Hard Coatings and Vapor Deposition Technologies
Room Town & Country D - Session B4-3-TuM

Properties and Characterization of Hard Coatings and Surfaces III

Moderators: Dr. Naureen Ghafoor, Linköping University, Sweden, **Dr. Marcus Günther**, Robert Bosch GmbH, Germany, **Dr. Fan-Yi Ouyang**, National Tsing Hua University, Taiwan

8:20am **B4-3-TuM-2 Is It Meaningful to Quantify Vacancy Concentrations of (Ti,Al)N Thin Films Based on Laser-Assisted Atom Probe Tomography Data?**, *Marcus Hans,* Materials Chemistry, RWTH Aachen University, Germany; *M. Tkadletz,* Department of Materials Science, Montanuniversität Leoben, Austria; *D. Primetzhofer,* Department of Physics and Astronomy, Uppsala University, Sweden; *H. Waldl,* Christian Doppler Laboratory for Advanced Coated Cutting Tools, Montanuniversität Leoben, Austria; *M. Schiester,* Materials Center Leoben Forschung GmbH, Austria; *M. Bartosik,* Department of Materials Science, Montanuniversität Leoben, Austria; *C. Czettl,* CERATIZIT Austria GmbH, Austria; *N. Schalk,* Christian Doppler Laboratory for Advanced Coated Cutting Tools, Montanuniversität Leoben, Austria; *C. Mitterer,* Department of Materials Science, Montanuniversität Leoben, Austria; *J. Schneider,* Materials Chemistry, RWTH Aachen University, Germany

Recently, it was proposed to quantify vacancy concentrations based on laser-assisted atom probe tomography (APT) data for a (Ti,Al)N film with a nanolamellar architecture, grown by chemical vapor deposition (CVD). However, the measurement accuracy of APT depends on the evaporation conditions. To determine, whether vacancy concentrations can be reliably estimated based on APT data, we systematically compare measurements with an ultraviolet (UV) as well as a green laser to ion beam analysis data. First, monolithic TiN and AlN films, which are stoichiometric within the measurement uncertainties of ion beam analysis, are investigated. In case of TiN an electric field strength of 39.4 V nm^{-1} and a nitrogen content of 49.0 at.%, consistent with ion beam analysis data, is obtained with both lasers, when using pulse energies of 5 pJ (UV laser) and 0.1 nJ (green laser). However, significant differences can be observed for monolithic AlN as nitrogen contents from 41.9 to 35.8 at.% and 48.4 to 41.4 at.% are measured, depending on variations of the pulse energies of the UV and green laser, respectively. In order to mimic nanolamellar architectures for correlative compositional analysis by ion beam analysis and laser-assisted APT, a multilayered TiN/AlN/TiN film is synthesized and significant deviations with respect to the nitrogen content are evident for the AlN layer. While the average N concentration from ion beam analysis is 51 at.%, N contents from laser-assisted APT data are only 38 at.% (UV laser) or 41 at.% (green laser). Hence, the nitrogen content of the AlN layer is underestimated from laser-assisted APT data by at least 10 and up to 13 at.% and this significant discrepancy cannot be explained by the measurement uncertainties. Thus, the here presented data emphasize that it is not meaningful to quantify vacancy concentrations of (Ti,Al)N thin films solely based on atom probe data.

8:40am **B4-3-TuM-3 The Oxidation Behavior of VMoN Thin Films Deposited by High Power Pulsed Magnetron Sputtering**, *Nan-Cheng Lai, J. Huang,* National Tsing Hua University, Taiwan
The purpose of this study was to investigate the oxidation behavior of VMoN thin film deposited by High Power Pulsed Magnetron Sputtering (HPPMS) with different duty cycles. Vanadium nitride (VN) and molybdenum nitride (MoN$_x$) are two promising materials for protective coatings on cutting tools because of the formation of Magnèli oxide phases at high temperature, thereby increasing the wear resistance and prolonging the service life of the industrial products. Due to the increasing demands of dry cutting, the oxidation during cutting and the accompanying severe degradation of the protective coatings becomes a crucial issue in the tool industry. Therefore, the oxidation behavior of VN and MoN coatings has been widely studied [1-2]. Previous research indicated that the tribological properties of Mo-N based coatings could be enhanced by adding vanadium [3]. The resultant ternary VMoN coatings possess better mechanical properties than the counterpart binary coatings, VN and MoN. However, there has been little research on the oxidation behavior of VMoN coatings. For the applications on tool industry, it is important to understand the oxidation behavior of VMoN coatings. In this study, the VMoN thin films with thickness of 1μm were deposited on both sides of Si substrate by high power pulsed magnetron sputtering (HPPMS). The duty cycles were controlled to be 3%, 5%, 7%, and 9%. After deposition, the ratios of V/Mo and (V+Mo)/N were determined using electron probe of microanalysis (EPMA) and the microstructure of the coatings was observed by scanning electron microscopy (SEM). X-ray diffraction (XRD) was used to characterize the crystal structure and the preferred orientation of the coatings. The residual stress of the specimens was measured by laser curvature method (LCM) and average X-ray strain (AXS) combined with nanoindentation methods [4,5]. The oxidation behavior of the coatings was investigated using thermo-gravimetric analysis (TGA) at temperature ranging from 300 to 800°C in Ar atmosphere. From the experimental results, the oxidation behavior of the VMoN coatings was discussed.

[1]   G.   Gassner   et   al.,   Tribol.   Lett.   17   (2004)   751.

[2]   T. Suszkoa et al., Surf. Coat. Technol. 194 (2005) 319.

[3]   W. Wang et al., Surf. Coat. Technol. 387 (2020) 125532.

[4]   C.-H.   Ma   et   al.,   Thin   Solid   Films   418   (2002)   73.

[5]   A.-N. Wang et al., Surf. Coat. Technol., 262 (2015) 40.

9:00am **B4-3-TuM-4 Correlation Between Microstructure and Mechanical Properties of B$_4$C Thin Films Deposited by Pulsed Laser Deposition**, *Falko Jahn, S. Weißmantel,* Laserinstitut Hochschule Mittweida, Germany
Being the third hardest known material with in addition outstanding thermal and chemical resistance, boron carbide is a very promising coating material for applications in the field of abrasive wear protection. We already could prove that B$_4$C thin films produced using pulsed laser deposition reliably show extraordinary mechanical properties like an indentation hardness up to 47 GPa. The substrate temperature during the deposition process turned out to be crucial for the extreme hardness [1]. However, the underlying mechanism to the found correlation remained unrevealed.

We now present the results of our investigations on the correlation between the mechanical properties and the microstructure of the produced boron carbide films. Furthermore, we propose and discuss a probable mechanism for the achieved super hardness. One important requirement to these studies was the improvement of the deposition process to significantly reduce the droplet incorporation. Thus, we were able to produce boron carbide films with film thicknesses > 3 μm that enable XRD and TEM analyses.

In addition, the influence of intrinsic film stresses on the mechanical film properties were investigated. These stresses result from the deposition technique of PLD. Furthermore, we present a laser-based relaxation method that can be fully integrated into the deposition process. That enables the deposition of completely stress-free, smooth and super hard boron carbide thin films.

[1]F. Jahn, S. Weißmantel, Properties of Boron Carbide Thin Films Deposited by Pulsed Laser Deposition, Surface and Coatings Technology (2021) 127480. https://doi.org/10.1016/j.surfcoat.2021.127480.

9:20am **B4-3-TuM-5 Evaluation of Fracture Toughness of Borided Materials by Cross-Sectional Scratch Testing**, *F. Alfonso-Reyes, André Ballesteros-Arguello, J. Martínez-Trinidad,* SEPI ESIME Instituto Politécnico Nacional, Mexico; *A. Ocampo-Ramírez,* Universidad Veracruzana, Mexico; *G. Rodríguez-Castro,* SEPI ESIME Zacatenco, Mexico; *A. Meneses-Amador,* SEPI ESIME Instituto Politécnico Nacional, Mexico
A numerical-experimental study of the fracture toughness of nickel and iron borides obtained by cross-sectional scratch test was carried out. The nickel borides were formed on an Inconel 718 superalloy and iron borides were formed on an AISI 316L steel. The powder-pack boriding process was developed at 1223 and 1273 K and 6 h of exposure time for the Inconel 718 superalloy and the AISI 316L steel, respectively. The scratch tests were carried out on the cross-sections of both borided materials using a CSM Revetest-Xpress commercial equipment with a Vickers indenter. The scratch distance was of 1.5 mm with a load range from 3 – 4.5 and 2.5 – 3.1 for the nickel and iron borides, respectively. The applied loads and damage observed at the samples surface (with half cone geometry) were used to estimate the fracture toughness of the system. The numerical model based on the finite element method of the cross-sectional scratch testing was developed considering the same test conditions. The numerical results were used to establish parameters employed in the methodology of fracture toughness by cross-sectional scratch testing.

9:40am **B4-3-TuM-6 Stress Evolution in Binary Metal Alloy Systems**, *Tong Su*, Brown University, USA; *J. Robinson, G. Thompson,* The University of Alabama, USA; *E. Chason,* Brown University, USA

While metal alloy films are used in many applications, there is limited stress evolution investigations during their growth as compared to elemental films. Here, we provide preliminary measurements of the stress evolution in the Mo-V and W-V systems, with each alloy forming a solid solution Different alloy compositions were sputter deposited at different growth rates with the stress measured by an in-situ wafer curvature measurement technique. For both systems, the steady-state stress was measured as a function of growth rate at these different compositions. The results are discussed in terms of stress-generating mechanisms that have been proposed for elemental systems, where the alloy stress is a superposition of the effects from the two components

10:00am **B4-3-TuM-7 Molecular Engineering of Inorganic Thin Film Interfaces for Accessing Multiple Novel Properties for Diverse Applications**, *Ganpati Ramanath,* Rensselaer Polytechnic Institute, USA
INVITED

Engineering the stability and properties of heterointerfaces in systems involving thin films and nanomaterials is essential for diverse applications, e.g., in electronics, energy conversion and storage. This talk will describe the use of molecular nanolayers to tailor chemical, mechanical, thermal and electronic properties of metal-ceramic and metal-thermoelectric interfaces. I will show that introducing molecular nanolayers (e.g., organosilanes, thiols, organophosphonates) at inorganic interfaces can produce remarkable multifold enhancements in interfacial fracture energy during static and dynamic loading, and thermal and electronic transport. These results are germane to engineering the chemical and mechanical stability of thin film composites, and accessing unusual mechanical responses, and tuning interfacial electrical and thermal transport for energy and electronics applications. Interfacial molecular nanolayers also open up new possibilities for studying interface fracture nanomechanics through macroexperiments. Electron and ion beam spectroscopy, and X-ray and electron diffraction, supported by theoretical calculations, show that the property enhancements are due to molecular nanolayer-induced alterations to the inorganic interface chemistry and structure. Key mechanisms include strong covalent bonding and chelation, interfacial oxide scavenging, diffusion curtailment, and altered phase formation pathways. Stacking molecularly-tailored inorganic interfaces can trigger unusual interfacial phenomena, such as, viscoelastic bandgaps, and the design of high-interface-fraction organic-inorganic nanocomposites wherein the molecularly-induced interface properties *become* materials properties.

Select References: Sci. Rep. 12, 10788 (2022); Nature Comm 9, 5249(2018); ACS Appl. Mater. Interf. (2017); ACS Appl. Mater. Interf.8, 4275 (2016); Nature Mater.12, 118 (2013); Scripta Mater. 121, 42-44 (2016); Phys. Rev. B 83, 035412 (2011); Nature 447, 299 (2007); ACS Appl. Mater. Interf. 9, 2001 (2017); ACS Appl. Mater. Interf. 8, 4275 (2016); Appl. Phys. Lett.109, 173904 (2016).

Author Index

Bold page numbers indicate presenter

— A —
Alfonso-Reyes, F.: B4-3-TuM-5, 1
— B —
Ballesteros-Arguello, A.: B4-3-TuM-5, **1**
Bartosik, M.: B4-3-TuM-2, 1
— C —
Chason, E.: B4-3-TuM-6, 2
Czettl, C.: B4-3-TuM-2, 1
— H —
Hans, M.: B4-3-TuM-2, **1**
Huang, J.: B4-3-TuM-3, 1
— J —
Jahn, F.: B4-3-TuM-4, **1**

— L —
Lai, N.: B4-3-TuM-3, **1**
— M —
Martínez-Trinidad, J.: B4-3-TuM-5, 1
Meneses-Amador, A.: B4-3-TuM-5, 1
Mitterer, C.: B4-3-TuM-2, 1
— O —
Ocampo-Ramírez, A.: B4-3-TuM-5, 1
— P —
Primetzhofer, D.: B4-3-TuM-2, 1
— R —
Ramanath, G.: B4-3-TuM-7, **2**
Robinson, J.: B4-3-TuM-6, 2

Rodríguez-Castro, G.: B4-3-TuM-5, 1
— S —
Schalk, N.: B4-3-TuM-2, 1
Schiester, M.: B4-3-TuM-2, 1
Schneider, J.: B4-3-TuM-2, 1
Su, T.: B4-3-TuM-6, **2**
— T —
Thompson, G.: B4-3-TuM-6, 2
Tkadletz, M.: B4-3-TuM-2, 1
— W —
Waldl, H.: B4-3-TuM-2, 1
Weißmantel, S.: B4-3-TuM-4, 1