

New Horizons in Coatings and Thin Films Room San Diego - Session F4-2

Functional Oxide and Oxynitride Coatings

Moderators: Jörg Patscheider, Evatec AG, Anders Eriksson, Oerlikon Balzers, Oerlikon Surface Solutions AG, Marcus Hans, RWTH Aachen University

1:50pm **F4-2-2 On the Thermal Stability of Cathodic Arc Evaporated (Al_{1-x}Cr_x)₂O₃ Thin Films**, *Valentin Dalbauer*, CDL-AOS at TU Wien, Austria; *J Ramm*, Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein; *S Kolozsvári*, Plansee Composite Materials GmbH, Germany; *C Koller*, CDL-AOS at TU Wien, Austria; *P Mayrhofer*, Institute of Materials Science and Technology, TU Wien, Austria

The thermo-mechanically excellently performing α -alumina (corundum-type) is a perfect candidate to protect tool or component surfaces suffering from mechanical loads in hazardous atmospheres. Thus α -alumina protective coatings significantly extend the tool-lifetime especially in oxidising environment and at high temperatures. However, a major concern is the formation of amorphous phase fractions and/or metastable Al₂O₃ polymorphs during low-temperature physical vapour deposition, which can effectively be counteracted by alloying with Cr, where the phase composition of (Al_{1-x}Cr_x)₂O₃ coatings strongly depends on the Cr content.

With respect to industrial application, the knowledge about structure-property-relationships of (Al_{1-x}Cr_x)₂O₃ as a result of thermal exposure is of utmost importance. We therefore study the structural evolution of arc evaporated (Al_{1-x}Cr_x)₂O₃ coatings, which have been prepared by Al_{0.75}Cr_{0.25}, Al_{0.70}Cr_{0.30}, Al_{0.50}Cr_{0.50}, or Al_{0.25}Cr_{0.75} cathodes.

The Cr-rich (Al_{0.49}Cr_{0.51})₂O₃ and (Al_{0.23}Cr_{0.77})₂O₃ coatings crystallise in a single-phase corundum-type structure (α -(Al,Cr)₂O₃) with pronounced columnar and faceted growth. Contrary, the Al-rich (Al_{0.72}Cr_{0.28})₂O₃ and (Al_{0.69}Cr_{0.31})₂O₃ coatings are multi-phased with a large metastable cubic-structured phase fraction and α -(Al,Cr)₂O₃.

Upon annealing to 800 and 950 °C, the metastable phases transform into a γ -type phase—with only minor indications for an intermediate θ -structure—and further to an α -type solid solution for temperatures above ~1080 °C. This structure stays stable up to the highest temperature tested, 1500 °C. The accompanied formation of bcc Cr phases indicates the decomposition of metallic droplets with—depending on the annealing conditions—subsequent oxidation of Al. Annealing within the spinodal-regime up to 6 h did not result in any phase separation towards α -Al₂O₃ and α -Cr₂O₃.

Thermo-mechanical properties of (Al_{1-x}Cr_x)₂O₃ show a stronger dependence on the microstructure than on the crystal structure of the as-deposited coatings. Although exhibiting a multi-phase constitution, Al-rich coatings demonstrate higher hardness than the single-phased α -(Al_{0.23}Cr_{0.77})₂O₃ coating, which consists of tapered crystallites. Highest H and E values of ~22 Gpa and ~300 Gpa are obtained for (Al_{0.49}Cr_{0.51})₂O₃, which combines a dense microstructure with a dominant α -character. Upon vacuum annealing—and therewith associated structural transformation and densification—H and E of the Al- and Cr-rich coating compositions converge with peak values of H ~27 Gpa and E ~450 Gpa at 1050 °C.

2:10pm **F4-2-3 Phase Evolution of RF Magnetron Sputtered Cr-rich (Cr,Zr)₂O₃ Coatings Studied by In-Situ Synchrotron Experiments during Annealing in Air or Vacuum Conditions**, *Ludvig Landälv*, Linköping Univ., IFM, Thin Film Physics Div. and Sandvik Coromant R&D, Sweden; *J Lu*, Linköping Univ., IFM, Thin Film Physics Div., Sweden; *D Ostach*, Zentrum für Material- und Küstenforschung GmbH, Germany; *M Ahlgren*, *E Göthelid*, Sandvik Coromant R&D, Sweden; *B Alling*, Linköping Univ., IFM, Theoretical Physics division and Zentrum für Material- und Küstenforschung GmbH, Sweden; *L Hultman*, Linköping Univ., IFM, Thin Film Physics Div., Sweden; *M Stüber*, Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany; *J Birch*, *P Eklund*, Linköping Univ., IFM, Thin Film Physics Div., Sweden

Physical vapor deposited binary oxide alloy hard coatings draw increasing attention, often focusing on the Cr-stabilized corundum α -(Al,Cr)₂O₃ phase by means of a template growth or alloying; Cr forms escolaita Cr₂O₃ that is isostructural with corundum [1,2]. A new and interesting oxide is obtained by exchanging Al with Zr in the Cr-Zr-O system. Spitz *et al.* explored (Zr,Cr)₂O₃ phases with respect to the Cr/Zr metal ratio in coatings prepared by reactive RF-magnetron sputtering, e.g., a solid solution α -(Cr,Zr)₂O₃

corundum structure at low Zr-content (< ~12 at %), a cubic-(Zr,Cr)₂O₃ based solid solutions at ~18 at % Zr, and a monoclinic/tetragonal solid solution (Zr,Cr)₂O₃ for higher Zr-content [3]. The as-deposited corundum structured coating from this study was the focus of an isothermal annealing study performed in vacuum with posterior HR TEM-characterization. It showed decomposition of a α -Cr_{0.28}Zr_{0.10}O_{0.61} coating into tetragonal ZrO₂ and bcc chromium upon loss of oxygen [5]. In another study on the Cr-rich part of the (Cr,Zr)₂O₃-system, as-deposited amorphous coatings were investigated by means of *in-situ* synchrotron X-ray diffraction during annealing in vacuum. This showed the increase in crystallization onset temperature for both α -(Cr,Zr)₂O₃ and tetragonal phases (Zr,Cr)₂O₃ with increasing Zr content (3-15 at %) in the as deposited coatings [4]. The phase-stability of such coatings are, however, expected to depend also on ambient atmosphere during service.

In order to study the effect of annealing atmosphere on the phase evolution of α -(Cr,Zr)₂O₃ coatings, we use *in-situ* synchrotron radiation experiments performed in air and in vacuum. We find that the phase evolution in α -(Cr,Zr)₂O₃ coating samples differs significantly depending on annealing atmosphere conditions: with retained α -Cr₂O₃ after air annealing with accompanying formation of tetragonal ZrO₂ and decomposition of the α -Cr₂O₃ structure if annealed in vacuum with formation of tetragonal ZrO₂ and possible monoclinic ZrO₂ after cooling to room temperature. The difference in phase evolution results in significant nano hardness difference ~22 and 8 GPa respectively and a largely changed microstructure observed with posterior HR-TEM characterization.

[1] Ramm, J., et al., Surface & Coatings Technology, 2007, **202**(4-7): p. 876-883.

[2] Khatibi, A., et al. Acta Materialia, 2013, **61**(13): p. 4811-4822.

[3] Spitz S., et al. Thin Solid Films, 2013, **548**: p. 143-149

[4] Rafaja D., et al, Thin solid Films, 2016, **516**: p. 430-436

[5] Landälv L., et al, Acta Materialia, 2017, **131**: p. 543-552

2:30pm **F4-2-4 Thick HS-PVD γ -Al₂O₃ Coatings for Challenging Cutting and Die Casting Applications**, *K Bobzin*, *T Brögelmann*, *C Kalscheuer*, *Martin Welters*, Surface Engineering Institute - RWTH Aachen University, Germany
In the last decades crystalline physical vapor deposition (PVD) Al₂O₃ coatings offered their great potential due to outstanding properties such as high hot hardness, high oxidation resistance and high wear resistance, especially concerning cutting and die casting applications. However, the properties of alumina strongly depend on the formed crystallographic phase. Thereby, the thermodynamically stable α -Al₂O₃ phase is the technical most interesting, exhibiting superior mechanical properties. The deposition of α -Al₂O₃ by chemical vapor deposition (CVD) is well-established, but requires high process temperatures. Thus, the deposition of α -Al₂O₃ on temperature sensitive-materials is not possible. Another promising candidate concerning cutting and die casting applications is γ -Al₂O₃. Depending on the initial conditions, the formation of the γ -Al₂O₃ phase starts at T \geq 450 °C, allowing lower deposition temperatures. Regarding the wear protection of turning tools, a higher coating thickness (s \geq 10 μ m) and thus a larger wear volume are beneficial. However, this requirement is hard to fulfill by typical PVD processes. A possibility to deposit thick PVD alumina coatings is the High-Speed PVD (HS-PVD) technology. In the present work thick, s \geq 20 μ m, γ -Al₂O₃ films are deposited on cemented carbides at a substrate temperature range between T = 500 °C and T = 850 °C, by means of HS-PVD. A thick, metallic (Cr,Al) bond coat was employed to improve the adhesion of γ -Al₂O₃. In order to analyze the influence of the bond coat regarding the adhesion of the coatings, scratch tests were conducted, as it is important regarding cutting and die casting operations. For determining the coating morphology and thickness, scanning electron microscopy (SEM) was used. Phase analysis was carried out by X-ray diffraction spectroscopy (XRD). The mechanical properties universal hardness (HU) and indentation modulus (E_{IT}) were determined by means of nanoindentation. Furthermore, thermal stability of the coatings was investigated via thermal exposure tests. Regarding the use in high temperature applications, especially the formation of γ -Al₂O₃ at substrate temperatures of T \approx 850 °C indicates that the use of the coatings is possible at equal high temperatures without phase transformation. The HS-PVD γ -Al₂O₃ coatings were compared to thin γ -Al₂O₃ films deposited by magnetron sputtering (MS), as they are state-of-the-art in industry. The comparison emphasizes the advantages of the coatings deposited by means of HS-PVD.

Wednesday Afternoon, April 25, 2018

2:50pm **F4-2-5 HiPIMS Deposition of Ta-O-N Coatings for Water Splitting Application**, *Jiří Čapek, Š Batková, J Houska, S Haviar*, University of West Bohemia, Czech Republic; *T Duchoň*, Charles University, Czech Republic

As reported in [1], Ta-O-N material can provide appropriate properties (i.e., band gap width and alignment) for splitting of water into H₂ and O₂ under visible light irradiation (without any external voltage). This could bring a great possibility to convert the solar light into a useful chemical energy. However, it is still a big challenge to prepare Ta-O-N electrodes exhibiting efficient water splitting performance.

In this work we first demonstrate that high-power impulse magnetron sputtering is a suitable technique for low-temperature (less than 250 °C) deposition of Ta-O-N coatings with a controllable oxygen to nitrogen (O/N) ratio and thus their properties. The band gap width of the coatings can be tuned for an effective visible light absorption at preserved proper alignment of the band gap with respect to the water splitting reactions. Subsequently, we focus on an optimization of the structure of the coatings with respect to the transport of the generated electron-hole pairs. For this purpose, the Ta-O-N coatings were either prepared at an elevated substrate temperature (up to 850 °C - limit of the substrate heater) or annealed in a vacuum furnace (up to 900 °C) after the deposition. The carried out X-ray diffraction analyses indicate that the coatings prepared at the elevated temperatures consist of a mixture of oxides and/or nitrides, while the annealed coatings (with a proper O/N ratio) are characterized by a single TaON phase. Moreover, the resulting TaON phase can be highly textured when a proper seeding layer (e.g., Pt) is used. This structure is very promising for the water splitting application due to a possibly reduced recombination rate of photogenerated electrons and holes.

[1] R. Abe, J. Photochem. Photobiol. C Photochem. Rev. 11 (2010) 179.

3:10pm **F4-2-6 Evolution of Microstructure and Mechanical Properties of Graded TiAlON Thin Films Investigated by Cross-sectional Characterization Techniques**, *Nina Schalk, M Tkadletz, V Terziyska*, Montanuniversität Leoben, Austria; *M Deluca*, Materials Center Leoben Forschung GmbH, Austria; *J Keckes, C Mitterer*, Montanuniversität Leoben, Austria

In the last years, oxynitrides have emerged as a new class of materials due to their tunable properties. Within the present work, a graded TiAl(O)N film was grown by magnetron sputter deposition, using TiAl targets with an Ti/Al atomic ratio of 40/60, constant nitrogen and stepwise increasing oxygen partial pressures over the film thickness. The microstructural evolution of the film was investigated by transmission electron microscopy and synchrotron X-ray nanodiffraction. The first layer, grown without the addition of oxygen, showed a dual phase structure consisting of a prevalent wurtzite phase fraction and a subordinate face centered cubic (fcc) phase fraction. The addition of small amounts of oxygen resulted in the stabilization of the fcc phase and the wurtzite phase vanished. With increasing film thickness and thus, increasing oxygen content, the texture of the fcc phase changed from dominating (111) to (100). Further, with increasing oxygen content increasing amounts of an additional amorphous phase fraction were observed. In the first layers, tensile residual stresses in the range of 1 – 2 GPa were determined, which turn compressive towards the film surface. Cross-sectional nanonindentation revealed increasing hardness and elastic modulus with increasing oxygen content in the first layers, however, towards the film surface the hardness decreases, which can be related to the increasing amounts of an amorphous phase fraction.

3:30pm **F4-2-7 Hard Transition Metal Oxynitride Thin Films: From Synthesis to Applications**, *Filipe Vaz, J Borges*, Minho University, Portugal
INVITED

The aim of this talk is to focus on the design, synthesis, properties and applications of different types of oxynitride protective and functional thin films and coatings. Multifunctional stable and metastable oxynitride coatings are expected to fill a gap between nitride and oxide based coatings. Therefore, they are considered to be of unique interest in fundamental research. Moreover, due to their combination of high oxidation resistance, chemical inertness, good mechanical properties at elevated temperatures and friction behavior, they have a wide application field. In fact, oxynitride thin films are rapidly emerging from the research laboratory, and there are actually several examples of successful industrial applications. Protective applications, decorative coatings for high-quality consumer products, gas barriers, optoelectronics, microelectronics, solar cells, are among the most important areas in which oxynitrides are revealing promising results.

Nevertheless, there is still a huge need for a comprehensive discussion of their fundamental properties and in-service response as a function of the different designs and basic characteristics.

This talk is focused on the development and understanding of the materials themselves and on relationships and knowledge-based correlations between process parameters, synthesis and growth, micro structure evolution and properties, providing a forum to discuss current and future applications of this class of thin films and coatings.

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