Protective and High-temperature Coatings
Room Palm 1-2 - Session MA1-2-TuA

Coatings to Resist High-temperature Oxidation, Corrosion, and Fouling II

Moderators: **Vladislav Kolarik**, Fraunhofer Institute for Chemical Technology ICT, Germany, **Francisco Javier Pérez Trujillo**, Universidad Complutense de Madrid, Spain

1:40pm **MA1-2-TuA-1 Fabrication, Characterisation and Fretting Wear Testing of Magnetron Sputtered Cr and CrN Coated Zr Alloy Cladding for Enhanced Accident Tolerance in Light Water Reactors**, *T. Rachid Netto,* Manchester Metropolitan University, Brazil*; A. Evans,* ***Peter Kelly (peter.kelly@mmu.ac.uk)***, Manchester Metropolitan University, UK*; D. Goddard, J. Cooper,* National Nuclear Laboratory, UK

Research into accident-tolerant fuels (ATFs) for light water reactors (LWRs) has focused on improving the safety of zirconium alloy fuel rod claddings and one of the more developed approaches is the use of chromium coatings deposited onto the claddings. In addition to performing in oxidising conditions, normal operation also causes fretting wear on the fuel rod surface, which requires tribological improvements.

The aim of this work, therefore, is to produce Cr and CrN coatings using the magnetron sputtering technique for Zr alloy nuclear fuel rod cladding material to enhance oxidation and mechanical resistance. This research is examining how the integrity and microstructure of the coating is affected by deposition conditions and coating thickness. The coatings were characterized by scanning electron microscopy (SEM), energy dispersive X-ray (EDX), X-ray diffraction (XRD), atomic force microscopy (AFM), optical profilometry and contact angle goniometry. A linear reciprocating wear tester was used to mimic fretting. Our results demonstrate that fretting resistance can be related to the different densities and thickness of coating produced and, in turn, related to the deposition parameters.

2:00pm **MA1-2-TuA-2 Fuel-cladding Thermochemical Interaction Study of Cr_2O_3 Coating Deposited by DLI-MOCVD on Zircaloy-2 Substrate**, ***Kenza Zougagh (kenza.zougagh@cea.fr)***, Université Paris-Saclay, CEA, Service de Recherche en Matériaux et procédés Avancés, France*; R. Chanson, A. Quaini, F. Rouillard, S. Gossé,* Université Paris-Saclay, CEA, Service de recherche en Corrosion et Comportement des Matériaux, France

In a nuclear reactor, the fuel cladding is the subject of particular attention since it constitutes the first safety barrier. Its mechanical integrity must therefore be guaranteed in a wide range of conditions from nominal operation to hypothetical incidental conditions.

The idea of improving the behavior of the zirconium-based claddings with the addition of external coatings in the frame of ATF (Accident Tolerant Fuels) is now widespread. However, internal thin films coatings can also be an effective solution to increase the resilience of fuel claddings under undesirable situations. There are many fewer developments proposing the addition of these internal coatings, probably due to the difficulties encountered in developing proper homogenous layers along the full-length.

In this work, chromium oxide is studied as a candidate material for an internal layer of the nuclear fuel cladding for the mitigation of pellet-cladding thermochemical interaction. This coating is deposited by the DLI-MOCVD process on a Zircaloy-2 substrate. This process has been already demonstrated relevant for coating the internal surface of nuclear fuel claddings [1]. This study highlights the influence of the process parameters on the coating properties. After satisfactory film deposition, physico-chemical and microstructural properties of the coating are characterized. The performance of the chromia layer against Zircaloy – UO_2 interaction is investigated at high temperature between 400 and 800°C using diffusion couple testing with natural UO_2 pellets. Moreover, the interaction between the chromia layer and Zircaloy is studied at temperatures up to 1200°C. All experimental results are compared to thermodynamic predictions using the Calphad method.

[1] Michau, A., F. Maury, F. Schuster, F. Lomello, J.-C. Brachet, E. Rouesne, M. Le Saux, R. Boichot, et M. Pons. « High-temperature oxidation resistance of chromium-based coatings deposited by DLI-MOCVD for enhanced protection of the inner surface of long tubes ». Surface and Coatings Technology 349 (2018): 1048-57. https://doi.org/10.1016/j.surfcoat.2018.05.088.

2:20pm **MA1-2-TuA-3 Evaluation of Wear and Corrosion Resistance in Acidic and Chloride Solutions of Pvd-Crn Coatings on Untreated and Plasma Nitrided Aisi 4140 Steel**, *A. Maskavizan, E. Dalibon,* National University of Technology (UTN), Faculty of Concepción del Uruguay, Argentina*; S. Farina,* CNEA and CONICET, Buenos Aires, Argentina*; J. Quintana,* CNEA (CAC), Buenos Aires, Argentina*;* ***Sonia P. Brühl (sbruhl@gmail.com)***, National University of Technology (UTN), Faculty of Concepción del Uruguay, Argentina

CrN coatings deposited by Physical Vapor Deposition (PVD) are widely used due to their high hardness and high wear resistance, low friction coefficient and superior corrosion resistance. The latter makes this coating appropriate for protecting forming tools, moulds and components used in chemical processing.

In this work, single layer CrN coatings were deposited on plasma nitrided and non treated AISI 4140 steel. The influence of nitriding on the wear resistance, coefficient of friction and corrosion resistance in acidic solutions and chloride solutions was studied.

Thickness of the coatings was measured using optical microscopy, and surface hardness was assessed with a Vickers microindenter. Adhesion was determined using Rockwell indentation applying 150 kg and Scratch test at different constant loads. Sliding wear resistance was studied with Pin-on-Disk tests under different normal loads and sliding distances, the coefficient of friction was registered during the tests and volume loss was calculated. Corrosion tests were carried out using a 3.5 % NaCl solution and a 0.5 M H_2SO_4 solution as electrolytes. Nitrided steel without any coating was used also as comparison.

Coating thickness was approximately (2.6 ± 0.4) µm and surface hardness reached a value of (1960 ± 160) $HV_{0.05,}$ being this a composed hardness because of the low film thickness. Adhesion was good for both substrates, non nitrided and nitrided steel, in both cases, it could be classified as HF1 according to VDI 3198 standard. In the case of the Scratch test, in the only coated samples, without nitriding as pre treatment the film cracking was observed at 50 N in the track, whereas in the duplex sample the coating had a better load bearing capacity and reached 70 N without damage. No delamination was detected around the scratch track in all cases. Wear volume loss was undetectable in the pin-on-disk test for the coated systems, whereas it was approximately 30 x 10^{-3} mm^3 for the nitrided steel and 150 x 10^{-3} mm^3 for the untreated steel. In the corrosion tests, the coating showed a passive behaviour as tested in NaCl solution and the corrosion current density was significantly lower for coated samples in the H_2SO_4 solution, proving that the CrN coating is suitable for protecting the steel substrate in both chloride and acidic media.

2:40pm **MA1-2-TuA-4 Deposition using CHC-PVD Method and High Temperature Oxidation of TiAlCrYSi Coatings on TiAl**, ***Radoslaw Swadzba (radoslaw.swadzba@git.lukasiewicz.gov.pl)***, Lukasiewicz Research Network – Uppersilesian Institute of Technology, Poland*; B. Mendala, L. Swadzba,* Silesian University of Technology, Poland*; U. Schulz, N. Laska, P. Bauer,* German Aerospace Center (DLR), Germany

This work concerns the application of Closed Hollow Cathode - Physical Vapor Deposition (CHC-PVD) method for the deposition of TiAlCrYSi on a 48-2-2 TiAl alloy. During the deposition process the samples were placed within the hollow cathode with diameter of 80 mm and length of 160 mm and nominal composition Ti-54Al-14Cr-0.5Si-0.5Y (at. %). The study involved the detailed analysis of the coating's growth mechanism, initial microstructure as well as phase transformations using high resolution Transmission and Scanning Transmission Electron Microscopy (HRTEM and STEM) as well as Scanning Electron Microscopy (SEM) and high temperature X-ray diffraction (HT-XRD). In the as-deposited state the obtained CHC-PVD TiAlCrYSi bond coating was found to be characterized by a columnar microstructure that contained both amorphous and crystalline regions. It has been found that the latter were composed of a strongly textured, hexagonal C14 $Ti(Al,Cr)_2$ Laves phase. It was shown that upon high temperature exposure the coating forms a dual phase microstructure composed of the $Ti(Al,Cr)_2$ Laves and TiAl phases. The coatings were pre-oxidized in pure oxygen atmosphere at 900 °C for 2 hours to form an adherent and stable Thermally Grown Oxide (TGO) and were then coated with Thermal Barrier Coatings (TBCs) using EB-PVD. The obtained coatings were tested under isothermal (50 hours) and cyclic oxidation (1000 1h cycles) conditions at 900 °C. Detailed microstructural investigations using STEM allowed to characterize the thermally grown oxide (TGO) scale. These investigations provided microstructural evidence for the Cr effect on the formation of Al_2O_3 during pre-oxidation treatment. Yttrium was found to segregate to the grain boundaries of alumina oxide scale during high temperature oxidation, indicating the occurrence of the reactive element (RE) effect.

4:00pm **MA1-2-TuA-8 Investigations of Water Vapor Enhanced Oxidation on TiAl-Based Alloys: Evaluation of Protective Coating Systems***, **Ronja Anton (ronja.anton@dlr.de)**, N. Laska,* German Aerospace Center (DLR), Germany

Currently, intermetallic γ-TiAl alloys are being used as material for turbine blades in the low-pressure turbine to replace the heavier Ni-based superalloys due to their due to their comparatively half the density. Their limitation to service temperatures below 800 °C is due to strength and creep resistance at elevated temperatures, as well as a reduced oxidation resistance. The latter can be surpassed with the aid of remarkably effective oxidation-protective coatings. These coatings result in the formation of a dense thermally grown oxide (TGO) scale, Al_2O_3. However, new turbine engine concepts, such as the Water Enhanced Turbofan (WET) engine concept or the use of hydrogen-based fuels in jet engines, introduce higher amounts of water vapor. Now, not only the γ-TiAl alloys need to be evaluated under more severe conditions, but also the highly studied protective coatings need to be tested in this harsher environment. The mechanism by which water vapor content and temperature may be affecting uncoated and coated γ-TiAl alloys needs to be understood.

For a further enhancement of the protection, a coating system with a ceramic top coat should be considered. Protective coating systems on SiC/SiC CMCs forming SiO_2 as an TGO layer, mostly contain Yb- or Y-silicates as a top coat due to their low oxygen diffusion and matching coefficient of thermal expansion (CTE). A protective coating system for γ-TiAl alloys with Al_2O_3-forming bond coats could be completed by Yb-aluminates, which also show low oxygen diffusion and CTE comparable to the alloys.

In the present work, γ-TiAl alloys were tested isothermally under water vapor enhanced oxidation up to 30 wt.% water in a tube furnace. The growth of a thick Al_2O_3/TiO_2 mixed oxide scale was analyzed on uncoated γ-TiAl alloys. Different coating concepts such as Ti-Al-Cr, Al-Si and Ti-Al-C deposited by DC magnetron sputtering could already improve the resistance of γ-TiAl alloys in dry oxidation conditions. In water vapor enhanced oxidation processes, the growth of the protective Al_2O_3 oxide scale is increased. In order to assess the need for ann ceramic top coat, the oxide growth as a function of temperature and different water contents was evaluated. Therefore, different analyses like SEM, EDX, XRD and thermogravimetric analyses were performed. Finally, first concepts of Yb-aluminates as a protective ceramic top layer by using the previously established layers as bond coating are introduced in terms of reactive sputter deposition, phase stability and improvement of the coating system.

4:20pm **MA1-2-TuA-9 Effect of Duty Cycle and N_2 Flow Rate on Structure and Oxidation Behavior of VN Coatings Deposited by High Power Impulse Magnetron Sputtering***, **Ruo-Syuan Chen (pamela.chan34@gmail.com)**, J. Huang,* National Tsing Hua University, Taiwan

Unlike traditional nitride metal protective coatings, VN coatings possess not only superior mechanical properties and corrosion resistance but also self-lubrication characteristics. The formation of Magnéli oxide phases at high temperature can enhance wear resistance [1]. Previous literature indicated that the duty cycle and N_2 flow rate have significant influence on the quality and properties of VN thin films [2-4]. Although there have been numerous studies on the oxidation behavior of VN coatings, the influence of nitrogen flow rate and duty cycle on their structure and oxidation behavior remains unclear. Therefore, this study aims to investigate the oxidation behavior of VN coatings deposited at different duty cycles and N_2 flow rates. VN coatings with a thickness of 1 mm were deposited on Si substrate by high power impulse magnetron sputtering (HiPIMS).The duty cycles were controlled to be 3% and 10%. The N_2 flow rates were set at 2 and 4 sccm. After deposition, the N/V ratios of the coatings were determined using X-ray photoelectron spectroscopy and the microstructure was observed by scanning electron microscopy (SEM). X-ray diffraction 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 measurement and average X-ray strain combined with nanoindentation methods [5,6]. The oxidation behavior of the coatings was investigated using thermo-gravimetric analysis at temperature ranging from 400 to 700°C in dry air atmosphere. From the experimental results, the oxidation behavior of the VN coatings was discussed.

[1] N. Fateh, G.A. Fontalvo, G. Gassner, C. Mitterer, Wear 262 (2007) 11521158.

[2]H. Hajihoseini, J.T. Gudmundsson, J. Phys. D: Appl. Phys. 50 (2017) 505302.

[3]X. Chu, S.A. Barnett, M.S. Wong, W.D. Sproul, J. Vac. Sci. Technol. A 14 (1996) 3124-3129.

[4]Y. Qiu, S. Zhang, B. Li, J.-W. Lee, D. Zhao,Procedia Eng. 36 (2012) 217-225.

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

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

4:40pm **MA1-2-TuA-10 Surface Modification of Copper by Electrical Discharge Coating using 3D-Printed SUS -420 Steel Electrodes***, **Siddanna Awarasang (siddanna.awarasang@gmail.com)**,* National Central University,Taiwan*; J. Hung,* National Central University, Taiwan

This study presents a novel approach to surface science by exploring the integration of 3D-printed SUS-420-steel coatings onto copper substrates through Electric Discharge Coating (EDC) processes. Unlike conventional methods, this approach utilizes 3D Printed electrodes (3DPE) for coating, offering a compact and efficient process. Through systematic optimization of process parameters, including discharge energy levels and coating processes, the study achieves significant improvements in coating thickness from 15.40 to 141.16 µm, microstructure, and composition. Surface analyses and Energy Dispersive X-ray Spectroscopy (EDS) scans reveal steel-rich areas, microcracks, and uniform distribution across the substrate. The resulting coatings exhibit enhanced mechanical properties, including increased hardness and improved resistance to corrosion and thermal degradation. This breakthrough not only opens new avenues in coating industries for complex surfaces but also underscores the potential for further innovation in material deposition technologies.

Author Index

Bold page numbers indicate presenter