

## Thin Films

### Room Naupaka Salons 4 - Session TF-TuE

#### Next-generation Protective Coatings and Tribological Applications

**Moderator:** Lars Hultman, Linköping University

##### 5:40pm TF-TuE-1 Effects of Ar:N<sub>2</sub> gas ratio on TiN and TiAlN Thin Films Synthesized via RF Magnetron Sputtering, *Jason Audrey Licerio, A Alibadbad, M Vasquez*, University of the Philippines, Philippines

There is a growing interest in using titanium nitride (TiN) and titanium aluminum nitride (TiAlN) as a hard coating in recent years because of their high hardness, low friction coefficient, and good wear and oxidation resistance. Lifetime of machining tools significantly increase when coated with these transition metal nitrides. Radio frequency (RF) magnetron sputtering was used to synthesize the films. In this study, the Ar:N<sub>2</sub> ratio of synthesized TiN and TiAlN films were varied and characterized using a single target magnetron. That is, thin film growth is achieved using either a Ti target or 1:1 TiAl composite target. Argon:nitrogen (Ar:N<sub>2</sub>) partial pressure ratios were varied at 9:1, 8:2, and 7:3 to grow the TiN and TiAlN films. Scanning electron microscope (SEM) images of TiN showed rough, 'pyramid-like' grains. Higher N<sub>2</sub> content resulted in more compact grains. The TiAlN films formed were dense 'cauliflower-like' grains. Cross-sectional SEM images showed both films having columnar structure with increasing grain diameter as N<sub>2</sub> content is increased. Energy dispersive x-ray spectroscopy mapping of TiN showed over-stoichiometric TiN<sub>x</sub>. TiAlN maps showed almost 1:1 Ti:Al ratio but an abundance of N, confirming the formation of TiAlN<sub>x</sub> films. X-ray diffraction (XRD) results of TiN showed presence of (111), (220), and (311) TiN crystallographic planes. Decreasing N<sub>2</sub> content in the system resulted in the increase in intensity of (111) and (220) planes while increase in N<sub>2</sub> resulted in broadening of (111) plane. TiAlN XRD results showed formation of (111), (200), and (220) peaks. Increasing N<sub>2</sub> enhances the (220) peak. The 80:20 Ar:N<sub>2</sub> ratio resulted in increase of (200) peaks. The performance of drill bits coated with TiN showed three-fold increase in number of holes drilled while TiAlN films showed a two-fold increase as compared to that of uncoated drill bits. This work succeeded in the synthesis of TiN and TiAlN films and improving drill bit performance.

##### 6:20pm TF-TuE-3 Formation Mechanism of Tribofilm of Silicon Carbide under Water Lubrication: Molecular Dynamics Simulation, *Fumiya Nakamura, Y Wang, N Miyazaki, Y Ootani, N Ozawa, K Adachi, M Kubo*, Tohoku University, Japan

Water lubrication has the characteristic of low environmental burden. It is known that silicon carbide (SiC) shows low friction coefficient due to the formation of a tribofilm by chemical reaction at sliding interfaces under water lubrication. Thus, understanding of the chemical reaction mechanism is essential to improve friction characteristic for practical use and application. However, it is difficult to observe directly such a complicated phenomenon including friction and chemical reaction by experiments. Therefore, in this study, molecular dynamics (MD) simulation using reactive force field, which can simulate chemical reaction, was conducted to analyze the structure and formation mechanism of tribofilm in the friction process of amorphous SiC under water environment.

In the simulation, we used a model in which amorphous SiC ball and disk were rubbed in water (See supplementary document (SD) Fig.1). The SiC ball was slid on the SiC surface with nominal pressure of 0.5 GPa and sliding speed of 100 m/s.

During the friction, the surface wears as the SiC ball and the SiC disk come into contact with each other. Silica (SiO<sub>2</sub>) particle and hydrocarbon were confirmed as wear debris. It was also observed that the SiO<sub>2</sub> particles dissolved in water and forms colloidal silica. Firstly, we investigated the changes in number of water molecules and Si-O-Si and C-H bonds during the friction (See SD Fig. 2, Fig.3). It was found that the number of water molecules decrease continuously while the number of Si-O-Si and C-H bonds increase correspondingly. This result indicates that hydrolysis reaction of SiC (SiC + H<sub>2</sub>O → Si-OH + C-H) occurs at the sliding interface. Next, we investigated the change in the number of Si and C contained in the wear debris (See SD Fig. 4). We found that the number of Si in the debris was always larger than that of C in the debris. This result indicates that the Si atoms are easily dissolved from the SiC surface as SiO<sub>2</sub> particle, whereas the C atoms tend to remain on the SiC surface. The distribution of C, Si, H, and O atoms except H<sub>2</sub>O molecules shows that the C and H atoms

were concentrated on the surface of the SiC disk and SiC ball (See SD Fig. 5, Fig. 6). On the other hand, the Si and O atoms were dissolved in water, forming the colloidal silica. Meanwhile, the Si and O atoms also located between the SiC disk and SiC ball. This fact indicates that the colloidal silica prevent the contact of the surfaces, leading to low friction. Thus, we concluded that colloidal silica, which is produced by the hydrolysis reaction of SiC surface, lowers the friction of SiC in water lubrication.

##### 6:40pm TF-TuE-4 Recent Advances in Surface Engineering, *Ivan Petrov*, Linköping University, Sweden, Frederick Seitz Materials Research Laboratory, University of Illinois

**INVITED**  
Surface Engineering (SE) is the science and technology of improving the surface properties of materials for protection in demanding contact conditions and aggressive environments. SE also encompasses engineering new multi-functional surface properties, such as electrical, optical, thermal, chemical, and biochemical properties. It involves multiple or hybrid processes which include substrate modification and deposition of overlayers in complex architectures. These processes enhance adhesion and optimize composition or microstructure to enhance protective properties coupled with other functionality. The substrates may be of complex shapes, like metal-cutting tools and automotive or aerospace components, and range in size from micrometers, such as in MEMS or NEMS devices, to meters, such as in architectural glass. The applications are wide-ranging, and include, for example, control of friction, wear-resistance, corrosion-resistance, thermal-barrier coatings, decorative coatings, bioimplants, antimicrobial layers, web-coatings, and thin films with engineered electrical and optical responses. Areas of scientific interest range from first-principle atomistic studies of new materials, to scientific and technological advances in synthesis methods, structural and chemical characterization techniques, property measurements, and performance characterization of surface-engineered parts. I will highlight a few selected SE advances from the past three years which include: complex SE architectures for joint-replacement implants [1], duplex coating for superior wear resistance of Ti alloy compressor blades or landing gear components [2], fracture-resistant thin-film metallic glass [3] and non-stick syringe needles[4]. TiB<sub>x</sub> thin films grown from compound TiB<sub>2</sub> targets by magnetron sputter deposition are typically highly over-stoichiometric due to differences in Ti and B preferential ejections angles and gas-phase scattering during transport. I will describe two methods to control of the B/Ti ratio in sputter deposited titanium diboride coatings, involving preferential ionization of sputter-ejected Ti atoms [5,6]. The ability to obtain stoichiometric TiB<sub>2</sub> films is a prerequisite to obtaining high-quality epitaxial transition metal diboride layers. Overall, Surface Engineering continues to be a vibrant interdisciplinary field in the area of interest of AVS.

<sup>1</sup> P Hovsepian et al, J. Mat. Sci: Mater Med (2016) 27:147

<sup>2</sup> D Goldbaum et al, Surf. Coat. Technol. 291 (2016) 264

<sup>3</sup> CC Yu et al, APL MATERIALS 4, 116101 (2016)

<sup>4</sup> JP Chu et al, Scientific Reports 6:31847

<sup>5</sup> I Petrov et al, J. Vac. Sci. Technol. A 35 (2017) 050601

<sup>6</sup> B Bakhit et al, J. Vac. Sci. Technol. A 36 (2017) 030604

##### 7:40pm TF-TuE-7 Influence of Defect Structures in MoS<sub>2</sub> Tribo-film Generated from MoDTC at DLC/DLC Interface on Friction Behavior: A Molecular Dynamics Simulation, *Masahiro Saito, N Miyazaki, Y Ootani, N Ozawa, M Kubo*, Tohoku University, Japan

MoDTC friction modifier for engine oil is well known to reduce friction under boundary lubrication where friction surfaces locally contact each other. MoDTC decomposes during friction and then, tribo-film of 2D-MoS<sub>2</sub> layers oriented at sliding interface is formed from the decomposition products of MoDTC, leading to low friction [1]. It is well known that the effect of MoS<sub>2</sub> largely depends on sliding condition. However, understanding of the dependency is not sufficient because of the difficulty of *in situ* observation at the sliding interface although sliding condition optimization is important to improve friction property. As one cause of this dependency, it is considered that the defect structure in MoS<sub>2</sub> tribo-film has some influence on friction. Thus, in order to investigate influence of defect structures in MoS<sub>2</sub> tribo-film generated from MoDTC at sliding interface on friction behavior, we performed molecular dynamics simulation by using reactive force field (ReaxFF), which takes into account the chemical reactions.

In the simulation, we prepared models in which some MoS<sub>2</sub> layers are sandwiched between two diamond-like carbon (DLC) substrates because DLC is a coating material used in engine cylinders. Here, we investigated

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the influence of the defects by comparing the friction behavior of the MoS<sub>2</sub> layers with and without defect structures. As the defect structures, we considered grain boundary structures in the MoS<sub>2</sub> layer and a distorted layer structure in which layers unoriented at the interface. In order to simulate friction process, one DLC substrate was fixed and the other was slid at 100 m/s with 3 GPa of a contact pressure.

The friction simulation the model without defect showed that the contact surface of DLC and MoS<sub>2</sub> was the sliding interface. The simulation the model with grain boundaries showed that the contact surface of MoS<sub>2</sub> and MoS<sub>2</sub> was the sliding interface since C-S bonds were formed between DLC and MoS<sub>2</sub> around grain boundaries. In addition, the MoS<sub>2</sub> layers with grain boundaries showed higher friction force because the grain boundaries in neighboring MoS<sub>2</sub> layers interact each other. The simulation the model with distorted layer structure showed that the MoS<sub>2</sub> edge adhered to DLC since C-S and Mo-C bonds were formed between DLC and MoS<sub>2</sub>. The shear stress acting on the unstable MoS<sub>2</sub> edge accelerated the chemical bond formation. In summary, we found that interactions between MoS<sub>2</sub> grain boundaries and formation of chemical bonds between MoS<sub>2</sub> and DLC sliding surface around defect are significant frictional resistance.

[1] J. Graham et al., *J. Tribol.*, 44 (2001) 4

8:00pm **TF-TuE-8 Diamond-like Carbon Thin Film Deposition using Low-energy Ion Beams**, *A Cuevas, M Ramos, A Catapang, Magdaleno, Jr. Vasquez*, University of the Philippines, Philippines

Diamond-like carbon (DLC) is a metastable form of carbon that has characteristics similar to diamond. High hardness, low wear rate, and chemically inert are some desirable properties of DLC that find a host of industrial applications. Diamond-like properties are greatly dictated by sp<sup>2</sup>/sp<sup>3</sup> ratio of hybridized carbon and hydrogen atoms that are present in the DLC matrix. High sp<sup>3</sup> content in DLC can be achieved when carbon ion energy incident on a substrate is in the range of 100 eV. In this work, we developed a two-electrode ion source system capable of extracting broad ion beams with mean ion energies around 100 eV. The ion reservoir is made of stainless steel with permanent magnets around the cylindrical body to realize a multicusp configuration. Quiescent plasma was produced using 0.3 mm dia tungsten wires as hot cathodes. Acetylene (C<sub>2</sub>H<sub>2</sub>) was used as the carbon source with argon (Ar) as background gas. Doping was also done by introducing nitrogen (N<sub>2</sub>) gas into the system. Retarding potential analyzer measurements suggest the successful generation of tunable broad ion beams with mean energies around 100 eV and current densities of around 10<sup>-6</sup> A/cm<sup>2</sup>. The dissociation of Ar/C<sub>2</sub>H<sub>2</sub> and Ar/C<sub>2</sub>H<sub>2</sub>/N<sub>2</sub> plasma were obtained using a residual gas analyzer. The mass spectra of the Ar/C<sub>2</sub>H<sub>2</sub> ion beam showed the presence of mostly hydrocarbon radicals such as C<sub>2</sub>H<sub>2</sub><sup>+</sup>, C<sub>2</sub>H<sup>+</sup>, CH<sup>+</sup>, as well as heavier C<sub>x</sub>H<sub>y</sub><sup>+</sup> radicals and monatomic carbon and Ar. For Ar/C<sub>2</sub>H<sub>2</sub>/N<sub>2</sub> ion beam, CN radicals, monatomic and diatomic N were also observed. Compositional analyses of the films via Raman spectroscopy revealed the successful growth of DLC with sp<sup>3</sup> content of up to 80%. Energy-dispersive x-ray spectroscopy measurements show up to 10% doping implying the successful and uniform incorporation of N in the DLC matrix. Improvement in adhesion was also observed for N-doped DLC films. X-ray photoelectron spectral measurements suggest the presence of sp<sup>2</sup> and sp<sup>3</sup> on the surface which supports the subplantation growth scheme of DLC. X-ray diffractometry suggests the presence of diamond and graphite phases in a generally amorphous films. Surface analyses employed using scanning electron microscopy showed good conformity of the DLC films with increasing thickness upon the subsequent increase in C<sub>2</sub>H<sub>2</sub> content. Hardness testing via nanoindentation show acceptable hardness values of around 8 GPa. These films may find applications in tribological coatings.

8:20pm **TF-TuE-9 A Study on Copper/Silver Core-shell Microparticles with Silver Nanoparticles Hybrid Ink and its Sintering Characteristics with Flash Light for High Oxidation Resistance**, *Jong-Whi Park, Y Jang, H Kim*, Hanyang University, Seoul, Korea

In this study, a silver(Ag) coated copper(Cu) core-shell microparticles ink were fabricated and screen-printed on Polyimide(PI) substrates. It was sintered via flash light sintering technique. Flash light irradiation condition (i.e. pulse duration, irradiation energy) was optimized to obtain high conductivity and good oxidation resistance characteristics of Ag coated Cu core-shell pattern. To increase the packing density of the electrodes and its oxidation resistance, Ag nanoparticles(NPs) were added to Cu/Ag core-shell microparticles (MP) ink. To determine optimal amount of the Ag NPs, the hybrid ink having different mass ratios of the Ag NPs and Cu/Ag core-shell MP were fabricated and tested. The sheet resistance of the hybrid ink was measured using the four-point probe method. To analyze the sintering

behavior and degree of oxidation of hybrid pattern, a scanning electron microscope (SEM) was used. To demonstrate the mechanism of the sintering process on hybrid ink, multiphysics COMSOL simulation and temperature monitoring was conducted. As a result, hybrid pattern sintered with flash light showed excellent oxidation resistance (resistance increase rate in 300°C for 5 hours: 54.34 %), and high electrical conductivity (9 μΩ-cm).

## Acknowledgments

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