Tuesday Afternoon Poster Sessions

Advanced Surface Engineering

Room: 4C - Session SE-TuP

Advanced Surface Engineering Poster Session

SE-TuP1 Protective Coatings of Extensible Biofibers, ***N. Holten-Andersen***, *F. Zok, J.H. Waite*, University of California, Santa Barbara

As thin film coatings are increasingly finding their way in engineering and biomedical applications, the demand for unique combinations of their material properties is increasing as well. A coatings protection of the underlying substrate against wear relies on its resistance to penetration, i.e. its hardness. Increasing hardness of the coating however, significantly lowers its extensibility. Protecting substrates undergoing large strains against wear is therefore a challenge beyond the reach of current engineering coating applications. By investigating natural coating materials adapted to high- and low-stress environments we have studied nature's solution to this problem. In the protective cuticles of mussel holdfast threads (self-assembled biological fibers), high wear resistance have in wave-exposed species been combined with high extensibility. Here, we demonstrate that the inclusion of deformable micro-particles within a stiff protein matrix allows the cuticle of these holdfast threads to exhibit sufficient hardness against wear without encumbering the elasticity of the thread. This unique composite design results in an impressive damage tolerance by arresting developing micro-cracks thereby preventing catastrophic failure of the coating up until an astounding 70% strain. Cuticles from mussel species in deeper and calmer habitats lack these deformable particles and fracture below 30% strain. This increase in extensibility of the granular composite cuticle parallels the behavior observed with rubber toughened polymers such as High Impact Poly-Styrene. However, whereas the inclusion of rubber particles significantly compromises the hardness of these synthetic composites, our study shows that only a small reduction in hardness is observed in the biological coating composite. Interestingly, the interior morphology of the micro-particles in the cuticle shares a striking similarity with the bi-continuous network morphologies observed in polymer micro-emulsions and block copolymer systems. The superior mechanical properties together with the self-assembling nature of the material, makes this study significant for the broad materials community.

SE-TuP2 Optimization of Process Parameters using Matrix Assisted Pulsed Laser Evaporation (MAPLE) for Deposition of Carbon Nanoparticles, ***M.H. Check***, University of Dayton, *A.A. Voevodin, C.N. Hunter,* Air Force Research Laboratory, *J.J. Hu*, University of Dayton Research Institute

Matrix Assisted Pulsed Laser Evaporation (MAPLE) is a thin film deposition technique that can be applied to a large range of polymeric and biological substances. The advantage of using MAPLE compared to other laser techniques is that deposition can be accomplished with little or no damage to the transported material. The technology was explored for preparation of tribological coatings with carbon nanopearls (~150 nm in size) encapsulated in metal (Au and Ag) and ceramic (TiN) matrices. The focus was placed on understanding how to control transport and uniformity of nanopearls on the deposition surface. The controlling parameters included laser fluence (200-800 mJ), repetition rate (1-30 Hz), solvent material (methanol and isopropanol), and background gas composition and pressure (5-30 mTorr of Ar and N2 mix). The characteristics of the synthesized 1-2 micron thick carbon/metal and carbon/ceramic composite films were correlated with area fraction of the nanoparticles, degree of dispersion of the nanoparticles and effect of the transport process on the properties of the nanoparticles. Results from electron microscopy, optical profilometry, and XPS are discussed.

SE-TuP3 High Rate Deposition of Photocatalytic TiO_2 Films with High Activity by Hollow Cathode Gas-Flow Sputtering, ***Y. Kubo***, Aoyama Gakuin University, Japan, *Y. Iwabuchi, M. Yoshikawa,* Bridgestone Co., Japan, *Y. Sato, Y. Shigesato*, Aoyama Gakuin University, Japan

Titanium dioxide (TiO_2) has been well known as a photocatalyst because of the strong oxidizing power of photo-generated holes. Reactive sputter depositions using a Ti metal target should be one of the most promising techniques for uniform coatings in large area with high packing density and strong adhesion. However, the deposition rate is very small of 2~5 nm/min for the conventional reactive magnetron sputtering to deposit fully oxidized TiO_2 films because the films should be deposited at the "oxide mode" where the target surface is oxidized and the sputtering yield is very smal.[1] In order for the high deposition rate of 30~90 nm/min, we have been reported on dual cathode sputtering system[2] or unipolor pulsing system[3] with plasma emission control systems[2-3]. As the much simpler and lower cost system, TiO_2 films were deposited on unheated alkali-free glass substrates by gas-flow sputtering using two Ti metal targets which were mounted parallel with each other. Ar (sputtering gas) was supplied between these two targets.O_2 (reactive gas) was supplied in the vicinity of the substrate. Ar and O_2 flows were 3.0 SLM and 10~50 sccm, respectively, and total gas pressure during the depositions was maintained at 45 Pa. In such pressure mean free path of gas atoms is very small and a gas flow is in viscous regime, that is why the process has been named gas-flow sputtering.[4] The photocatalytic activity was evaluated by photo-decomposition of acetaldehyde and contact angle for water after UV illumination (black light lamp, 0.4 mW/cm^2). Both of the as-deposited films and the post-annealed films at 300 °C in air performed the photocatalytic decomposition. Especially the post-annealed films performed extremely high photocatalytic activities. The highest deposition rate to deposit such photocatalytic TiO_2 films were 162 nm/min.

[1] M. Yamagishi, S. Kuriki, P. K. Song and Y. Shigesato, Thin Solid Films, 442 (2003) 227.

[2] S. Ohno, D. Sato, M. Kon, Y. Sato, M. Yoshikawa, P. Frach, Y. Shigesato, Jpn. J. Appl. Phys., Vol. 43, No.12 (2004) 8234.

[3] S. Ohno, N. Takasawa, Y. Sato, M. Yoshikawa, K. Suzuki, P. Frach and Y. Shigesato, Thin Solid Films 496 (2006) 126.

[4] K. Ishii, J. Vac. Sci. Technol., A7 (1989) 256.

SE-TuP4 High Rate Deposition of Photocatalytic WO_3 Thin Films with Visible Light Activity by Gas-Flow Sputtering, ***M. Fukuyama***, *M. Kikuchi*, Aoyama Gakuin University, Japan, *Y. Iwabuchi, M. Yoshikawa*, Bridgestone Corporation, Japan, *Y. Sato, Y. Shigesato*, Aoyama Gakuin University, Japan

In recent years, we have been reported on the visible-light induced photocatalytic properties on polycrystalline WO_3 films deposited by reactive dc magnetron sputtering on heated glass substrate at around 600 oC.[1,2] However deposition rate was very low of about 10 nm/min for the conventional reactive magnetron sputtering to deposit fully oxidized WO_3 films because the films should be deposited at the "oxide mode" where the target surface is oxidized and the sputtering yield is very small. In this study, polycrystalline WO_3 films were deposited by on fused quartz glass substrate by gas flow sputtering using two W metal target which were mounted parallel with each other. Ar was used as sputtering gas and O_2 was used as reactive gas, which were supplied between these two targets. Total gas pressure was maintained at 70Pa. Ar and O_2 gas flows were 5.0 SLM and 50 sccm, respectively. WO3 films were deposited on the substrate without heating or heated upto 500 oC, 600 oC or 700 oC. The films deposited on the unheated substrate were post-annealed at 500 oC, 600 oC or 700 oC for an hour in the air. The crystal structure of the WO_3 films were analyzed by X-ray diffraction (XRD). The transmittance and reflectance of the films in UV-VIS region were measured using spectrophotometer in order to estimate absorption coefficient by Newton-Raphson's method. The photocatalytic activity was evaluated by decomposition of acetaldehyde and contact angle for water after UV (black light lamp : 0.4mW /cm^2, center wavelength : 352 nm) light and VIS (Xe lamp with a 410-500 nm band pass filter : 1.0, 7.0 mW/cm^2 respectively, center wavelength : 450 nm) light irradiation. Both of the films deposited at 500-700 oC and the films post-annealed at 500-700 oC performed the visible-light induced photocatalytic activity. The highest deposition rate to deposit such photocatalytic WO_3 films was 230nm/min.

[1] M.Ebihara, Y.Shigesato, et al., Proceedings of the 3rd ICCG), (2000) 137.

[2] M. Kikuchi, Y. Shigesato, et al., Proceedings for 6th International Conference on Coatings on Glass and Plastics (ICCG-6), (2006) 365.

SE-TuP5 Photocatalysis of Dense and Porous Bilayers of Cuprite and Titania, ***M.H. Wu***, *M.S. Wong*, National Dong Hwa University, Taiwan

Titanium dioxide with anatase phase couples with different materials contributing better or worse photocatalysis. Transferring of electrons and holes in junction is caused by the different energy levels of conduction band and valence band. Dense and porous bilayers of cuprous oxide and titanium dioxide with various microstructures and thickness were prepared by magnetron sputtering and electron beam evaporation with glancing-angle deposition technique. The photocatalysis of the films was tested via photo-degradation of methylene blue. Porous columnar titania films covered with Cu2O layer allow good carrier transfer and high specific surface area, where the photo-generated electrons and holes can be separated and function at different area of the columnar structure, resulting better photocatalytic performance.

SE-TuP6 Preparation of TiO_2 Thin Films by Laser Ablation for Photocatalytic Applications, *W.-T. Chang*, ***J.-Y. Ciou***, National Dong Hwa University, Taiwan, *S.-J. Wang*, National Taipei University of Technology, Taiwan, *M.-K. Wei, M.S. Wong*, National Dong Hwa University, Taiwan

Thin titanium dioxide (TiO2) films were deposited by KrF excimer laser ablation deposition system using a titanium oxide target. The effects of substrate temperature and oxygen partial pressure on the phase formations of various microstructures were investigated by X-Ray diffraction (XRD), scanning electron microscopy (SEM), Raman scattering spectroscopy and UV-Vis spectrophotometer, respectively. Increasing the substrate temperature can improve the quality of anatase phase of crystalline TiO2 films that were obtained from the amorphous structure hybridized with rutile and anatase phases. However, the oxygen pressure in the range between 15 to 60 mTorr shows a single anatase phase in TiO2 films that the rutile and anatase phases were observed elsewhere. The bandgap of TiO2 films varied from 2.72eV to 3.27 eV with more oxygen partial pressure in the film deposition indicates the phase changed from rutile phase to anatase phase. The surface area of TiO2 films was increased as more oxygen partial pressure involved in the fabrication. The photocatalytic effect measured by exposing the methylene blue in UV light that was distinguishable in the TiO2 films with high anatase phases and surface area.

SE-TuP7 Effect of Internal Pressures for TiO_2 based Colloidal Sols during Hydrothermal Process, ***C.R. Yoon***, *H.J. Oh, N.H. Lee, Y. Guo, S.J. Kim*, Sejong University, Korea

Transparent TiO_2 sols were prepared by hydrothermal synthesis to heat Ti precursor solutions, from Ti hydroxides obtained with neutralizing aqueous $TiOCl_2$ solutions having various concentrations of NaCl by aqueous NaOH solution, in the autoclave at 120°C, and then their photocatalytic abilities using glass beads coated with the sol for gaseous benzene were evaluated. Because it was possible to prepare brookite phase TiO_2 sol by external pressurization into the autoclave during the synthesis, the internal pressure in the autoclave was controlled using a technique with capturing Na ions in the lattice of Ti hydroxide. As a result, it was found that due to the increase of brookite phase in TiO_2 by controlling the concentration of Na ion the optical absorption of TiO_2 increases toward long wavelength but that in the range of short wavelength becomes relatively low and consequently the photocatalytic performance of TiO_2 thin film for benzene gas rather decreases, compared to that of composite film of anatase and brookite phases. These results suggest that in order for coated TiO_2 thin film to have high dissociation performance for benzene gas it is effective to form anatase and brookite phases compositely in TiO_2.

SE-TuP8 Photoinduced Friction Force Variation of Polycrystalline Anatase Thin Films, ***N. Arimitsu***, *A. Nakajima, Y. Kameshima, K. Okada*, Tokyo Institute of Technology, Japan

Titanium dioxide (TiO_2) thin film has attracted much attention as a photocatalyst. TiO_2 surface exhibits conventional photocatalytic oxidation reactions and photoinduced highly hydrophilic conversion. These reactions result in useful properties such as antibacterial functions, self-cleaning, and antifogging. The photoinduced reaction on TiO_2 surface has been well studied by various techniques. According to a friction force microscopy (FFM) study using a Si_3N_4 cantilever, it was revealed that rutile single crystal produce a unique microdomain structure in the surface with a contrast difference by UV illumination.[1] Since the tip of the cantilever is hydrophilic, the image contrast implies the difference in hydrophilicity on the surface. Recently, it is reported that the contrast difference after UV illumination was also obtainable on polycrystalline anatase thin film as in the case of rutile single crystal.[2] In the present study, we prepared polycrystalline anatase thin films on Si substrates using sol-gel process and O_2 plasma treatment[3] and investigated the relationship between photoinduced friction force change and photoinduced hydrophilicity of the film. The photoinduced friction force change was evaluated by FFM with a Si_3N_4 cantilever. Upon UV illumination, the average friction force decreased gradually with decreasing water contact angle until it reached the lower limit. Then, the friction force began to increase with increasing UV illumination time. Detailed relationship among contact angle change, UV illumination period, and friction force change will be discussed.

[1] R. Wang et al., Nature 388 (1997) 431.

[2] K. Katsumata et al., Surf. Sci. 579 (2005) 123.

[3] N. Arimitsu et al., Surf. Coatings Technol. 201 (2006) 3038.

SE-TuP9 Pretreatment by High Power Impulse Magnetron Sputtering - Interface Structure and Stress Evolution, ***D. Jädernäs***, *M. Lattemann, U. Helmersson*, Linköping University, Sweden

Substrate pretreatment using metal ion bombardment is an effective way of promoting film-substrate adhesion. In this work we have used high power impulse magnetron sputtering (HIPIMS) to produce the Cr-ions that are bombarding the high speed steel substrates with an applied negative substrate bias, U_b, between 200 and 1100 V. During pretreatment and subsequent film growth, the stress evolution was measured and the adhesion of the films was evaluated using scratch testing. Some samples were also post-annealed at a temperature of 900 K. The results showed that all pretreatment conditions result in a compressive stress that can be correlated to U_b. The stress induced during pretreatment was also shown to affect the growth of the subsequently grown film. For U_b below 600 V significant etching did not occur and a Cr-layer was formed. In this case, the native oxide on the steel remained. For higher U_b values the oxide layer was removed. For the non-annealed films a strong correlation between U_b and adhesion was observed. Substrates with the oxide layer intact showed low film adhesion. After annealing all samples showed an increased adhesion and no clear trend between different pretreatments and adhesion could be observed. The interfacial chemistry and structure were examined in order to find the correlation between structure, chemistry and adhesion. The results show that strong interfaces, capable of resisting an applied force, can be produced even though an oxide is still present.

SE-TuP10 Nanostructure and Properties of TiAlN/a-C Composite Coatings, ***M. Nose***, *T. Kawabata*, University of Toyama, Japan, *S. Khamthe*, Graduate School of Science and Engineering, Japan, *K. Matsuda, T. Nagae, S. Ikeno*, University of Toyama, Japan, *K. Nogi*, Osaka University, Japan

Aluminum/magnesium pressure die-casting needs protective coatings to the molding dies in order to extend die life. When applied to cast liquid aluminum or magnesium alloy into molding parts, die surface faced harsh conditions such as soldering and erosion at temperatures over 600 °C. DLC (diamond like carbon) or a-C (amorphous carbon) coating has been widely applied to machine-tools for aluminum, due to enhanced tribological properties in terms of low friction, high hardness and non-affinity to aluminum. However, DLC or a-C becomes thermally unstable at temperatures higher than 300 °C when coating hardness drastically drops with temperature. Nanocomposite coatings consisting of transition metal nitride/carbide and amorphous carbon are expected to be stable at higher temperatures and to reduce adhesion of nonferrous alloy. In this study, TiAlN/C nano-composite coatings synthesized by PVD process were examined the effects of sputtering conditions on the microstructure and mechanical properties, and evaluated as potential applications in molding dies. Coating films were synthesized by the co-sputtering of TiAl (pulsed-d.c. sputtering) and C (d.c. sputtering) targets using a Facing Target-type Sputtering system (FTR-2, Osaka Vacuum Co., Ltd.) under an environment with a mixture of Ar and N_2 on square plates of Si and high speed steel (ANSI M2). The structure of the films was investigated by means of XRD, XPS and HRTEM with GIF (Gatan Imaging Filter). Mechanical properties of coating films were measured in detail by a submicron indentation system (H-100, Fischer). Although TiAlN or a-C films showed hardness of about 30 or 10 GPa, one of TiAlN/a-C films containing several % of a-C showed higher hardness of 43 GPa. The Zero-loss image indicated that a change of contrast accompanies the change of composition of Ti and Al. Nanometer-size of Al agglomerates were observed and Ti distribution corresponded to that of Al. XPS analysis of C1s spectrum revealed that carbon in the films bound almost as C-C with a few bondings of Ti-C or Al-C and C-N. Ti2p and Al2p spectrum indicated that these transition metals bound mostly with nitrogen. These results indicated that nano-composite structure consisting of complicated mixture of nanocrystalline Ti-Al-N phase and a-C phase (with a small amount of C:N phase and metal carbide phase) existed in the TiAlN/a-C films.

SE-TuP11 Wear Behavior of Unbalanced Magnetron Sputtered Multilayer CrN/TiAlYN Coatings Deposited on Plasma Nitrided Steels, ***M. Flores***, *E. Rodriguez*, Universidad de Guadalajara, México, *E. De las Heras, P. Corengia*, Instituto Nacional de Tecnología Industrial, Argentina, *L. Huerta*, Universidad Nacional Autonoma de México

The influence of pretreatment on the wear behavior of tool steels coated with TiN, CrN and CrN/TiAlYN multilayers were experimentally investigated. The substrate materials were nitrided using plasma nitriding. The thin films were deposited using unbalanced magnetron sputtering technique. A comparison between the wear resistances of nitrided, coated, nitrided and coated samples were made. The nitrided coatings and CrN/TiAlYN multilayer grown on pulse plasma nitriding steels have been characterized by using X-ray diffraction (XRD), scanning electron microscope (SEM), micro-indentation and abrasive wear tests. The depth profiles were studied by X-ray photoelectron spectroscopy (XPS) and Rutherford Backscattering spectroscopy (RBS). The duplex coatings showed a low wear respect to the coated samples. The out-performance of the prenitrided TiN, CrN and CrN/TiAlYN coatings can be attributed to the presence of a nitrided subsurface.

SE-TuP12 Power Supplies to Enable High Power Impulse Magnetron Sputtering, ***D. Ochs***, HÜTTINGER Elektronik GmbH, Freiburg, Germany, *R. Spencer*, Alacritas Consultancy Ltd., Leicestershire, U.K.

High Power Impulse Sputtering (HIPIMS or HPPMS) receives more and more attention as a technique to produce very dense films. It relies on the creation of high density plasma in front of the sputtering source and by that way a large fraction of the sputtered atoms are ionized. These ionized atoms can be used for surface pretreatment and deposition as well. The interfaces and layers so produced show superior properties in many applications. Currently the most investigated and promising application is use for hard coatings as wear and corrosion protection. Popular layers are for example CrN and TiN. To enable the HIPIMS process a specially designed power supply for powering the magnetron cathode is needed. This power supply consists of 3 modules. The DC module contains a converter which charges a capacitor bank in the pulse module. A semiconductor switch is activated by the pulse control unit. The third module is an impedance matching circuit to shape the output current pulse in order to match the requirements of the cathode. Several power supply configurations have been realized in order to fulfill the different process needs. HIPIMS power supplies with a max. pulse power of up to 18MW, a voltage of 1kV to 3kV and a current of 1kA to 6kA will be presented with practical results from industrial coating applications.

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