Hard Coatings and Vapor Deposition Technologies
Room California - Session B4-2-TuA

Properties and Characterization of Hard Coatings and Surfaces II

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

1:40pm **B4-2-TuA-1 Fracture Toughness Enhancement in Superlattice Hard Coatings**, ***Rainer Hahn***[1], *M Bartosik, H Riedl,* TU Wien, Institute of Materials Science, Austria*; H Bolvardi,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; S Koloszvári,* Plansee Composite Materials GmbH, Germany*; P Mayrhofer,* TU Wien, Institute of Materials Science, Austria

Physical vapour deposited (PVD) ceramic hard coatings are widely used in industrial applications as protective, wear reducing coatings. Their combination of good mechanical properties such as high hardness, a low friction coefficient, and their chemical resistance enable the application in harsh environments. However, a strong limitation is the relatively low fracture tolerance (brittle behaviour), depicting especially in cutting applications a major challenge.

In this contribution, we show experimental results of *in-situ* microcantilever bending tests on nanolayered TiN–CrN coatings, referred to as superlattices, overcoming this unfavourable behaviour. We found a maximum in fracture toughness (K_{IC}) at bilayer periods of ~6 nm [1], similar to the well-known peak for the indentation hardness reported by Helmersson et al. [2]. For both, K_{IC} and the hardness, we observe an increase by ~50 % compared to the rule of mixture of the constituents. The beneficial effect of a careful structural design on the fracture toughness will be shown for reactive magnetron sputtered as well as arc evaporated superlattice coatings. Importantly, the coatings synthesized in the industrial scale arc evaporation plant (Oerlikon Balzers Innova) show an even more pronounced superlattice effect and thus unite high hardness with reasonable toughness.

While mechanisms based on dislocation activity explain the increase in hardness, the linear elastic behaviour during our micromechanical tests suggests a different mechanism responsible. To describe this, we conducted density functional theory (DFT) calculations as well as finite element studies.

Complementary, we studied the microstructure of our coatings by X-ray diffraction experiments, scanning electron microscopy and high-resolution transmission electron microscopy. The thermal stability of our films was investigated by annealing in vacuum and ensuing experiments (XRD, hardness and fracture toughness) [3] along with differential scanning calorimetry (DSC) investigations.

[1] R. Hahn, M. Bartosik, R. Soler, C. Kirchlechner, G. Dehm, P.H. Mayrhofer, Superlattice effect for enhanced fracture toughness of hard coatings, Scripta Mat. 124 (2016) 67.

[2] U. Helmersson, S. Todorova, S.A. Barnett, J.-E. Sundgren, L.C. Markert, J.E. Greene, Growth of single-crystal TiN/VN strained-layer superlattices with extremely high mechanical hardness, J. Appl. Phys. 62 (1987) 481.

[3] R. Hahn, M. Bartosik, M. Arndt, P. Polcik, P.H. Mayrhofer, Annealing effect on the fracture toughness of CrN/TiN superlattices, Int. J. Refract. Met. H. 71 (2018) 352-356.

2:00pm **B4-2-TuA-2 Simultaneous Topographical and Electrochemical Mapping using Scanning Ion Conductance Microscopy - Scanning Electrochemical Microscopy (SICM-SECM)**, *W Shi, G Mendoza,* ***Byong Kim****, K Lee,* Park Systems Corporation, USA

Lately, scanning ion conductance microscopy (SICM), has emerged as a versatile non-contact imaging tool. To obtain spatially-resolved electrochemical information, scanning electrochemical microscopy (SECM), also known as the chemical microscope, has been developed. Hybrid SICM-SECM techniques have been developed, in which the SICM compartment provides the accurate probe-sample distance control, while the SECM compartment measures the faradaic current for electrochemical information collection.

In this work, we demonstrate the use of an Atomic Force Microscopy (Park NX10) in combination with an ammeter for concurrent topography imaging and electrochemical mapping. The SICM-SECM probe consisted of a Au crescent electrode (AuE) on the peripheral of a nanopipette. High resolution probe-substrate distance control was obtained by the ion current feedback from SICM, while simultaneous electrochemical signal collection was achieved via the AuE from SECM. As a proof-of-concept experiment, a Au/Pyrex pattern standard sample was imaged with the SICM-SECM technique. The Au bar and the Pyrex substrate were clearly resolved from the SICM topography image, with the bar height and pitch width closely matching the actual values. In terms of the electrochemical property mapping, higher Faradaic current was seen when the probe was scanned over Au bar as a result of redox cycling, while lower Faradaic current was observed when the probe was over Pyrex substrate due to hindered diffusion. The capability of the SICM-SECM technique described here holds promise of many exciting applications in the field of electrochemistry, battery research and metallurgical coatings.

4:00pm **B4-2-TuA-8 Performance Comparison of Two Diffusion Models for Describing the Growth Kinetics of Iron Boride Layers**, *M Ortiz-Domínguez,* Universidad Autónoma del Estado de Hidalgo, México*; O Gómez-Vargas,* ***José Solis-Romero****,* Instituto Tecnológico de Tlalnepantla, México*; G Ares de Parga,* Instituto Politécnico Nacional, México*; J Oseguera-Peña,* Tecnológico de Monterrey, México

In selecting and designing materials for certain engineering applications is an important factor. Likewise, one of the most important reasons for the machinery parts to suffer damage and fail is wear. The boriding process is adequate to increase the surface hardness and a very significant resistance against some acids, bases, metal solutions and high temperature oxidizing are among the advantages of boriding over other surface hardening methods to extend its lifetime. An indispensable tool to choose the suitable process parameters for obtaining boride layer of an adequate thickness is the modeling of the boriding kinetics. Moreover, the simulation of the growth kinetics of boride layers has gained great interest in the recent years. In this study, the AISI O1 steel was pack-borided in the temperature range of 1123-1273 K for different treatment times ranging from 2 to 8 h. Two kinetic models were proposed for estimating the boron diffusion coefficients through the Fe_2B layers. Displacements of the interface (Fe_2B/substrate) resulted from a difference of the arrival flux of the interstitial boron atoms to one phase. The mass balance equations were formulated. The measurements of the thickness (Fe_2B), for different temperature of boriding, were used for calculations. As a result, the boron activation energy for the AISI O1 steel was estimated as 197.20 kJ mol^{-1}. This value of energy was compared between both models and with other literature data. In addition, to extend the validity of the present models, two additional boriding conditions were done. The Fe_2B layers grown on AISI O1 steel were characterized by use of the following experimental techniques: X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDS) .

4:20pm **B4-2-TuA-9 Microstructure and Surface Strength of Chemically Modified WC-Co for Adhesive Strength Improvement**, ***Daichi Kiyokawa****, C Tanaka, T Saito, N Okamoto,* Osaka Prefecture University, Japan*; A Kitajima, K Higuchi,* Osaka University, Japan

Chemical vapor deposited (CVD) or physical vapor deposited (PVD) hard material carting technique is widely used the cemented-tungsten carbide (WC-Co) for molds and cutting tools, which plays an important role in a lot of manufacturing industry. However, the adhesive strength is one of the issues for reliable mold preparation.

In this study, substrate is pretreated by chemical treatment with aqua regia ($3HCl:HNO_3$) for 1 to 5 min at 25 to 60°C to remove Co from the WC-Co surface and to increase surface roughness to enhance adhesion strength. The hardness of films was measured by dynamic ultra-micro hardness tester (Shimadzu Co. DUH-211). Pretreated WC-Co substrates are measured for bulk strength with 200 gf of test load as well as for surface strength with 25 gf of test load.

Figure 1 shows Martens hardness (HM) of WC-Co bulk after pretreatment. Hardness of pretreated substrate became gradually lower. Figure 2 shows HM of WC-Co surface after pretreatment. Hardness of pretreated substrate became lower, even after 1min/25°C treatment. In addition, the difference in HM increased with higher temperature an longer treatment period. The brittleness of WC-Co surface after surface treatment should be eliminated. The TiC-based hard coating deposition of surface treated WC-Co will be discussed.

[1] **Student Award Nominee**

Author Index

Bold page numbers indicate presenter