Hard Coatings and Vapor Deposition Technologies
Room California - Session B5-1

Hard and Multifunctional Nanostructured Coatings

Moderators: Jiri Capek, University of West Bohemia, Robert Franz, Montanuniversität Leoben

10:00am **B5-1-1 Synthesis and Characterization of HfNbTiVZr High Entropy Alloy Thin Films***, **Stefan Fritze**, D Karlsson, P Berastegui, D Rehnlund, L Nyholm, M Sahlberg, E Lewin, U Jansson,* Uppsala University, Angstrom Laboratory, Sweden

High entropy alloys (HEAs) are multicomponent alloys with at least five elements in approximately equimolar concentrations. Due to the high entropy of mixing, solid solutions of e.g. a simple bcc or ccp phase are formed. Many HEAs exhibit unique properties such as extremely high strength, ductility, high thermal stability and corrosion resistance. Recently, we have also demonstrated that a HfNbTiVZr alloy with a bcc structure has exceptional hydrogen storage capability [1].

In this study we report the first successful deposition of highly textured HfNbTiVZr thin films by non-reactive unbalanced magnetron sputtering using five metal targets. The films were characterized with SEM, XPS, XRD and nanoindentation. Bragg-Brentano XRD analyses of these coatings show that the HfNbTiVZr films crystallize in a simple bcc structure with a strong (110) orientation. No additional phases were observed in the as-deposited films ensuring that the sample is a single phase HEA. The SEM cross-sections exhibit a dense microstructure and EDS mapping shows a random distribution of all five elements with no noticeable segregation.

The as-deposited films exhibited a hardness of 5.4 GPa. This is more two times higher than expected from rule of mixture. The high hardness can be explained by a significant lattice strain due to large differences in atomic radii. Upon annealing, XRD shows the formation of a second alloy phase which is unexpected for a true HEA. The precipitation of a second phase leads to a further hardness increase with at least 100%. The phase stability and the precipitation of secondary phases in the HfNbTiVZr films will be discussed based on lattice strain effects in the alloy. Finally, the electrochemical properties of the HfNbTiVZr films have been investigated. The films exhibited, compared to steel alloys, a very high corrosion resistance in chlorine-containing solutions.

[1] M. Sahlberg, D. Karlsson, C. Zlotea and U. Jansson, submitted

10:20am **B5-1-2 Structural Stability of ZrN/SiN$_x$ Multilayered Coatings under Harsh Environments***, **Gregory Abadias**,* Institut P', Université de Poitiers-UPR 3346 CNRS-ENSMA, France*; I Saladukhin, V Uglov, S Zlotski, V Shymasnki,* Belarusian State University, Belarus

Synthesis of nitride-based multilayered structures is prospective for enhancement of mechanical properties and wear resistance as well as for their resistance to harsh environments exposure, in particular, to high temperature oxidation and ion irradiation. Multilayered ZrN/SiN$_x$ films (with bilayer thickness ranging from 6 to 40 nm) with a total thickness of about 300 nm were deposited at 300°C by reactive magnetron sputtering by sequentially alternating ZrN and SiN$_x$ layers [1]. Annealing under air atmosphere was carried out for temperature intervals ranging from 400 to 950°C using *in situ* temperature XRD. Ion irradiation by Xe ions (180 keV, doses 5x10^{16} cm^{-2} 1x10^{17} cm^{-2}) was performed at room and high (800°C) temperatures.

According to TEM and XRD analysis the multilayered films consist of nanocrystalline ZrN and X-ray amorphous SiN$_x$ layers. While pure ZrN films are characterized by [111] preferred orientation, the presence of SiN$_x$ layers results in its change to [200]. Multilayered ZrN/SiN$_x$ films show the improved oxidation resistance compared to ZrN reference layer. For pure ZrN film, the oxidation starts at 550°C. Higher oxidation resistance is observed for ZrN/SiN$_x$ films and it strongly depends on ZrN fraction and number of layers. So, for ZrN/SiN$_x$ (5 nm/10 nm) film the onset of oxide phase formation is delayed up to 950°C and nitride ZrN phase still remains. The presence of SiN$_x$ layer favors the formation of tetragonal ZrO$_2$ phase during annealing.

There is no evident change of ZrN/SiN$_x$ film structural state after Xe ion irradiation as it was proved by XRD investigations. However, the lattice parameter increase occurs that is connected with Xe incorporation. It was revealed by RBS analysis that the maximum concentration of Xe in the film bulk is about 4 at.% after irradiation at room temperature and about 5 at.% after high temperature irradiation. The shape of Xe concentration profile also changes. TEM studying indicates amorphization of ZrN layers and Xe bubbles formation in the film. There is a tendency of Xe depth penetration decrease with the SiN$_x$ layer thickness increase. Thus multilayered ZrN/SiN$_x$ films are considered to be promising for oxidation and irradiation resistance enhancement.

1. G. Abadias, V.V. Uglov, I.A. Saladukhin et al., Surf. Coat. Technol., under press

10:40am **B5-1-3 Magnetron Sputtered High-Temperature Hf–B–Si–C–N Films with Controlled Electrical Conductivity and Optical Transparency***, **Veronika Simova**, J Vlcek, S Zuzjakova, R Čerstvý, J Houška,* University of West Bohemia, Czech Republic

The present work focuses on the effect of nitrogen addition into hard and electrically conductive Hf–B–Si–C films [1] in order to significantly improve their thermal stability in air at very high temperatures (above 1200°C). Our motivation has been to develop new hard thin-film materials with a very low electrical and thermal conductivity, and high optical transparency or with a sufficiently high electrical conductivity for high-temperature protective coatings of electronic and optical elements, and for harsh-environment sensors.

Hf–B–Si–C–N films were deposited onto Si(100) and SiC substrates using pulsed magnetron co-sputtering of a single B$_4$C–Hf–Si target (at a fixed 15% Hf fraction and a 20% Si fraction in the target erosion area) in Ar + N$_2$ gas mixtures at the N$_2$ fraction ranging from 0% to 50%. A planar unbalanced magnetron (127×254 mm^2 target) was driven by a pulsed dc power supply operating at a repetition frequency of 10 kHz with an average target power of 500 W in a period and voltage pulse durations of 50 µs and 85 µs (duty cycles of 50% and 85%). The substrates were held at a floating potential and a temperature of 450 °C.

An increasing N content (from 0 to 52 at.%) in the films was compensated by decreasing contents of B (from 39 to 24 at.%), Si (from 24 to 15 at.%), Hf (from 25 to 4 at.%) and C (from 7 to 3 at.%). The structure of the Hf–B–Si–C film prepared in pure argon was nanocomposite, while the Hf–B–Si–C–N films were amorphous. An increase in the N$_2$ fraction in the gas mixture, resulting in an increasing N content in the films, led to a rapid rise in the optical transparency and the electrical resistivity of the films. All films exhibited a high hardness in the range of 17–21 GPa.

The as-deposited, optically non-transparent Hf$_7$B$_{23}$Si$_{22}$C$_6$N$_{40}$ film with 2 at.% of Ar possessing a hardness of 20 GPa and electrical resistivity of 4 Ωm, which was prepared with the 15% N$_2$ fraction in the gas mixture at the voltage pulse duration of 50 µs, and the as-deposited, highly optically transparent and electrically insulating Hf$_6$B$_{21}$Si$_{19}$C$_4$N$_{47}$ film with 3 at.% of Ar possessing a hardness of 20 GPa, which was prepared with the 25% N$_2$ fraction in the gas mixture and at the same voltage pulse duration, exhibited a very high oxidation resistance in air even up to 1600°C.

[1] J. Kohout, J. Vlcek, J. Houska, P. Mares, R. Cerstvy, P. Zeman, M. Zhang, J. Jiang, E.I. Meletis, S. Zuzjakova, Hard multifunctional Hf–B–Si–C films prepared by pulsed magnetron sputtering, Surf. Coat. Technol. 257 (2014) 301–307.

11:00am **B5-1-4 Reactively Sputtered Multicomponent (TiZrHfVNb)N Thin Films***, **Kristina Johansson**, E Lewin,* Uppsala University, Angstrom Laboratory, Sweden

(TiZrHfVNb)N thin films, synthesised by reactive DC magnetron sputtering, demonstrate a large homogeneity range for a solid solution phase with the NaCl-type structure. The films have been deposited using elemental targets of the respective element and a gas mixture consisting of Ar and N$_2$ (15 % of total gas flow). In earlier studies, (TiZrHfVNb)N films have been synthesised by cathodic arc vapour deposition using a high entropy alloy of Ti-Zr-Hf-V-Nb as cathode material. These films have showed very interesting mechanical properties, such as high hardness and high wear resistance.[1] However, there are no previous studies on sputter deposited (TiZrHfVNb)N films. By using this deposition technique it could allow for more design possibilities, which is explored in this study by varying composition of the material. The films were characterised by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM).

Large variations in metallic ratio were obtained for the (TiZrHfVNb)N coatings, about 10-50 % for Ti, 20-35 % for Zr,10-50 % for Hf,10-30 % for V and 5-15 % for Nb. XPS spectra for each transition metal showed that the films are fully nitrided. The coatings were found to be of single NaCl type phase for all studied compositions. The lattice parameter varied from 4.32 Å for Ti rich coatings to 4.44 Å for Hf rich coatings, which is within the range of the corresponding binary nitrides (4.13 Å for VN and up to 4.58 for

ZrN) and thus indicating a solid solution phase of all constituent elements. Cross sections of the coatings studied by SEM showed a columnar growth which varied in density depending on deposition conditions such as substrate temperature and bias.

Reference:

[1] A.D. Pogrebnjak *et al*., *Mater. Chem. Phys.,* 147 (2014) 1079

11:20am **B5-1-5 Deposition of Fluor-doped WS_2-C Coatings on Nanostructured Anodized Aluminum Alloy Substrates for Wettability Control***, S Rodrigues,* SEG-CEMUC, Portugal*;* ***Sandra Carvalho,*** University of Minho and University of Porto, Portugal*; A Cavaleiro,* SEG-CEMUC, Portugal

Currently, lubrication procedures of mechanical components in automotive industry, such as ignition systems, are often stopped for tool cleaning or replacement due to high friction phenomena faced because of lubricant accumulation. Then, the development of a functional surface; addressing either longer lifetime due to an improvement of the wear resistance, or energy savings, by the decrease of the friction, is now welcome particularly when they can also avoid or reduce the excessive use of liquid lubricants which are harmful for the environment and the human health.

This work intends to create a new surface acting as solid lubricant, gathering the outstanding self-cleaning and *nearzero* friction properties of fluor-doped WS_2-C coatings. These coatings can be deposited onto different porous anodized aluminum alloy surfaces in order to be able to control the water and oil wettability.

W-S-C-F coatings were produced by magnetron sputtering in reactive mode using an Ar/CF_4 gas mixture. The fluorine insertion in the produced coatings was controlled by varying the CF_4 gas flow aperture (0-20%).

Top view and cross-sectional morphologies, chemical composition/bonding, structure and wettability characterization of the coatings were respectively performed through FIB/SEM-EDS, XRD techniques and water/oil contact angle measurements. Mechanical properties such as hardness, elastic modulus and adhesion were also conducted under nanoindentation procedures and *scratch* testing.

The results revealed that the fluorine insertion on the W-S-C coatings did not change significantly the structure and morphology in relation to pure W-S-C coatings. However, a decrease on the mechanical properties was observed. Furthermore, the changes in the contact angles values show a potential for the control of the wettability behaviour in relation to water and oils.

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