

Tuesday Morning, October 19, 2010

Advanced Surface Engineering

Room: Cimmaron - Session SE-TuM

Hard and Nanostructured Coatings

Moderator: I. Petrov, University of Illinois at Urbana-Champaign

8:00am **SE-TuM1 PVD-Oxide Coatings for Tribological Applications, H. Rudigier, J. Ramm, OC Oerlikon Balzers AG, Liechtenstein INVITED**

In the past, oxide coatings for tribological applications were almost exclusively deposited using chemical vapour deposition technology. The synthesis of corundum type Al-Cr-O coatings at temperatures of the order of 500°C using physical vapour deposition - cathodic arc evaporation in the case of Al-Cr-O - has triggered research activities to explore the potential of oxide materials for wear protection and other tribological applications. An overview of the various attempts to deposit oxides will be given, as well as a discussion of their properties and applications.

8:40am **SE-TuM3 Nanostructure, Bonding, and High Temperature Oxidation of SiZrON Thin Films, M.S. Byrne, R.J. Lad, University of Maine**

SiZrON thin films have potential applications as hard high temperature coatings since they combine the oxidation resistance and hardness of oxides with the toughness of nitrides. In this study, a range of $\text{Si}_x\text{Zr}_y\text{O}_z\text{N}_{1-x-y-z}$ thin films with a nominal thickness of 200 nm were deposited onto r-cut sapphire and fused silica substrates at 200°C using reactive RF magnetron co-sputtering of Zr and Si targets in $\text{N}_2/\text{O}_2/\text{Ar}$ gas mixtures. The films were characterized using high resolution scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) in the as-deposited state as well as after annealing treatments up to 1000°C both in air and in vacuum. Grazing incidence XRD indicates that the as-deposited are amorphous for oxygen-rich and Si-rich film stoichiometries, but nanocrystalline ZrN or ZrO_2 phases form within an amorphous matrix for N-rich and Zr-rich films. XPS shows a decrease in the Si, Zr, O, and N Auger parameters as the chemical bonding becomes more ionic with increasing O+Si content. For the different films, the N1s XPS lineshape indicates different states involving Si-N-O, Zr-N-O, and/or O-N bonding. When annealed to 1000°C in vacuum, negligible changes in stoichiometry or nanostructure are observed. However, when the films are heated to 1000°C in air, N depletion and Si enrichment at the film surface is observed, accompanied by the formation of tetragonal phase ZrO_2 nanocrystallites and changes in nanomorphology as observed by SEM. Argon ion depth profiling with XPS was used to investigate the kinetics of the high temperature oxidation process.

9:00am **SE-TuM4 Spinodal Decomposition of $\text{Ti}_{0.33}\text{Al}_{0.67}\text{N}$ Thin Films Studied by Atom Probe Tomography, L.J.S. Johnson, Linköping University, Sweden, M. Thuvander, K. Stiller, Chalmers University of Technology, Sweden, M. Odén, L. Hultman, Linköping University, Sweden**

The metastable solid solution of fcc-TiAlN is of interest both from an industrial perspective, since it is extensively used as a coating for cutting tools, and from a scientific perspective; as questions pertaining to the details of phase transformations in the system, not least spinodal decomposition, remain [1]. Here, the isostructural decomposition of $\text{Ti}_{0.33}\text{Al}_{0.67}\text{N}$ thin films deposited by cathodic arc evaporation has been studied by atom probe tomography with close to atomic resolution. As-deposited films were found to deviate slightly from a random solid solution, and so be in the earliest stage of decomposition. After annealing at 900 °C for 2 h the films exhibited a spinodally decomposed nanostructure, in an intermediate stage. Results indicate that N segregates to the Al-rich domains in the annealed sample, causing the TiN-domains to be understoichiometric. Furthermore, a possible Kirkendall effect was detected in the annealed sample, with a modulation of the local stoichiometry by 1-2 at. % along the decomposition gradient. The implication of the findings for the age hardening of TiAlN alloy films will also be discussed.

[1] L. J. S. Johnson, Nanostructuring and Age Hardening in TiSiCN, ZrAlN, and TiAlN Thin Films, Licentiate Thesis no. 1442, Linköping University, 2010, <http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-56221>

9:20am **SE-TuM5 Structure, Mechanical Properties and Thermal Stability of Zr-Al-N Thin Films, P.H. Mayrhofer, L. Chen, D. Holec, D. Luef, R. Rachbauer, University of Leoben, Austria, Y. Du, Central South University**

$\text{Zr}_{1-x}\text{Al}_x\text{N}$ thin films were synthesized by magnetron sputtering with AlN mole fractions x ranging from 0 to 0.9. We reveal, via X-ray diffraction (XRD) and transmission electron microscopy (TEM) that the films crystallize in the cubic NaCl (c) structure with $x \leq 0.32$ and the wurtzite ZnS (w) structure with $x \geq 0.75$. For AlN mole fractions between 0.32 and 0.75 the films crystallize with multiple phases and contain a fully percolated disordered phase. This is in agreement with *ab initio* calculations suggesting that within a broad x range of 0.38–0.75 the cubic, wurtzite and hexagonal (BN structure) are equally preferred with respect to their energy of formation. Lower AlN mole fractions prefer the cubic structure whereas higher AlN fractions favor the wurtzite structure. The maximum hardness of $H \sim 36$ GPa with an indentation modulus of $E \sim 303$ GPa is observed for the single-phase cubic $\text{Zr}_{0.68}\text{Al}_{0.32}\text{N}$ coating. For higher Al contents the hardness rapidly decreases to ~ 22 GPa with $x \sim 0.45$ and then slightly decreases further to ~ 21 GPa for even higher Al contents. This is in perfect agreement with the structural investigations. During thermal annealing to 1500 °C in inert atmosphere the supersaturated phases of the films decompose towards their stable constituents c-ZrN and w-AlN. This is connected with a change in their mechanical properties where two major differences can be observed. The hardness of as deposited single-phase cubic $\text{Zr}_{1-x}\text{Al}_x\text{N}$ slightly increases with annealing to $T_a \sim 1000$ °C due to the formation of cubic Zr- and Al-rich domains. Contrary to this observation the hardness of as deposited multi-phase $\text{Zr}_{1-x}\text{Al}_x\text{N}$ coatings with x values between 0.38 and 0.5 increases by ~ 10 GPa during annealing to ~ 900 °C. Here, the observed hardness increase is mainly based on the structural rearrangement during annealing which results in the formation of crystalline areas with compact interface boundaries. As soon as w-AlN is formed, at around 1100 °C, the hardness decreases for as deposited single-phase cubic and multi-phase $\text{Zr}_{1-x}\text{Al}_x\text{N}$ coatings.

9:40am **SE-TuM6 Growth and Microstructure Analysis of Hafnia-Based Nanostructured Coatings, M. Noor-A-alam, C.K. Roy, C.M. Bradely, A.R. Choudhuri, C.V. Ramana, University of Texas at El Paso**

The aim of this work is to develop nano-structured Hafnia-based coating which can withstand with high temperature environment. Yttria stabilized hafnia (YSH) coatings have been fabricated on Nickel-based super alloy Inconel-738 and stainless steel using PVD method. The coatings have been produced at various temperatures. The thickness of the coating was about 500 nm as demonstrated in the cross-sectional imaging by Scanning Electron Microscopy (SEM). The structural characterization performed by X-ray diffraction (XRD) indicates the cubic crystal structure of YSH coating. Columnar structure has been noticed in all the coatings. The microhardness investigated by using a diamond tip microhardness testing machine indicates 3 Gpa hardness coatings. The temperature stability of these coatings has been examined. The result will be discussed in detail.

10:40am **SE-TuM9 Low Temperature Synthesis of $\alpha\text{-Al}_2\text{O}_3$ Films, K. Jiang, F. Nahif, RWTH Aachen University, Germany, K. Sarakinos, Linköping University, Sweden, S. Konstantinidis, University of Mons, Belgium, D. Music, J.M. Schneider, RWTH Aachen University, Germany**
In this study, we deposit Al_2O_3 films using plasma assisted chemical vapor deposition (PACVD) in an $\text{Ar-H}_2\text{-O}_2\text{-AlCl}_3$ atmosphere and by filtered cathodic arc.

During PACVD a novel generator is employed delivering four times larger power densities than those obtained in conventional PACVD approaches. This mode of operation enables the increase of the efficiency of the AlCl_3 dissociation in the gas phase, as well as a more intense energetic bombardment of the growing film. We demonstrate that these deposition conditions allow for the growth of dense films $\alpha\text{-Al}_2\text{O}_3$ with negligible Cl incorporation and elastic properties similar to those of the bulk $\alpha\text{-Al}_2\text{O}_3$ at a temperature of 560 ± 10 °C.

$\alpha\text{-Al}_2\text{O}_3$ films are deposited employing a monoenergetic Al^+ beam generated by a filtered cathodic arc. A critical Al^+ ion energy of 40 eV for the formation of the $\alpha\text{-Al}_2\text{O}_3$ phase at a substrate temperature of 720 °C is determined. This energy is used as input for classical molecular dynamics and Monte-Carlo based simulations of the growth process, as well as *ab initio* calculations. The combination of theory and experiment indicates that in addition to the well known surface diffusion the previously non considered diffusion in sub-surface regions is an important atomistic mechanism in the phase formation of Al_2O_3 .

11:00am **SE-TuM10 Al-Si-N-O Hard Coatings Prepared by Reactive Magnetron Sputter Deposition from Composite Targets**, *J. Patscheider*, *M. Parlinska-Wojtan*, *A. Pélisson*, Empa, Switzerland, *P. Polcik*, Plansee Composite Materials GmbH, Germany, *P. Pecher*, Glas Troesch AG, Switzerland

The applicability of hard nitride coatings on a large industrial scale often depends on the sensitivity of their properties on oxygen contaminations. Following the experience of reactive magnetron sputter deposition of optically transparent Al-Si-N thin films by co-sputtering from two elemental targets in a confocal arrangement, the possibility to prepare similar films from powder metallurgical Al-Si targets of different Al/Si ratios in mixed Ar-N₂-O₂ is investigated. This arrangement is especially interesting when such coatings have to be prepared on an industrial scale. In this work, the effect of oxygen on the coating properties is examined, as reactive elements like Al often cause oxygen to be incorporated as a contamination. It is shown that hardness values up to 28 GPa are reached at oxygen concentrations of several atomic percent. The deliberate addition of O₂ to the reactive gas mixture of Ar/N₂ leads to the incorporation of oxygen up to 20 atomic %. Despite these very high concentrations hardness values of 25 GPa are reached. Similar to silicon, oxygen additions cause grain refinement and a gradual disappearance of the columnar structure with increasing oxygen content. It is shown that the hardness is primarily influenced by the plasma density and to a lower extent by other factors like silicon content and preferred orientation.

11:20am **SE-TuM11 A New Approach to the Synthesis of Adherent Hard Coatings with High Toughness**, *A.N. Ranade*, Northwestern University, *L.R. Krishna*, International Advanced Research Centre (ARCI), India, *Y.W. Chung*, Northwestern University

Traditional ceramic coatings provide abrasive wear protection due to high hardness. However, these coatings have low fracture toughness, making them susceptible to surface or internal flaws and failure under high impact loads. In addition, when ceramics are deposited onto metal substrates, lower thermal expansion coefficients compared to those of metals can cause thermal stress that may result in delamination. This paper explores a new approach to the synthesis of adherent hard coatings with high toughness. The approach begins with a metal matrix identical to that of the substrate, followed by the incorporation of nanoscale hard particles to increase hardness by Orowan strengthening. Theoretical estimates indicate that incorporation of 10 vol. % of such nanoscale particles can raise the hardness by as much as 20 GPa. The coating matrix is identical to that of the substrate, resulting in maximum adhesion and minimum thermal stress. Furthermore, by choosing nanoscale particles whose structure is semi-coherent with the metal matrix, local stress at the particle-matrix interface may activate the motion of screw dislocations, thus preserving the high fracture toughness of the matrix. This paper will present initial results of this exploration, using Ti as the matrix and semi-coherent TiB₂ nanoparticles as the strengthening agent. Characterization tools include x-ray diffraction (structure), AFM (surface roughness), SEM/TEM (size and distribution of nanoparticles), nanoindentation (elastic modulus, hardness, and fracture toughness), and scratch testing (adhesion), as a function of nanoparticle concentration. These studies should provide a general strategy for designing adherent hard coatings with high toughness.

11:40am **SE-TuM12 Oxidation and Diffusion Study on AlCrVN Hard Coatings using Oxygen Isotopes ¹⁶O and ¹⁸O**, *R. Franz*, University of Leoben, Austria, *J. Schnoeller*, *H. Hutter*, Vienna University of Technology, Austria, *C. Mitterer*, University of Leoben, Austria

In the commonly applied procedure to study the oxidation behavior of hard nitride and carbide coatings, the sample is heated to a certain temperature and exposed to an oxygen-containing atmosphere during a defined period of time. Subsequently, the oxidized specimen is analyzed as to the thickness and morphology of the oxide layer or the composition and chemical nature of the oxides. In order to gain more information about the mechanisms active during oxidation the procedure can be split into two stages where different isotopes, ¹⁶O and ¹⁸O, are introduced in each step. An analysis by means of secondary ion mass spectrometry depth-profiling with its inherent isotope selectivity allows for an investigation of the general oxidation behavior as well as the oxygen diffusion during the oxidation process. In the present case, two AlCrVN coatings of equal composition but different crystal structure were studied. The single-phase coating with its face-centered cubic (fcc) structure presents a higher oxidation resistance as compared to the dual-phase coating containing a wurtzite and a fcc phase. After the annealing treatment, the surface of the latter is entirely covered by VO₂ and V₂O₅ as evidenced by Raman spectroscopy. The single-phase coating, on the other hand, reveals unoxidized coating material and AlVO₄ crystals. However, even though exhibiting a significantly different oxidation resistance, the oxygen diffusion is similar. In both cases peak values of ¹⁸O, which was introduced in the second stage, were found near the oxide-nitride interface indicating that O atoms diffused through the

already formed oxides. Additional experiments using a gas mixture comprising natural water vapor H₂¹⁶O and ¹⁸O₂ revealed that mainly the molecular oxygen serves as source for the formation of oxides as with increasing water vapor partial pressure the oxide layer thickness was significantly reduced.

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