Tribology and Mechanics of Coatings and Surfaces
Room Town & Country B - Session MC2-2-WeM

Mechanical Properties and Adhesion II

Moderators: Jazmin Duarte, MPI für Eisenforschung GMBH, Germany, **Bo-Shiuan Li**, National Sun-Yat Sen University, Taiwan

8:00am **MC2-2-WeM-1 *In Situ* Micromechanical Characterization of Thin Films: Strain Rate, Size and Microstructure Related Experiments in the SEM**,
Szilvia Kalacska (szilvia.kalacska@cnrs.fr), CNRS LGF, Mines St. Etienne, France; *L. Petho,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland; *G. Kermouche,* Mines St. Etienne, France; *J. Michler,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland; *P. Ispanovity,* Eötvös Loránd University, Hungary **INVITED**

Creating multi-layered thin films with alternating dissimilar sublayers is proposing unusual (electric, thermal, optical, etc.) properties to be experimentally investigated. In such a system where grain size and texture can be controlled by the deposition/annealing process represents a unique opportunity to focus on some aspects of the deformation processes driven by the collective behaviour of dislocation. Our aim was to create a system with large enough grains (500-800 nm in diameter) and engineer flat grain boundaries to study plastic deformation modified by the presence of barriers.

A hybrid thin film deposition system (Swiss Cluster) was used to create the samples by combining atomic layer deposition (ALD) and physical vapour deposition (PVD) [1]. Sequential deposition of approx. 1 µm thick multilayers were separated by 10 nm thick Al_2O_3 interlayers. The initial 100-250 nm grain size was increased by extensive heat treatment (@800°C for 4h under Ar atmosphere, Fig. 1a). Such final specimen was quite challenging to create without porosities or major delamination from the substrate after heat treatment.

Afterwards, micropillars were fabricated using focused ion beam (FIB) milling close to the edge of the bulk sample (Fig.1b). These micropillars were then compressed at various strain rates (0.1-1000/s) using a nanodeformation setup (Alemnis AG). High (angular) resolution electron backscatter diffraction (HR-EBSD) was applied to study the geometrically necessary dislocation (GND) density distribution after low and high strain rate deformations. Sequential FIB-slicing [2] was applied to create 3D reconstructions of the deformed volumes.

References

[1] T. Xie, T.E.J. Edwards, N.M. della Ventura, D. Casari, E. Huszár, L. Fu, L. Zhou, X. Maeder, J.J. Schwiedrzik, I. Utke, J. Michler, L. Pethö, *Thin Film Solids*, **2022**, 711, 138287.

[2] S. Kalácska, J. Ast, P.D. Ispánovity, J. Michler, X. Maeder, *Acta Materialia*, **2020,** 200, 211-222.

8:40am **MC2-2-WeM-3 Assessing Brittleness of Indium Tin Oxide Layers on Glass Substrates with Nanoindentation**,
Kurt Johanns (kurt.johanns@kla.com), *S. Varma, J. Hay, B. Crawford,* KLA-Tencor, USA

Many of the materials used in manufacturing semiconductors are susceptible to cracking, i.e., exhibit brittle failure during processing and in application.While the definition of brittle is well understood, assigning a “brittleness” value to a given material or system of materials is not easy as “brittleness” is not a material property.Here, we define a simple set of nanoindentation experiments in an effort to assess the brittleness of Indium Tin Oxide (ITO) layers and provide feedback to semiconductor manufacturers looking to mitigate latent defects that may initiate and propagate during processing. Multiple ITO film thicknesses in different residual stress states of ITO are tested. Results show that indentation testing is capable of assessing the brittleness of ITO on glass when experimental and material system artifacts are taken into account. Multiple examples of nanoindentation and nanoscratch testing are provided with a focus on advantages and improved sensitivity over related techniques.

9:00am **MC2-2-WeM-4 The Effect of Nitrogen Flow Rate and Deposition Power on the Mechanical Properties and Microstructure of TiN Thin Film Deposited by HCD-IP Method**,
Ching-Cheng Chen (moricechen@gmail.com), *K. Lan,* National Tsing Hua University, Taiwan

Due to the high strength-to-weight ratio, aluminum alloys are widely used in various industries. However, relatively low surface hardness limits the development of aluminum alloys. Various coatings deposited by PVD method have been proposed to enhance the surface hardness and corrosion resistance. Due to the excellent hardness, TiN coating is commonly used as a protective film. In addition, its dense structure effectively inhibits the corrosion of metal substrate. It was reported that substrate bias significantly affects the ZrN film structure deposited on AISI stainless steel 304, resulting in improved corrosion resistance [1]. Elevated deposition temperature helps the growth of ZrN thin film with a high quality. However, aluminum alloys might loss its hardness after high temperature depositions, and there are few articles discussing the effect of bias on the mechanical properties and corrosion resistance of TiN thin film when depositing under low-temperature by hallow cathode deposition ion-plating method (HCD-IP) on an aluminum alloy substrate.

Therefore, the purpose of this study was to investigate the effect of substrate bias on the mechanical and corrosion properties of TiN thin films coating on the aluminum alloy 6061. The TiN thin films were deposited by HCD-IP system under low temperature (<200℃). After deposition, the structure and texture of TiN thin films were confirmed by scanning electron microscope (SEM) and X-ray diffraction (XRD). Scratch test and nanoindentation were carried out to measure the adhesion strength and surface hardness. Salt spray test and polarization curve were used to evaluate the corrosion resistance of the TiN coated samples.

[1] J.-H. Huang, C.-Y. Hsu, S.-S. Chen, G.-P. Yu,”Effect of substrate bias on the structure and properties of ion-plated ZrN on Si and stainless steel substrates”, Materials Chemistry and Physics 77 (2002) 14–21

9:20am **MC2-2-WeM-5 Effect of Metal Interlayers on Stress Relief of Mo_2N/Mo and Mo_2N/Ti Bilayer Coatings on Si Substrate by High Power Impulse Magnetron Sputtering**,
Yun-Yang Sun (yysunk@gapp.nthu.edu.tw), *J. Huang,* National Tsing Hua University, Taiwan

The purpose of this study is to investigate the effect of different metal interlayers and interlayer thickness on the relief of residual stress in g-Mo_2N/metal bilayer coatings. Previous studies [1,2] have indicated that the metal interlayers such as Ti and Zr in transitional metal nitride/metal bilayer systems can significantly relieve stress, where the interlayer with a sufficient thickness can act as a buffer layer and relieve stress through plastic deformation, and the interlayer is usually under tensile stress state. However, when the thickness of interlayer is insufficient, the metal interlayer will act as a transitional layer to transfer the stress to the substrate. Mo is one of the metals that is commonly used in metal interlayer. However, from our previous study [1], the plastic properties of the metal interlayer, such as strength coefficient and strain hardening coefficient, may strongly affect the behavior of plastic deformation and change the capability of stress relief. Therefore, this study aimed to investigate the elastic and plastic properties of Mo and Ti interlayers on stress relief of Mo_2N coating on Si substrate. Mo_2N coatings were deposited on Si substrate by high power impulse magnetron sputtering (HiPIMS). The thickness of the coatings was controlled at about 1000 nm and Ti and Mo interlayers were set at 100, 150, 200, and 250 nm deposited by dc-UBMS. After deposition, the Mo/(Mo+N) ratio was determined by electron probe microanalysis, and the thickness of specimens was measured by the cross-sectional images from scanning electron microscopy and confirmed by the compositional depth profiles using Auger electron spectroscopy. X-ray diffraction were used to characterize the crystal structure and texture. The residual stress was measured by laser curvature measurement and average X-ray strain methods. Hardness and elastic constant were assessed by nanoindentation, and the atomic force microscopy was used to measure the surface roughness.

[1] J.-H. Huang, I-S. Ting, T.-W. Zheng, Surf. and Coat. Technol. 434 (2022) 128224.

[2] J.-H. Huang, I-S. Ting, P. -W. Lin, J. Vac. Sci. Technol. A 41 (2023) 023104.

9:40am **MC2-2-WeM-6 Microstructure and Mechanical Behavior of Magnetron Co-Sputtering Mo-Ta-N Coatings**, ***JIA-YI HSU (u0978750703@gmail.com)**, F. Wu,* Department of Materials Science and Engineering, National United University, Miaoli , Taiwan

The binary refractory metal nitride, Mo-Ta-N, coatings were fabricated and characterized in this study. The relationship between its microstructure and mechanical properties of the magnetron sputtering Mo-Ta-N coatings were investigated. The coatings were deposited using radio frequency reactive magnetron co-sputtering technique with input power control. The Mo-Ta-N thin films were prepared under a fixed inlet gas Ar/N_2 ratio and input power of 12/8 sccm/sccm and 150 W on Mo, respectively. The input power of Ta was tuned from 50 to 150 W to adjust the microstructure and composition. The addition amount of Ta and the deposition rate increased monotonically from 3.7 to 16.8 at.% and from 5.4 to 6.7 nm/min, respectively, as a function of Ta input power, while the (Mo+Ta)/N ratio kept a steady value around 1.0. The Mo-N film showed well-defined Mo_2N (111) and (200) facets with minor MoN (111) and (220) reflections. The Mo-Ta-N coatings exhibited a polycrystalline microstructure with MoN(111), Mo_2N(111), Mo_2N(200), TaN(111), TaN(200) and TaN(220) multiple phases and showed the nano-crystalline structure according to the broadened diffraction peaks. A maximum hardness of 18 GPa was found for the Mo-Ta-N coating deposited at an input power of 150/100 W/W. A sufficient adhesion was revealed and a better wear resistance was realized for Mo-Ta-N coatings with 6.8 and 10.4 at.% Ta and nanocrystalline multiple phase feature.

Keywords: refractory metal nitride, Mo-Ta-N, co-sputtering, multiple phase, nanocrystalline.

11:00am **MC2-2-WeM-10 Function of Mo Metal Interlayer in γ-Mo_2N/Mo Bilayer Coatings on D2 Steel Deposited by High Power Pulsed Magnetron Sputtering**, *Y. Fang, **Jia-Hong Huang (jhhuang@mx.nthu.edu.tw)**,* National Tsing Hua University, Taiwan

The purpose of this study was to investigate the function of Mo metal interlayer in the γ-Mo_2N/Mo bilayer coatings deposited by high power pulsed magnetron sputtering (HPPMS) on D2 steel substrate. The interlayer thickness was designed from 50 to 150 nm, and the thickness of γ-Mo_2N was controlled at 1000 nm. The results indicated no significant change in chemical compositions, microstructure, and mechanical properties of the Mo_2N coatings by adding a Mo interlayer. The residual stress of the bilayer coatings was measured by two methods. Laser curvature method was applied to measure the overall stress of the bilayer samples on Si substrate. The stress in individual layers was measured by the average X-ray strain method. For samples on Si substrate, the compressive stress in Mo interlayer was higher than that of the Mo_2N coating, which was also much higher than the yield strength of Mo ($\sigma_{y,Mo}$). This is quite different from the expected function that the interlayer can relieve stress by plastic deformation. The stress measurements on samples on D2 steel substrate showed that the Mo interlayer is under a very high compressive stress (> $6\sigma_{y,Mo}$), indicating that the interlayer cannot relieve stress by plastic deformation. Instead, the interlayer serves as a transitional layer that transfers the stress in Mo_2N to D2 steel substrate, where the D2 steel near the interface relieve the stress by plastic deformation, and the extent of stress relief is related to the interlayer thickness. The high strength coefficient and strain hardening exponent may be the reason that Mo cannot serve as a buffer layer but become a transitional layer. All samples show quite low wear rate, where the formation of the self-lubricating Magnéli oxides may be the major factor. Although the Mo interlayer can increase the adhesion strength of Mo_2N coating on D2 steel substrate, it is not necessary to add a Mo interlayer because the adhesion strength of Mo_2N on D2 steel substrate is sufficient for the wear test. Moreover, adding a Mo interlayer withinadequate thickness (50 nm) may not be beneficial to the stress relief of the Mo_2N coatings.

11:20am **MC2-2-WeM-11 Micro-Arc Oxidation of Commercially Pure Titanium Subjected to Hydrostatic Extrusion**, ***Lukasz Maj (l.maj@imim.pl)**,* Institute of Metallurgy and Materials Science, Polish Academy of Sciences, Poland*; F. Muhaffel,* Istanbul Technical University, Turkey*; A. Jarzebska, A. Trelka, D. Wojtas, K. Trembecka,* Institute of Metallurgy and Materials Science, Polish Academy of Sciences, Poland*; J. Kawalko,* AGH University of Science and Technology, Poland*; M. Kulczyk,* Unipress Extrusion, Poland*; M. Bieda,* Institute of Metallurgy and Materials Science, Polish Academy of Sciences, Poland*; H. Cimenoglu,* Istanbul Technical University, Turkey

Micro-arc oxidation (MAO) proved itself as very efficient method of the surface modification of so-called “valve metals” like titanium, aimed at improving their properties like wear resistance, bioactivity, antibacterial performance, etc. Enhancement of above-mentioned properties is connected with formation of well adhering oxide coating on the top of the substrate material thanks to the electrochemical reactions driven by the ions exchange between the substrate and electrolyte. Thus, not only the selection of proper electrolyte and MAO process conditions is important, but also microstructure of the substrate material. The plastic deformation of the substrate material may also affect the mechanisms of the oxide formation.Grain refinement and formation of higher density of low angle (LAGB) and high angle grain boundaries (HAGB) allows many more sites for the oxides nucleation to be formed what accelerates the coating formation. Application of severe plastic deformation techniques such as hydrostatic extrusion provided amazing results in terms of strengthening of metallic materials such as titanium, allowing for its widespread application, especially as future dental implants. Owing to the hydrostatic extrusion characteristics microstructure refinement down to the nanometric scale may be achieved, increasing strongly the density of LAGB and HAGBs, also having a huge impact on eventual surface modification with the methods like MAO.However, there is a lack of information about microstructure and tribological properties of the MAO coatings deposited on the surface of hydrostatically extruded titanium. In this work, titanium grade 4 substrates was subjected to 3-pass hydrostatic extrusion and subsequent rotary swaging reducing the initial diameter from 50 mm down to 5 mm.The rods were cut into diameter and subjected to MAO process in phosphate-based electrolyte with the help of the bipolar pulsed power supply.Such power supply allows for far better control of the electrochemical reactions during the deposition process than direct current or unipolar pulsed ones.Before the MAO coatings deposition, the cp-Ti substrates were thoroughly investigated in terms of determination of the HAGB and LAGB density with the SEM/EBSD method in order to determine their influence on the properties of the forming oxide surface layer. The microstructure observations (SEM/TEM) supported by phase and chemical analysis (XRD, SAED, EDS) allowed us discuss the mechanisms of oxide coating formation and correspond to their tribological behavior.

Acknowledgement: This research was funded by the National Science Centre of Poland, grant number UMO-2020/39/D/ST8/01783.

11:40am **MC2-2-WeM-12 Effect of Ultrasonic-Assisted Machining for Surface Functionalization of Innovative Work-Hardening Multi-Principal-Element Alloys**, ***Marcel Giese (marcel.giese@bam.de)**, D. Schroepfer, M. Rhode,* Bundesanstalt für Materialforschung und -prüfung, Germany*; B. Preuss, T. Lindner, N. Hanisch, T. Lampke,* Institute of Materials Science and Engineering (IWW), Chemnitz University of Technology, Germany

Multi-principal-element alloys (MPEAs) are an alloying concept consisting of at least two main alloying elements resulting in unique microstructures and potentially superior physical, mechanical and chemical properties, for instance a high work hardening capacity. These characteristics are determined by four core effects: sluggish diffusion, severe lattice distortion, high-entropy and cocktail effect. The development of MPEAs is a promising approach to extend the range of applications of conventional alloys by exploiting these core effects. In the present study, as reference to the conventional high-manganese steel X120Mn12 (ASTM A128), characterized by particularly high work hardening capacity generating exceptional mechanical properties, work-hardening MPEAs based on the equimolar composition CoFeNi in combination with Mn and C were developed. Specimens were produced as bulk material by melting via an electric arc furnace. In a second step the specimens undergo a surface finishing via milling process. Therefore, a hybrid milling process was used which, in addition to producing defined surfaces, also has the potential to reduce tool wear and increase surface integrity by introducing compressive stresses and increasing hardness through pronounced work hardening in comparison to conventional machining. The so-called ultrasonic-assisted milling (USAM) is characterized by an axial oscillation of the tool during the milling process. The machining parameters were varied to analyze the effect on work hardening together with process forces during milling and resulting surface integrity. Subsequently, microstructure evolution, hardness as well as resulting wear resisting capacity were investigated and correlated with the composition and the USAM parameters. For the MPEA CoFeNi-Mn12C1.2 a pronounced lattice strain and grain refinement due to the plastic deformation during the USAM was recorded, especially at high USAM amplitude and lower cutting speed due to the greater number of tool oscillations per cutting engagement. Consequently, a hardness increase of up to 380 HV0.025 was induced for the aforementioned MPEA exhibiting a higher wear resistance compared to the X120Mn12. This shows the promising approach for the development of work-hardening materials based on new alloy concepts such as MPEAs allowing also coatings required for applications in tribological systems. As conventional hard and wearresistant coatings are challenging in machining due to massive tool wear this approach of functional coating materials with high hardening capacity during USAM have the potential to reduce tool wear and ensure a adequate surface integrity and wear resistance.

12:00pm **MC2-2-WeM-13 Metal/Oxide Nanolaminates of Al/Al2O3 by PVD-ALD: Understanding & Maximising Strength-Ductility**, ***Thomas Edwards (thomas.edwards@empa.ch)***, NIMS (National Institute for Materials Science), Japan*; B. Putz, T. Xie, L. Vogl, H. Jansen, A. Groetsch, M. Watroba, J. Michler,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland

The extent of the embrittlement in ductile-brittle multilayers often depends on the modulation period ($t_{brittle}$ + $t_{ductile}$) as well as on the modulation ratio ($t_{brittle}/t_{ductile}$) [1]. In this work, ductile-brittle multilayers of Al / Al_2O_3 / Al... were produced on Si substrates by a unique combination of atomic layer (ALD, Al_2O_3) and physical vapour deposition (PVD, Al) within a single deposition system. Using this ALD/PVD combination, neighbouring layer thicknesses can easily differ by one order of magnitude or more. In particular, the ability to deposit continuous sub-nm layers with ALD opens up a wide range of otherwise unachievable modulation and thickness ratios. The thicknesses and structures of the ALD layers were verified by HR-TEM imaging of lift-outs. The amorphous oxide layer thickness was previously optimised in the 0.1 nm – 10 nm range by microcompression, considering crack onset and propagation as a function of oxide layer thickness in tensile tested multilayer films. Here, the crystalline metal layer thickness is varied (10 nm – 250 nm) to optimise strength. The multilayer structure has good adhesion between individual layers and the oxide layers show increasing stretchability with decreasing film thickness. *In situ* TEM tensile loading was performed to evaluate the role of the amorphous-crystalline interfaces on dislocation motion in metallic layers, whilst microcompression at variable temperature and strain rate was used to quantify the activation parameters; this is compared with molecular dynamics simulations. The thermal stability of such multilayer films was also studied up to 0.9 T/T_m.

[1]K. Wu, J.Y. Zhang, J. Li, Y.Q. Wang, G. Liu, J. Sun, Acta Mater. 100 (2015) 344–358.

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