

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. Veprek¹, 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.,¹ followed by the publication of the generic design concept,^{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 1,2⁴. This finding was recently confirmed by the work of Oden et HYPERLINK "mailto:al.@footnote"al.@footnote 5⁵ on the preparation of high-quality heterostructures where the highest hardness enhancement was achieved for one monolayer of Si₃N₄. The first principle DFT calculations by C. Stampfl et HYPERLINK "mailto:al.@footnote"al.@footnote 6⁶ lend further support to this concept and show that, as predicted (see references quoted in⁴), 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 nanocomposites⁴ and of a finite activation volume for the initiation of plastic deformation within an amorphous HYPERLINK "mailto:phase.@footnote"phase.@footnote 7⁷. 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 8⁸. 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. ⁹FootnoteText⁹ ¹⁰S. Z. Li, Y. Shi and H. Peng, Plasma Chem. Plasma Process. 12 (1992) 287. ¹¹S. Veprek and S. Reiprich, Thin Solid Films 268 (1995) 64. ¹²S. Veprek, S. Reiprich and S. Z. Li, Appl. Phys. Lett. 66 (1995) 2640. ¹³S. Veprek, M. G. J. Veprek-Heijman, P. Karvankova and J. Prochazka, Invited Review, Thin Solid Films 476 (2005) 1. ¹⁴M. Oden, invited paper at the 51st Int. Symp. of the American Vacuum Society, Anaheim, November 14 – 19, 2004. ¹⁵S. Hao, B. Delley, and C. Stampfl, School of Physics, The University of Sydney, to be published. ¹⁶M. J. Demkowicz and A. S. Argon, Phys. Rev. Lett. 93 (2004) 025505-1. ¹⁷R. G. Veprek, D. M. Parks, A. S. Argon, and S. Veprek, to be published.

¹ John A. Thornton Memorial Award Winner

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.

Monday Morning, October 31, 2005

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 Al₂O₃ 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 + Al₂O₃ 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/O₂/N₂ 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, Al₂O₃/Si₃N₄ 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.

Advanced Surface Engineering Room 201 - Session SE-MoA

MAX Phases: Nanolaminates and Nanomechanical Measurements

Moderator: D. Gall, Rensselaer Polytechnic Institute

2:00pm SE-MoA1 The MAX Phases: Ductile, Machinable Ternary Carbides and Nitrides, *M.W. Barsoum*, Drexel University **INVITED**

With over 100 refereed publications and 8 patents in the past 8 years we have made tremendous progress in understanding the properties of a class of layered, hexagonal ternary carbides and nitrides with the general formula: $M_{n+1}AX_n$ (MAX), where $n = 1$ to 3, M is an early transition metal, A is an A-group element and X is C or N. The MAX phases combine some of the best attributes of metals and ceramics. Like metals, they are electrically and thermally conductive, readily machinable, not susceptible to thermal shock, plastic at high temperatures, and exceptionally damage tolerant. Like ceramics, some are elastically rigid, lightweight, and maintain their strength at high temperatures. Ti_3SiC_2 is also creep, fatigue and oxidation resistant. Furthermore, basal planes of Ti_3SiC_2 possess very low friction coefficients (3×10^{-2}) that are quite robust vis-a-vis exposure to the atmosphere. Two characteristics distinguish these phases from other layered solids: i) the metallic-like nature of the bonding, and ii) they deform by a unique combination of kink and shear band formation resulting from the glide of basal-plane dislocations. Polycrystalline Ti_3SiC_2 cylinders can be repeatedly compressed at room temperature, up to 1 GPa. The stress-strain curves outline fully reversible, reproducible closed loops whose size and shape depend on grain size, but not strain rate. The energy dissipated per cycle is of the order of 1 MJ/m³. At the grain level we have shown that it is possible to nanoindent grains of Ti_3SiC_2 with up to 10 GPa, dissipate roughly 25 % of the mechanical energy and not be able to find any trace of the indentation. Both phenomena are attributed to the formation and annihilation of incipient kink bands. The technological implications of having these naturally nanolayered materials will be discussed.

2:40pm SE-MoA3 Alternating Covalent-Ionic and Metallic Bonding in Nanolaminated Cubic Perovskites, *D. Music, J.M. Schneider*, RWTH Aachen, Germany

Using ab initio calculations, we have studied 35 cubic perovskites of RM_3X stoichiometry, where R and M are metals and X is a 2p nonmetal. In this structure (space group Pm-3m, prototype $CaTiO_3$), R atoms fill primitive cubic sites, M atoms are located at face centered cubic positions, and X is placed at body centered cubic Bravais nodes. We show that the coupling between M-R and M-X layers in RM_3X can be switched from predominantly covalent-ionic to metallic in character by varying the population of the M and R d-shells. As the X 2p population increases, the bulk modulus decreases, which can be understood by changes in bonding character from more covalent to more ionic due to splitting in density of states. We will also discuss transport properties obtained from phonon calculations. Based on the electron density distribution resemblance to the so-called MAX phases, it is reasonable to assume that alternating covalent-ionic and metallic bonding in these compounds may give rise to similar properties as observed for MAX phases.

3:00pm SE-MoA4 Observation of the Growth and Microstructural Development of MAX Phase Ti_2AlN Thin Films during Magnetron Sputtering using Synchrotron Radiation, *N. Schell, M. Beckers, R.M.S. Martins, A. Mücklich, W. Möller*, Forschungszentrum Rossendorf, Germany

The heteroepitaxial growth of MAX phase Ti_2AlN ($M_{n+1}AX_n$ with $M = Ti$, $A = Al$, $X = N$ and $n = 1$) on single crystal substrates $MgO(001)$ and $MgO(111)$, deposited by reactive magnetron co-sputtering from Ti and Al targets in an Ar/N₂ atmosphere at a temperature of 690°C, has been studied in situ. Using real-time specular x-ray reflectivity, layer-by-layer growth first of an approximately 10 nm thick epitaxial B1-cubic $Ti_0.63Al_0.37N$ seed layer, then, after changing the deposition parameters, of the MAX phase itself was observed, with an increased surface-roughening on $MgO(001)$ substrate. Using off-plane Bragg-Brentano x-ray scattering, the heteroepitaxial growth of Ti_2AlN to the underlying seed-layer as well as MgO was established with lattice parameters of $c = 1.3463$ nm and $a = 0.2976$ nm. From ex-situ pole figures at a laboratory source the epitaxial relationship between film and substrate lattice was determined to be $MgO \{111\} //$

$Ti_2AlN \{1012\} [1; \bar{2}; 0]$ regardless of choice of substrate orientation during deposition, e.g. a non-basal plane epitaxial growth of the Ti_2AlN thin films along MgO directions, leading to a threefold grain orientation as also seen in cross-sectional transmission electron microscopy. In temperature dependent four-probe measurements at room temperature a specific resistivity of $37 \mu\Omega/cm$ has been derived.

3:20pm SE-MoA5 The Materials Science of MAX Phase Thin Films, *L. Hultman*, Linköping University, Sweden **INVITED**

This presentation is a review of the materials research on M_n phase thin films. We have deposited epitaxial films from the Ti-Si-C, Ti-Ge-C, and Ti-Sn-C as well as Ti-Al-N systems on Al_2O_3 or $MgO(111)$ substrates at temperatures of 700-1000C employing DC magnetron sputtering. This was done using mainly growth from elemental sources, but also demonstrating single source deposition from compound targets. We report single-crystal growth of the previously known phases Ti_3SiC_2 , Ti_3GeC_2 , Ti_3SnC_2 , and the discoveries of two phases Ti_4SiC_3 and Ti_4GeC_3 as well as intergrown structures of stoichiometries $Ti_5Al_2C_3$ and $Ti_7Al_2C_5$ in the Si and Ge systems. Characterization studies will be reported using XRD, TEM, four-point (resistivity) probe, and nanoindentation. Comparison will also be made with the phase composition in nanocomposite M-A-X films forming during deposition at reduced temperature.

4:00pm SE-MoA7 The Promise of High Power Pulsed Magnetron Sputtering (HPPMS), *W.D. Sproul*, Reactive Sputtering Consulting **INVITED**

High power pulsed magnetron sputtering (HPPMS) applies a very large power pulse to the target in a short period of time. Typical power densities are on the order of 1,000 to 3,000 W/cm² with pulse durations of 100-150 μsec. This power density is about 100 times the typical power densities used in conventional sputtering. Depending on the size of the sputtering target, the peak power can reach the megawatt range. The very interesting feature of HPPMS is that there is a high degree of ionization of the sputtered species due to electron impact ionization, and most of the ionized species are singularly ionized although there are reports of small amounts of multiply ionized species of the target material. These ionized species can be used to improve the structure and properties of the deposited film, and the ionized species will follow field lines to a biased substrate producing a dense film in side wall features as has been demonstrated by Alami et al. In many respects HPPMS is very much like the cathodic arc process where there is a very high degree of ionization of the evaporant, but unlike the arc process there are few if no droplets produced in the process. HPPMS has been used for reactive sputtering of conducting materials such as chromium nitride, and it has also been used for the reactive sputter deposition of the oxides of Al, Ta, and Ti. The one disadvantage of the HPPMS process that has come to light so far is that its deposition rate is only 25-30% of the rate for an equivalent amount of power used during conventional DC sputtering. A model by Christie has been developed to explain this loss of rate for the HPPMS process, and the model provides insights that hopefully will bring a solution to this loss of rate issue. In this talk, the current state of the art for HPPMS will be reviewed with an eye toward the future to see where HPPMS can be used to benefit the thin film community.

4:40pm SE-MoA9 Towards Large Area Deposition of Cr_2AlC on Steel, *C. Walter, D.P. Sigumonrong*, RWTH Aachen, Germany; *T. El-Raghy*, 3-One-2 LLC; *J.M. Schneider*, RWTH Aachen, Germany

Cr_2AlC belongs to the MAX phases, which are promising materials for protective coatings on steel due to their unique combination of properties like corrosion and oxidation resistance and damage tolerance. Here the deposition by magnetron sputtering of a Cr-Al-C compound target was investigated varying the substrate temperature and the substrate bias potential. It was found that the MAX phase structure is stable in a substrate temperature range between 850 and 450 °C. At lower substrate temperatures the structure of the film is X-ray amorphous. Varying the DC substrate bias potential between floating potential and 310 V, no significant influence on the film composition and structure was observed. A phase purity of more than 90 % MAX phase in the films was reached and the equilibrium volume measured by X-ray diffraction is in excellent

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agreement with our own ab initio calculations. The method discussed here may provide a pathway towards large area MAX phase deposition on steel.

Advanced Surface Engineering Room 201 - Session SE-TuM

Hard Coatings and Wear Mechanisms of Protective Coatings

Moderator: A.A. Voevodin, Air Force Research Laboratory

8:20am SE-TuM1 Structure and Properties of TiBN Coatings Deposited by Reactive Arc Evaporation, J. Neidhardt, C. Mitterer, University of Leoben, Austria; Zs. Czigány, Research Institute for Technical Physics and Materials Science, Hungary; M. O'Sullivan, Plansee AG, Austria

TiBN based coating systems have been shown to have a high potential as wear protective coating owing to their outstanding mechanical properties as well as their chemical and thermal stability. However, the industrial scale synthesis has been very limited so far, presumably due to the sensitivity of the target materials and the therefore low deposition rates as well as the commonly high intrinsic stresses. This study reports, thus, on high-rate (30 - 40 nm-min@super -1@) TiBN coating deposition by reactive arc evaporation in a commercial Balzers Rapid Coating System at different N@sub 2@ partial pressures. Decreasing the bias voltage to -20V is shown to reduce the intrinsic stress and in turn to improve the adhesion on various substrates, e.g. high speed steel and (100) Si. XRD as well as high-resolution transmission electron microscopy in combination with selected area electron diffraction revealed that all coatings contain fcc crystallites, whereas the increasing lattice parameter at lower N@sub 2@ partial pressures indicates a supersaturated solid solution of B in fcc TiN. At higher N@sub 2@ partial pressures an amorphous BN phase forms, whereas its extent scales with the N@sub 2@ fraction. Nano-indentation revealed a maximum in hardness at approximately 40 GPa for the TiBN single phase solid solution which drops to 22 GPa for the coating grown in pure N@sub 2@. Ball-on-disc tests against alumina at 5N showed that the high hardness of the single phase material results in a by one order of magnitude reduced wear coefficient with respect to the coating containing the additional amorphous phase, even though the coefficient of friction remained constant at 0.7 to 0.8

9:00am SE-TuM3 The Origin of the Hysteresis Effect in Reactive Sputtering Processes, S. Berg, T. Nyberg, O. Kappertz, T. Kubart, D. Rosen, Uppsala University, Sweden

INVITED

Sputtering is a well known and widely used thin film coating technique. The way the energetic incoming particle generates a collision cascade in the target that causes some of the surface atoms to be ejected is reasonable well understood. Since there is negligible consumption of the inert gas (normally argon) process control is not a problem. The sputtering process may easily be modified. By adding a reactive gas to a sputtering system it is possible to obtain a reactive sputtering process. This process, however, exhibits a significantly more complex processing behaviour than inert sputtering. The processing curves will form hysteresis loops where the processes have a tendency to make avalanche like abrupt transitions at the edges of the hysteresis width. Before the transition a metal rich film may be formed at high deposition rate while after the transition a compound film will be deposited at a low deposition rate. Without a sophisticated feedback control system no compositions in between these two extremes can be reached. Unfortunately the most attractive processing point is located at one of the critical edges of the hysteresis loop. This complicates industrial production carried out by these processes. The aim of this presentation is to describe the cause of the hysteresis loop and point out how different processing parameters will influence the hysteresis. The possibility to eliminate the hysteresis and obtain non-critical stable processing conditions will also be discussed. In addition comments will be made about common mis-information in reporting data from reactive sputtering processing experiments.

9:40am SE-TuM5 Nanostaircases: An Atomic Shadowing Instability during Epitaxial CrN(001) Layer Growth, D. Gall, Rensselaer Polytechnic Institute
Epitaxial CrN(001) layers, 57 and 230 nm thick, were grown on MgO(001) at 700 °C by ultra-high-vacuum magnetron sputter deposition in pure N@sub 2@ discharges. An oblique deposition angle @alpha@ = 80° was utilized to purposely increase the effect of atomic shadowing on surface morphological and microstructural evolution. The layers are single crystals with a surface morphology that is characterized by dendritic ridge patterns extending along orthogonal directions superposed by square shaped super mounds with edges. The ridge patterns are due to a 2D growth instability related to a gradient in the adatom density while the supermounds form

due to atomic shadowing. The supermounds protrude out of the surface and capture a larger deposition flux than the surrounding layer. This leads to both vertical and lateral growth and the formation of inverted pyramids that are epitaxially embedded in a single crystalline matrix. The inverted pyramids are terminated by 1-3 nm wide tilted voids that form nanostaircases due to kinetic faceting along orthogonal {100} planes.

10:00am SE-TuM6 The Effects of Si Additions on the Structure and Mechanical Properties of Mo-Si-C and Zr-Si-C Thin Films, J.E. Krzanowski, University of New Hampshire

The effects of Si additions on the mechanical properties of molybdenum carbide and zirconium carbide thin films have been examined in this study. Mo-Si-C and Zr-Si-C thin films were deposited by magnetron co-sputter deposition using carbide targets. The films were deposited onto Si substrates at 350C for Mo-Si-C and 450C for Zr-Si-C. The structure, texture and crystallinity of the films were analyzed using x-ray diffraction, and high-resolution transmission electron microscopy was used to study film microstructure. X-ray photoelectron spectroscopy (XPS) was used to determine film composition and also to assess the chemical state of the carbon, as well as oxygen impurities, in the films. For Mo-C films with no or little Si, the structure was hexagonal; as the Si content increased, a transition to a face-centered cubic structure was observed. At the highest Si contents (10-14%) the structure was essentially amorphous. The TEM studies showed as Si was added, the grain size was reduced and confirmed the amorphous structure at the high Si contents. The texture of the films also evolved with Si content, showing oriented films at low Si but random grain structures (continuous Debye rings) at intermediate Si concentrations. The mechanical properties of the films were analyzed using nano-indentation, and showed little change in hardness over the entire range of film compositions. Zr-Si-C films were similarly studied, and showed a stronger tendency for amorphization as Si was added. The nano-indentation tests on these films showed a peak in hardness near 18% Si, where the hardness of near 30 GPa was more than 50% higher than for ZrC films alone, while the film modulus increased only slightly. Initial TEM studies show that films with added Si have a higher density, which may be a factor contributing to the observed hardness increase.

10:20am SE-TuM7 The Effects of Water Vapor on the Friction Coefficient of Near Frictionless Carbon, W.G. Sawyer, P.L. Dickrell, University of Florida; A. Erdemir, Argonne National Laboratory

INVITED

Diamond-like carbon (DLC) films are of tribological interest due to their low friction, low wear rate, high hardness, and chemical inertness. These films can potentially be used in a wide range of applications, such as bearings, cutting tools, submersible parts, and biomedical applications. One class of diamond-like carbon coatings termed near frictionless carbon (NFC) that was developed at Argonne National Laboratory have been shown to sustain superlow coefficients of friction ($\mu < 0.003$) and wear rates ($K < 3-10$ mm³/Nm) in self-mated contacts. The tribological behavior of these films is sensitive to the environment, only realizing their low coefficient of friction and wear rate in inert, dry, or vacuum environments. Using a microtribometer that is enclosed in a controlled environmental chamber the coefficient of friction over a range of surface temperatures and gaseous water vapor pressure was measured. The normal load for these experiments was 100 mN, the reciprocating speed was 18 mm/s, and the reciprocating path length was 0.6 mm. The oxygen partial pressure was measured to be less than 10 ppm for all experiments. The relative humidity varied from nominally dry to approximately 40%. The surface temperatures varied from 35C to 100C. The friction coefficient data will be presented with an accompanying uncertainty analysis. Using the friction coefficient to estimate the fractional coverage of adsorbate or percentage of effected sites, the data set was fit to an adsorption and desorption equation. This curve fitting revealed an activation energy of approximately 50 kJ/mol, which is consistent with the activation barrier for water.

11:20am SE-TuM10 Tribological Behavior and Thermal Stability of TiC/a-C:H Nanocomposite Coatings, Y.T. Pei, D. Galvan, J.Th.M. De Hosson, University of Groningen, The Netherlands

Advanced TiC/a-C:H nanocomposite coatings have been produced via reactive deposition in a closed-field unbalanced magnetron sputtering system (Hauzer HTC-1000). These wear-resistant coatings are targeted for automotive applications where high-load bearing capacity, low friction and wear rate are the primary requirements. In this paper, the tribological behavior of the nanocomposite coatings is scrutinized by means of ball-on-disc tribo-tests in the temperature range of 20-400°C and in different environments, in conjunction with detailed examinations of the mechanical properties. The influence of the volume fraction and grain size of TiC

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nanocrystallites on the coating properties has been examined. The thermal stability of the coatings in terms of critical temperatures, at which the degradation of wear resistance and friction of the coatings starts, are monitored in comparison with the variation of hardness and elastic modulus of the coatings with temperature. In-situ monitoring the thickness of transfer films formed on the counterpart (100Cr6 ball) reveals that the dynamic and super-low friction ($\mu=0.01-0.05$ in air) behavior is directly related to the thickening of transfer films that contributes self-lubrication. The lowest friction and wear rate are obtained when the size of TiC particles become of the same dimension as the separation distance of amorphous hydrocarbon matrix, maximizing also the toughening effects in the composite system. These phenomena have been understood based on a physical model.

Tuesday Afternoon Poster Sessions, November 1, 2005

Advanced Surface Engineering Room Exhibit Hall C&D - Session SE-TuP

Advanced Surface Engineering Poster Session

SE-TuP1 HPPMS Growth of High Sputtering Yield Metallic Films, S.L. Rohde, University of Nebraska; D.J. Christie, Advanced Energy; S. Sevvana, S. Chennadi, D.M. Mihut, J. Li, University of Nebraska

Ionization levels as high as 70-90% have been reported using High-Power Impulse Magnetron Sputtering (HPIMS), also known as HPPMS, as compared with 5-10% ionization typical in conventional dc magnetron sputtering. Unfortunately, the overall deposition rates observed in most HPPMS studies is significantly lower than (~30%) for conventional dc magnetron sputtering. In the present study, the deposition rate of HPPMS films has been studied as a function of the impulse voltage (or charge voltage). The studies have been carried out for both high sputtering yield metals including Al and Cu, as well as low sputtering yield compounds, such as CrB₂. While the overall deposition rate increases with increasing impulse voltage or pulse power; this relationship does not follow the same linear relationship observed for dc sputtering. Additionally, under specific conditions it has been shown that dynamic deposition rate [nm/(watt*s)] can exceed that obtained using comparable dc power levels. This trend is observed only for materials with very high sputtering yields, but in all cases there are distinct changes in film properties, such as texture, surface roughness and residual stress, as a function of impulse voltage or power. Other variables considered include: substrate bias, supplemental discharge confinement and angle of inclination. Discussed are some of the implications of and possible explanations for this variation in dynamic deposition rate, making it possible to envision applications where HPPMS techniques might have significant advantages over conventional magnetron sputtering.

SE-TuP2 Low Temperature Deposition of α -Al₂O₃ by Plasma Chemical Vapor Deposition, D. Kurapov, J.M. Schneider, RWTH Aachen, Germany

Al₂O₃ coatings were deposited on tempered hot working steel substrates (X38CrMoV5-1) by plasma enhanced chemical vapor deposition. The influence of the substrate temperature on the constitution of the alumina films was investigated in the temperature range from 500 to 600 °C and normalized ion flux values of 100, 140, 270, and 480. The constitution of the deposited films was analyzed by grazing incidence x-ray diffraction (GIXRD). Additional information about phases formed was obtained from atomic force microscopy (AFM) of polished films. It was found that the phase formation was strongly affected by the normalized ion flux. α -Al₂O₃ films were obtained at a growth temperature as low as 500 °C. The hardness and elastic modulus of the deposited films were evaluated by nanoindentation. The correlation between deposition parameters and mechanical properties of Al₂O₃ films can be understood in terms of the density reduction due to changes of the ion flux. It was found that maximum hardness and elastic modulus values were obtained at low normalized ion flux values.

SE-TuP3 Laser Processing of Crystalline Technologically Relevant Glass-Forming Alloys for Enhanced Corrosion Resistance, J.M. Fitz-Gerald, J.G. Hoekstra, M.A. Jakab, S.J. Poon, G.J. Shiflet, J.R. Scully, University of Virginia

Over the past 25 years, investigations concerning the use of continuous and pulsed lasers for surface modification have met with reasonable success in areas of alloying element modification, enhanced surface hardness, structure manipulation, and improvements in corrosion resistance. There are several critical attributes of laser surface modification (LSM) that lead to the formation of an amorphous surface, including the ability to promote near-surface compositional uniformity, and due to the use of a pulsed laser (nanoseconds), rapid solidification at quench rates on the order of 10⁸ to 10¹⁰ K/s are possible. Moreover, since only the first few micrometers are re-solidified, LSM presents the opportunity to explore the surface amorphization of materials without sacrificing desirable bulk properties such as strength and toughness. This research focuses on the Al-Co-Ce and Fe-Cr-Mo-Er-C-B alloy systems with enhanced glass forming chemistries. In this research, the homogeneity of the starting crystalline ingot has been found to have a major impact on the ability to form an amorphous surface. The LSM surfaces showed several amorphous characteristics in terms of backscattered imaging, diffraction spectra, and corrosion behavior, all of which are signatures of these classes of amorphous materials.

Electrochemical analysis of the modified materials showed increased pitting potentials and several characteristics similar to that of fully amorphous, melt spun metallic glass alloy standards. Characterization was performed with scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDXS), Auger electron spectroscopy (AES), conventional and glancing angle X-ray diffraction (XRD), and electrochemical analysis. @FootnoteText@ @footnote 1@ K.G. Watkins, M.A. McMahon, and W.M. Steen, Mat. Sci. and Eng. 231, p. 55 - 61 (1997).

SE-TuP4 Structure and Bonding of V@sub 2@AIC Studied by Theoretical and Experimental Means, J.M. Schneider, R. Mertens, D. Music, RWTH Aachen, Germany

We have studied V@sub 2@AIC (space group P6@sub 3@/mmc, prototype Cr@sub 2@AIC) by ab initio calculations and used DC magnetron sputtering to synthesize a thin film. The density of states (DOS) of V@sub 2@AIC for antiferromagnetic (AFM), ferromagnetic (FM), and paramagnetic (PM) configurations are also presented. Based on a comparison of the cohesive energies as well as the DOS for the spin polarized structures, we have identified the FM/AFM configuration to be metastable. According to our partial DOS analysis, V@sub 2@AIC can be described as a strongly coupled nanolaminate [Z. Sun, D. Music, R. Ahuja, S. Li, and J. M. Schneider, Phys. Rev. B 70, 092102 (2004)]. Furthermore, we have observed good agreement between the calculated and measured equilibrium volume.

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