Advanced Surface Engineering
Room 303D - Session SE-TuM

Hard and Low Friction Coatings with Advanced Designs

Moderator: D. Gall, Rensselaer Polytechnic Institute

8:20am **SE-TuM1 Tribological Coatings: Synthesis, Structure, and Properties*, D.V. Shtansky,*** Moscow State Institute of Steel and Alloys, Russia **INVITED**

Various approaches to design and evolution of tribological coatings are review and refer to our recent results on the deposition, characterization, testing, and application of multicomponent nanostructured thin films. The targets for PVD based on the systems TiN+TiB@sub 2@, Ti@sub 5@Si@sub 3@+Ti, Ti@sub 5@Si@sub 3@+TiN, TiB@sub 2@+Si, TiB@sub 2@+SiC, TiB+Ti@sub 9@Cr@sub 4@B+Cr@sub 2@Ti, CrB@sub 2@, TiB@sub 2@+TiAl+Ti@sub 2@AlN, TiC+Ti@sub 3@SiC@sub 2@+TiSi@sub 2@, TiC@sub 0.5@+ZrO@sub 2@, TiC@sub 0.5@+CaO, Ti@sub 5@Si@sub 3@+ZrO@sub 2@, and TiC@sub 0.5@+Nb@sub 2@C were manufactured by means of self-propagating high-temperature synthesis (SHS). Multicomponent films were deposited by DC magnetron sputtering of composite targets either in an atmosphere of argon or reactively in a gaseous mixture of argon and nitrogen. The BN and WSe@sub x@ films were deposited using a sintered hexagonal BN and a cold compacting WSe@sub 2@ target, respectively. The WSe@sub x@ films were deposited by pulsed laser deposition (PLD) and ion-assisted PLD technique. The microstructure and chemical composition of films were studied by means of AES, EDXS, XRD, SEM, TEM, high-resolution TEM, XPS, and EELS. The films were characterized in terms of their hardness, elastic modulus, elastic recovery, adhesion, surface topography, friction, and wear. The biocompatibility of the medical films was evaluated by both in vitro and in vivo experiments. Three groups of films are considered: 1) nanostructured hard, tribological coatings Ti-B-N, Ti-Cr-B-N, Ti-Si-N, Ti-Al-B-N, Ti-Si-C-N, Ti-Si-B-N, BN, and Cr-B-N; 2) double-layer self-lubricating/hard coatings WSe@sub x@/TiC, WSe@sub x@/TiCN, WSe@sub x@/TiSiN, and 3) biocompatible hard coatings for medicine Ti-Ca-C-O-(N), Ti-Zr-C-O-(N), Ti-Zr-Si-O-(N), and Ti-Nb-C-(N). Particular attention is paid to the analysis of the structure of the films in the nanometric scale and the evaluation of the properties of the individual nanostructures.

9:00am **SE-TuM3 New Concepts for Low-friction Coatings*, C. Mitterer,*** University of Leoben, Austria

Hard coatings deposited by plasma-assisted vapor deposition are widely used to reduce tool wear. The presently applied transition metal nitride coatings show high friction against steels, which restricts their applicability with reduced or without coolant. Tool temperatures for different machining operations are extremely different ranging from relatively low temperatures for deep drawing to above 1000°C for dry cutting. Presently applied low-friction coatings are essentially based on diamond-like carbon and MoS@sub2@, which often begin to fail with increasing temperature, in humid atmosphere or due to oxidation. The aim of the present contribution is thus to present now concepts for low-friction coatings for different temperature ranges. Examples for low-temperature lubrication approaches to be described include Cl-alloyed TiN coatings, where low-friction coefficients are provided by the Cl-induced formation of rutile layers on top of the coating in humid air, and CrC/a-C:H, where graphitization of the a-C:H phase is responsible for low friction coefficients. Approaches for lubricant phases at high temperatures (i.e. above 600°C) are based on the formation of Magneli phase oxides, in particular V@sub2@O@sub5@, due to oxidation of VN in Ti@sub1-x@Al@subx@N/VN superlattices or V in V-alloyed Ti@sub1-x-y@Al@subx@V@suby@N coatings. Using these concepts, friction coefficients of 0.2-0.4 against steel can be obtained for temperatures of 700°C, where lubrication is achieved by melting of the V@sub2@O@sub5@ phase. Another high-temperature low-friction approach is the application of thin top layers based on intermetallic phases on hard coatings. In particular, the Al@sub2@Au phase is stable up to 850°C without oxidation, shows a pink color and yields friction coefficients of 0.45 at 700°C. These nanoscale design approaches allow the utilization of functional properties facilitating the development of next generations hard coatings.

9:20am **SE-TuM4 Why do DLC and MoS@sub x@-based Amorphous Coatings Have Similar Friction and Wear Behavior?*, I.L. Singer,*** Naval Research Laboratory **INVITED**

Amorphous coatings based on MoSx and hydrogenated carbon (a-C:H) exhibit dry sliding friction and wear behavior that qualifies them as ideal solid lubricating coatings. Both exhibit friction coefficients of 0.05 or less in dry air; in load-dependent friction tests, both coatings show interfacial shear strengths around 25 MPa in dry air. Both can have lifetimes of the orders of millions of cycles even though the coatings are one micrometer or less thick. However, their tribological behavior could not have been predicted based on common understanding of solid lubricants. The lubricity of MoS@sub 2@ is associated with easy shear of the basal planes, yet the MoSx-based coatings are amorphous. Often called diamond like carbon, a-C:H is a very hard material (12 - 16 GPa), with no easy shear planes. These discrepancies - between materials properties and tribological properties - can be reconciled by recognizing the role that third bodies play in the friction and wear of the two coatings. The low friction is associated with a film that transfers from the coating to the (counterface) slider and the velocity accommodation mode - interfacial sliding - between the transfer film and the parent coating. The higher friction coefficients of both in humid air is also explained by interfacial sliding and attributable to a higher interfacial shear strength in the presence of humidity. Earlier studies demonstrated that third body recycling from reservoirs contributed to the long life of MoS@sub 2@ coatings, and recent in situ tribometry studies also suggest ways in which the transfer film contributes to long life of diamond-like carbon, as well. Thus, both the friction behavior and the long life of these two otherwise different coating materials can be accounted for by third body effects on sliding contacts.

10:00am **SE-TuM6 In-situ Quantitative Nano-scale Metrology of Thin Coatings*, N. Gitis,*** *A. Daugela, A.K. Sikder, M. Vinogradov, A. Meyman,* Center for Tribology, Inc.

Quantitative nano-metrology tools have become a standard in semiconductor, data storage and other hi-tech industries where products are tested for coating properties. Though it is critical to characterize advanced thin films and coatings, todayâ?Ts off-line nanoscale metrology tools can capture only limited number of manufacturing process stages. A quantitative nano/micro-instrument mod. UNMT with both SPM and optical microscope imaging integrated into it was developed to characterize mechanical properties of thin films and coatings and monitor their changes during indentation, scratching, reciprocating, rotating and other tribology tests. Both the materials properties and surface topography can be assessed at various stages of the tests. A 5-um thick copper layer on a silicon wafer was tested for changes in material properties during tribology test. Integrated SPM type imaging and nano-indentation tests revealed changes in elastic modulus, hardness and surface topography at nanometer scale. Dynamics of the copper layer hardening was recorded at several hundreds time steps during the entire tribology test.

10:20am **SE-TuM7 Effect of Impurities and Deposition Condition on the Mechanical Properties of Superhard Nanocomposites with High Thermal Stability*, S. Veprek,*** Technical University Munich, Germany **INVITED**

Nano-Sized and Nano-Structured materials represent the leading edge of the research and technological development in many different areas from inorganic to biological ones. This paper will address the preparation and properties of superhard nanocomposites with a high thermal stability and an unusual combination of mechanical properties which were developed on the basis of our generic design concept that was published in 1995. These superhard nanocomposites were recently introduced into a large-scale industrial production. Because many researchers have recently claimed a lack of reproducibility of our results, the emphasis of my lecture will be on the deposition conditions needed for a reproducible preparation of these nanocomposites. A special attention will be paid to the detrimental role of impurities in these and other nano-structured coatings. It will be shown that minor oxygen impurities of @>=@0.4 at. % are the most probably reason why a number of researcher were unable to reproduce our data.

11:00am **SE-TuM9 Development of Hybrid Deposition Techniques for Nanocomposite Coating Growth*, A.A. Voevodin,*** *J.G. Jones, J.S. Zabinski,* Air Force Research Laboratory

Development of hybrid processes, combining filtered vacuum arc deposition, magnetron, sputtering, and laser ablation for synthesis of functionally gradient and nanocomposite materials are discussed. Hybrid techniques facilitate a high degree of structural control and allow growth of nanostructured materials at low temperature by mixing plasma streams from various sources. Special attention was given to process instrumentation for plasma chemistry and energy control. Spectroscopic, imaging and time of flight analysis techniques are discussed. Interesting plasma interactions were found in a hybrid of laser ablation and ion beam deposition, where short-lived interactions between two plasma sources were explored to produce alumina oxinitride films. In addition, studies of a combination of laser ablation with magnetron sputtering (MSPLD) are presented. In this hybrid process, highly energetic plasma plumes from laser ablation were intersected with a magnetron-generated plasma containing sputtered metal atoms. Another hybrid process combined filtered vacuum arc and magnetron sputtering. All processes were tuned to produce advanced tribological coatings for wear protection of engineering components, combining metals, oxides, carbides, and dichalcogenides into various nanocomposite coating designs.

11:20am **SE-TuM10 Growth and Characterization of Zirconium Nitride/Inconel Nanocomposite Structures***, **S.M. Aouadi**, M. Debessai,* Southern Illinois University*; J. Xu, S.R. Mishra,* University of Memphis*; D.M. Mihut, S.L. Rohde,* University of Nebraska

This paper reports on the first study of the physical, chemical, and mechanical properties of reactively sputtered zirconium nitride/inconel nanocomposite films as a function of chemical composition, and substrate bias. Several sets of samples were deposited on Si(111) substrates at room temperature with bias voltages in the -45 to -160 V range. The chemical composition was deduced from X-ray photoelectron spectroscopy and energy dispersive X-ray fluorescence measurements, and was found to be influenced by the sputtering power and substrate bias. The phase composition and the grain size were determined using X-ray diffraction. The grain size was found to decrease with the increase in power to the inconel gun. The optical constants were measured using spectroscopic ellipsometry. A correlation between film structure/composition and optical constants was established. The hardness and elastic modulus of each sample were measured by nanoindentation. The resistance to plastic deformation, as measured by the ratio H3/E2, was optimized (H3/E2=1.0) with a substrate bias of -100 V. Finally, the tribological behavior of these films was studied using a nanowear tester. Nanowear results correlated well with the resistance to plastic deformation deduced from nanoindentation measurements.

11:40am **SE-TuM11 Microstructure and Properties of Ti-Al-Si-N Coatings Prepared by r.f.-Reactive Sputtering in Facing Targets-type Sputtering (FTS) System***, **M. Nose**,* Takaoka National College, Japan*; W.A. Chiou,* Univ. of California at Irvine*; H. Suzuki,* Toyama Univ., Japan*; E. Honbo,* Toyama Industrial Research Center, Japan*; S. Ikeno, H. Anada,* Toyama Univ., Japan*; S. Nogi,* Osaka Univ., Japan

Ti-Al-N films have been widely used in the coating industry as a superior wear protection material in comparison with its predecessor, TiN; however, the discovery of Ti-Si-N nano-composite film (by Veprek et. al. in 1995) has sparked recent interest in the study of quaternary system coatings such as Ti-Al-Si-N. Research on the influence of Si content on the mechanical properties of the quaternary system has been reported, however, the studies of microstructure and properties of Ti-Al-Si-N films containing high Al content are scarce. The effect of Si concentration on the microstructure and on high aluminum-content systems (such as (Ti@sub0.5@A1@sub0.5@)@sub50@-N@sub50@ film), remain unclear. Thin Ti-Al-Si-N films were synthesized by r.f. reactive sputtering in a facing target-type sputter (FTS) system on the hight speed steel substrates. A pair of composite targets consisting of a Ti@sub50@-Al@sub50@ plate and Si chips was used. During the deposition the substrate was heated from room temperature up to 300° C. The crystallite size of the deposited film without bias voltage decreased from 14 nm to 7 nm with the increase of Si content up to about 7 at. %. XRD patterns of Ti-Al-Si-N films suggested two phases, the cubic B1 NaCl type structure and an amorphous phase, were presented in the film. XPS analysis exhibited a peak that corresponded to the Si@sub3@N@sub4@ phase. TEM investigation of (Ti@sub48@-Al@sub0.48@-Si@sub0.04@)@sub50@-N@sub50@ films revealed a nano-column structure. The nano-column structure has a long aspect ratio ranging from 3 to 10 with an average around 7 to 9. Without applying substrate bias, the hardness of the films increased from 35 GPa for Ti-Al-N films, reaching a maximum of 38GPa for Ti-Al-Si-N films containing approx. 4 at. % Si. Based on thermal-gravity measurement by oxidation of films at 900° C in the air, the oxidation ratio of the Ti-Al-Si-N films was only a quarter of that in Ti-Al-N films. These special characteristics of the Ti-Al-Si-N films are potential results from the formation of an amorphous Si@sub3@N@sub4@ phase.

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