-series samples by scanning electron microscopy revealed that the microstructure of the coatings changed from dense to a loosely packed columnar structure for the specimen deposited at the highest working pressure of 10 mTorr, where high roughness, high electrical resistivity, and low residual stress were also measured.

Keywords: TiZrN; high power pulse magnetron sputtering (HPPMS); duty cycle; working pressure

9:40am **MA3-1-TuM-6 Superstoichiometric (Al,Cr)N$_x$ Coatings with Superior Hardness, Fracture Toughness, and Wear Resistance**, ***Fedor F. KLIMASHIN,*** Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland; *Martin Učík,* PLATIT a.s., Czechia; *Martin Matas, David Holec,* Montanuniversität Leoben, Austria; *Martin Beutner,* Otto-von-Guericke-Universität Magdeburg, Germany; *Jan Klusoň, Mojmír Jílek,* PLATIT a.s., Czechia; *Andreas Lümkemann,* PLATIT AG, Switzerland; *Johann Michler, Thomas E. J. Edwards,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Many transition-metal carbides, nitrides, and oxides are inherently non-stoichiometric compounds, characterised by broad homogeneity ranges in their phase diagrams. Deviations from stoichiometry, defined as the ratio of non-metal to metal atoms (x), can drastically affect properties. While substoichiometric compounds (x<1) have been widely studied, superstoichiometric compounds (x>1) remain largely unexplored.

Here we present our finding on superstoichiometric (Al,Cr)N$_x$ coatings sputter-deposited from an $Al_{60}Cr_{40}$ target at power densities reaching 840 W/cm^2. Experimental and computational analyses reveal that excess nitrogen predominantly occupies interstitial lattice sites. Upon surpassing a critical concentration (x≈1.06), grain renucleation rates increase, disrupting columnar growth and altering the preferential orientation from (111) to (220). The coatings exhibit a single-phase, face-centred cubic structure, a dense microstructure, and reduced surface roughness compared to benchmark coatings produced by cathodic arc evaporation.

Remarkably, hardness, fracture toughness, and wear resistance equal or exceed those of the benchmark coatings. Our findings highlight the advantages of superstoichiometric (Al,Cr)N$_x$ as effective wear-resistant materials for advanced engineering applications, while also suggesting broader implications for the utilisation of superstoichiometric nitrides across various industries.

10:00am **MA3-1-TuM-7 Connecting Phase Stability and Mechanical Properties of Ti–-B–N Thin Films**, ***Rebecca Janknecht,*** Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland; *Tomasz Wójcik,* TU Wien, Austria; *Fedor F. Klimashin,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland; *Johann Michler,* EMPA, Switzerland; *Paul H. Mayrhofer, Rainer Hahn,* TU Wien, Austria

Understanding the relationship between thermally induced decomposition in metastable material systems and their mechanical properties is critical for designing thin films with improved wear resistance and thermal stability. Our previous work revealed that achieving improved solubility of B in fcc-TiN requires a deviation from the TiN-TiB tie line toward Ti-rich compounds, facilitated by the formation of vacancies in the non-metal sublattice. This deviation was achieved by non-reactive co-sputtering of a Ti target alongside TiN and TiB_2 targets, allowing full incorporation of 8.9 at.% B into the fcc-TiN lattice. In contrast, co-sputtering TiN and TiB_2 yielded compositions along the TiN-TiB_2 tie line, with excess B forming amorphous grain boundary phases [1]. In this study, we systematically annealed (1) a single-phase fcc-Ti–B–N coating with a composition of $Ti_{1.08}B_{0.18}N_{0.74}$ and (2) a Ti–B–N coating with amorphous B-rich grain boundary phases with a $Ti_{1.01}B_{0.21}N_{0.78}$ stoichiometry. Annealing was performed at 700°C, 800°C, 900°C, 1000°C, 1200°C and 1400°C for 10 minutes. Both coatings retained high hardness of 30±1 GPa up to 1200°C. The results of micro-cantilever bending tests indicate an inverse relationship between fracture toughness (K_{IC}) and annealing temperature (T_a). The $Ti_{1.01}B_{0.21}N_{0.78}$ coating exhibits a K_{IC} of 2.1 ± 0.1 MPa·m$^{0.5}$, which increases to 3.8 ± 0.3 MPa·m$^{0.5}$ upon increasing T_a to 1000°C, but K_{IC} for the $Ti_{1.08}B_{0.18}N_{0.74}$ sample was observed to decrease from 2.7 ± 0.1 MPa·m$^{0.5}$ in the as-deposited state to 2.3 ± 0.1 MPa·m$^{0.5}$ at T_a=1000°C. X-ray diffraction (XRD) and transmission electron microscopy (TEM) analyses confirm that K_{IC} improves only when metastable Ti–B–N decomposes into co-existing thermodynamically more stable fcc-TiN and hcp-TiB_2 phases without the formation of additional hcp-Ti precipitates. These findings highlight the critical influence of compositional and structural control on the thermal and mechanical stability of Ti–B–N thin films, providing new pathways for their use in high-performance applications.

[1] R. Janknecht et al., *A strategy to enhance the B-solubility and mechanical properties of Ti–B–N thin films*, Acta Mater., 271 (2024), Article 119858, 10.1016/j.actamat.2024.119858 [https://doi.org/10.1016/j.actamat.2024.119858]

10:20am **MA3-1-TuM-8 Effect of Oxygen Content and Thickness on the Property and Structure of Zr(O,N) Thin Film**, ***Chi Feng Hung,*** *Jia Hong Huang,* National Tsing Hua University, Taiwan

Transition metal nitrides (TMeNs) have been widely applied as the protective coatings for tools due to their excellent properties. Zirconium nitride (ZrN) coatings, in particular, attract attention for the outstanding mechanical properties, corrosion resistance, and attractive golden color. It has been extensively reported that by adding oxygen in ZrN, the coating becomes Zr(N,O), where the ionic/covalent bond ratios can be tuned by adjusting the nitrogen-to-oxygen (N/O) ratio, and consequently influencing the optical, electrical, and mechanical properties of the coatings. However, most studies of Zr(N,O) coatings are on the effect of phase transition on structure and properties within a wide range of N/O contents, while limited research was conducted with range of oxygen content where Zr(N,O) remains a single phase. The purpose of this study is to explore the effect of oxygen content and film thickness on the structure and properties of single-phase Zr(N,O) films. In this study, the Zr(N,O) coatings were prepared using dc unbalanced magnetron sputtering with different durations and oxygen flow rates. Four different oxygen flow rates were used to control the oxygen content, and the coating thickness was controlled by varying the deposition times. The preferred orientation of the coatings was observed by X-ray diffraction. The results showed that dominant (111) and (200) textures appeared in the specimens with low and medium oxygen contents, respectively; in contrast, the texture of the specimens with high oxygen contents varied from random to (200) with increasing thickness. The hardness and Young’s modulus of the coatings were nearly constant for all samples, with no observable trends with respect to thickness or oxygen content. The results revealed that the electrical resistivity increased with increasing oxygen content. The variation of residual stress with increasing oxygen content could be divided into two regimes, where compressive stress dropped sharply when the texture changed from (111) to (200) and then gradually decreased with further increase of oxygen content. The specimens with higher oxygen contents exhibited a significant decrease in electrical resistivity with decreasing thickness, while the specimens with medium oxygen contents showed a less distinct decrease, and the specimens with the lowest oxygen contents showed no change in resistivity with thickness. The residual stress also showed two trends, in which residual stress decreased with thickness for the specimens with the lowest oxygen contents, while residual stress increased with thickness for the other specimens.

10:40am **MA3-1-TuM-9 Effect of Fluence on Zirconium Nitride Coating Irradiated by 5-MeV-Proton**, ***Rou-Syuan Chen,*** Department of Engineering and System Science, National Tsing Hua University, Taiwan (ROC); *Kuan-Che Lan,* Institute of Nuclear Engineering and Science, National Tsing Hua University, Taiwan (ROC)

The development of advanced nuclear reactors and small modular reactors (SMR) will require nuclear fuel at a higher enrichment, which can introduce higher fluence of ionizing radiation such as fission products, neutron and proton etc. It will bring a severe challenge for fuel cladding materials. Zirconium nitride (ZrN) thin films are known for their thermal stability, high hardness, low resistivity, and better tribological properties, and they are widely used as hard coatings on deposited on the edge surface of cutting. Previous studies have also shown that ZrN exhibits great resistance to ionizing radiation. However, report about the irradiation damage of ZrN thin film as a function of proton fluence are rare. The objective of this study is to investigate on effect of fluence on ZrN thin film irradiated by 5-MeV-proton. Post irradiation examination of ZrN thin film will be performed to analyze the electronic properties, crystal structure, hardness and young’ s modulus. The crystal structure and grain size of each sample are characterized by X-ray diffraction (XRD). The electronic resistivity is measured by a four-point probe. The film thickness is examined by scanning electron microscope (SEM). The residual stress is assessed by the laser curvature method (LCM) and average X-ray strain (AXS) method. The surface hardness and young’ s modulus are measured by nanoindentation (NIP).

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