

## 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 ( $K < 3-10$  mm<sup>3</sup>/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.

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