Hard Coatings and Vapor Deposition Technologies
Room California - Session B4-1-TuM

Properties and Characterization of Hard Coatings and Surfaces I

Moderators: Naureen Ghafoor, Linköping Univ., IFM, Thin Film Physics Div., **Ulrich May**, Robert Bosch GmbH, Diesel Systems, **Fan-Bean Wu**, National United University, Taiwan

8:20am **B4-1-TuM-2 Preparation and Characterization of Hard and Tough Coatings of Ion-assisted Co-sputtered Transition Metal Borides***, **Ming-Show Wong,*** National Dong Hwa University, Taiwan **INVITED**

Transition metal borides (TMeB) are frequently explored around the globe due to their superior mechanical, tribological, electrical properties and chemical stability. Titanium diboride (TiB_2) is the most promising and explored material, while the other TMeBs like zirconium and tantalum diboride (ZrB_2 and TaB_2) sharing the same crystal structure and common properties receive relatively low attention. TMeBs are usually hard but brittle, which limit their wide spread applications. To prepare both hard and tough coatings of TMeBs, various approaches have been taken including doping, solid solution, ion bombardment, and multilayer. In the Ti-Zr-Ta-B system, ceramic-meal composites like TiB_2-Zr, ZrB_2-Ta composites, $TiZrB_2$ and $TiTaB_2$ solid solution and TiB_2/ZrB_2 multilayer films were explored by co-sputtering the corresponding TMeB ceramic target and/or metal target under various substrate bias voltages. Appropriate doping, solid solution, multilayer and ion bombardment could result in textured films with preferred structure with enhanced properties. Ion bombardment on the growing film greatly affects the crystal preferred orientation, crystallinity, composition, grain size, surface roughness, stress, toughness and hardness of the TMeB films. The change in target power ratio for solid solution films and in bilayer thickness for multilayer all affected the structure of the obtained films influencing intensity of texture, distortion of crystal lattice and residual stress. Superhard and tough films with hardness over 50 GPa and fracture toughness over 3 MPa.m$^{1/2}$ have been achieved consistently

9:00am **B4-1-TuM-4 Strategy for Increasing Both Hardness and Toughness in Transition-metal Diboride Thin Films***, B Bakhit,* Linköping Univ., IFM, Thin Film Physics Div., Sweden*; I Petrov,* University of Illinois, USA, Linköping University, Sweden, USA*; J Greene,* University of Illinois, USA, Linköping University, Sweden, National Taiwan Univ. Science & Technology, Taiwan*; L Hultman, J Lu, J Rosén, G Greczynski, **Naureen Ghafoor,*** Linköping Univ., IFM, Thin Film Physics Div., Sweden

Refractory transition-metal (TM) diborides exhibit inherent hardness. However, this is not always sufficient to prevent failure in applications involving high mechanical and thermal stresses, since hardness is typically accompanied by brittleness leading to crack formation and propagation. Toughness, the combination of hardness and ductility, is required to avoid brittle fracture. Here, we propose a strategy for enhancing *both* the hardness and ductility of ZrB_2 thin films, selected as a model TM diboride, grown by hybrid high-power pulsed and dc magnetron co-sputtering (HiPIMS/DCMS) in pure Ar. A Ta target operated in HiPIMS mode, with a substrate bias synchronized to metal-rich portions of HiPIMS pulses, supplies energetic Ta ions to the growing film, while a compound ZrB_2 target operated in DCMS mode provides a continuous flux of Zr and B atoms. The average power P_{Ta} applied to the HiPIMS Ta target, and the HiPIMS pulse frequency, are varied from 0 to 1800 W (300 Hz) in increments of 600 W. All other deposition parameters are maintained constant. The resulting boron-to-metal ratio, y = B/(Zr + Ta), in as-deposited $Zr_{1-x}Ta_xB_y$ films continuously decreases from 2.4 to 1.5 as P_{Ta} is increased from 0 to 1800 W, while x increases from 0 to 0.3. A combination of XTEM, analytical Z-contrast STEM, EELS, EDX, and XRD analyses, reveal that all films have the AlB_2 hexagonal crystal structure with a columnar microstructure. Layers with $x < 0.2$ have B-rich column boundaries, whereas those with $x \geq 0.2$ have Ta-rich column boundaries. This microstructural transition results in an increase of ~20% in hardness, from 35 to 42 GPa, with a simultaneous increase of ~50% in the nanoindentation toughness, from 3.5 to 5.2 MPa√m.

9:20am **B4-1-TuM-5 Tribocorrosion Resistance of Borided ASTM F1537 Alloy***, I Campos-Silva, **Angel Manuel Delgado-Brito,*** Instituto Politecnico Nacional Grupo Ingeniería de Superficies, México*; J Oseguera-Peña,* Tecnologico de Monterrey-CEM, México*; J Martinez-Trinidad,* Instituto Politecnico Nacional, Grupo Ingenieria de Superficies, México*; R Perez Pasten-Borja,* Instituto Politecnico Nacional, SEPI ENCB, Mexico*; D Lopez-Suero,* Instituto Politecnico Nacional, Grupo Ingenieria de Superficies, México*; A Mojica-Villegas,* Instituto Politecnico Nacional, ENCB, México

New results about the tribocorrosion resistance of borided ASTM F1537 alloy, immersed in Hanks' solution were estimated in this study. A CoB-Co_2B layer, with around 30 microns of thickness, was obtained at the surface of the alloy using the powder-pack boriding process at 1273 K with 6 h of exposure. Before the tribocorrosion tests, indentation properties such as hardness, fracture toughness, the residual stresses were obtained at the surface of the borided cobalt alloy. Otherwise, the tribocorrosion tests were carried out in a linear reciprocating tribometer coupled with a standard three-electrode electrochemical cell, in which a 5 mm diameter alumina ball worn the specimen surface immersed in Hanks' solution. A constant load of 20 N was applied over the surface of the material considering a stroke length of 2.5 m, and a total sliding distance of 100 m.

To estimate the material loss due to wear only, corrosion only, and the component due to the wear-corrosion synergism, four tests were conducted according to the ASTM G119 procedure: two wear tests, a) one in which the total material loss due to wear and corrosion (T) was estimated, b) another performed at 1 V cathodic of the open circuit to eliminate the corrosion component, defined as W_o. In the case of the corrosion tests, c) the polarization resistance was evaluated (C_o), without the influence of the wear component, and finally, d) the influence of the wear component in the corrosion behavior (C_w) was estimated. In all the cases, and to evaluate the influence of the boride layer developed at the surface of the ASTM F175 alloy, the experimental procedure was also established on the untreated material.

The results established that the presence of CoB-Co_2B layer decreases the total material loss due to wear and corrosion synergy compared to the untreated material. For the untreated material, the 62 % of the material loss was attributed to the wear-corrosion synergism in comparison with the 38 % estimated for the borided cobalt alloy. Finally, the influence of wear affected in greater extent than corrosion in the untreated material, while for the borided alloy the interaction between corrosion and wear was equal.

9:40am **B4-1-TuM-6 Corrosion Behavior of TiAlSiN Doped with Ag Coating Deposited by Co-sputtering in Physiological Fluids***, **Alvaro Danilo Caita Tapia**, S Rodriguez Arevalo, E Borja Goyeneche, J Olaya Florez, B Gamboa Mendoza,* Universidad Nacional de Colombia, Colombia

In this work it was studied the influence of the variation on weight percentage of Ag in TiAlSiN coating deposited on TiAlV substrate with co-sputtering technique. The structural analysis was performed by X-ray diffraction (XRD) and chemical composition was performed using Energy-dispersive X-ray spectroscopy (EDS). It was evaluated the corrosion response at one hour of Electrochemical Impedance Spectroscopy (EIS) performed on samples in different solutions that simulate physiological fluids such as 3.5%NaCl at human body temperature (aprox. 38°C), physiological serum and ringer lactate. Those results were compared with an EIS corrosion test in 3.5%NaCl solution at an ambient temperature. It is shown that there is a peak in silver content for which is reached the best corrosion resistance performance, wich in addition to the antibacterial capacities of Ag, makes this coating an optimal candidate for biomedical applications.

10:00am **B4-1-TuM-7 Adhesion Strength of Titanium Carbide Thin Film Coatings on Surface Microstructure Controlled WC-Co***, **Takeyasu Saito**, C Tanaka, N Okamoto,* Osaka Prefecture University, Japan*; A Kitajima, K Higuchi,* Osaka University, Japan

Chemical vapor deposited (CVD) or physical vapor deposited (PVD) hard material coating technique on the cemented-tungsten carbide (WC-Co) is widely used for molds and cutting tools, which plays an important role in a lot of manufacturing industry. Plasma enhanced chemical vapor deposition (PECVD) and PVD have some merits like lower deposition temperature (< 500°C) than thermal CVD and high through-put, however, the films usually have low adhesion strength. Then, life of molds and cutting tools obtained PVD are usually shorter than that with CVD.

In this study, several surface pretreatment methods were investigated to increase surface roughness to enhance adhesion strength. The procedure include, dry etching by CF_4 plasma discharge for 15 to 120 min in the temperature change from R.T. to 500°C. Chemical treatment with aqua regia (3HCl:HNO_3) for 3 min at 25 to 60°C. After pretreatment, TiC coatings were formed by sputtering with TiC target or PECVD with $TiCl_4$ and CH_4. Surface roughness, deposition rate, composition ratio and chemical bond, hardness and adhesion strength of WC-Co and TiC coating film ewre evaluated AFM, surface profiler, XPS, dynamic ultra-micro hardness tester, and scratch tester, respectively.

Figure 1 shows the relationship between the surface roughness (Ra) and critical load of sputtered TiC hard coating layer on surface treated WC-CO. With the CF_4 plasma treatment, the maximum load of 12.1 N with Ra = 46 nm. However, with the aqua regia treatment, the maximum load of ca. 70 N more than Ra = 80 nm. There are still scatters less than Ra = 80 nm. The cause of delamination was thought to be the detailed substrate morphology or chemical states after etching and poor step coverage of sputtered TiC coating layer. Figure 2 shows the relationship between the surface roughness (Ra) and critical load of PECVD TiC hard coating layer on surface treated WC-CO with aqua regia. Compared with fig. 2(right), the critical load is worse. We are still investigating the reason but are considering that the quality PECVD TiC film is poor at this moment

Author Index

Bold page numbers indicate presenter