Hard Coatings and Vapor Deposition Technologies
Room California - Session B4-2

Properties and Characterization of Hard Coatings and Surfaces

Moderators: Ulrich May, Robert Bosch GmbH, Diesel Systems, Chau-Chang Chou, National Taiwan Ocean University, Taiwan, Farwah Nahif, eifeler-Vacotec GmbH

2:10pm B4-2-3 Measurement of Residual Stress on Transition Metal Nitride Hard Coatings by Combining Average X-ray Strain Method and Nanoindentation, *Jia-Hong Huang, A Wang, G Yu,* National Tsing Hua University, Taiwan **INVITED**

Among the nondestructive techniques for measuring residual stress in thin films, X-ray diffraction (XRD) is one of the well-established techniques, by which the strain tensors and crystal structure can be simultaneously determined. However, using conventional XRD $sin^2\psi$ and the like methods to measure residual stresses in textured thin films are usually problematic. We previously developed an XRD technique named $cos^2\alpha sin^2\psi$ method to solve the problem by using grazing incidence asymmetrical diffraction configuration that effectively increased the irradiation volume from a thin-film specimen, thereby generating higher intensity for high-angle Bragg peaks compared with the conventional Bragg-Brentano geometry. The $cos^2\alpha sin^2\psi$ method has been successfully applied on single layer thin films, thin film with interlayer and multiphase oxynitride thin films. Nevertheless, the X-ray residual stress (XRS) is usually deviated from the stress measured by optical curvature method, even up to 30%, which is normally attributed to the use of incorrect elastic constants determined by mechanical methods such as nanoindentation. On the other hand, if X-ray elastic constants (XECs) are adopted, the uncertainty of the measured stress can be within 10%; however, the XECs are not readily available for most hard coatings. In this study, we proposed a method where the average X-ray strain (AXS) was determined using $cos^2\alpha sin^2\psi$ XRD technique at several rotational (f) angles, combining with elastic constant measured by nanoindentation (E_{NI}), to improve the accuracy of the measurement of XRS. The major concept was to increase sampling volume by measuring X-ray strain at multiple rotational angles. TiN hard coating on Si (100) substrate was selected as the model system, where the residual stress was determined by laser curvature technique and the accompanying AXS was measured by $cos^2\alpha sin^2\psi$ method at several rotational angles. By using AXS and elastic constant measured by nanoindentation (E_{NI}) to calculate X-ray stress, the stress deviation from that by laser curvature method could be substantially reduced even down to 3 % with sufficient sampling points. The results also indicated that AXS could be accurately measured down to a thickness of 350 nm by using lab X-ray source; however, the resolution of AXS was not sufficient to differentiate the strain for a specimen with a thickness less than 160 nm, which was mainly due to insufficient sampling volume. Therefore, AXS may serve as a convenient parameter, when combining with E_{NI}, in X-ray stress measurement, by which residual stress of hard coatings comparable to that by laser curvature method can be obtained without using XECs.

2:50pm B4-2-5 Investigation of the Tribocatalysis Mechanisms involved in the Extraction of Amorphous Carbon Boundary Films from Base Oils, *Giovanni Ramirez, O Eryilmaz, B Narayanan, Y Liao, G Kamath, S Sankaranarayanan, A Erdemir,* Argonne National Laboratory, USA

Aimed at solving some of the durability and efficiency problems existing in current mechanical systems, we have been studying the interactions between lubricants and solid surfaces and how one can possibly mitigate friction and wear in components with the use of novel environment friendly technologies. As an innovative approach, here we present the mechanisms involved in the extraction of carbon-based tribofilms directly from the hydrocarbon molecules of the base oils with the use of catalytically active nanocomposite coatings, and without the need of antiwear additives [1].

In this work, we present the tribocatalysis phenomena that allow the extraction of carbon-based tribofilms when surfaces are made of nanocomposite thin films/coatings that include a metal catalyst and called catalytically active nanocomposite coatings. Such metal catalysts (i.e., Cu, Ni, Co, etc.) seems to be responsible for lowering the activation energy that is required for first dehydrogenation and then cracking of the hydrocarbon molecules into dimers and trimers that in the end recombine under pressure to form a carbon-based deposit resembling a hydrogenated diamond like carbon film. To study these processes and show the presence of protective carbon tribofilms, not only several tribometers, but also advance surface characterization techniques such like Raman microscopy, TOF-SIMS and transmission electron microscopy were employed to elucidate the fundamental mechanisms involved. Further, detailed MD simulations were performed using classical and ab-initio molecular dynamics to explain the specific steps in the creation of a protective tribofilm that outperforms the more traditional boundary films resulting from ZDDP and other types antiwear additives. We will discuss the effects of having less catalyst on the coating on the formation of the carbon-based tribofilms.

[1] Ali Erdemir, Giovanni Ramirez, Osman L. Eryilmaz, Yifeng Liao, Badri Narayanan, Subramanian Sankaranarayanan. Carbon-based Tribofilms from Lubricating Oils. Nature (536) 67-71 (2016).

3:10pm B4-2-6 Phase Stability and Strain Evolution in TiZrAlN Coatings During Annealing, *Lina Rogström, R Pilemalm, N Ghafoor,* Nanostructured Materials, IFM, Linköping University, Sweden*; L Johnson,* Sandvik Coromant, Sweden*; N Schell,* Helmholtz-Zentrum Geesthacht, Germany*; M Odén,* Nanostructured Materials, IFM, Linköping University, Sweden

TiAlN-based coatings are widely studied, and quaternary alloys within this system can further improve the mechanical properties as well as the thermal stability of hard and wear resistant coatings. TiZrAlN is still a relatively unexplored material system, while there are studies showing that addition of Zr to TiAlN can delay the formation of wurtzite AlN in the coating [1]. Theoretical results show that the decomposition route in TiZrAlN coatings is expected to vary depending on chemical composition [2] while the effect of chemical composition on the thermal stability of TiZrAlN coatings remains to be clarified.

Here, we study the phase stability and the strain evolution in TiZrAlN coatings during annealing. TiZrAlN coatings with Zr-contents on the metal sublattice between 24 and 69 at.% were grown by cathodic arc evaporation on polished WC-Co substrates. The coatings have a columnar structure and consist of a solid solution cubic (c) NaCl structure TiZrAlN phase which grows with a strong preferred 200 orientation. In situ wide angle scattering during annealing reveal that the thermal stability of the c-TiZrAlN phase depends on chemical composition. The coating containing 69 at.% Zr on the metal sublattice displays high stability. After 3 h at 1100 °C there is only a very small change in the lattice parameter of the c-TiZrAlN phase indicating that a small change in composition takes place, corresponding to formation of small amounts of other phases, or that point defects are annihilated. The strain in this coating relaxes during annealing above 800 °C. For the coatings containing less Zr, domains enriched in ZrN and TiAlN form during annealing above 600 °C. In the low Zr-content sample the microstructure is anisotropic with Al-rich domains elongated in the in-plane direction while the domains are more equiaxed in the case of higher Zr-content. The decomposition is associated with a large increase in compressive in-plane strain of the c-TiZrAlN phase. For a Zr-content of 48 at.%, the strain relaxes above 950 °C while for the lowest Zr-content the strain remains high throughout the 3 h anneal. The strain in the formed ZrN-rich domains depends on the composition of the coating and is largest for the low Zr-content (24 at.%) sample. The strain evolution is discussed in terms of microstructure and elastic properties.

[1] L. Chen et al., Thin Solid Films 519 (2011) 5503.

[2] H. Lind et al., AIP Advances 4 (12) (2014) 127147.

3:30pm B4-2-7 Gas Inlet and Input Power Modulated Sputtering Molybdenum Nitride Thin Films, *JianYing Xiang,* National United University, Taiwan

The molybdenum nitride films were produced by RF magnetron sputtering with various structural features by the input power and gas flow ratio control. With Ar/N gas flow ratio s from 10/10 to 18/2 and RF input powers from 150 to 300W, the molybdenum nitride films evolved from significant columnar to amorphous structure. The coating deposited at an Ar/N_2 ratio of 16/4 and an input power of 300W showed an intensified Mo_2N microstructure with preferred (111) orientation. In comparison, the crystalline phase of the coating fabricated at an Ar/N_2 ratio of 10/10 and an input power of 150W was suppressed. The thickness, deposition rate and

crystallinity of the molybdenum nitride increased with Ar/N_2 ratio and power input. To enhance the protective behavior of the molybdenum nitride coating, the crystalline and amorphous nitride layers were alternately stacked to form a nanolayered film. Hardness, Young's modulus, and tribological characteristics of the molybdenum nitride multilayer films were investigated. The correlation between structural evolution and mechanical behavior was discussed.

3:50pm **B4-2-8 Transition Metal Nitrides Deposition by HiPIMS in DOMS Mode**, *João Oliveira, F Ferreira, R Serra, F Fernandes, A Cavaleiro,* University of Coimbra, Portugal

Transition metal nitrides (TMD) coatings are well known for their unique combination of outstanding mechanical properties (hardness and Young's modulus), high thermal and chemical stability and excellent resistance to wear and corrosion. TMD are commonly used in industry to improve the performance and enhance lifetime of tools and components in a wide range of applications, including automotive, energy, electronic, and machining applications. During the past decade huge investments have been made aiming at further improving their properties and thus reduce the costs due to wear and corrosion. High-power Impulse Magnetron Sputtering (HiPIMS) is a recently developed deposition process that already demonstrated a huge potential for coatings properties improvement. HiPIMS relies on the application of very high target power densities to ionize the sputtered material and thus allows a more effective control of the bombarding species during film growth than in D.C. Magnetron Sputtering (DCMS). In this work the properties of TMD thin films deposited by Deep Oscillations Magnetron Sputtering (DOMS), a variant of HiPIMS, are summarized and compared to their DC MS counterparts. Results obtained in four different coatings systems (CrN, TiN, TaN and TiSiN) are presented and discussed in light of the Ion Energy Distributions of metal and gaseous species impinging on the growing films.

The TMD coatings were deposited using a wide range of deposition conditions leading to very different bombardments regimes. The effect of the peak target power on the films properties was systematically studied. The structure, morphology, surface topography and mechanical properties of the films were characterized and related to the bombarding conditions. It was concluded that HIPIMS-DOMS allows using different sets of energy and incidence angle of the bombarding species as compared to DCMS and, therefore, enables the deposition of thin films with improved properties.

4:10pm **B4-2-9 Advanced HIPIMS Solution for R&D and Process Development**, *Jason Hrebik,* Kurt J. Lesker Company, USA*; R Bandorf,* Fraunhofer IST, Germany

When HIPIMS was first introduced to the thin film coating industry, it was considered an advanced technique for production applications, which would provide optimal film properties and wear resistance. The HIPIMS supply options were very large scale directly suited to the production industry. However, it was found to have significant limitations in rate, which minimized its acceptance in production applications.

Recently, the introduction of smaller scale supplies triggered an emergence of the technology into the R&D community. This enabled a high rate of enhancements and helped innovate a more efficient capability and process optimization that could be utilized by HIPIMS supplies. This ultimately re-energized the interest and potential of HIPIMS in the thin film coating industry.

One of the solutions to emerge from the crowd was the IMPULSE supply, which brings a unique range of features to the HIPIMS community. The IMPULSE is a 2kW supply that is offered in a single and dual configuration. It features touch panel controllability, the fastest pulse frequency, 200A peak current, and the most competitive pricing in the industry. The supply is slave capable and can be scaled from its 2kW standard configuration by adding additional units. This makes it an excellent option for process development.

Test results will be shared that show its unique performance capabilities and compatibility with higher scale power requirements.

4:30pm **B4-2-10 Determining of the Critical Loads of Transition Metal Nitrides on Steels**, *Aysenur Keles,* Ataturk University Faculty of Engineering, Turkey*; H Cicek,* Erzurum Technical University, Turkey*; O Baran,* Erzincan University, Turkey*; Y Totik, I Efeoglu,* Ataturk University, Turkey

Transition metal nitride coatings are very attractive materials due to their hardness and toughness. On the other hand, adhesion properties of these coatings are generally low because of their brittleness. To overcome this disadvantage, this type of coatings are produced with different coating techniques. In this work, V and Nb doped ternary TiN-based coatings were deposited on M2 and H13 substrates with pulsed-dc closed field unbalanced magnetron sputtering (CFUBMS) system. The films microstructure were examined by SEM. The thicknesses of the films changed from 400 nm to 360 nm. The maximum nano hardnesses were meausred 35 GPa and 26 GPa for M2 and H13 steels, respectively. The critical load values of the coatings were pointed out using scratch tester. For M2 steel; the highest Lc value was obtained 63 N and for H13; the highest Lc value was obtained 47 N. It was cleary seen that pulsed-dc created very dense microstructure and utilized to improve the adhesion of transition metal nitride coatings on the steels.

4:50pm **B4-2-11 Tribocorrosion Behaviour of Nanocomposite TiSiCN Coatings Tested in PBS Solution**, *Andre Hatem,* Pontifícia Universidade Católica do Paraná, Brazil*; J Lin, R Wei,* Southwest Research Institute, USA*; R Torres, C Laurindo, P Soares,* Pontifícia Universidade Católica do Paraná, Brazil

Recent articles have investigated the tribological performance of nanocomposite TiSiCN coatings mainly because of their high hardness, low friction coefficient and good adhesion to many substrates, especially, when compared to other ternary system coatings (TiSiN, TiCN). These properties are mainly attributed to the microstructure of the nanocomposite TiSiCN coatings which generally consists of TiC_xN_y nanocrystals embedded in an amorphous Si_3N_4 matrix. The proportional between these phases is much related to the silicon content presented in the coating. Higher silicon contents increase the amorphous matrix and hence decrease the nanocrystals size, which to some extent, provide nanocomposite TiSiCN coatings with higher hardness. Despite the nanocomposite TiSiCN coating appears as interesting candidate for severe wear applications, there are few wear studies under corrosive environments. Therefore, the main purpose of this study is evaluate the tribocorrosion performance under phosphate-buffered saline (PBS) solution of nanocomposite TiSiCN coatings with different silicon contents applied on Ti-6Al-4V samples. Plasma enhanced magnetron sputtering (PEMS) of Ti in a gas mixture of Ar, N_2 and silicon precursors, trimethylsilyl (TMS) and hexamethyldisilazane (HMDSN), were utilized to obtain the nanocomposite TiSiCN coatings in this study. The coatings silicon content could be varied by controlling the inlet flow of silicon precursors in the deposition chamber. Reciprocal sliding tribocorrosion tests were conducted under PBS solution on the nanocomposite TiSiCN coatings and compared to a Ti-6Al-4V bare alloy sample. Moreover, microstructure and composition of the coatings were evaluated using scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDS), X-ray diffraction (XRD) and Raman spectroscopy while mechanical properties were studied by scratch and nanoindentation tests. The results of tribocorrosion tests revealed that exists an optimal silicon content range where occur much lower wear rates. The same behaviour was observed to the mechanical properties of the samples in this same silicon content range. In conclusion, the TiSiCN nanocomposite deposited by PEMS emerge as a new generation of quaternary system coatings that promise high wear performance in corrosive environment since their deposition parameters are optimized for a desirable proportion between the nanocrystalline and amorphous phases.

Author Index

Bold page numbers indicate presenter

— B —
Bandorf, R: B4-2-9, 2
Baran, O: B4-2-10, 2
— C —
Cavaleiro, A: B4-2-8, 2
Cicek, H: B4-2-10, 2
— E —
Efeoglu, I: B4-2-10, 2
Erdemir, A: B4-2-5, 1
Eryilmaz, O: B4-2-5, 1
— F —
Fernandes, F: B4-2-8, 2
Ferreira, F: B4-2-8, 2
— G —
Ghafoor, N: B4-2-6, 1
— H —
Hatem, A: B4-2-11, **2**
Hrebik, J: B4-2-9, **2**

Huang, J: B4-2-3, **1**
— J —
Johnson, L: B4-2-6, 1
— K —
Kamath, G: B4-2-5, 1
Keles, A: B4-2-10, **2**
— L —
Laurindo, C: B4-2-11, 2
Liao, Y: B4-2-5, 1
Lin, J: B4-2-11, 2
— N —
Narayanan, B: B4-2-5, 1
— O —
Odén, M: B4-2-6, 1
Oliveira, J: B4-2-8, **2**
— P —
Pilemalm, R: B4-2-6, 1

— R —
Ramirez, G: B4-2-5, **1**
Rogström, L: B4-2-6, **1**
— S —
Sankaranarayanan, S: B4-2-5, 1
Schell, N: B4-2-6, 1
Serra, R: B4-2-8, 2
Soares, P: B4-2-11, 2
— T —
Torres, R: B4-2-11, 2
Totik, Y: B4-2-10, 2
— W —
Wang, A: B4-2-3, 1
Wei, R: B4-2-11, 2
— X —
Xiang, J: B4-2-7, **1**
— Y —
Yu, G: B4-2-3, 1