Hard Coatings and Vapor Deposition Technologies
Room Town & Country C - Session B5-1-WeM

Hard and Multifunctional Nanostructured Coatings I

Moderator: Tomas Kozak, University of West Bohemia, Czechia

8:20am **B5-1-WeM-2 Enhanced Thermal Stability of (Ti,Al)N Coatings by Oxygen Incorporation***, **Damian M. Holzapfel (holzapfel@mch.rwth-aachen.de)*** [1], RWTH Aachen University, Germany*; D. Music,* Malmö University, Sweden*; M. Hans,* RWTH Aachen University, Germany*; S. Wolff-Goodrich,* Max-Planck-Institut für Eisenforschung GmbH, Germany*; D. Holec,* Montanuniversität Leoben, Austria*; D. Bogdanovski,* RWTH Aachen University, Germany*; M. Arndt,* Oerlikon Balzers Coating Germany GmbH, Germany*; A. Eriksson, K. Yalamanchili,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; D. Primetzhofer,* Uppsala University, Sweden*; C. Liebscher,* Max-Planck-Institut für Eisenforschung GmbH, Germany*; J. Schneider,* RWTH Aachen University, Germany

Thermal stability of protective coatings is one of the performance-defining properties for advanced cutting and forming applications as well as for energy conversion. To investigate the effect of oxygen incorporation on the high-temperature behavior of (Ti,Al)N, metastable cubic (Ti,Al)N and (Ti,Al)(O_xN_{1-x}) coatings are synthesized using reactive arc evaporation. X-ray diffraction of (Ti,Al)N and (Ti,Al)(O_xN_{1-x}) coatings reveals that spinodal decomposition is initiated at approximately 800°C, while the subsequent formation of wurtzite solid solution is clearly delayed from 1000°C to 1300°C for (Ti,Al)(O_xN_{1-x}) compared to (Ti,Al)N. This thermal stability enhancement can be rationalized based on calculated vacancy formation energies in combination with spatially-resolved composition analysis and calorimetric data: Energy dispersive X-ray spectroscopy and atom probe tomography data indicate a lower O solubility in wurtzite solid solution compared to cubic (Ti,Al)(O,N). Hence, it is evident that for the growth of the wurtzite, AlN-rich phase in (Ti,Al)N, only mobility of Ti and Al is required, while for (Ti,Al)(O,N), in addition to mobile metal atoms, also non-metal mobility is required. Prerequisite for mobility on the non-metal sublattice is the formation of non-metal vacancies which require larger temperatures than for the metal sublattice due to significantly larger magnitudes of formation energies for the non-metal vacancies compared to the metal vacancies. This notion is consistent with calorimetry data which indicate that the combined energy necessary to form and grow the wurtzite phase is larger by a factor of approximately two in (Ti,Al)(O,N) than in (Ti,Al)N, causing the here reported thermal stability increase.

8:40am **B5-1-WeM-3 Metastable Single- or Dual-Phase Structures in Magnetron Sputtered W-Zr Thin-Film Alloys: Properties and Thermal Behavior***, M. Cervena, S. Haviar, R. Cerstvy, J. Rezek,* ***Petr Zeman (zemanp@kfy.zcu.cz)***, University of West Bohemia, Czechia

Metastable solid materials such as amorphous or nanocrystalline alloys, supersaturated solid solutions, high-temperature or high-pressure phases persisting at normal conditions, have been of great interest due to a possibility to explore novel structures with unknown properties. These materials are kinetically determined and can be therefore synthesize only by non-equilibrium processes. Magnetron sputtering is thus a suitable technique for their preparation as thin films.

The present study focuses on preparation of thin-film alloys from the W-Zr system by non-reactive magnetron sputtering and systematic investigation of their structure, properties, and thermal behavior at elevated temperature. The films were sputter-deposited in argon gas using two unbalanced magnetrons equipped with a W and Zr target, respectively. The elemental composition of the films was controlled in a very wide composition range (0-100 at.% Zr), by varying the deposition rate from the individual targets.

Using magnetron sputtering, we were able to prepare W-Zr thin-film alloys with several metastable structures in respect to the equilibrium phase diagram [1]. Up to 24 at.% Zr, the structure of W-rich films is characterized by a supersaturated bcc α-W(Zr) solid solution with a highly oriented structure, columnar dense microstructure, enhanced hardness and very low residual stress. In a wide range between 33 and 83 at.% Zr, an amorphous structure with features indicating metallic glass behavior is observed. These films exhibit a very smooth surface, a moderate compressive stress, and a constant electrical resistivity. Above 83 at.% Zr, high-temperature bcc β-Zr(W) and high-pressure hcp ω-Zr(W) phases with an enhanced hardness are prepared in Zr-rich films. Moreover, a very interesting dual-phase structure with crystalline columnar submicrometer-sized conical domains surrounded by a metallic glass is spontaneously formed at 28 at.% Zr [2].

Preliminary results on the thermal behavior indicate that the stability of the metastable α-W(Zr) solid solution in the W-rich films reaches at least 1000°C and its oxidation resistance is improved by an Zr addition. The stability of the amorphous of W-Zr films with metallic glass behavior depends on their elemental composition and can be as high as 1400°C. Moreover, the oxidation of these films to 600°C leads to a homogenously oxidized amorphous structure with twice higher hardness than in the as-deposited state.

[1] M. Červená, R. Čerstvý, T. Dvořák, J. Rezek, P. Zeman, J. Alloy. Compd. 888 (2021) 161558.

[2] P. Zeman, S. Haviar, M. Červená, Vacuum 187 (2021) 110099.

9:00am **B5-1-WeM-4 A Conformable SiAlN/Mo Thermal Barrier Layer for Titanium Alloys Deposited by Magnetron Sputtering***, Z. Gao,* The University of Manchester, UK*; **Justyna Kulczyk-Malecka (j.kulczyk-malecka@mmu.ac.uk)**, P. Kelly,* Manchester Metropolitan University, UK*; P. Xiao,* The University of Manchester, UK

Titanium and its alloys are widely used in the aeronautical and automotive industries, as well as in bio-medical implants due to their low density, high specific strength, and excellent corrosion resistance at lower temperature ranges. Nevertheless, at temperatures above 500ºC Ti alloys exhibit a rapid oxidation, which leads to the formation of a less protective brittle oxide scale that limits its application. To mitigate the formation of a detrimental oxide scale, a protective bilayer coating consisting of an amorphous SiAlN top layer and a Mo interlayer were deposited onto Ti alloys using pulsed DC reactive magnetron sputtering. Coated Ti samples were then exposed to oxidative corrosion in air at 800°C for up to 200 hr and the degradation and thermal barrier ability of the bilayer nitride coatings were studied and correlated with the coating thickness and the presence of the Mo interlayer.

It was found that the thermal barrier nature of the bilayer coating stack is attributed to the interfacial reaction between the Ti substrate and the Mo interlayer and the formation of mechanical twinning within the interfacial reaction product, i.e. a $TiN_{0.26}$ conformable interlayer, which accommodates the thermal mismatch strain between the coating and the substrate upon thermal cycling. The degradation mechanism of SiAlN/Mo coatings is determined by the depletion of the coating induced by interfacial diffusion and reaction between the elements composing the coating and the Ti substrate. The morphology of as-deposited and oxidised samples was characterised using imaging techniques, such as SEM and TEM, the physiochemical properties of the coating were investigated using XPS and EDS and residual stresses in the SiAlN coatings were obtained using a FIB milling-stress driven buckling method. This work, therefore, provides a new coating stack design for aeronautical applications displaying exceptional environmental protection for Ti at high temperatures through the interfacial reaction mechanism, which controls the coating degradation.

9:20am **B5-1-WeM-5 Thermal Decomposition of Hard Coatings - Insights from Nanometer-Scale Characterization***, **Marcus Hans (hans@mch.rwth-aachen.de)**,* RWTH Aachen University, Germany*; Z. Czigány,* Centre for Energy Research, Hungary*; D. Neuß, J. Sälker, H. Rueß, J. Krause, P. Ondračka,* RWTH Aachen University, Germany*; D. Music,* Malmö University, Sweden*; S. Evertz, D. Holzapfel,* RWTH Aachen University, Germany*; G. Nayak, D. Holec,* Montanuniversität Leoben, Austria*; D. Primetzhofer,* Uppsala University, Sweden*; J. Schneider,* RWTH Aachen University, Germany **INVITED**

Three-dimensional atom probe tomography is a powerful technique to characterize the local chemical composition of materials. Since the spatial resolution at the nanometer scale is ideally suited to identify decomposition-relevant mechanisms, the thermal stability of (V,Al)N hard coatings is the focus of this talk.

Based on thermodynamic considerations of $d^2\Delta G/dx^2 < 0$, spinodal decomposition is predicted for NaCl-structured $V_{1-x}Al_xN$ with $x \geq 0.35$ by ab initio calculations. Consistent with these predictions, metastable single-phase cubic $(V_{0.64}Al_{0.36})_{0.49}N_{0.51}$ thin films exhibit chemical modulations after annealing at 900°C, which implies spinodal decomposition into V- and Al-rich cubic nitride phases. However, the formation of thermodynamically stable wurtzite AlN occurs concurrently and the higher mobility of Al in (V,Al)N in comparison to (Ti,Al)N may be understood by the smaller lattice parameter difference of the cubic VN and AlN phases.

[1] **Graduate Student Award Finalist**

Systematic investigations by post-deposition vacuum annealing revealed the onset of spinodal decomposition after cyclic vacuum annealing at 700°C. Moreover, at this temperature, evidence for Al diffusion to grain boundaries and triple junctions is provided by correlation of transmission electron microscopy and atom probe tomography data. The formation of Al-rich regions can be understood by the more than 25% lower activation energy for bulk diffusion of aluminum compared to vanadium as obtained from ab initio calculations. The significantly larger equilibrium volume of wurtzite AlN compared to the cubic phase explains its initial formation exclusively at triple junctions and grain boundaries. Interestingly, the formation of the wurtzite phase at grain boundaries and triple junctions can be tracked by resistivity measurements, while X-ray diffraction and nanoindentation data do not support an unambiguous wurtzite phase formation claim for annealing temperatures < 900°C.

Hence, it is evident that previously reported formation temperatures of wurzite AlN in transition metal aluminum nitrides, determined by other characterization techniques than chemical and structural characterization at the nanometer scale and/or resistivity measurements, are overestimated.

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