

Monday Morning, October 19, 2015

Advanced Surface Engineering

Room: 212A - Session SE+AS+NS+TR-MoM

Nanostructured Thin Films and Coatings

Moderator: Robert Franz, Montanuniversität Leoben, Austria, Andrey Voevodin, Air Force Research Laboratory

8:20am **SE+AS+NS+TR-MoM1 Reactively Sputter Deposited Ternary AlN-based Coatings**, *Joerg Patscheider*, Empa, Switzerland, *E. Lewin*, Uppsala University, Sweden

The protection of surfaces against preventing premature failure by abrasion-resistant nitride coatings has been investigated and put into daily operation ever since. Despite these efforts, the wide range of available protective coatings cannot be used, when glass and other optically transparent materials have to be protected due to the opacity of transition metal nitrides for visible light. For such applications thin films based on Al-A-N with additions of elements from group 14 with A = Si, Ge or Sn are attractive candidate materials, as their transparency in the visible range opens new opportunities of applications. Furthermore, the addition of these elements causes the formation of solid solutions and of nanocomposites, leading to enhanced hardness in the case of A = Si and Ge. Once nanocomposites are formed, enhanced hardness of more than 30 GPa is observed in the case of Al-Si-N and more than 20 GPa for Al-Ge-N and Al-Sn-N. The choice of the additional A element allows for the preparation of highly transparent coatings for the case of Si and the control of color in the range from yellow to red by tuning of the UV absorption edge in the case of Ge and Sn. The role of deposition conditions and their implications on the structure these ternary nitride coatings will be discussed.

8:40am **SE+AS+NS+TR-MoM2 Mo₂BC Coatings for Metal Forming: Interactions Between Tool Surface and Aluminium by Theory and Experiment**, *Jochen Schneider*, RWTH Aachen University, Germany, *H. Bolvardi*, Oerlikon Balzers, Liechtenstein, *D. Music*, RWTH Aachen University, Germany

Low temperature growth strategies for Mo₂BC coatings are reviewed and initial theoretical and experimental data pertaining to the applicability of these coatings during forming of Al based alloys are discussed. A Mo₂BC(040) surface was exposed to O₂. The gas interaction was investigated using *ab initio* molecular dynamics and x-ray photoelectron spectroscopy (XPS) of air exposed surfaces. The calculations suggest that the most dominating physical mechanism is dissociative O₂ adsorption whereby Mo - O, O - Mo - O and Mo₂ - C - O bond formation is observed. To validate these results, Mo₂BC thin films were synthesised utilizing high power pulsed magnetron sputtering and air exposed surfaces were probed by XPS. MoO₂ and MoO₃ bond formation is observed and is consistent with here obtained *ab initio* data. Additionally, the interfacial interactions of O₂ exposed Mo₂BC(040) surface with an Al nonamer is studied with *ab initio* molecular dynamics to describe on the atomic scale the interaction between this surface and Al to mimic the interface present during cold forming processes of Al based alloys. The Al nonamer was disrupted and Al forms chemical bonds with oxygen contained in the O₂ exposed Mo₂BC(040) surface. Based on the comparison of here calculated adsorption energy with literature data, Al - Al bonds are shown to be significantly weaker than the Al - O bonds formed across the interface. Hence, Al-Al bond rupture is expected for a mechanically loaded interface. Therefore the adhesion of a residual Al on the native oxide layer is predicted. This is consistent with experimental observations. The data presented here may also be relevant for other oxygen containing surfaces in a contact with Al or Al based alloys for example during forming operations.

9:00am **SE+AS+NS+TR-MoM3 Molecular Dynamics Simulations of TiN/TiN(001) Growth**, *Daniel Edström*, *D.G. Sangiovanni*, *V. Chirita*, *L. Hultman*, Linköping University, Sweden, *J.E. Greene*, *I. Petrov*, University of Illinois at Urbana Champaign

The Modified Embedded Atom Method (MEAM) interatomic potential within the classical Molecular Dynamics (MD) framework enables realistic, large-scale simulations of important model materials such as TiN. As a step toward understanding atomistic processes controlling the growth of TiN on a fundamental level, we perform large-scale simulations of TiN/TiN(001) deposition using a TiN MEAM parameterization which reproduces experimentally-observed surface diffusion trends, correctly accounts for Ehrlich barriers at island step edges [1], [2], and has been shown to give results in excellent qualitative and good quantitative agreement with *Ab Initio* MD based on Density Functional Theory (DFT) [3], [4]. 85% of a monolayer of TiN is deposited on 100x100 atom

TiN(001) substrates at a rate of 1 Ti atom per 50 ps, resulting in simulation times of 212.5 ns. The TiN substrate is maintained at a typical epitaxial growth temperature, 1200 K during deposition using N:Ti flux ratios of 1:1, 2:1, and 4:1 and incident energies of 2 and 10 eV to probe the effects of N₂ partial pressure and substrate bias on TiN(001) growth modes. We observe nucleation of Ti_xN_y molecules; N₂ desorption; the formation, growth and coalescence of mixed <100>, <110>, and <111> faceted islands; as well as intra- and interlayer mass transport mechanisms. For equal flux ratios at 2 eV incidence energy, islands begin to form atop existing islands at coverages ≥ 0.25 ML, leading to 3D multilayer growth. Increasing the N:Ti flux ratio shifts the growth mode to layer-by-layer growth and changes the stoichiometry from under- to over-stoichiometric. We discuss the implications of these results on thin film growth and process tailoring. Our classical MD predictions are supported and complemented by DFT-MD simulations.

[1] D. G. Sangiovanni, D. Edström, L. Hultman, V. Chirita, I. Petrov, and J. E. Greene, "Dynamics of Ti, N, and TiN_x (x=1-3) ad molecule transport on TiN(001) surfaces," *Phys. Rev. B*, vol. 86, no. 15, p. 155443, 2012.

[2] D. Edström, D. G. Sangiovanni, L. Hultman, V. Chirita, I. Petrov, and J. E. Greene, "Ti and N adatom descent pathways to the terrace from atop two-dimensional TiN/TiN(001) islands," *Thin Solid Films*, vol. 558, pp. 37-46, 2014.

[3] D. G. Sangiovanni, D. Edström, L. Hultman, I. Petrov, J. E. Greene, and V. Chirita, "Ab initio and classical molecular dynamics simulations of N₂ desorption from TiN(001) surfaces," *Surf. Sci.*, vol. 624, pp. 25-31, 2014.

[4] D. G. Sangiovanni, D. Edström, L. Hultman, I. Petrov, J. E. Greene, and V. Chirita, "Ti adatom diffusion on TiN(001): Ab initio and classical molecular dynamics simulations," *Surf. Sci.*, vol. 627, pp. 34-41, 2014.

9:20am **SE+AS+NS+TR-MoM4 Stress Design of Multi-layered Coatings**, *Wolfgang Seidl*, Christian Doppler Laboratory for Application Oriented Coating Development at the Institute of Materials Science and Technology, Vienna University of Technology, 1040 Vienna, Austria, *M. Arndt*, Oerlikon Balzers, Oerlikon Surface Solutions AG, 4946 Balzers, Liechtenstein, *P. Polcik*, Plansee Composite Materials GmbH, 86983 Lechbruck am See, Germany, *P.H. Mayrhofer*, Vienna University of Technology, Austria

Residual stresses within physical vapour deposited coatings are a major concern, as they are often the origin of failure and delamination. Furthermore, stresses, which typically scale with the thickness, limit the thickness of the coating. With increasing stresses, the interface region is increasingly stressed and weakened, promoting delamination and buckling effects. CrN coatings are known to allow for moderate compressive or even tensile stresses, enabling the preparation of coating thicknesses above 20 μ m. Although CrN coatings exhibit excellent tribological and wear resistance properties, their thermal stability with respect to Cr-N dissociation is limited to 900 °C, which limits their application field. However, several applications require higher thermal stability in combination with relatively thick ceramic coatings. Therefore, we study in detail the requirements to develop nitride-based coatings with thicknesses exceeding 20 μ m.

The residual stresses of arc evaporated TiN, CrN, TiAlN, CrAlN, and TiAlTaN coatings, prepared with an industrial sized coating plant (Balzers Oerlikon INNOVA), are investigated as a function of their thicknesses by measuring the curvature of one-side coated Si(100) cantilevers. Based on these studies we developed multilayer arrangements of TiN/CrN, TiAlN/CrN, TiAlN/CrAlN, and TiAlTaN/CrAlN thick coatings. Their stresses are designed through variations in bilayer period and arrangements of the cathodes at the sidewalls of the industrial chamber.

The individual coatings and multilayers are additionally investigated with respect to growth morphology (by cross sectional scanning electron microscopy), hardness and indentation moduli (by nanoindentation), structure and crystallographic phases (by X-ray diffraction).

9:40am **SE+AS+NS+TR-MoM5 Atomistic Guided Development of Hard Coatings and Thin Films for Severe Applications**, *Paul Mayrhofer*, Vienna University of Technology, Austria **INVITED**

This work summarizes recent developments on applying thin film structure and architecture concepts to hard coatings for optimized performance in various application fields.

The hardness of materials rapidly decreases at elevated temperatures as generally the density of structural defects, such as point defects, dislocations, and grain boundaries, decreases. Additional strengthening can be provided by age-hardening mechanisms, which originate from decomposition-processes of supersaturated phases to form new obstacles

retarding plastic deformation. Furthermore important is the resistance against oxidation and corrosive attack.

By using ab initio calculations and sophisticated experimental methods we will have a detailed insight into various mechanisms responsible for excellent mechanical strength, thermal stability and oxidation resistance properties of Ti–Al–N based hard coatings. For these materials we will also compare the effect of various architecture and alloying concepts with e.g., Y, Zr, Hf, Nb, and Ta.

Another important class of hard coatings is based on the material systems CrN and Cr–Al–N. After a short overview on ab initio and experimental studies in comparison to their sister system Ti–Al–N, we will have a small excursion on the influence of architecture – using the model system CrN/AlN multilayers or their superlattices – on the mechanical properties and especially fracture toughness. Furthermore, based on recent ab initio investigations suggesting that the inherent fracture toughness of CrN can be increased by alloying with Mo or W, we will explore in detail the challenges in studying Cr–Mo–N or Cr–W–N materials by ab initio and experiments.

The various thin film structure and architecture concepts allow the utilization of multifunctional properties facilitating the development of next generation's hard coatings.

10:40am **SE+AS+NS+TR-MoM8 Crystallographic Stabilization of δ -WC Thin Films by Alloying with B, using Reactive Magnetron Sputtering of W in Trimethylboron (CH_3)₃B.** *Hans Högborg, L. Tengdelius, M. Samuelsson, G. Greczynski, F. Eriksson, L. Hultman, Linköping University, Sweden*

The hardness, oxidation resistance, and high temperature stability of hexagonal δ -WC (B_h) in cemented carbide is a key component in metal cutting. Such a property envelop suggest many potential thin film applications. However, the literature shows that thin film growth of δ -WC by for instance magnetron sputtering is complicated typically resulting in the deposition of films containing the phase γ -WC (B1) with a carbon content lower than nominal, i.e. WC_{1-x} . As the properties of this phase is less favorable compare to those of δ -WC, growth of WC_{1-x} must be avoided in an optimized thin film material. In this study, we attempt to promote the formation of δ -WC films by alloying with B. Our hypothesis is that the preferred growth of WC_{1-x} films depends on the preference of C to occupy octahedral sites found in the B1 structure and where the larger B atom may act to stabilize the B_h structure by better filling out the larger trigonal prism interstitials in this structure. We use reactive magnetron sputtering of W, using trimethylboron (CH_3)₃B (TMB) as C and B precursor. The 5 min depositions were carried on Si(100) substrates in a Kr plasma held at a constant pressure of 0.53 Pa. The gaseous TMB was introduced close to the substrates. The influence of TMB flow, ranging from 1-10 mln, was studied for a growth temperature of 500 °C. Also, the influence of growth temperature, from room temperature to 900 °C, was investigated for a constant TMB flow of 10 mln. X-ray photoelectron spectroscopy shows that the content of B and C scales with the flow into the plasma with no B and ~3 at.% C at 1 mln and 6.5 at.% B and 17.8 at.% C at 10mln. In contrast, temperatures up to 600 °C show no impact on the B and C content in the films, while higher temperatures give a solid state reaction with the substrate. X-ray diffraction shows broad peaks indicative of small grain sizes and with peaks at 2θ angles matching those of the phases WC_{1-x} or W. In the in the temperature range 300 to 600 °C, 100-textured WC_{1-x} films are deposited and with a shift to a weak 111 orientation at lower temperatures. At 500 °C, TMB flows of 5 to 10 mln results in the growth of 100-textured WC_{1-x} films, while lower flows yield W films. Films are deposited with thicknesses up to ~1000 nm, corresponding to a deposition rate of 3.3 nm/s. The microstructure is generally fine-grained, but with broken columns at 500 and 600 °C and a TMB flow of 1 mln. The mechanical properties of the films will be reported.

11:00am **SE+AS+NS+TR-MoM9 Epitaxial and Polycrystalline WN_x and MoN_x Films Deposited by Reactive DC Magnetron Sputtering.** *Brian Ozsdolay, K. Balasubramanian, Rensselaer Polytechnic Institute, C.P. Mulligan, U.S. Army Armament Research Development & Engineering Center, Benét Laboratories, M.J. Guerette, L. Huang, D. Gall, Rensselaer Polytechnic Institute*

WN_x layers, 1.45- μm -thick, were deposited by reactive magnetron sputtering on MgO(001), MgO(111), and Al_2O_3 (0001) in 20 mTorr N_2 at $T_s = 500$ -800 °C. X-ray diffraction ω - 2θ scans, ω -rocking curves, ϕ scans, and reciprocal space maps show that all layers deposited from 500-700 °C exhibit the cubic rock-salt structure, with a relaxed lattice constant that decreases from 4.299 to 4.171 Å as the N-to-W ratio decreases from $x = 1.20$ for $T_s = 500$ °C to $x = 0.83$ for $T_s = 700$ °C, as measured by energy dispersive and photoelectron spectroscopies. $T_s = 500$ -600 °C yields a polycrystalline 111-textured microstructure on all substrates. In contrast, deposition at 700 °C results in epitaxial growth of WN(111) and WN(001)

on MgO(111) and MgO(001), respectively, while deposition on Al_2O_3 (0001) yields a 111-preferred orientation, misoriented cubic WN grains as well as N-deficient BCC W. $T_s = 800$ °C causes nitrogen loss and WN_x layers with primarily BCC W grains and $x = 0.04$ -0.06. The measured elastic modulus ranges from 110-260 GPa for $T_s = 500$ -700 °C and decreases with increasing N-content, and increases to 350 GPa for $T_s = 800$ °C. For samples deposited at $T_s = 700$ °C, nanoindentation on WN on MgO(001), MgO(111), and Al_2O_3 (0001) provides hardness values of 9.8 ± 2.0 , 12.5 ± 1.0 , and 10.3 ± 0.4 GPa, and elastic moduli of 240 ± 40 , 257 ± 13 , and 242 ± 10 GPa, respectively. The corresponding shear moduli measured by Brillouin light scattering are 127 ± 2 GPa, 121 ± 2 GPa and 115 ± 2 GPa. MoN_x layers, 1- μm -thick, deposited on MgO(001) also exhibit a cubic rock salt structure with x decreasing from 1.18 for $T_s = 500$ and 600 °C to $x = 0.76$ for $T_s = 800$ °C but remaining approximately constant for $T_s = 800$ -1000 °C. Layers with $T_s > 700$ °C contain both epitaxial MoN_x (001) and 111-oriented grains. The out-of-plane lattice constant decreases from 4.22 to 4.18 Å for 111 oriented grains and from 4.17 to 4.06 Å for epitaxial 001-oriented grains, as T_s is increased from 700 °C to 1000 °C.

11:20am **SE+AS+NS+TR-MoM10 Phase Stability and In Situ Growth Stresses in Thin Cu/Nb Multilayered Films.** *Qianying Guo, L. Wan, R.L. Martens, G.B. Thompson, University of Alabama*

As the length scale of individual layers are reduced in a Cu/Nb multilayer, fcc to bcc and bcc to fcc transformations were noted for Cu and Nb respectively. These transitions have been modeled using a thermodynamic phase diagram where interfacial and volumetric energy considerations determine stability and the bilayer thickness of the multilayer is a state variable for predicting those transformations. Using HRTEM, the evolution of the interface from incoherent-to-semicoherent-to-coherent is determined and related to the structural component of the interfacial energy reduction that drives the crystalline transformations. When equal thicknesses of each layer were < 1 nm, the layers underwent an additional transformation from a crystalline to amorphous structure. This has been rationalized by the positive enthalpy of mixing between these two species as they intermixed during the sputter deposition process. The chemical intermixing and local clustering at and near the interface has been quantified by atom probe tomography. These phase transformations have been related to real-time, intrinsic growth stress measurements. All of the multilayers were in a compressive stress state, but a notable reduction in the compressive stress value occurred with each transformation. The collective characterization of the film, via TEM, atom probe, and stress evolution, have provided insights into the structural stability of crystalline phases at the nanoscale.

11:40am **SE+AS+NS+TR-MoM11 Droplets in Cathodic Arc Evaporated (Al,Cr)₂O₃-based Coatings and the Nucleation of Dedicated Crystalline Structures.** *Christian M. Koller, CDL AOS, TU Wien, Austria, R. Hahn, TU Wien, Austria, J. Ramm, Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein, S. Koložvári, Plansee Composite Materials GmbH, Germany, P.H. Mayrhofer, CDL AOS, TU Wien, Austria*

Corundum-type Al_2O_3 coatings demonstrate excellent thermo-mechanical properties, giving rise to widespread applications as protective films on, e.g., cutting inserts or components. These coatings are typically synthesised by chemical vapour deposition (CVD) at temperatures of 900 °C or higher, which excludes temperature sensitive substrates. Physical vapour deposition (PVD) proved to be a suitable method for low temperature synthesis of nitrides with excellent properties. However, the growth of single-phased corundum-type α - Al_2O_3 by PVD is still a difficult task under standard production conditions. In general, a mixed phase composition of metastable cubic phases is observed, which influence the thermo-mechanical performance of the coating. The utilisation of targets produced by powder metallurgical methods allows for the combination of aluminium with other elements, suitable to promote dedicated crystal structures as demonstrated by AlCr and more recently AlCrFe, where dense crystalline coatings with an increased amount of hexagonal phase fractions were realised. Although the alloying with Cr and Fe is a promising concept with good prospects, the mechanism to form the hexagonal structure in these materials is yet not understood. Therefore, the aspect of layer-nucleation is investigated in more detail. A significant part of hexagonal crystallites in (Al,Cr,Fe)₂O₃ coatings is triggered by nucleation onto small particles incorporated in the coating. They originate from the cathode surface and are generated during the cathodic arc process. Cathode surface modifications, macroparticle incorporation and the associated coating microstructures are elucidated by detailed X-ray diffraction and electron microscopy studies. Implications on the coatings' properties and possible technological concepts are discussed.

Authors Index

Bold page numbers indicate the presenter

— A —

Arndt, M.: SE+AS+NS+TR-MoM4, 1

— B —

Balasubramanian, K.: SE+AS+NS+TR-MoM9, 2

Bolvardi, H.: SE+AS+NS+TR-MoM2, 1

— C —

Chirita, V.: SE+AS+NS+TR-MoM3, 1

— E —

Edström, D.: SE+AS+NS+TR-MoM3, **1**

Eriksson, F.: SE+AS+NS+TR-MoM8, 2

— G —

Gall, D.: SE+AS+NS+TR-MoM9, 2

Greczynski, G.: SE+AS+NS+TR-MoM8, 2

Greene, J.E.: SE+AS+NS+TR-MoM3, 1

Guerette, M.J.: SE+AS+NS+TR-MoM9, 2

Guo, Q.Y.: SE+AS+NS+TR-MoM10, 2

— H —

Hahn, R.: SE+AS+NS+TR-MoM11, 2

Högberg, H.: SE+AS+NS+TR-MoM8, **2**

Huang, L.: SE+AS+NS+TR-MoM9, 2

Hultman, L.: SE+AS+NS+TR-MoM3, 1;
SE+AS+NS+TR-MoM8, 2

— K —

Koller, C.M.: SE+AS+NS+TR-MoM11, **2**

Kolozsvári, S.: SE+AS+NS+TR-MoM11, 2

— L —

Lewin, E.: SE+AS+NS+TR-MoM1, 1

— M —

Martens, R.L.: SE+AS+NS+TR-MoM10, 2

Mayrhofer, P.H.: SE+AS+NS+TR-MoM11, 2;
SE+AS+NS+TR-MoM4, 1;
SE+AS+NS+TR-MoM5, 1

Mulligan, C.P.: SE+AS+NS+TR-MoM9, 2

Music, D.: SE+AS+NS+TR-MoM2, 1

— O —

Ozsdolay, B.D.: SE+AS+NS+TR-MoM9, **2**

— P —

Patscheider, J.: SE+AS+NS+TR-MoM1, **1**

Petrov, I.: SE+AS+NS+TR-MoM3, 1

Polcik, P.: SE+AS+NS+TR-MoM4, 1

— R —

Ramm, J.: SE+AS+NS+TR-MoM11, 2

— S —

Samuelsson, M.: SE+AS+NS+TR-MoM8, 2

Sangiovanni, D.G.: SE+AS+NS+TR-MoM3, 1

Schneider, J.M.: SE+AS+NS+TR-MoM2, **1**

Seidl, W.M.: SE+AS+NS+TR-MoM4, **1**

— T —

Tengdelius, L.: SE+AS+NS+TR-MoM8, 2

Thompson, G.B.: SE+AS+NS+TR-MoM10, 2

— W —

Wan, L.: SE+AS+NS+TR-MoM10, 2