Advanced Surface Engineering
Room 2007 - Session SE-ThA

Hard and Nanocomposite Coatings: Synthesis, Structure, and Properties

Moderator: A. Anders, Lawrence Berkeley National Laboratory

2:00pm **SE-ThA1 Characterization of Inorganic Nanomaterial Composite Coatings**, *J.J. Hu, J. Steffens, J.S. Zabinski, J.H. Sanders,* ***A.A. Voevodin****,* Air Force Research Laboratory

Inorganic nanomaterials including metals, oxides, carbides and sulfides etc. are mostly lager-scale synthesized and commercially available in powder/colloid states. Therefore, for some special applications such as surface protection and lubrication, there is a strong request to make or incorporate the inorganic nanomaterials into coatings. High density and uniformity of the nanomaterial distribution in coatings are deserved for pursuing the extraordinary properties of precursor nanomaterials. In this study, the coatings containing nanomaterials were deposited using laser ablation from frozen liquid targets, where the original liquid material was loaded with nano-tubes and nanosized particles. This laser ablation source was operated in a high vacuum chamber and was assisted with magnetron sputtering of metals and ceramics to adhere and encapsulate nanomaterials into a composite coatings. The chemistry and microstructure of the coatings were characterized using X-ray diffraction (XRD), X-ray energy dispersive spectrometry, scanning electron microscopy (SEM), focused ion beam (FIB) and transmission electron microscopy (TEM). Some advantages of the laser ablation technology from frozen liquid targets for insertion nanomaterials into coatings include: (1) good coating uniformity and smooth surface topography; (2) enhanced coating adhesion to substrates; and (3) being free of solvent molecules and contamination-free. Nanomaterial composite coating benefits for wear protection will be discussed.

2:20pm **SE-ThA2 Microstructure and Surface Properties of Ti-Si-C Nanocomposite Thin Films Deposited by dc Magnetron Sputtering**, ***P. Eklund****, J. Emmerlich, J. Frodelius, C. Virojanadara, L.I. Johansson,* Linköping University, Sweden*; O. Wilhelmsson, U. Jansson,* Uppsala University, Sweden*; H. Hogberg, L. Hultman,* Linköping University, Sweden

Nanocomposites from the Ti-Si-C system are of growing interest as a multifunctional coating material in electrical and tribological applications. We have previously demonstrated beneficial electrical contact properties and a ductile deformation behavior for Ti-Si-C nanocomposite thin films deposited by magnetron sputtering from a Ti@sub 3@SiC@sub 2@ compound target@footnote 1@ at substrate temperature below 300 °C.@footnote 2@ Here, we report on detailed characterization of the microstructure and surface conditions of Ti-Si-C nanocomposites. As evidenced by XRD, TEM, and XPS, the Ti-Si-C films consist of TiC nanocrystallites (<20 nm), embedded in a matrix of amorphous SiC with presence of graphitic carbon. The nc-TiC/a-SiC/g-C nanocomposite exhibited nanoindentation hardness and elastic-modulus values of 20 GPa and 290 GPa, respectively. The ductility of the material can be attributed to rotation and gliding of nc-TiC grains in the matrix. Furthermore, photoemission studies of as-deposited films on Si substrates show a native oxide thickness of 3-4 nm. The thermal stability of the coating was investigated by annealing in vacuum. Upon heating to 1000 °C, the oxide layer is removed and large amounts of free surface carbon appear, as well as surface silicon. This can be interpreted as C and Si segregation during the annealing. @FootnoteText@ @footnote 1@Maxthal, courtesy of Kanthal AB@footnote 2@P. Eklund et al J. Vac. Sci. Technol. B 23(6) 2486 (2005).

2:40pm **SE-ThA3 Characterisation of Nanocomposite Alumina-Zirconia Thin Solid Films Deposited by Reactive Dual RF Magnetron Sputtering**, ***D.H. Trinh****,* Linköping University, Sweden*; M. Collin, I. Reineck,* Sandvik Tooling AB, Sweden*; S.S. Nonnenmann, J.E. Spanier,* Drexel University*; L. Hultman, H. Högberg,* Linköping University, Sweden

Alumina-zirconia composites are of interest for a wide range of applications. These include wear resistant coatings, requiring a combination of high hardness, thermal and chemical stability, and more advanced high-k dielectric thin films for microelectronics, which require the inherent insulating properties of both phases. A deeper understanding of the microstructure is required to fully harness the potential of the mixed oxide system and, in particular, nanocomposites within the aforementioned system. This is complicated, however, by the spontaneous phase separation process into binary oxides and the variety of possible stable and metastable phases that form within each respective binary system. In this study dual RF reactive magnetron sputtering has been utilised to deposit pure and mixed oxide films at a substrate temperature of 450°C on substrates such as Si (100) and WC-Co. High-resolution electron microscopy revealed that the films are nanocomposite in nature with grain sizes <50nm and that phase separation between alumina and zirconia occurs. The phase composition of the films was studied by x-ray diffraction. Complementary electron energy loss spectroscopy (EELS) and Raman scattering spectroscopy were performed for more in depth studies of the atomic arrangement and bonding. The pure zirconia films feature the monoclinic zirconia phase, while the pure alumina films consist of @gamma@-alumina phase. The composite films are nanocrystalline and are comprised of a mixture of phases that included the metastable zirconia phases, @gamma@-alumina, and some amorphous phase. The mechanical properties of the films were characterised by nanoindentation.

3:00pm **SE-ThA4 Tailoring the Nanostructure and Surface Properties of Nanocrystalline Diamond Thin Films on Micro-End Mills for Micro-manufacturing Applications**, ***A.V. Sumant****, P. Heaney, F. Pfefferkorn, R.W. Carpick,* University of Wisconsin-Madison

The growing interest in high-precision machining to fabricate miniaturized parts with meso-scale machine tool systems (mMTs) for medical devices, and optical components requires high-performance micro-end mills with diameters ranging from 10 to 500 microns. This technology complements standard silicon-based microfabrication processes by its ability to directly produce true 3D structures with high accuracy, low cost, and short cycle time from metals. Presently, tungsten carbide (WC) with cobalt binder is widely used as a standard cutting tool material. However, these tools suffer from a limited operational life and have difficulty in machining adhesive metals such as aluminum and copper. Nanocrystalline diamond (NCD) thin films are an attractive possibility for coating these tools, because of its high hardness and the low friction and wear rate of its surface. We have developed a new approach using CH4/H2/Ar growth chemistry to grow a conformal, sub-micron thick coating of NCD on tungsten carbide micro-end mills using Hot Filament Chemical Vapor Deposition (HF-CVD). The percentage of Ar in the gas phase is varied to simultaneously optimize the grain size and the high sp3 content. The characterization of the sp3 content of the NCD coatings is performed using Raman and near edge x-ray absorption (NEXAFS) spectroscopy. The performance of the uncoated and NCD-coated tools have been evaluated by performing dry slot milling experiments on aluminum. The initial test results show a substantial dependence of the performance of the tool on the sp3 content of the film. Dramatic improvement in the tool integrity, extremely low wear, no observable adhesion of aluminum, and a significant reduction in the cutting forces (~ 50%) with improved surface finish are observed for NCD films with high sp3 content. This translates into a micro-machining process with minimal environmental impact, and offers great promise for micro and meso-scale manufacturing applications.

3:20pm **SE-ThA5 Growth Study of TiN- and TiCxNy-based Superhard Nanocomposite**, *E. Bousser,* Ecole Polytechnique, Canada*; P. Jedrzejowski,* Plasmionique*; A. Amassian, L. Martinu,* ***J.E. Klemberg-Sapieha****,* Ecole Polytechnique, Canada

Recent advances in the area of aerospace, automobile and biomedical industries, in microsystems and manufacturing of specialized industrial componentry stimulate the development of new functional coating materials and surface engineering processes that provide an ever increasing mechanical and tribological performance. In the present work, we investigate in situ and in real-time the growth of superhard ternary nanocomposite nc-TiN/a-Si3N4 and quaternary nc-TiCxNy/a-SiCN. These materials were synthesized by plasma enhanced chemical vapor deposition (PECVD) from TiCl4/CH4/SiH4/N2 gas mixtures at substrate temperature of 500oC. Using nondestructive, noncontact spectroscopic ellipsometry and appropriate ellipsometric models, we determine the variation of optical constants, film resistivity, and electron scattering time and mean free path as a function of thickness and particle size. We will show how real-time in situ measurements allow one to evaluate the evolution of the electrical properties that can be described on the basis of existing models (Thompson, Fuchs-Sondheimer, Mayadas-Shatzkes), and related to electron scattering due to phonons, point and line defects (grain boundaries), and surface effects. The films' electrical characteristics derived from optical measurements were confirmed by direct four-point evaluations, and interpreted in terms of the evolution of their microstructure and chemical composition. This approach then became the basis for a generalized microstructural model that takes into account the microstructural features including grain size, inter-grain spacing and interfaces, that are closely related to the film hardness (>50 GPa), and the highest reported H3/E2 ~ 1.8 GPa parameter characterizing resistance to plastic deformation obtained for such nanocomposite films. High resolution TEM micrographs of the evolution of the nanostructures are also presented in support of the structural model.

3:40pm **SE-ThA6 Preparation and Characterization of Reactively Sputtered Al@sub x@CoCrCuFeNi Oxide Films***, **T.K. Chen**, M.S. Wong,* National Dong Hwa University, Taiwan, ROC

Multicomponent Al@sub x@CoCrCuFeNi (x=0.5, 1 and 2) metallic and oxide thin films were prepared by reactive sputtering using single alloy target in a mixture of argon and oxygen gases with various oxygen/argon flow ratio. The dependence of the oxygen to argon ratio, such as the evolution of films structure and properties was investigated in this study. At low oxygen flow rate, the oxygen atoms seemed to be incorporated into the metallic films as solute atoms. At higher oxygen to argon fraction, new crystalline oxide phases, matching the XRD patterns of spinel-structured AB@sub 2@O@sub 4@ like NiCr@sub 2@O@sub 4@ were detected. The films resistivity increased from hundreds of micron ohm-cm for metallic films to nearly 1000 ohm-cm for oxide films grown at high oxygen/argon ratio. UV-Vis absorption spectra of the oxide films revealed a narrow transmission band that only light with wavelength between 650 nm to 850 nm was allowed to pass. These oxide films exhibited unexpected high hardness, compared with their metal and metal nitride counterparts, to a value of 20 GPa.

4:00pm **SE-ThA7 Magnetron Sputtered Nanolaminate Coatings for Debonding of Segmented Structures***, **J.D. Demaree**, J.K. Hirvonen,* US Army Research Laboratory*; M.P. Blickley,* The Pennsylvania State University*; N.A. Soroka,* United States Military Academy*; P.G. Dehmer, M.A. Minnicino,* US Army Research Laboratory

Reactive coatings consisting of repeated bilayers of aluminum and nickel/vanadium capable of self-propagating reactions were deposited onto carbon composite and steel coupons using magnetron sputtering. Such sacrificial coatings, when embedded in an adhesive joint, can provide reliable on-demand debonding of segmented structures when ignited. Adhesion of the metallic nanocomposite coating to carbon composite substrates was enhanced by in-vacuum plasma treatments. The energy required to initiate the self-propagating intermetallic reaction and the propagation velocity of that reaction was measured before and after low temperature annealing, using a spark gap and high speed video photography. Rutherford backscattering spectrometry (RBS) was used to calibrate the deposition process and to characterize the interfacial interdiffusion induced by annealing. Increases in required initiation energy and decreases in propagation velocity were observed with increased anneal times and temperatures, in agreement with the RBS results and existing literature discussion of reaction mechanisms that show sensitivity of these to interface reactions. Initiation sensitivity and propagation velocity were both impacted by varying the stoichiometric ratio of Al to Ni/V, and the propagation rate was also affected by the nature of the substrate. These results allow for the optimization of both reliable initiation and long term, low temperature storage stability of said reactive coatings as required for Army applications. Scale-up demonstration of this process has begun, which will use a dual-source magnetron sputter system with a computerized sample manipulator, and will be capable of coating structural segments of carbon composite or steel up to 20 inches long. Once the adhesion, reactivity, and durability of these reactive coatings has been demonstrated on a component scale, such coatings are envisaged to become useful debonding agents in a number of future Army systems.

4:40pm **SE-ThA9 Dimensional Attributes of Enhancements in Nanocrystalline Ta-V Layered Structures***, **A.F. Jankowski**,* Univ. California - Lawrence Livermore National Laboratory

The scaling of structure to the micro- and nano-scale is a known method of enhancing the physical properties of many materials. For example, the strength and hardness of nanocrystalline metals and laminates can be increased several fold. At present, we evaluate how the dimensional attribute of nanoscale affects the mechanical properties of body-centered-cubic Ta and V thin films. The samples for this study are prepared by magnetron sputter deposition and characterized using the methods of x-ray diffraction, transmission electron microscopy, and nanoindentation. Systematic increases in hardness, for example, are measured to a factor of ten or more above the comparative value of fully annealed samples. To asses underlying structural origin, single and layered structures of each metal are evaluated separately as well as in the form of layered structures. That is we examine Ta, Ta/Ta, V, V/V, and Ta/V films as deposited on silicon substrates. At small layer-pair spacings, as 3 nm, it is found that strained layered superlattices are formed in Ta/V. Dimensional attributes of the nanoscale effects are considered in accounting for the origin of mechanical property enhancements in all these Ta and V nanostructured materials. Specifically, we assess the nanoscale features that are parallel versus perpendicular to the growth plane of the films, i.e. the relative effects of grain size versus the layer pair spacing. Although layer spacing is commonly associated with the effects of superlattice distortions in correlating effects of elastic properties, it is seen that grain size is a dominant contributor to plastic deformation associated with strength and hardness in the Ta-V films. This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

Author Index

Bold page numbers indicate presenter