Advanced Surface Engineering
Room 201 - Session SE-MoM

Nanocomposites and Coatings with Enhanced Thermal Stability

Moderator: J.M. Schneider, RWTH Aachen

8:20am **SE-MoM1 John Thornton Memorial Award Lecture: Understanding of the Preparation and Properties of Superhard Nanocomposites***, **S. Veprek**[1],* Technical University Munich, Germany **INVITED**

Since the first report on the strong enhancement of hardness to 60-70 GPa in the Ti-Si-N system by Li Shizhi et al.,@footnote 1@ followed by the publication of the generic design concept,@footnote 2,3@ a large number of papers were published on this and similar systems which have led to some misunderstanding and controversies regarding the suitable deposition techniques and conditions, the maximum achievable value of hardness, the mechanism of the hardness enhancement, thermal stability and others. So far, plasma induced deposition techniques, such as glow discharge CVD, reactive sputtering and vacuum arc evaporation were used to prepare thin films of such materials. In my lecture I shall try to answer some of the open questions. First it will be shown how to differentiate between the superhard nanocomposites and coatings in which the hardness enhancement is due either to energetic ion bombardment during deposition or to solution hardening. The focus will be on the recent results regarding the spinodal nature of the phase segregation in this system, and on the thermodynamic and kinetic conditions needed to complete it during the deposition to obtain superhard nanocomposites with high thermal stability. The high hardness enhancement achieved in these materials is associated with the formation of a nanostructure where few nanometer small crystals of a hard transition metal nitride are "glued" together by about one monolayer of silicon nitride, as reported in our earlier HYPERLINK "mailto:work.@footnote"work.@footnote 1,2@ This finding was recently confirmed by the work of Oden et HYPERLINK "mailto:al.@footnote"al.@footnote 5@ on the preparation of high-quality heterostructures where the highest hardness enhancement was achieved for one monolayer of Si@sub 3@N@sub 4@. The first principle DFT calculations by C. Stampfl et HYPERLINK "mailto:al.@footnote"al.@footnote 6@ lend further support to this concept and show that, as predicted (see references quoted in@footnote 4@), such nanostructure reaches the ideal strength. The unusual combination of a high hardness, high resistance against crack formation and high elastic limit is a simple consequence of the almost flaw-free nature of these nanocomposites@footnote 4@ and of a finite activation volume for the initiation of plastic deformation within an amorphous HYPERLINK "mailto:phase.@footnote"phase.@footnote 7@) In order to correctly describe the mechanical properties of these materials, a new constitutive material's model was elaborated that accounts for the pressure enhancement of elastic moduli and of the flow stress. To be able to quantitatively describe the plastic deformation under conditions of a pressure dependent flow stress, the von Mises yield criterion had to be expressed in terms of a critical deviatoric strain. This model was then implemented into an advanced Finite Element Method code and the behavior of the materials upon indentation was studied in some HYPERLINK "mailto:detail.@footnote"detail.@footnote 8@ An important result of this work is the strong stiffening for both, elastic and plastic deformation due to the increase of the elastic moduli and of the flow stress by the high pressure under the indenter which is not found in conventional materials. The lecture will conclude with a brief overview of the recent industrial applications. @FootnoteText@ @footnote 1@ S. Z. Li, Y. Shi and H. Peng, Plasma Chem. Plasma Process. 12 (1992) 287. @footnote 2@ S. Veprek and S. Reiprich, Thin Solid Films 268 (1995) 64. @footnote 3@ S. Veprek, S. Reiprich and S. Z. Li, Appl. Phys. Lett. 66 (1995) 2640. @footnote 4@ S. Veprek, M. G. J. Veprek-Heijman, P. Karvankova and J. Prochazka, Invited Review, Thin Solid Films 476 (2005) 1. @footnote 5@ M. Oden, invited paper at the 51st Int. Symp. of the American Vacuum Society, Anaheim, November 14 – 19, 2004. @footnote 8@ S. Hao, B. Delley, and C. Stampfl, School of Physics, The University of Sydney, to be published. @footnote 7@ M. J. Demkowicz and A. S. Argon, Phys. Rev. Lett. 93 (2004) 025505-1. @footnote 8@ R. G. Veprek, D. M. Parks, A. S. Argon, and S. Veprek, to be published.

9:00am **SE-MoM3 Effect of Momentum Per Arriving Atom on nc-TiN/a-Si@sub x@N@sub y@ Nanocrystalline Composite Thin Film Properties in a Pulsed DC Magnetron Sputtering System***, **P. Sunal**, M.W. Horn,* The Pennsylvania State University

The mid-frequency pulsed dc range of 50-250 kHz was used to co-sputter nanocrystalline-TiN/a-Si@sub x@N@sub y@ films. A combinatorial process was performed in a reactive nitrogen environment from pure Ti and Si targets. An asymmetric bipolar pulsing frequency affects the plasma properties and results in a change in the density and energy of arriving ions at the growing film surface. The plasma potential, electron density, and electron temperature have been determined using a Langmuir probe and used with ion specie results from an energy resolved mass spectrometer to calculate the momentum per arriving atom. Using nanoindentation, the reduced modulus and hardness of the films were characterized and related to the plasma properties during deposition. The momentum per arriving atom shows threshold values for changes in the morphology, which result in different mechanical properties. Finally, the plasma properties were studied against the sputter pressure. At higher pulsing frequencies, the plasma potential increases causing energetic bombardment which yields smaller nanocrystal diameters and a stronger (200) preferred crystallographic orientation. Oxygen contamination of the thin films leads to degradation of the film properties and was investigated by using a silicon nitride capping layer to hermetically seal the film before leaving vacuum.

9:20am **SE-MoM4 Columnar Growth, Nanostructure and Properties of TiC/a-C:H Nano-Composite Coatings***, **D. Galvan**, Y.T. Pei, J.Th.M. De Hosson,* University of Groningen, The Netherlands

TiC/a-C:H coatings were deposited through closed field unbalanced magnetron sputtering (CFUBMS) reactive deposition. Different acetylene gas flow and substrate bias values were employed to vary the coatings composition and nanostructure. To improve adhesion between substrate and coating a Cr-Ti/Ti-TiC graded interlayer was introduced. Various techniques were employed to study the formation of TiC particles within the a-C:H matrix, e.g. EPMA, XPS, grazing angle XRD and high-resolution transmission electron microscopy (HR-TEM). The investigations provide detailed information about the TiC particles volume fraction, particle size and their size distribution in different coatings. It turns out that the Ti content affects to a great extent the columnar features. It is influenced by processing parameters such as deposition temperature or ion flux to atom flux ratio (ion number). An explanation of this effect is provided based on the observed nanostructure and the deposition technique employed. The mechanical performance of coatings with various chemical compositions was investigated through nano-indentations, focused ion beam (FIB) and TEM observations. It was found that the C-enriched columnar boundaries are the locations of crack nucleation and propagation. The investigations confirmed that a coating of low elastic modulus favors the redistribution of the applied load over a larger area, delaying the onset of plastic deformation and subsequent coating failure in these systems. The influence of the toughness of the coatings on their tribological performance is discussed.

9:40am **SE-MoM5 Smart Nanocomposite Tribological Coatings with Chameleon Behavior***, **A.A. Voevodin**,* Air Force Research Laboratory **INVITED**

A review of a recent progress in developing new tribological materials for operating across multiple environments relevant to aerospace applications is provided. New coating materials were designed to rearrange their structure and chemistry on demand to adapt to variable surface conditions (environment humidity, temperature). These materials have been dubbed chameleon because of their ability to change their surface chemistry and structure to avoid wear. The chameleon coating concept involves a nanocrystalline/amorphous nanocomposite structure, where individual phases are arranged to provide a high degree of mechanical and thermal stability and, at the same time, serve as nano reservoirs for tribological surface self-reconstruction. The stored materials are released from nanophase reservoirs in the process of wear and tribological surface chemistry and structure change to continuously reduce friction and wear. This surface response is triggered by changes in the operating environment and/or temperature. Several mechanisms are employed, including self-induced crystallization of amorphous dichalogenide phases, nucleation of nanograins of low melting point metals, formation of low melting point glassy ceramics, and change in the electron hybridization of carbon. These mechanisms were explored in sliding wear tests performed in controlled humidity air, dry nitrogen, and vacuum, as well as at high temperature in air.

[1] **John A. Thornton Memorial Award Winner**

10:20am **SE-MoM7 Optimization of Multilayer Wear-resistant Thin Films Using Finite Element Analysis***, **R.K. Lakkaraju**, F. Bobaru, S.L. Rohde,* University of Nebraska

Extensive research has been carried out by researchers on the growth and characterization of multilayer protective coatings, but the design of these coatings still remains largely empirical. In this regard, recent progress has been made in developing a design approach for optimizing multilayer coating structure before deposition which would help in saving time and material. In pursuit of optimal design, finite element analysis using a plane strain, hertzian contact model was developed to investigate the stress/strain behavior within the layers of the system. The present study looks to find optimal thicknesses of individual layers in the multi-layer coating-substrate system. First test case is a multiobjective optimization of a multilayer system performed by minimizing the strain discontinuities at the coating/substrate interface and the stresses developed in top layer, under combined normal and tangential load conditions. Another option is a single objective optimization (minimizing the strain discontinuity) by constraining the stress values below yield strength. We discuss the use and efficiency of optimization algorithms such as genetic algorithm and gradient based routines used in the present work, and the preliminary results are compared to pin-on-disk wear results of empirically designed coatings.

10:40am **SE-MoM8 Investigation on the Thermal Cycling Behaviour of Graded and Multilayered Lanthanum Zirconate as EB-PVD Thermal Barrier Coating***, K. Bobzin, E. Lugscheider, **N. Bagcivan**,* Surface Engineering Institute (IOT) RWTH Aachen, Germany

Thermal cycling behavior of thermal barrier coatings (TBC) is essential for the increase of efficiency of gas turbines. Traditionally Yttria partially stabilized Zirconia (YPSZ) coatings are used as TBCs on turbine blades. One approach within the collaborative research center (SFB) 561 "Thermally highly loaded, porous and cooled multilayer systems for combined cycle power plants" is to develop innovative TBCs to increase the overall efficiency of the power plant from 58% up to 65%. Investigations on some materials with perovskite, spinelle and pyrochlore structure have shown a great potential of Lanthanum Zirconate (pyrochlore) as thermal barrier coating. In this work Lanthanum Zirconate has been developed as TBC using electron beam physical vapour deposition (EB-PVD). TBCs deposited by EB-PVD show a columnar grain microstructure. A columnar grown TBC is able to balance the difference in thermal expansion between base material and TBC by the relative movement of the single columns. Two different coating architectures have been developed for the TBCs. First a multilayered TBC consisting of YPSZ and Lanthanum Zirconate has been deposited. In the second approach a graded TBC with a transition from YPSZ to Lanthanum Zirconate has been deposited by EB-PVD. The thermal cycling behavior of these coatings on Inconel Alloy 600 has been investigated by a thermal cycling test at 1050°C. Additionally the coatings have been characterized by x-ray diffraction (XRD), scanning-electron microscopy (SEM), energy dispersive X-ray analysis (EDX), and nanoindentation. The results of thermal cycling test show an increase of number of cycles before fatigue from 1380 cycles for YPSZ to 3390 cycles for graded YPSZ/Lanthanum Zirconate and 4140 cycles for multilayered YPSZ/Lanthanum Zirconate.

11:00am **SE-MoM9 Established Protective Cutting Tool Coatings for Difficult Machining Operations***, **K. Bobzin**, M. Maes, C. Pinero,* RWTH Aachen University, Germany **INVITED**

This paper presents a review of the most important thin coatings developed for the protection of cutting tools. Special attention was given to the development of promising coatings for difficult machining operations. Because of the increasing of the complexity in the aircraft and nuclear industry and the elevated operating temperatures, super alloys were developed from simple nickel-chromium matrix to multi-element, multi-phase systems. These new nickel-based super alloys are specially favored for their exceptional thermal resistance and ability to retain mechanical properties at elevated temperatures. However, they are classified as difficult-to-machine materials due to their high shear strength, work hardening tendency, highly abrasive carbide particles in the microstructures, strong tendency to weld and form built-up edges. Also, their tendency to maintain a high strength at the elevated temperatures generated during machining because of their low thermal conductivity constitutes an important challenge. Nowadays, TiAlN is well known because of its excellent overall performance in cutting operations. Also crystalline Al@sub 2@O@sub 3@ shows a high potential for the protection of cutting tools due to its very good chemical and thermal properties. However an adequate coating system for machining super alloys was not found yet. In order to obtain the appropriated properties combination in a single coating system, different TiAlN + @gamma@-Al@sub 2@O@sub 3@ coating system combinations were deposited on cemented carbide cutting inserts and characterized by X-ray diffractometry (XRD) and scanning electron microscopy (SEM). Surface energy of the coated samples was measured. Tribological and chemical properties were analyzed at room and high temperatures.

11:40am **SE-MoM11 Multifunctional SiAlON Ceramic Coatings for High Temperature Applications***, J.I. Krassikoff, D.J. Frankel, T.A. Dunn, D.R. Southworth, **R.J. Lad**,* University of Maine

SiAlON ceramics possess oxidation resistance, high strength, and thermal shock resistance, which make them extremely attractive for applications in 1000-1500°C oxidation environments. We have investigated well-defined SiAlON thin films deposited by rf magnetron co-sputtering of Al and Si targets in Ar/O@sub 2@/N@sub 2@ mixtures. By precisely controlling film architecture at the nanometer level, coating structures having homogenous, gradient, or multilayer compositions that span the full range of O/N and Al/Si ratios have been synthesized, and their chemical, thermal, and mechanical properties have been characterized. Nitride-rich SiAlON film compositions are extremely wear resistant, yet they become oxidized during thermal treatments in air between 1000-1500°C. Compositionally graded coatings with oxide-rich terminations show improved oxidation resistance. Similarly, Al@sub 2@O@sub 3@/Si@sub 3@N@sub 4@ laminate structures exhibit low wear and chemical stability at high temperature. Photolithographically patterned thin film metal resistors embedded at the SiAlON/substrate interface have been used to quantify the oxygen penetration rates through the SiAlON film structures during isothermal annealing and thermal cycling experiments. Accelerated testing consisting of rapid thermal cycling in various reactive environments was accomplished using a microfabricated heater platform. The role of film stress on resulting mechanical properties was investigated using microfabricated cantilever structures.

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