Hard Coatings and Vapor Deposition Technologies
Room Pacific F-G - Session B5-ThM

Hard and Multifunctional Nanostructured Coatings

Moderators: Dr. Rainer Hahn, TU Wien, Institute of Materials Science and Technology, Austria, **Dr. Tomas Kozak**, University of West Bohemia, Czechia

9:00am **B5-ThM-4 High-Temperature Properties of Multicomponent Nitride Coatings Deposited by PVD*, Yuxiang Xu,*** Guangdong University of Technology, China **INVITED**

Al-containing transition metal nitrides possess high hardness and excellent wear resistance and, therefore, have been widely applied as protective coatings on tools and components. Whereas the development of advanced machining techniques and the application of difficult-to-cut materials require high-performance surface coatings, especially at elevated temperatures. This work used the alloying method to construct multicomponent nitrides to tailor their thermal stability, oxidation resistance, and tribological properties.

The TiAlCrZrTaWN coating with a mixing entropy of 14.8 J/mol·K was deposited using DC magnetron sputtering. Upon annealing, a retarded spinodal decomposition to AlN-rich and AlN-depleted nanosize domains can be recognized in the TiAlCrZrTaWN coating, accompanied by age-hardening. The occurrence temperature of peak hardness shifts from 800 C of TiAlN to 900 °C of TiAlCrZrTaWN. Moreover, a high hardness of ~31 GPa can be obtained for TiAlCrZrTaWN after annealing at 1100 °C. The coherent precipitation of wurtzite AlN was detected at the grain boundaries at 1000 °C.

For oxidation behavior, arc-evaporated TiAlCrTaWN coating was investigated in detail. The synergistic effect of Cr, Ta, and W significantly improves the oxidation resistance of TiAlN coatings. During the oxidation process, Cr promotes the formation of a dense Al_2O_3 layer in the early stage, Ta slows down the rate of inward diffusion of O through the TiO_2 layer in the middle stage, and W forms nano-oxides at the interface to improve the combination of oxide scale and underneath nitride. Thermal stability and oxidation resistance are jointly improved in the TiAlCrTaWN system.

To decrease the high-temperature friction of nitride coatings, Mo and Cu were introduced to the TiAlN coating. Alloying with Mo can reduce the friction coefficient at room temperature with water vapor aid and distinctly increase the wear resistance. While the tribological behavior of TiAlMoN is similar to TiAlN at 600 °C. The co-addition of Mo and Cu promotes the formation of Mo–O/Cu–O oxide tribolayer with the novel nanocore-shell structure during friction at 600 °C. The array of Mo–O/Cu–O nanopillars inside the wear track provides low shear resistance and decreases the friction pair's contact area, thus decreasing friciton from high temperatures.

In a word, alloying is versatile in changing the high-temperature properties of hard nitride coatings. And alloying elements need to be explicitly selected for specific goals.

9:40am **B5-ThM-6 Effect of Ion Density Flux Ratio on Properties of Protective Hard (Ti,V)B_2 Coatings Sputtered by Cylindrical Magnetron*, Daniel Karpinski,*** *P. Karvankova, C. Krieg,* Platit AG, Switzerland*; J. Kluson,* Platit a.s., Czechia*; B. Torp,* Platit Inc., USA*; A. Lümkemann,* Platit AG, Switzerland

Titanium diboride dopped by vanadium (Ti,V)B_2 coating as well as pure TiB_2 due to their densely packed hexagonal structure with strongly covalently bonded boron atoms separated by metallically bonded metal layers exhibits very high hardness H ≥ 40 GPa, high elastic modulus E ≥ 500 GPa, very high melting point about 3000 °C, high chemical inertness, and therefore low sticking to soft metals. Thanks to these outstanding properties, the TiB_2 has nowadays become very attractive as a protective coating in industrial applications e.g., non-ferrous metal machining such as aluminum-based, and titanium-based metals, etc. and coin stamping. The hard TiB_2 is becoming a good alternative to hard tetrahedrally amorphous carbon (ta-C) with high amounts of diamond bounds (sp^3), due to its high deposition rate, low roughness, and cleaner process. Moreover, both TiB_2 as well as ta-C coatings often exhibit high compressive macro-stress above -5 GPa which can lead to adhesion failure. High compressive stress can be relaxed already by small additions of VB_2 [1], and/or can be tuned by controlling the ion density flux to deposition flux ratio (J_i/J_d) [2]. On top of that, the addition of V to TiB_2 has no significant effect on the mechanical properties unlike the J_i/J_d. Except varying the bias voltage and/or magnetron power, the J_i/J_d controlling is not possible in most conventional sputtering systems. In this study the industrially developed SCIL® (sputter coatings induced by lateral glow discharge) technology was used to independently control the J_i. In the SCIL® technology [2], the coating is deposited by sputtering of the central cylindrical cathode, and in the meantime, a secondary discharge (LGD) is also ignited between two cylindrical lateral electrodes. One of these lateral electrodes is acting as an anode – powered by a positive potential (LGD®), while the other is a typical arc cathode. During the sputtering process, the arc cathode has been shielded to avoid the deposition of the evaporated materials on the substrates. Where the J_i is then controlled by tuning the electron current to the anode (LGD®).

[1] Ch. Mitterer, V. L. Terziyska, M. Tkadletz, L. Hatzenbichler, D. Holec, V. Moraes, A. Lümkemann, M. Morstein, P. Polcik, *Synthesis and characterization of sputtered (Ti,V)B_2 hard coatings*, ICMCTF (2019) oral contribution.

[2] R. Zemlicka et al., *Enhancing mechanical properties and cutting performance of industrially sputtered AlCrN coatings by inducing cathodic arc glow discharge*, Surface & Coatings Technology 422 (2021) 127563.

10:00am **B5-ThM-7 Development of TiB2 Coatings in a New Generation Industrial Reactor Based on Hybrid DC-Pulsed and HIPIMS Magnetron Sputtering on HSS Steels – A Tribological Study*, Gonzalo Garcia Fuentes,*** *J. Fernández, J. Fernández-Palacio,* AIN, Spain*; H. Gabriel,* PVT Vakuum Technik, Germany

Titanium di-boride (TiB_2) coatings exhibit excellent combination of hardness and low adhesion to cutting metal alloys such as these based on Ti, Al or Ni, and it has been used since a decade on cutting tools in the aerospace sector. TiB_2 is well known to exhibit low moderate toughness, which limits it applicability under complex 3D shaped cutting tools, or tools subject to very high loads. Pulsed DC sputtering as well as other conventional vapor deposition techniques are being developed to this purpose. In our approach, a hybrid HIPIMS/DC_pulsed industrial scale system equipped with 4 sputtering evaporators and a 500/300 mm H/W effective working volume is chosen to implement the TiB2 coating formulations.

TiB2 coatings were prepared on M2 HSS tool steel using HIPIMS conditions as a function of the BIAS potential, and tuning those pulse length and frequencies providing the maximum sputtering yield of the diboride target. In addition, the hybrid HIPIMS/DC_pulsed mode was implemented using two targets in opposition around the sample holder volume. Alternative deposition configurations such as gradient (increasing) DC_pulse power mode on constant power HIPIMS have been designed and characterized.

The coating microstructures have been characterized using x-ray diffraction and scanning electron microscopy in top and cross-sectional view. Nano-indentation hardness and standard wear rate were carried out to frame the overall mechanical properties at room temperature. It has been found that the HIPIMS coatings (without DC_pulse co-sputtering) exhibit good adhesion on M2-steel, and less tendency to crack under indentation loading as the BIAS potential decreases. On the other hand, the indentation hardness of the hybrid deposited coatings (HIPIMS and DC_sputtered) decrease as the DC_pulsed/HIPIMS power ratio of the opposing targets increases.

The frictional properties of the TiB2 coatings are tested against aluminium. A test matrix of variables such as temperature (RT-300ºC) and sliding-speed (10-50 cm/s) has been set in order to identify the mild-to-severe galling threshold conditions at the TiB2 - Aluminium interfaces. The comparison of the frictional properties of the deposited TiB2 coatings with benchmark TiN and CrN HIPIMS sputtering coatings sliding against aluminium clearly indicated that the TiB2 can be considered an effective antigalling coating.

10:20am **B5-ThM-8 Nanoporous/Nanocomposite Thin Films by Magnetron Sputtering Deposition in Helium and Other Light Gases: New Materials and Applications*, Asunción Fernández,*** Instituto de Ciencia de Materiales de Sevilla (CSIC-US), Spain **INVITED**

He ions (100 eV-500 keV) and He plasma-surface interactions have been widely investigated due to their technological interest related to damage in nuclear reactor materials. The formation of He filled high pressure nano-bubbles and porous fuzz structures have been widely reported as undesired damage effects. The work to be presented aims to transform the formation of defects (i.e. gas bubbles, porosity) in a solid matrix into an opportunity for the controlled fabrication of nano-structured thin films and coatings by using “magnetron sputtering (MS)” deposition with He and N_2 as process gas. Results on this bottom-up fabrication methodology and the characterization of microstructure and composition will be shown for the case of nanoporous He-charged silicon [1] and N_2-charged silicon oxinitride [2] films. A revision of up to now proposed applications will be presented with special details for the use of the new “solid-gas” nanocomposite materials as ^{4}He and ^{3}He solid targets for nuclear reaction studies [3]. Among others the reduction of the refractive index or the fabrication of nanostructured catalytic coatings are proposed. The use of flexible supports and electron tomography for the 3D reconstruction at the nano-scale will be respectively illustrated for newly investigated matrix elements as Co and Cu with Helium as process gas.

In summary the presented results will show a perspective interdisciplinary and collaborative international research covering the synthesis, advanced characterization and applications of functional thin films and coatings prepared by plasma assisted magnetron sputtering deposition in He and other light gases.

[1] R. Schierholz, B. Lacroix, V. Godinho, J. Caballero-Hernández, M. Duchamp, A. Fernández. *Nanotechnology* 26 (2015) art.nr. 075703

[2] V. Godinho, T. C. Rojas, A. Fernández.*Microporous and Mesoporous Materials* 149 (2012) 142-146

[3] A. Fernández, D. Hufschmidt, J.L. Colaux, J.J. Valiente-Dobón, V. Godinho, M.C. Jiménez de Haro, D. Feria, A. Gadea, S. Lucas. *Materials & Design* 186 (2020) art.nr. 108337.

11:00am **B5-ThM-10 Mechanical Properties of Epitaxial TiN(001)-TiC(001) Superlattices**, ***Moishe Azoff-Slifstein,*** Rensselaer Polytechnic Institute, USA*; S. Lee,* University of Connecticut, USA*; D. Gall,* Rensselaer Polytechnic Institute, USA

Superlattices of 1-µm-thick epitaxial TiN(001)-TiC(001) layers are deposited on MgO(001) at 1100 °C in order to explore superlattice hardening in a cubic nitride-carbide materials system. The processing gas during reactive magnetron sputtering is alternately switched between Ar/N_2 and Ar/CH_4 mixtures to obtain TiN-TiC superlattice films with equal nitride and carbide fractions and a variable superlattice bilayer period Λ = 1.5-30 nm, as measured using X-Ray diffraction (XRD) ϑ-2ϑ superlattice peaks. XRD ω-rocking curves indicate strong crystalline alignment with a peak width increasing from 0.1 - 0.6° with decreasing Λ. Reciprocal space maps confirm a cube-on-cube epitaxy of alternating rock-salt structure TiN(001) and TiC_x(001) layers and indicate fully-strained TiN(001)-TiC(001) superlattices which are coherent with the MgO(001) substrate for Λ = 3 and 30 nm but are partially relaxed for Λ = 6 and 13 nm. Scanning electron microscopy analyses show surface protrusions due to misoriented grains which increase in density from ρ = 0.4 to 1.0 μm^{-2} for Λ = 1.5 to 3 nm but then decrease back to ρ = 0.06 μm^{-2} for Λ = 30 nm. The misoriented grains cause large variations in nanoindentation measurements, resulting in an artificial depth-dependent hardness H for 20, 80, and 10% of indentations for multilayers with Λ = 1.5, 6, and 30 nm, respectively. Accounting for these deviations allows to determine H and the elastic modulus E as a function of Λ: The TiN-TiC superlattice system demonstrates an increase in H from 23 to 34 GPa with increasing Λ = 1.5 to 6 nm, followed by a decrease to H = 30 GPa for Λ = 30 nm. Similarly, E increases from 450 GPa for Λ = 1.5 nm to a maximum of 750 GPa for Λ = 6 nm and a subsequent drop to E = 450 GPa for Λ = 30 nm. The observed superlattice hardening is attributed to local strain variations and dislocation pinning at the TiN-TiC interfaces.

11:20am **B5-ThM-11 Tensile and Compressive Stress in Sputtered Cu/W Nanomultilayers: Correlation with Microstructure, Thermal Stability, and Thermal Conductivity**, ***Giacomo Lorenzin,*** Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; M. bin Hoque,* University of Virginia, USA*; D. Ariosa,* Universidad de la Republica, Montevideo, Uruguay*; L. Jeurgens,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; E. Hoglund, J. Tomko, P. Hopkins,* University of Virginia, USA*; C. Cancellieri,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Physical vapor deposition (PVD), in particular magnetron sputtering, is a commonly adopted technique to produce nanomultilayer (NML) materials because it allows a full control of thickness, period, and interface roughness by tuning deposition parameters. During the growing procedure, however, internal residual stress is generated in the forming multilayer. Stress represents one of the main factors determining failure and reliability issues, hence affecting the durability and the performance of functional coatings. Nevertheless, for some specific applications, a controlled level of stress is desirable to enhance target properties like mechanical strength, thermal stability, and thermal conductivity. For this reason, it is of paramount importance to study the relation between deposition parameters and stress states in NMLs. Copper-tungsten (Cu/W) multilayers are one of the most widely used nanomaterials in electronic, optical, and sensing devices because of the combination between the electrical and thermal properties of Cu and the mechanical strength of W.

In this work, Cu/W multilayers were deposited by magnetron sputtering, achieving configurations with opposite stress values (i.e., tensile and compressive) by tuning deposition parameters. Stress was monitored both in-situ by measuring the substrate curvature and ex-situ by XRD. Stress values derived with these two technique were compared and the difference was ascribed to interface stress, whose values have opposite signs in tensile and in compressive multilayers. Samples with opposite stresses exhibit also different microstructures, which were characterized by SEM, STEM, XRD, and sputter depth profiles acquired with XPS. In particular, tensile NMLs have a more disordered structure than the compressive ones. When annealed at temperatures >700°C, Cu/W NMLs degrade and transform into nanocomposites (NCs) with W nanoparticles embedded in a Cu matrix. Stress states and microstructure affect the transition temperature, with compressive NMLs exhibiting a better thermal stability and resistance to degradation. In addition, out-of-plane thermal conductivity was extensively characterized in NMLs and in NCs and, once again, compressive samples outperform the tensile counterpart. Within this work, we were able to show how a fine tuning of deposition parameters can lead to Cu/W NMLs with different stress states and microstructures, and we highlighted the effects on the thermal stability and the thermal conductivity. This paves the way to stress tailoring in multilayers for specific properties and applications.

11:40am **B5-ThM-12 Investigation of Thermal Properties of PECVD Ti-Si-C-N Nanocomposite Coatings**, ***Alexander Thewes,*** *L. Broecker,* IOT TU Braunschweig, Germany*; H. Paschke, T. Brueckner,* Fraunhofer Institute for Surface Engineering and Thin Films IST, Germany*; C. Sternemann, M. Paulus,* DELTA TU Dortmund, Germany

Ti-based nanocomposite coatings are known for high hardness values, drawing attention to tribological applications, where the wear reduction on tool surfaces can be achieved by protective thin films. In this case, nanocomposite structures are made of nanocrystalline (nc–) grains embedded in an amorphous (–a) matrix, increasing the hardness due to the Hall-Petch effect. In addition to high hardness, this is due to outstanding properties concerning the coefficient of friction (e.g. Ti–C–N) and the oxidation resistance (e.g. Ti–Si–N). In this study, Ti–Si–C–N nanocomposite coatings were investigated and possibly combining advantageous properties of Ti–C–N and Ti–Si–N coatings. The coating deposition was tailored to form a graded system, beginning with TiN and gradually increasing the amount of Si and C to form Ti–Si–C–N. The a–matrix partially consists of Si_3N_4 phases, which are highly resistant against oxidation, act as diffusion barrier for O_2, and enclose the nc–Ti(C,N) grains, that are vulnerable towards oxidation. To understand the fundamental principles behind Ti–Si–C–N nanocomposite coatings and their thermal properties, the phase composition and micro- and nanostructure were investigated by means of X-ray diffraction, Raman spectroscopy, SEM, and tempering behavior of samples. EPMA analysis was used to correlate the chemical composition with the coatings build-up and thermal properties. Ti(C,N) phases were identified under use of X–ray diffraction, with a strong pronunciation of the (200) reflex. The 2D detector enabled an analysis of preferential orientations of crystalline lattices. By these means, a texture was identified. Via Raman spectroscopy, a–C was detected as a mixture of D-band and G-band phases. *In-situ* X–ray diffraction experiments at 900 °C showed only minor signs of oxidation compared to room temperature. A sample tempered at 900 °C for 1 h in air composed of 2.5 µm oxide layer with 0.8 µm of as-deposited Ti–Si–C–N coating underneath. These results are promising to use Ti–Si–C–N as a protective coating in high temperature applications, e.g. on extrusion dies in hot extrusion of copper.

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