

# Thursday Afternoon Poster Sessions

## Advanced Surface Engineering

Room: Hall B - Session SE-ThP

### Poster Session

**SE-ThP1 Gas Barrier Properties of Hydrogenated Amorphous Carbon Films Synthesized by Atmospheric Pressure Plasma on Nitrogen-Plasma-Treated Polyethylene Terephthalate Substrates, Y. Futagami, T. Hirako, M. Noborisaka, A. Shirakura, T. Suzuki, Keio University, Japan**

Gas barrier properties of hydrogenated amorphous carbon (a-C:H) films synthesized at atmospheric pressure have been investigated for applications to packaging materials. In this study, a-C:H films were synthesized on N<sub>2</sub>-plasma-treated polyethylene terephthalate (PET) substrates by atmospheric pressure plasma enhanced chemical vapor deposition method. PET substrates were treated with various plasma treatment time at atmospheric pressure prior to synthesis of 500-nm-thick a-C:H films. The effects of N<sub>2</sub> plasma treatment on the properties of PET surface and a-C:H/PET were investigated in terms of chemical binding structure, surface free energy, roughness, adhesion and oxygen transmission rate (OTR). Formation of new C-N bonds were observed on the PET surfaces by N<sub>2</sub> plasma treatment from X-ray photoelectron spectroscopy analysis, and the adhesion strength between a-C:H films and PET substrates was improved in tape tests. As the plasma treatment time increased from 0 to 5 s, OTR of the a-C:H films on N<sub>2</sub>-plasma-treated PET substrates decreased from 5.6 to 3.1 cc/(m<sup>2</sup>·24h·atm), which is five times less OTR than those of uncoated PET substrates. However by increasing the plasma treatment time from 5 to 40 s, the surface roughness of PET substrate and OTR of a-C:H/PET were increased to 10.5 nm and 4.2 cc/(m<sup>2</sup>·24h·atm). This result indicates that the proper time of N<sub>2</sub> plasma treatment on PET substrates is effective for improving adhesion and gas barrier properties of a-C:H films.

**SE-ThP2 Recycling and Diffusion of Ions in High Power Impulse Magnetron Sputtering Plasmas, L. Meng, P. Raman, H. Yu, D.N. Ruzic, University of Illinois at Urbana Champaign**

\*\*\*PLEASE NOTE THAT D. RUZIC CANNOT BE THE PRESENTER. HE IS ALREADY AN INVITED SPEAKER AND YOU MAY PRESENT ONE PAPER (ORAL OR POSTER) IN THE SYMPOSIUM\*\*\* In high power impulse magnetron sputtering (HiPIMS), ions either diffuse towards the substrate for the deposition or are recycled to sputter or self-sputter the target. Both processes were studied here to further understand the underlying mechanisms. For the diffusion, plasma across the entire chamber was characterized using a 3D scanning triple Langmuir probe. An obvious plasma expansion originated from the "race track" region was observed. The expansion speed and orientation varied with both pulsing parameters and magnetic field strength. These parameters were also found to affect the metal ionization fraction on the substrate. A lower magnetic field strength gave a higher ion fraction (e.g. up to 60% for Cu in a 200 Gauss field while about 30% in an 800 Gauss field) despite a lower plasma density. The corresponding lower plasma potential drop across the bulk plasma was accounted for the effect. Then, the fluxes of plasma species towards the cathode were directly measured through an orifice on the target. Quartz crystal microbalance and current collecting plate behind grid filters were used to determine the fluxes of argon ions, metal ions, and metal atoms. The self-sputtering effect during HiPIMS was supported by a higher fraction of metal ions obtained at a higher pulse peak current. A delayed detection of ion flux for 10 to 40 μs from the onset of pulse likely supported the theory of localization of ionization zone during the HiPIMS ignition.

**SE-ThP3 Mechanical Properties and Impact Resistance of CrAlSiN and TiAlSiN Coatings, Y.Y. Chang, Y.C. Yang, Y.K. Chou, J.X. Liu, National Formosa University, Taiwan, Republic of China**

The extension of the tool life is a considerable goal for high speed precision forming tools. Therefore, it is interested to reduce the friction and wear for such tools. The employment of hard coatings, in form of metal and ceramic, increases the production and maintenance costs. In this study, CrAlSiN and TiAlSiN coatings have been deposited on cemented carbide tools by using cathodic-arc evaporation with plasma enhanced duct equipment. Titanium, TiAl, TiSi and CrAlSi alloy cathodes were used for the deposition. The alloy content of the deposited coating was correlated with the evaporation rate of cathode materials. The microstructure of the deposited coatings was characterized by using a field emission gun high resolution transmission electron microscope (FEG-HRTEM, FEI Tecnai G<sup>2</sup> 20 S-Twin), equipped with an energy-dispersive x-ray analysis spectrometer (EDS), operated at 200 keV for high-resolution imaging. Glancing angle X-ray diffraction was used to investigate the microstructure and phase identification of the films. The composition and depth profile were assessed by wavelength-dispersive

x-ray spectroscopy (WDS). Mechanical properties, such as the hardness and elastic modulus, were measured by means of nanoindentation. To evaluate the correlation between impact fracture resistance and hardness/elastic modulus ratio of the deposited coatings, an impact test was performed using a cyclic loading device with a tungsten carbide indenter as an impact probe. The design of CrAlSiN and TiAlSiN coatings is anticipated to inhibit the grain growth, and leads to grain refinement effect, which expected to increase the hardness and impact resistance of coatings.

**SE-ThP4 Preferential Growth of Oxide Nanorods on Multicomponent TiAlSiN Coated Stainless Steels after Thermal Oxidation, Y.Y. Chang, Y.C. Yang, National Formosa University, Taiwan, Republic of China**

Transition metal nitrides, such as TiN and CrN, have been used as protective hard coatings due to their excellent tribological properties. Recently, multicomponent TiAlSiN coatings have been developed in order to possess high hardness and good thermal stability at temperature exceeding 800 °C. In this study, a series of TiAlSiN coatings with different alloy contents (Ti<sub>0.67</sub>Al<sub>0.32</sub>Si<sub>0.01</sub>N, Ti Al Si N, and Ti<sub>0.85</sub>Al<sub>0.03</sub>Si<sub>0.12</sub>N) were deposited onto an SS304 substrate by using cathodic arc evaporation. Cathodes of Ti, TiAl (50 at.% of Al and 50 at.% of Si) and Ti<sub>0.8</sub>Si<sub>0.2</sub> (80 at.% of Al and 20 at.% of Si) alloy targets were used. The as-deposited films were annealed at 800 °C for different time from 20 minutes to 100 minutes in air to analyze the different preferential oxidation behaviors of TiAlSiN coatings. The surface morphology and microstructure of the deposited and oxidized coatings was investigated by field emission scanning electron microscopy (FESEM) equipped with an energy-dispersive x-ray analysis spectrometer (EDS). X-ray diffractometry was performed using PANalytical X'pert Pro diffractometer with a high resolution  $\psi$  goniometer and Cu radiation in both glancing angle and high-angle configurations for phase identification. The correlation between the preferential growth of oxide nanorods and the deposited multicomponent TiAlSiN coatings was discussed. During the oxidation process, Ti, Al, and Si would diffuse outward to form oxidative layers of Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and SiO<sub>2</sub> at high temperature. The Ti<sub>0.67</sub>Al<sub>0.32</sub>Si<sub>0.01</sub>N with higher Al content ratio showed that needle-like  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> oxides preferentially grow from the macroparticle defect sites. Oxide nanorods were uniformly found on the oxidized Ti<sub>0.8</sub>Al<sub>0.17</sub>Si<sub>0.03</sub>N with smaller content of Al. The Ti<sub>0.85</sub>Al<sub>0.03</sub>Si<sub>0.12</sub>N with the highest Si and the lowest Al contents showed only short TiO<sub>2</sub> nanorods uniformly grow on the surface. Therefore, the kinetic oxidation behavior of TiAlSiN coatings varied with the alloy content and phase segregation via high temperature oxidation.

**SE-ThP5 Oxidation Resistance and Hardness of CrAlN based Films Deposited by the Arc Ion Plating Method, T. Mori, T. Suzuki, Keio University, Japan**

In the field of hard coatings, oxidation resistance and high hardness of the coatings are among the main concerns. In this study, CrAlSiYN films with various silicon content were synthesized and investigated their oxidation resistance and hardness. The films were deposited on cemented carbide, silicon and SUS304 substrates by the arc ion plating method. X-Ray Diffraction results showed that the CrAlSiYN films had NaCl-type structure. With increasing the silicon content, the lattice parameter *a* for cubic CrAlSiYN films decreased from 0.416 nm to 0.413 nm. The solid solubility limit of silicon into CrAlYN film was about 3 at. %. Hardness of CrAlSiYN films was measured using conventional micro-Vickers hardness tester and the result showed that CrAlSiYN films with high Si content exhibited high hardness (about 30 GPa). Using the flow discharge optical emission spectrometry depth profiling method, an oxygen peak was only observed around surface of films after annealed at 1000°C for 1 hour in air. The cross-sectional transmission electron microscopy observation of oxide layer of CrAlSiYN films showed that yttrium stimulated the formation of amorphous oxide, and its silicon or yttrium oxide prevented diffusion of oxygen and metal such as chromium. Incorporation of silicon and yttrium maintained the stable oxidation layer of Cr<sub>2</sub>O<sub>3</sub> or Al<sub>2</sub>O<sub>3</sub> produced at the surface under high temperature and improved oxidation resistance of CrAlN films.

**SE-ThP7 Structure and Mechanical Properties of Tungsten-Yttrium Based Coatings, G. Martinez, C.V. Ramana, University of Texas at El Paso**

The challenging environment associated with a fusion reactor will require the utilization of advanced materials in order to enable successful development of fusion energy for the future. Tungsten(W)-based materials have been considered for nuclear reactor applications for its outstanding properties such as high melting point, low vapor pressure, high thermal conductivity, and low thermal expansion coefficient. However, pure W exhibits low fracture toughness at all temperatures and a high ductile to brittle transition, which depends on the chemical and microstructure. The

present work was focused on the W-Y based alloy coatings grown by sputter-deposition. The sputtering was performed using a W-Y target to fabricate coatings on to MgO(100) substrates. W-Y coatings were made at various growth temperatures ( $T_s$ ) ranging from room temperature to 500 °C. The structural and mechanical properties of the coatings were evaluated as a function of  $T_s$ . While the ultimate goal is to investigate the performance of W-Y coatings as a structural material in the next generation nuclear reactors, preliminary results obtained on the crystal structure, composition, stress evolution and mechanical properties of the coatings are presented and discussed.

**SE-ThP8 A New Testing Method for Surfaces Subjected to Combined Impact and Sliding Loads.** *P. Epaminonda, C. Rebolz*, University of Cyprus

There are a large number of factors involved in wear processes (e.g. mechanical, physical and chemical properties, surface topography, loading), making the precise theoretical and quantitative approach of wear a challenge even for “simple” tribo-systems. Many of these factors are hard to measure, may vary with time and space, and there is not yet a general theory available of how to link the basic properties with the tribological response. Several well established testing methods (e.g. pin-on-disk, fretting and impact tests) have been widely used to study treated surfaces and coatings on various substrates. However, many of these existing techniques have limitations in their ability to characterize materials, since they mainly focus on a single mode of loading and wear (e.g. only impact or sliding).

In this study, a new Dynamic Impact and Sliding Test (DIST) for the tribo-mechanical evaluation of surfaces under complex loading conditions is presented, where the surfaces are simultaneously subjected to sliding and impact loading. Such modes exist in many critical applications, from biomedical (e.g. hip/knee implants) to automotive applications (e.g. diesel injectors, engine valves, cam shafts), in cutting tools, general machine parts and systems, etc. Instruments and techniques for combined loading situations (such as the proposed DIST) are a feasible way for fast, economical and reliable evaluation of complex tribo-systems with high practical and industrial interest. Expected benefits include the time and cost effective evaluation of various surfaces and the better understanding of their peculiarities under such multi mode loading conditions. Some of the unique characteristics of the DIST (e.g. combined impact and sliding testing; wear area in a single point; pre-setting of desired maximum wear depth possible; evaluation of materials’ properties and behavior in a single run) are presented.

**SE-ThP9 Exploring Crater Roughness for Durable Sol-Gel Derived Superhydrophobic Coatings.** *B. Dyett, A. Wu, R. Lamb*, The University of Melbourne, Australia

Characterized as exhibiting water droplet contact angles  $> 150^\circ$  and sliding angles  $< 5^\circ$ , superhydrophobic films have attracted considerable research attention as a result of their remarkable non-wetting properties and potential applications in self-cleaning, anti-fouling and anti-icing. The combination of hydrophobic chemistry and surface roughness necessary for imparting such non-wetting characteristics presents a challenge towards industrial applicability due to the intrinsic frail nature of highly rough surfaces.[1] Sol-gel synthesis offers a versatile and scalable means for producing superhydrophobic films. However, traditional sol-gel approaches are often reliant on ‘needle-like’ aggregations of nanoparticles to impart surface roughness. This surface structure, whilst ideal for minimizing solid-water interactions is inherently fragile.[2, 3] Upon contact, high aspect-ratio asperities experience excessive pressures usually exceeding the mechanical properties of the material[4], consequently such superhydrophobic films are very easy to abrade and damage. To overcome this challenge a templating method was used to engineer more robust structures. Discrete polymer spheres were embedded within an alkoxysilane sol-gel to form a continuous, robust, thin film. Roughness was then engineered into the film by thermally degrading the polymer spheres within the gel network, leaving behind crater-like structures with durability far exceeding its predecessor’s. The resultant crater-like films exhibited pencil hardness exceeding 4H, eclipsing traditional films’ pencil hardness, typically of the order 8B – HB. This avenue may provide a scalable approach for controlling roughness features in durable superhydrophobic films and allow for large scale application in areas of self-cleaning and anti-fouling.

References

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**SE-ThP10 Abrasion Resistance and Adhesion Promotion for SiOC(-H) / Polycarbonate System using Nanosilica Contained Acrylic Intermediate Layers.** *T. Masuko, M. Noborisaka, T. Mori, A. Shirakura, T. Suzuki*, Keio University, Japan

SiOC(-H) films were synthesized on polycarbonate substrates from mixture of trimethylsilane (TrMS) and  $O_2$  gases by radio frequency plasma enhanced chemical vapor deposition (RF-PECVD) method to improve the abrasion resistance of polycarbonate substrates.

In order to improve the adhesion to polycarbonate substrates, we applied the acrylic intermediate layer prepared by ultraviolet curing method between SiOC(-H) films and polycarbonate substrates. The nanosilica particles were mixed with pentaerythritol triacrylate and pentaerythritol tetraacrylate at various concentrations to control the hardness of the intermediate layer.

The scratch resistance of SiOC(-H) films deposited on polycarbonate substrates with the intermediate layer was improved as the pencil hardness of the intermediate layer increased. After the taber abrasion tests of the SiOC(-H) films deposited on polycarbonate substrates with the intermediate layer, the occurrence of delamination was inspected by digital microscope. The delamination was confirmed to be markedly suppressed as the hardness of the intermediate layer increased.

The haze difference ( $\Delta H_{\text{haze}}$ ) between before and after the abrasion tests exhibited sufficient abrasion resistance of 3.5% after 1000 revolutions when the 500 nm thick-SiOC(-H) film was deposited on polycarbonate substrates with the intermediate layer contained 25 wt.% nanosilica particles.

**SE-ThP11 Highly Conformal and Size-Controlled Nanofabrication of Macro-scale Three-Dimensional Biotemplated Inorganic Nanonetworks.** *H. Ceylan, C. Ozgit-Akgun, T.S. Erkal, I. Donmez, R. Garifullin, F. Genisel, A.B. Tekinay, A.K. Okyay, M.O. Guler, N. Biyikli*, Bilkent University, Turkey

By combining organic and inorganic nanomaterials using two different material growth techniques (self assembly and atomic layer deposition), we demonstrate a facile and reliable fabrication method for  $TiO_2$  and ZnO semiconductor nanonetworks. Self-assembled peptide-amphiphile nanofibers are used as three-dimensional organic nano-templates, whereas subsequently atomic layer deposited metal-oxide films formed the conformal inorganic functional nano-coatings. Apart from the traditional organic templates, we used a fully dried, three-dimensional (cm-scale), highly interconnected peptide nanofibrous network template, which enabled atomic layer deposition (ALD) precursors to be homogeneously deposited with exceptional conformity. The wall thickness of the inorganic nanotubes can be precisely controlled by simply altering the number of ALD cycles.  $TiO_2$  and ZnO nanonetworks demonstrated superior performance compared to the unstructured  $TiO_2$  and ZnO substrates in photocatalytic activity because of the enhanced specific surface area of the photocatalysts with nanostructured morphology. Importantly, immobilization of the photocatalysts on a solid support enabled recycling of the material, which can dramatically reduce the treatment cost and prevent secondary contamination of the water sources with inorganic materials. Furthermore, we discovered that there is an optimal wall thickness for gaining photocatalytic advantage through nanostructuring for both  $TiO_2$  and ZnO. This optimum nanotube wall thickness was found to be around ~8 nm for both  $TiO_2$  and ZnO. These results demonstrate significant potential of using peptide-based organic templates to fabricate high-quality  $TiO_2$  and ZnO nanostructures not only for photocatalysis, but for several applications where increased surface area plays a crucial role: chemical/gas sensing, dye synthesized solar-cells, etc. Further studies can be extended to other transition-metals and their compounds, such as oxides, nitrides, and sulfides. As a result of the rapid and convenient scaling of the peptide nanofibers into macro-size networks, new opportunities could be available for fabrication of a wider range of inorganic materials.

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