Wednesday Afternoon, October 22, 2008

Advanced Surface Engineering
Room: 204 - Session SE+NC-WeA

Hard and Nanocomposite Coatings: Synthesis, Structure, and Properties II
Moderator: J. Patscheider, EMPA, Switzerland

1:40pm **SE+NC-WeA1 Structural Development and Mechanical Properties of TiN-Ni Nanocomposite Coatings**, ***J.P. Riviere***, University of Poitiers, France, *A. Akbari*, Sahand University of Technology, Iran, *C. Templier*, University of Poitiers, France **INVITED**

Superhard nanocomposite coatings represent an important class of new materials with enhanced mechanical properties. The synthesis of these coatings has been principally obtained by both techniques: plasma-assisted chemical vapour deposition or reactive magnetron sputtering. It appears that dual ion beam assisted deposition could be also an effective tool for tailoring the structure and properties of nanocomposite coatings because it permits independent control of the process variables such as particle nature, energy, flux. A particular important effect of the bombardment of a growing film with energetic ions is the enhanced adatom mobility which plays an important role in the renucleation of nanograins and on the formation of the percolation network of the intergranular phase We have investigated the formation of hard nanocomposite coatings with improved toughness consisting of TiN nanograins embedded in a soft metallic intergranular phase of Ni using reactive ion beam assisted deposition. A composite Ti-Ni target was sputtered with 1.2 keV Ar^+ ions and the growing films were simultaneously bombarded with a mixture of 50 eV Ar^++$N2^+$+N^+ ions. The chemical composition was deduced from RBS analysis and a N/Ti ratio of ~ 0.85 independent of the Ni content was determined. Phases, grain size, and texture of the coatings were investigated by XRD and HRTEM. In the composition range 0-22,5 at% Ni, δ-TiN is the only crystalline phase and Ni appears as an X Ray amorphous phase. The hardness increases up to a maximum of 41 Gpa at 6 at.% Ni which corresponds to a TiN crystallite size of ~ 8 nm and a Ni intergranular phase thickness of roughly 1 monolayer. Stress analysis was performed by XRD using the crystallite group method (CGM) developed for textured materials and coatings. It is shown that the hardness enhancement in TiN-Ni nanocomposite coatings is not correlated with residual stresses, but rather with the intrinsic nanostructure. An important improvement in wear resistance is observed however the highest wear resistance is obtained for the coatings exhibiting the highest toughness and not the highest hardness. These results show the beneficial influence of the ductile metallic amorphous intergranular phase on the mechanical behaviour of nanocomposite coatings.

2:20pm **SE+NC-WeA3 Processing and Characterization of Polymer-Ceramic Nanolaminate Thin Films**, ***A.R. Waite***, Air Force Research Labs/UTC, Inc./University of Dayton, *J.O. Enlow*, Air Force Research Labs/UES, Inc., *C. Muratore*, Air Force Research Labs/UTC, Inc., *J.G. Jones*, Air Force Research Labs, *H. Jiang*, Air Force Research Labs/Materials Science & Technology Applications, LLC, *T.J. Bunning*, *A.A. Voevodin*, Air Force Research Labs

Polymer-ceramic nanolaminate thin films were synthesized by coupling chemical and physical vapor deposition processes. Highly cross-linked fluoropolymer layers were deposited by room temperature plasma enhanced physical vapor deposition from octafluorocyclobutane (OFCB) precursor gas. Gas flow rates, substrate position and rf power were examined to produce a dense polymer coating with a minimum refractive index of 1.38. Magnetron sputtering processes were investigated for deposition of amorphous TiO_2 with a high refractive index. Stoichiometric TiO_2 with a refractive index >2.3 was produced via reactive sputtering and sputtering of a titania target in pure Ar, however, reactive sputtering in an oxygen atmosphere resulted in decomposition of the polymer film. Multiple polymer-ceramic film architectures were investigated, including a quarter wave stack notch filter consisting of alternating TiO_2 and fluoropolymer layers (3 and 2 layers, respectively). Analysis of nanoindentation results was used to compare the fracture toughness and other mechanical properties of multilayered and monolithic films. The combination of optical and mechanical properties for different nanolaminate architectures revealed that the coupling of polymer-ceramic thin film materials has potential for the development of useful electro-optical devices with remarkable toughness and flexibility compared to the current state of the art.

2:40pm **SE+NC-WeA4 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 because of 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 deposited onto metal substrates, lower thermal expansion coefficients of ceramic coatings 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. Since the coating matrix is identical to that of the substrate, this should result 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 TiB_2 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.

3:00pm **SE+NC-WeA5 Influence of Nb on Structure, Properties, and Phase Stability of Ti-Al-N Hard Coatings**, ***P.H. Mayrhofer***, *R. Rachbauer*, Montanuniversität Leoben, Austria, *L. Hultman*, Linköping University, Sweden

Metastable $Ti_{1-x}Al_xN$ thin films synthesized by plasma-assisted vapour deposition crystallize in the industrially preferred cubic NaCl (c) structure with AlN mole fractions (x) ≤ 0.7. We reveal, via X-ray diffraction (XRD) and transmission electron microscopy (TEM), that the addition of niobium to c-$Ti_{1-x}Al_xN$ has only a minor influence on the structure and morphology of as deposited coatings. By a combination of differential scanning calorimetry, XRD, and TEM investigations we can conclude that the onset temperature for decomposition of the formed metastable phases increases with increasing Nb content. After annealing at 1450 °C the coating decomposed into c-$Ti_{1-y}Nb_yN$ and h-AlN phases. This decomposition process is initiated via spinodally formed cubic Ti-rich and Al-rich domains. As these domains influence plastic deformation during the nanoindentation experiments an increased hardness is observed after annealing at temperatures in the range 800—1000 °C. At higher temperatures c-AlN transforms to h-AlN. Due to the reduced mechanical properties of h-AlN compared to c-AlN this transformation is accompanied by a hardness reduction. The experimentally observed results are corroborated by a combination of ab intio and continuum-mechanical calculations.

4:00pm **SE+NC-WeA8 Development of MoN-Ag-Based Nanocomposite Films for Severe Tribological Applications**, ***A. Erdemir***, *O.L. Eryilmaz*, Argonne National Laboratory, *M. Urgen*, *V. Ezirmik*, *K. Kazmanli*, Istanbul Technical University, Turkey

Using the principles of a crystal-chemical model, we designed and produced novel nanocomposite coatings that are made of hard MoNx and soft Ag phases. Because of the very high ionic potentials of the complex sulfides and phosphates that they form during lubricated sliding tests in formulated engine oils, these nanocomposite coatings are able to drastically reduce friction and at the same time increase resistance to wear and scuffing under severe boundary lubricated sliding regimes. In this paper, we will concentrate on the fundamental tribological mechanisms that control the sliding friction and wear behaviors of these nanocomposite coatings. The major implications of this study is that using such a fundamental approach one can design and manufacture coatings that are very compatible with lubricants and hence suitable for a wide range of rolling, rotating and sliding bearing applications in engines and other lubricated mechanical systems.

4:20pm **SE+NC-WeA9 Process Variables Effect of PVD Nitride Hard Coatings Deposited on Chromium-Based Tool Steel Substrates**, ***A. Neira***, North Carolina State University, *F. Sequeda, A. Ruden,* Universidad del Valle, Colombia, *J.M. Gonzales*, Universidad Nacional, Colombia

Process variables parameters as substrate temperature, bias voltage and N2/Ar ratio were studied during the deposition of IV, V and VI group materials in the form of nitrides, (TiAlVN, ZrN and CrN). Those coatings were deposited on chromium-based steels, like AISI H-13 and AISI-4140 commonly used for high mechanical performance even after long exposure at high working temperatures and AISI D-3 designed for high resistance to wear or to abrasion and for resistance to heavy pressure. This work was done using available coating production techniques like Plasma Assisted Physical Vapor Deposition (PAPVD) and DC-Reactive Magnetron Sputtering and physical properties resulting from modifying the process parameters like crystal structure, film texture, and mechanical properties like strain micro deformation, hardness, wear resistance friction coefficient and adhesion of the coating to the substrate were addressed in this study and conducted through film characterization techniques such as X-Ray Diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscope (SEM), micro and nanoindentation, wear and adhesion test. An special attention was given to the deposition of TiAlVN due to the differences on bonding types between components Al and V considered as "film stabilizers" increasing the film hardness and promoting the Magneli phase formation type (VxO3X-1), offering a reduction in the friction coefficient for auto lubrication phenomena, increasing its use for tribological coating applications.

4:40pm **SE+NC-WeA10 Water Adsorption on Phosphorous-Carbide Thin Films**, ***E. Broitman***, Carnegie Mellon University, *A. Furlan, G.K. Gueorguiev,* Linköping University, Sweden, *Zs. Czigány,* Research Institute for Technical Physics and Materials Science, Hungary, *A.J. Gellman*, Carnegie Mellon University, *S. Stafström, L. Hultman*, Linköping University, Sweden

Amorphous phosphorous-carbide films have been considered as a new tribological coating material with unique electrical properties. However, the coatings cannot be practically used until now because CP_x films rapidly oxidize/hydrolyze and delaminate when in contact with air. Recently we demonstrated that CP_x thin solid films with a fullerene-like structure can be deposited by magnetron sputtering. Thus, the introduction of P atoms in the graphene structure induces the formation of bent and interlinked grapheme planes.[1,2] In this work we compare the uptake of water of amorphous phosphorous-carbide (a-CP_x) films, with fullerene-like phosphorous-carbide (FL-CP_x) and amorphous carbon (a-C) films. Films with thickness in the range 10-300 nm were deposited on quartz crystal substrates by reactive DC magnetron sputtering. The film microstructure was characterized by X-ray photoelectron spectroscopy, and transmission electron microscopy and diffraction. A quartz crystal microbalance placed in a vacuum chamber as described in[3] was used to measure their water adsorption. Measurements indicate that the amount of adsorbed water is highest for the pure a-C films and that the FL-CP_x films adsorbed less water than a-CP_x. To provide additional insight into the atomic structure of defects in the FL-CP_x, a-CP_x and a-C compounds, we performed first-principles calculations within the framework of Density Functional Theory. Emphasis was put on the energy cost for formation of vacancy defects and dangling bonds in relaxed systems.[4] Cohesive energy comparison reveals that the energy cost formation for dangling bonds in different configurations is considerable higher in FL-CP_x than for the amorphous films. These simulations thus confirm the experimental results that dangling bonds are less likely in FL-CP_x than in a-CP_x and a-C films.

[1] A. Furlan, G.K. Gueorguiev, Zs. Czigány, H. Högberg, S. Stafström, and L. Hultman, Phys. Stat. Solidi Rapid Research Letters (2008) in press

[2] G.K. Gueorguiev, A. Furlan, H. Högberg, S. Stafström, and, L Hultman, Chem. Phys. Lett. 426 (2006) 374

[3] E. Broitman, VV. Pushkarev, A.J. Gellman, J. Neidhardt, A. Furlan, and L. Hultman, Thin Solid Films 515 (2006) 979

[4] E. Broitman, G. K. Gueorguiev, A. Furlan, N. T. Son, A.J. Gellman, S. Stafstrom, and L. Hultman, ICMCTF, San Diego, CA (May 2008).

5:00pm **SE+NC-WeA11 Structure-Property Relationships of Galvanic Nickel-NanoDiamond Composite Coatings**, *D.L. Schulz,* ***R.A. Sailer***, North Dakota State University, *G.E. McGuire, O. Shenderova*, International Technology Center

Galvanic nickel coatings have been in use for decades and have many desirable properties including corrosion resistance and relative ease of application. Recently, work has been performed to enhance the tribological properties of nickel-based coatings by incorporation of diamond nanoparticles as a wear-resistant component of this functional coating.[1] In this previous study, detonation nanodiamonds (DNDs) produced from a mixture of carbon-containing explosives were used. The DNDs were then employed as a hard filler in nickel electroplated films giving Ni-DND composite coatings. It was found that the presence of the DNDs significantly affected the properties of the coatings in an intriguing fashion. Toward that end, Ni-DND coatings exhibited improved microhardness and wear resistance when compared to Ni-only control coatings but the latter showed better erosion resistance.[1] These observations warrant a better understanding of the structure of the Ni-DND coatings and the effect on various mechanical properties. The work presented in this paper relates to an investigation of the structure/tribological properties of Ni-DND composite coatings. Characterization data to be discussed includes wear rates, hardness profiles and composite structure as measured by pin-on-disk, nanoindentation and high resolution SEM test methods.

[1] I. Petrov, P. Detkov, A. Drovosekov, M.S. Ivanov, T. Tyler, O. Shenderova, N.P. Voznecova, Y.P. Toporova, D. Schulz, Diamond & Related Materials 15 (2006) 2035–2038.

5:20pm **SE+NC-WeA12 Deposition of Various Nitride and Oxiceramic Coatings by an Industrial-Scale LAFAD Process**, ***V. Gorokhovsky***, *C. Bowman, D. VanVorous, J. Wallace*, Arcomac Surface Engineering, LLC

Nearly defect-free nitride and oxiceramic coatings were deposited by the unidirectional dual large area filtered arc deposition (LAFAD) process. One LAFAD dual arc vapor plasma source was used in both gas ionization and coating deposition modes with and without vertical magnetic rastering of the plasma flow. Substrates made of different metal alloys, as well as carbide and ceramics were installed at different vertical positions on the 0.5 m diameter turntable of the industrial scale batch coating system which was rotated at 12 rpm to assess coating thickness uniformity. Targets of the same or different compositions were installed on the dual cathodic arc sources of the LAFAD plasma source to deposit a variety of coating compositions by mixing the metal vapor and reactive gaseous components in a magnetized strongly ionized plasma flow. The maximum deposition rate typically ranged from 1.5um/hr for TiCr/TiCrN to 2.5 um/hr for Ti/TiN multilayer and AlN single layer coatings, and reached up to 6 um/hr for AlCrO based oxi-ceramic coatings. The vertical coating thickness uniformity was +/-15% inside of the 150mm area without vertical rastering. Vertical rastering increased the uniform coating deposition area up to 250 mm. The coating thickness distribution was well-correlated with the output ion current distribution as measured by a multi-sectional ion collector probe. Coatings were characterized for thickness, surface profile, adhesion, hardness and elemental composition. Estimates of electrical resistivity indicated good dielectric properties for most of the AlCrO based oxi-ceramic coatings. The multi-elemental LAFAD plasma flow consisting of fully ionized metal vapor with reactive gas ionization rate in excess of 50% was found especially suitable for deposition of nanocomposite, nanostructured coatings. Potential applications of this highly productive coating deposition process are discussed.

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