Advanced Surface Engineering
Room 303D - Session SE-MoM

Nanolayered and Gradient Coatings for Surface Engineering

Moderator: A.A. Voevodin, Air Force Research Laboratory

8:20am **SE-MoM1 Structure and Hardening in TiN/a-SiNx Multilayers and Self Organizing Ti1-xAlxN Films***, M. Oden,* Lulea University of Technology, Sweden **INVITED**

This talk will cover two distinctly different mechanically hard films. The first is a dual reactive magnetron sputtered mulilayer consisting of alternating polycrystalline TiN and amorphous SiNx layers. The TiN layers exhibit a preferred 200 orientation for layer thicknesses below 10 nm. For thicker layers 111 orientations are also observed. The amorphous SiNx layers provides for TiN renulcleation in each layer yielding a column free microstructure. Nanoindentation was used to evaluate the hardness which varied between 18 to 32 GPa depending on the layer modulation. For large wavelength (>20 nm), Hall-Petch dependence is observed with a generalized power of -0.4. For shorter wavelengths superhardening yields a deviation from the Hall-Petch relationship. The highest hardness is observed for mulilayers having thin SiNx -layers (< 1nm) for which HRTEM reveals a transformation from amorphous to crystalline SiNx layers growing cube on cube on the TiN crystals. The formation of crystalline SiNx and its influence on hardening is discussed. The second material system to be reviewed is arc evaporated Ti1-xAlxN with a range of compositions (x=0 to 0.74). As-deposited coatings with xï,£0.66 had metastable cubic structures. Annealing at 1100 Â°C of these films resulted in phase separation of c-TiN and h-AlN, via spinodal decomposition of c-TiN and c-AlN. The high hardness (~37 GPa) and texture of the Ti1-xAlxN coatings are retained for annealing temperatures up to 950ï,°C, which indicates a superior stability of this system compared to TiN and Ti(C,N) coatings. It is proposed that competing mechanisms are responsible for the effectively constant hardness; softening by lattice defect annihilation is balanced by hardening from formation of a nano-composite structure of c-AlN volumes by spinodal decomposition.

9:00am **SE-MoM3 Structure and Optical Behavior of As-Grown and Annealed Titania/Alumina Nanolaminate Films***, M.A. Omari, R.S. Sorbello, C.R. Aita,* University of Wisconsin-Milwaukee

Titania-alumina nanocomposites are of current interest for optical, catalytic, and sensor applications. A wide range of desirable properties can be obtained by varying the amount of each constituent. A convenient way of incorporating tailored nanocomposites in thin film structures is by using a nanolaminate structure. We report here the fabrication, structure, and optical behavior of titania-alumina nanolaminates. 150 nm-thick multilayer films were grown at room temperature on silica substrates by sequential reactive sputtering of metal targets in argon/20% oxygen rf discharges. The nominal titania layer thickness was varied from 1.25 to 45 nm, and the alumina layer thickness was kept constant at 5 nm. X-ray diffraction and spectrophotometry were used for film analysis. The films were cyclically annealed at 700 and 1000 deg. C from 15 min to 10 h. Alumina was amorphous in as-grown and annealed films. Titania in as-grown films consisted of rutile nanocrystals embedded in an amorphous matrix. No anatase was present, nor was anatase formed by annealing. High temperature annealing produced a series of crystalline (Ti,Al)-oxide interface phases. Optical band gap and refractive index measurements indicate that significant interfacial mixing occurred in as-grown films, as well.

9:20am **SE-MoM4 The Growth of Depth-Graded WSi@sub 2@/Si Multilayer Linear Zone Plates****, C. Liu, R. Conley, A.T. Macrander, J. Maser, H.C. Kang, G.B. Stephenson,* Argonne National Laboratory

Fresnel zone plates, consisting of alternating transparent and opaque rings designed according to Fresnel phase conditions, are widely used to focus x-rays. Zone plates are commonly made using lithographic techniques and have achieved high spatial resolution on the order of 20 nm in the soft x-ray range. For hard x-rays, to achieve an optimum efficiency, the thickness of the zone plate needs to be several microns. The required high aspect ratio is difficult for lithography and imposes a limit to the focus spot size. Techniques have been developed using sectioned multilayer-coated wires to obtain a high aspect ratio, with concentric multilayers as the zone-plate rings. We have recently explored a linear zone-plate concept, by first growing a depth-graded multilayer on a flat substrate and then sectioning the multilayer and assembling several sections to focus the x-rays. The structure of the multilayer is calculated according to the desired focus parameters with corresponding Fresnel phase conditions. We have grown a depth-graded WSi@sub 2@/Si multilayer on a Si substrate using dc magnetron sputtering to test the linear zone-plate idea. The multilayer has a total of 469 alternating layers with thickness gradually increasing from ~15 nm to ~60 nm. It has a total coating thickness of ~11.27 µm and took ~45 h to coat. The sample has been sectioned and polished and studied using a scanning electron microscope and synchrotron radiation x-rays. The challenges and solutions for the growth of this kind of depth-graded multilayer will be discussed. @FootnoteText@ @footnote *@ This work is supported by the U. S. Department of Energy, under Contract No. W-31-109-ENG-38.

10:00am **SE-MoM6 Early Stages of Oxidation at 800°C for CrAlON Superlattice Coatings used to Improve Oxidation Resistance of Steel Plates for Applications as SOFC Interconnects@footnote *@***, R.J. Smith, A. Kayani, C.V. Ramana, P.E. Gannon, M.C. Deibert,* Montana State University-Bozeman*; V.I. Gorokhovsky,* Arcomac Surface Engineering, LLC*; V. Shutthanandan, D. Gelles,* Pacific Northwest National Laboratory

The requirements of low cost and high-temperature corrosion resistance for bipolar interconnect plates in solid oxide fuel cell stacks has directed attention to the use of metal plates with oxidation resistant coatings. We have investigated the performance of steel plates with superlattice coatings consisting of CrAlON (oxynitrides). The coatings were deposited using large area filtered arc deposition technology@footnote 1@, with various O/N pressure ratios, and subsequently annealed in air for up to 25 hours at 800°C. The composition, structure and morphology of the coated plates were characterized using RBS, nuclear reaction analysis, XPS and AFM techniques. Area specific resistance was measured as a function of time and temperature. By altering the architecture and composition of the coatings, the rate of oxidation was reduced by more than an order of magnitude relative to the uncoated steel plates. @FootnoteText@ @footnote 1@Vladimir I. Gorokhovsky, Rabi Bhattacharya and Deepak G. Bhat, Surface and Coating Technology, 140 (2) 2001, pp. 82-92.@footnote *@Work supported by DOI and DOE subcontract from PNNL, number 3917(413060-A). Work at PNNL (EMSL) supported through OBER (DOE) .

10:20am **SE-MoM7 Oxide Nanolaminate Coatings for Protection Against Perforated Pitting Corrosion in Stainless Steel***, W.F. Gaertner, C.R. Aita,* University of Wisconsin-Milwaukee

Perforated pitting corrosion is disastrous in stainless steel (SS) medical implants where even a low released cation concentration causes rejection by the surrounding tissue. Protection by oxide nanolaminates on 316L SS in saline is reported here. The behavior of constituent oxide single-layer films is also reported. We previously found [1] that a tetragonal ZrO@sub 2@/A1@sub 2@O@sub 3@ smart nanolaminate protects a rough 316L SS substrate (15 µm finish) against pitting. We constructed a model for corrosion prevention after a pit has initiated. This model involves mesoscopic film fracture accompanied by passivation of the underlying exposed SS. Here, we apply this model to (a) films on highly polished (1 micron finish) substrates where adhesion can be a problem, and (b) to a TiO@sub 2@/A1@sub 2@O@sub 3@ nanolaminate (which is not a smart coating) on both rough and substrates. 200 to 250 nm thick films were grown at room temperature by sequential sputtering of metal targets in Ar with 20% O@sub 2@ rf discharge. Cyclic polarization was used to determine the corrosion current, i@sub o@, as a function of applied potential after a steady state open circuit potential (OCP) was established. Samples were examined by scanning electron microscopy and energy dispersive spectroscopy. The results show that: (1) Corrosion current in all samples was low, on the order of 1 to 100 nA/cm@super 2@. (2) Single layer ZrO@sub 2@ and TiO@sub 2@ films did not protect against perforated pitting in polarized samples of either surface finish. (3) Single layer A1@sub 2@O@sub 3@ did prevent pitting but catastrophically failed after a single polarization cycle.(4) Nanolaminates protected by the synergic effect of a tough (ZrO@sub 2@, TiO@sub 2@) nanolayer combined with a brittle (A1@sub 2@O@sub 3@) became important in 316L SS with a rough finish. @FootnoteText@ NSF-CMS Grant No. 9988892 is acknowledged. [1]W.F.Gaertner,et al.,JVST A 22, 272 (2004).

10:40am **SE-MoM8 Environmentally Friendly Plasma Electrolytic Processes for Corrosion and Wear Protection of Lightweight Metals***, A.L. Yerokhin,* Sheffield University, UK, U.K.*; A. Matthews,* Sheffield University, UK **INVITED**

The paper discusses both fundamentals and applied aspects of novel Plasma Electrolytic Oxidation (PEO) processes which can be successfully used for wear and corrosion protection of Al, Ti and Mg alloys. Being a high-voltage electrochemical oxidation process, PEO is featured by a plasma discharge that occurs at the metal/electrolyte interface in the form of discrete short-lived microdischarges moving across the metal surface. This alters the kinetics of the main electrode processes, i.e. anodic oxidation and dissolution, complementing them with high rate gas evolution triggered by plasma enhanced thermochemical reactions at the metal surface. As a result, surface layers with composition and structure substantially different to those of conventional anodic oxide films can be formed in environmentally friendly diluted alkaline solutions. Electrolyte species tend to be more strongly incorporated into the surface layer, forming mixed oxide compounds. Rapid local heating and quenching of the surface during the microdischarge events promotes formation of high temperature oxide phases with fused-like structure, controllable porosity and a graded coating/substrate interface. Oxide ceramic surface layers produced by PEO as well as composite coatings based on these layers are proven to possess excellent tribological and anti-corrosion properties, which show promise for a number of industrial applications.

11:20am **SE-MoM10 Evaluation of Plasma Polymer Coatings in Corrosion Protection of Aluminum Alloys***, **Q.S. Yu,*** University of Missouri-Columbia, US*; Y.F. Chan, H.K. Yasuda,* University of Missouri-Columbia

As a pretreatment method, chromate conversion coatings are being widely used for corrosion protection of aircraft aluminum alloys. Pretreatment by chromate conversion layer is used to ensure good paint adhesion and provide corrosion inhibition. Due to the hazardous and toxic effects of chromates to environment and human heath, however, pressure from EPA has promoted research efforts focusing on the replacement of chromate conversion coatings with more environmentally friend systems. One promising alternative method is the use of plasma polymer coatings as pretreatment for metallic materials. Plasma polymerization process is a dry and â?ogreenâ? process which can produce high quality and chemically inert coatings with strong adherence to various substrates including metallic materials. Our recent studies have demonstrated that interface engineered plasma coating systems provide excellent corrosion protection of various aircraft Al alloys. In this study, the roles of plasma polymer coatings in interface engineering and fabrication of environmentally benign coating systems are further investigated. Electrochemical measurements including potentiodynamic polarization and electrochemical impedance spectroscopy are employed to characterize the corrosion resistance and interface properties of plasma coated Al alloys. The results obtained through this study will be presented and discussed.

11:40am **SE-MoM11 Nano-coatings for Complex Uneven Surfaces Cellular Foams & Nano-fibers of Carbon***, S.M. Mukhopadhyay, **R.V. Pulikollu,** P.P. Joshi,* Wright State University

The concept of surface coatings to enhance or prevent bonding with a second phase is not new, but when the surface in question has complex shape, and the coating needs to be effective at the nanometer scale, new challenges emerge. In this presentation, effectiveness of plasma-assisted nano-coatings (4-5nm thick) on two carbon structures will be presented. These are: (i) microcellular foam that has about 80% porosity and the surface consists of open, interconnected cell walls, and (ii) vapor-grown fibers having diameter of about 200nm. Both these structures are useful as reinforcing materials for composites. Coatings for enhancement surface wettability are obtained in microwave plasma using siloxanes. This treatment forms a strongly bound SiO_2-type layer on the surface and causes noticeable enhancement of polar fluid infiltration in these materials. This results in micro-structural differences and enhancement of mechanical properties of composites formed. A different type of coating, that makes the surface inert by attaching CF_2 groups on it, is effective in making these surfaces moisture-repellent. This coating appears to influence composite behavior in different ways. Additional aspects of these coatings, specific to different applications, such as bonding with metals and polymers, and possibility of creating multi-layer and multi-functional nano-coatings will be discussed.

Author Index

Bold page numbers indicate presenter