Hard Coatings and Vapor Deposition Technologies
Room California - Session B6-ThM

Coating Design and Architectures

Moderators: Shou-Yi Chang, National Tsing Hua University, **Paul Heinz Mayrhofer**, Institute of Materials Science and Technology, TU Wien, Austria

8:00am **B6-ThM-1 The Mechanical and Tribological Properties of Boron Based Films Grown by HiPIMS Under Different N_2 Contents***, A Keleş, **Ihsan Efeoğlu**, Y Totik,* Ataturk University, Turkey

The cubic phase of boron nitride (c-BN) has significant technological potential for thin film applications. It is generally compared with diamonds due to c-BN properties. c-BN is a semi-stable, high temperature and high pressure (HPHT) stable phase with high strength covalent bond and the second highest hardness. However, c-BN film has low adhesion at the interface due to high compressive internal stress. To overcome this problem, c-BN films were coated with HiPIMS-CFUBMS under three different N_2 contents (2.5 sccm, 3 sccm, 3.5 sccm). Before deposition of c-BN film, Ti-TiN-TiB_2-TiBN-TiBCN graded composite layers were coated for improving the adhesion. The structural properties were identified using SEM. The chemical properties were determined using XPS. The c-BN content and internal compressive stress were calculated using FT-IR. The mechanical properties were carried out by microhardness tester and scratch tester. The tribological properties were experimented with pin-on-disc tribometer. The maximum hadness (45GPa) and minimum critical load (Lc»69N) values were obtained from the lowest N_2 content (2.5sccm). Also, the minimum friction coefficient value was 0.622. The results showed that c-BN films coated with HiPIMS is very up-and-coming.

8:20am **B6-ThM-2 Peculiar Oscillations in Nano-scale AlN/TiN and Other Nitride-based Superlattices***, **Nikola Koutna**,* Institute of Materials Science and Technology, TU Wien, Austria*; P Řehák,* Institute of Physics of Materials, Academy of Sciences of the Czech Republic, Czech Republic*; Z Zhang,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria*; M Černý,* Central European Institute of Technology, CEITEC VUT, Brno University of Technology, Czech Republic*; M Bartosik,* Institute of Materials Science and Technology, TU Wien, Austria*; M Friák, M Šob,* Institute of Physics of Materials, Academy of Sciences of the Czech Republic, Czech Republic*; P Mayrhofer,* Institute of Materials Science and Technology, TU Wien, Austria*; D Holec,* Department of Physical Metallurgy and Materials Testing, Montanuniversität Leoben, Austria

Superlattices with layer thicknesses of only a few nm cannot be simply understood based on the knowledge of their monolithic building components. Different phases and/or their mutual orientation together with the presence of interfaces may lead to peculiar physical phenomena, such as partial structural transformations, superhardening or supertoughening effects.

This talk centers around an AlN/TiN multilayered system, combining materials that are very popular in industrial applications. Though considerable experimental as well as modelling efforts have been devoted to AlN/TiN system, the atomic-scale effects of the interface are not fully understood. Our ab initio calculations reveal interplanar spacing oscillations stemming from the presence of the interface and the corresponding changes in the electronic structure. The character of these oscillations differs significantly in each material–AlN and TiN–based on the superlattice-forming phases (metallic TiN vs. semiconducting AlN, or cubic vs. hexagonal AlN) and their orientation (e.g., (001) vs. (111)), influencing the critical distance from the interface above which the oscillations disappear. The oscillatory behaviour of atomic displacements have also important consequences for elastic constants as well as the cleavage properties in terms of theoretical critical stress and energy for brittle cleavage. Our Density Functional Theory calculations are corroborated with observations from high resolution transmission electron microscopy. Consequently, atomistic reasons for superior mechanical properties of AlN/TiN multilayered systems are proposed. Our findings are compared with the relevant predictions for other superlattice architectures containing (meta)stable phases of transition metal nitrides.

8:40am **B6-ThM-3 Impact Fatigue and Mechanical Properties of AlTiCrN and AlTiCrSiN Hard Coatings with Optimal Design of Interlayers***, **Yu-Ju Yang**, Y Chang, S Weng,* National Formosa University, Taiwan

Optimal design of interlayers of a hard coating can offer an efficient way of controlling residual stress, improving adhesion strength and enhancing toughness. Transition metal nitrides, such as AlTiCrN, have been used as protective hard coatings due to their high hardness and high resistance to high temperature oxidation. In this study, AlTiCrN and AlTiCrSiN coating was deposited by cathodic-arc evaporation (CAE). During the coating process of AlTiCrN and AlTiCrSiN, TiN and CrN were deposited, respectively, as interlayers with different graded structures to control residual stress, toughness and adhesion strength between the coatings and substrates. The microstructure of the coatings was characterized by using a field emission scanning electron microscope (FE-SEM), equipped with an energy-dispersive x-ray analysis spectrometer (EDS). Glancing angle X-ray diffraction (XRD) was used to characterize the microstructure, phase identification and residual stress. The chemical composition was also evaluated. The thickness and alloy content of the deposited coating were correlated with the evaporation rate of cathode materials. Mechanical properties, such as the hardness and elastic modulus, were measured by means of nanoindention and Vickers hardness measurement. To study the correlation between impact fracture resistance and hardness/elastic modulus ratio of the deposited coatings, an impact test was performed at 500 °C using a cyclic loading device with a tungsten carbide indenter as an impact probe. The results indicated that all the AlTiCrN and AlTiCrSiN coatings exhibited (Al,Ti,Cr)N solid solution phases with NaCl-type structure. The design of AlTiCrN hard coatings with optimal designed interlayers of CrN and AlTiCrN/CrN can decrease residual stress, enhance hardness and toughness, which were effective to elimination of cracking of hard coatings. The AlTiCrN and AlTiCrSiN hard coatings with multilayered interlayers of CrN and AlTiCrN/CrN possessed the best resistance to plastic deformation and the highest impact fatigue resistance. The AlTiCrN and AlTiCrSiN hard coatings with optimal design of interlayers can be good candidates for piercing, punching and molding applications.

9:00am **B6-ThM-4 Improvement of CrMoN/ SiN_x Multilayered Coatings on Mechanical and High Temperature Tribological Properties***, **Wei-Li Lo**, L Yeh-Liu, J Lee, J Duh,* National Tsing Hua University, Taiwan

In this study, CrMoN/SiN_x multilayered coatings were deposited by controlling the shutter-open time of two sputtering guns in a radio frequency magnetron sputtering system. CrMoN/SiN_x thin films with different bi-layer periods were fabricated on both Si-wafer and Inconel-718 substrates. The chemical composition of as-deposited CrMoN/ SiN_x coatings were obtained by a field emission electron probe micro-analyzer (FE-EPMA). The confirmation of multilayered structure and crystallization characterization were carryied out using a transmission electron microscope (TEM). The phases of the coatings were analyzed by a grazing incidence X-ray diffraction (XRD). Mechanical and high-temperature tribological properties were estimated using a nano-indenter and a high-temperature tribometer (ball-on-disc), respectively.

The grain refinement phenomenon was verified using XRD peak broadening at high angles, indicating inhibition in the column structure and the formation of an amorphous phase. The CrMoN/SiN_x multilayered coatings exhibited high-temperature tribological properties for a specific bi-layer period, which was attributed to the multilayer strengthening mechanism. Multilayered structure provided enormous benefit to COF improvement, which was reduced by 50% of the value of CrMoN. In the meanwhile, the toughening effect of the multilayered structure design also improved the wear resistance ability of the coatings. Moreover, the best bi-layer period was identified, resulting in favorable mechanical and high-temperature tribological properties. Eventually, a CrMoN/SiN_x multilayer coating with enhanced high-temperature characteristics was demonstrated and discussed in this study.

9:20am **B6-ThM-5 Tuning the Hardness–toughness Relationship by Combining MoN with TaN***, F Klimashin, N Koutna, L Lobmaier,* TU Wien, Institute of Materials Science and Technology, Austria*; D Holec,* Montanuniversität Leoben, Austria*; **Paul Heinz Mayrhofer**,* TU Wien, Institute of Materials Science and Technology, Austria

Recently we showed that cubic-structured Mo–N and Ta–N exhibit an inherent driving force for vacancies at the nitrogen and metal sublattice, respectively. To shed light on their interaction and effects on structural evolution and mechanical properties within the ternary system Mo–Ta–N, we have synthesised coatings by means of reactive magnetron sputtering with varying nitrogen partial pressure. Low nitrogen partial pressures, resulting in high concentration of vacancies on the N sublattice, allow one to stabilise single-phase cubic-structured solid solutions up to a high metal fraction of Ta of x = Ta/(Mo+Ta) of at least 0.76. These solid solutions form with vacancies predominantly at the nitrogen sublattice, with increasing vacancy concentration upon increasing x. Furthermore, with increasing x to 0.56, also the compressive residual stresses increase to -2 GPa, the hardness increases to 36 GPa, and the fracture toughness increases to 7 MPa√m. Schottky defects, energetically favoured at higher tantalum concentration (at least up to x = 0.76), cause in turn the relaxation of compressive residual stresses to -1.3 GPa and reduction in hardness to 29 GPa and fracture toughness to 5 MPa√m. On the contrary, high nitrogen partial pressures favour vacant sites on the metal sublattice of cubic-structured solid solutions, which are the major constituent in these dual-phased coating. The hardness of these dual-phase coatings is mainly determined by the fraction of the coexisting hexagonal phase, which appears to be the harder constituent. However, neither hexagonal phases nor vacancies at the metal sublattice are desirable when aiming to combine high hardness with high fracture toughness in this Mo–Ta–N system. The fracture toughness would be reduced to 2.5 MPa√m. The binary γ-$MoN_{0.89}$ with partially ordered vacancies on metal and non-metal sublattices possesses the highest toughness among all coatings studied with 8 MPa√m, while showing a moderate compressive residual stress of -2 GPa and hardness of 28 GPa. Our findings show that by combining materials with a driving force for metal or nitrogen vacancies, both routes of structural evolution can be designed, allowing to tune their mechanical and elastic properties.

9:40am **B6-ThM-6 Microstructure, Mechanical and Tribological Performance of Complex TiAlTaN-[TiAlN/TaN_n] Coatings: Understanding the Effect of Volume Fraction***, Elbert Contreras, J Cortínez,* Universidad de Antioquia, Colombia*; A Hurtado,* Centro de Investigación en Materiales Avanzados CIMAV, Mexico*; M Gómez,* Universidad de Antioquia, Colombia

Recent studies have shown that by modifying the coatings architecture it is possible to obtain significant improvements in their mechanical and tribological properties. In the present work four complex TiAlTaN-[TiAlN/TaN_n] coatings were deposited, varying the volume fraction of the top quaternary coating (TiAlTaN) and the base multilayer coating (TiAlN/TaN) with percentages of: 20/80, 40/60, 60/40 and 80/20, and evaluating their effect on mechanical and tribological performace of the complex coatings. The cross-sectional images obtained by FIB-SEM showed the interface between each of the constituent monolayers, a well-defined columnar structure was also observed for the TiAlN/TaN multilayer coating, while in the quaternary TiAlTaN coating a refinement was observed in the columns with denser and compact structures. High-resolution TEM analysis revealed well-formed multilayer composites with very smooth layers. The complex TiAlTaN-[TiAlN/TaN_n] coatings did not exhibited a significant difference in their crystalline structure, however, once calculating the residual stresses by XRD, it was found that by increasing the volume fraction of the multilayer in the coatings there is a decrease in the compressive residual stresses. Regarding the mechanical properties, it was possible to observe an increase between 20-25% when increasing the volume fraction of the multilayer, as well as an increase in resistance to plastic deformation (H^3/E^2), fracture toughness and in the adhesion of complex architecture coatings. With respect to tribological properties, TiAlTaN-[TiAlN/TaN_n] coatings exhibited lower friction coefficients and wear rates compared to constituent monolayers. Using cross-section FIB it was possible to observe initial deformation in the constituent layers followed by the propagation of cracks along the interfaces between TiAlTaN, TiAlN and TaN layers, in nanoindentation tests, scratch tests and tribological tracks.

10:00am **B6-ThM-7 Plastic Deformation in Transition-Metal Nitrides and Carbides via Density-Functional Molecular Dynamics***, Davide Sangiovanni,* Linköping University, Sweden, Ruhr-Universität Bochum, Germany **INVITED**

Hard refractory transition-metal nitrides and carbides (TMN and TMC) possess unique combinations of outstanding physical and mechanical properties. As most ceramics, however, TMN and TMC are typically inherently brittle. Recent theoretical and experimental results have demonstrated that TMN can be made *bothhard* (~20 – 25 GPa) *and ductile* via manipulation of electronic structures and control of phase stability. This surprising finding addressed a long-standing question in materials science on whether hardness and ductility are necessarily mutually exclusive properties in a single-crystal ceramic phase. Nevertheless, it is still puzzling how high hardness and excellent ductility may coexist given that the two properties are affected in opposite manner by plastic deformation.

This seminar will be divided in three parts. (*i*) I will first describe density-functional theory results to explain the effects induced by valence electron concentrations and phase stabilities on toughness of TMN and TMC; (*ii*) Then, I will show the results of finite-temperature *ab initio* molecular dynamics (AIMD) simulations of tensile, shear deformation, and nanopillar compression to clarify the atomistic pathways with associated changes in electronic structures responsible for brittleness (TiN and VN) vs. supertoughness (VMoN, VN_x); (*iii*) Finally, I will give an overview of AIMD simulations for slip system activation/quenching as a function of temperature and pressure to demonstrate unusual non-Schmid behavior in TMC. All first-principles results will be discussed in comparison with, and supported by, experimental findings.

10:40am **B6-ThM-9 Phase Evolution and Mechanical Properties of Isostructural Decomposing $W_{1-x}M_xB_2$ Thin Films***, Vincent Moraes, L Zauner,* TU Wien, Institute of Materials Science, Austria*; H Bolvardi,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P Polcik,* Plansee Composite Materials GmbH, Germany*; H Riedl, P Mayrhofer,* TU Wien, Institute of Materials Science, Austria

The increasing demand in various industrial applications calls for a target-driven development of protective coatings with exceptional properties. Therefore, transition metal nitrides have been studied and developed extensively. However, the exploration of new protective coating systems is required to meet upcoming challenges not only in machining applications. A rather new promising class of materials – to be used as protective thin films – are borides. Especially, multinary borides are rather unexplored compared to their nitride-based counterparts. Coherent phase separation effects of supersaturated single-phased structures such as age hardening in $Ti_{1-x}Al_xN$ based thin films was a key-factor for the success being nowadays one of the most important material combination in thin film industries. The formation of coherent domains through spinodal decomposition ($Ti_{1-x}Al_xN$ into TiN- and AlN-rich cubic domains) allows for significant strengthening effects at elevated temperatures (for example, as obtained during application). Transferring the concept of two competing phases from nitrides to borides is a promising approach to find new materials with outstanding properties already in the as deposited state. Different ab initio and experimental studies [1-3] already showed that WB_{2-z} thin films preferable crystallize in their metastable α-AlB_2 modification (space group 191), being an excellent origin for ternary alloying concepts considering the decomposition to its stable ω-W_2B_{5-x} configuration (space group 194).

In this study, we experimentally investigated the structural and mechanical evolution for selected ternary $W_{1-x}M_xB_2$ based thin films concerning spinodal decomposition. Especially, not only the effect of coherent phase separation on the hardness but also fracture toughness has been correlated with temperature. This aspect is highly important, as most of the α-AlB_2 structured diborides (e.g. TiB_2, ZrB_2, or CrB_2) suffer extremely low damage tolerance. In addition, the phase evolution with respect to structural defects (e.g. metal or boride vacancies) was also investigated by ab initio based calculations.

Keywords: W_2B_{5-x} based diborides; multinary borides; mechanical properties; coherent phase separation;

[1] B. Alling, H. Högberg, R. Armiento, J. Rosen, L. Hultman, Sci. Rep. 5 (2015) 9888.

[2] V. Moraes, H. Riedl, C. Fuger, P. Polcik, H. Bolvardi, D. Holec, P.H. Mayrhofer, Sci. Rep. 8 (2018) 9288.

[3] V. Moraes, C. Fuger, V. Paneta, D. Primetzhofer, P. Polcik, H. Bolvardi, M. Arndt, H. Riedl, P.H. Mayrhofer, Scr. Mater. 155 (2018) 5–10.

11:00am **B6-ThM-10 Van der Waals Layer Promoted Heteroepitaxy in Sputter-deposited Thin Films***, Koichi Tanaka, P Arias, M Liao, Y Wang, H Zaid, A Aleman, M Goorsky, S Kodambaka,* University of California, Los Angeles, USA

We demonstrate that the crystallinity of sputter-deposited thin films can be significantly improved using two-dimensional (2D) van der Waals (vdW) layered materials as the buffer layers on substrates. Using hexagonal boron nitride (hBN) (a = 0.250 nm and c = 0.667 nm) as the 2D vdW buffer layer, we grow trigonal-structured Ta_2C (a = 0.310 nm and c = 0.494 nm) thin films of desired thickness (t = 17 ~ 75 nm) on Al_2O_3(0001) substrates via ultra-high vacuum direct current magnetron sputtering of TaC compound target in 20 mTorr pure Ar gas atmospheres at 1373 K. hBN layers are deposited via pyrolytic cracking of borazine (~600 L) onto Al_2O_3(0001) substrates at 1373 K. The as-deposited Ta_2C films are characterized *in situ* using Auger electron spectroscopy and low-energy electron diffraction and *ex situ* using X-ray diffraction (XRD) and transmission electron microscopy (TEM) based techniques. For the same Ta_2C film thickness, the notable differences in the layers deposited on hBN-covered Al_2O_3(0001) compared to those grown on bare substrates are: observation of 6-fold symmetric LEED pattern, significantly stronger (20x´) 0002 reflection intensity in ω-2θ XRD scans, and observation of Laue oscillations around the 0002 peak. Furthermore, we show that inserting hBN layers at regular intervals results in highly-0002-oriented growth and suppression of polycrystallinity in thicker Ta_2C films.

11:20am **B6-ThM-11 Improvement of Tribological Properties for Hard Coatings by Stress Control**, ***Tianmin Shao,*** State Key Laboratory of Tribology, Tsinghua University, China

For the application of hardcoatings, stress level in coating/substrate systems is one of the main factors influencing their tribological properties. In many applications, effective control of stresses is of great importance for the performance and working life of hard coatings. Generally, the stress inside coatings subjected during service is a combination of external stress and intrinsic stress. The external stress is mainly determined by the applied working load, and the intrinsic stress depends on the coating material, the structure of coating, property mismatch between coating and substrate, coating production process, etc. In this presentation, control of intrinsic stress by properly design of coating/substrate system is studied. As examples, studies on stress control by textured coating technique and design of layered structures are introduced. Tribological properties of several hard coatings are experimentally studied and the results are discussed based on stress analysis. Results show that both textured coating and layered structure can be used for stress control of coating/substrate systems, and eventually improving their tribological properties.

Keywords: stress control; tribological property; hard coating; textured coating; layered structure

11:40am **B6-ThM-12 Is WB_{2-z} a Proper Base System for Designing Ternary Diboride based Thin Films?**, ***Helmut Riedl***, *V Moraes, C Fuger, H Euchner, R Hahn, T Wojcik,* TU Wien, CDL AOS at the Institute of Materials Science, Austria; *M Arndt,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein; *P Polcik,* Plansee Composite Materials GmbH, Germany; *P Mayrhofer,* TU Wien, Institute of Materials Science, Austria

Future tasks in many different fields of academia and industry are directed towards environmental sustainability, and hence the application of ultra-stable materials featuring novel properties. A rather new and highly promising class of thin film materials are borides. Especially, transition metal borides (TMBs) exhibit a tremendous potential to be applied in various applications ranging from wear and corrosion resistant coatings, to superconductive thin films, or as superhard and extremely stable protective layers in diverse fields of engineering. In contrast to classic diborides – such TiB, ZrB_2,WB_2, or ReB_2, which has been theoretically predicted to be the most incompressible material exceeding the properties of diamond – are ternary or even multinary diborides (e.g. $W_{1-x}M_xB_2$) relatively unexplored. Based on atomistic modelling studies [1,2] (Density Functional Theory calculations) is the stabilization of ternary diborides dominated by two hexagonal competing structure types – α–AlB_2-prototype (SG-191) vs. ω-W_2B_{5-x}-prototype (SG-194) – as well as structural defects (especially vacancies). These facts emphasize distinct difficulties for PVD based synthesis of ternary diboride thin films.

Within this study, we want to address the challenges in depositing ternary diborides in a prototype based on α-$W_{1-x}M_xB_2$ solid solutions, applying non-reactive sputtering processes, whereas M represents different transition metals such as Ta or Ti [2]. Due to the strong tendency of WB_2 to be stabilized through structural defects in the AlB_2 structure type – exhibiting distinct advantages concerning the relatively low ductility of TMBs in general – it can be an excellent base system for studying various alloying concepts utilizing physical vapour deposition (PVD) techniques. To gain an in-depth insight on the specific effects of selected transition metals on α structured $W_{1-x}M_xB_2$ coatings, we correlated the synthesis parameter with structure property relationships applying a set of high-resolution characterization techniques as well as micro-mechanical testing methods – also after exposing to diverse aggressive- environments in terms of oxidation and thermal treatments.

References

[1] B. Alling, et al., A theoretical investigation of mixing thermodynamics, age-hardening potential, and electronic structure of ternary $M(1)_{1-x}M(2)_xB_2$ alloys with AlB_2 type structure, Sci. Rep. 5 (2015) 9888.

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