Coatings for Use at High Temperatures
Room Pacific Salon 2 - Session A1-1-TuM

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

Moderators: Justyna Kulczyk-Malecka, Manchester Metropolitan University, **Lars-Gunnar Johansson**, Chalmers University of Technology, Sweden, **Shigenari Hayashi**, Hokkaido University

8:00am **A1-1-TuM-1 Modeling the Influence of Heat Treatment and Base Alloy Composition on the Performance of Aluminide Coatings for High Performance Engine Valve Alloys***, **Rishi Pillai**, S Dryepondt, B Armstrong, Q Guo, K Unocic, G Muralidharan,* Oak Ridge National Laboratory, USA

Ni-based alloys are currently being used for engine valves in internal combustion engines.The currently employed valve alloys have reached their operational limit and the need to increase engine efficiency and hence operating temperatures combined with the added challenge of low component cost tolerance makes high temperature materials selection for durability and cost a primary concern since there are fewer lower-cost materials which possess sufficient oxidation, creep and fatigue resistance.

Protective metallic nickel aluminide (NiAl) diffusion coatings enhance the oxidation and corrosion resistance of the underlying high temperature materials.However, the substrate composition and specimen geometry influence the final coating microstructure during the aluminising process and govern the high temperature behavior of the coating system during subsequent exposure.Potentially detrimental phases may form in the interdiffusion zone (IDZ) during the aluminizing process.The formation of a protective alumina scale and the diffusion from the coating into the substrate during subsequent service result in the loss of Al and thereby the dissolution of the ß-NiAl phase in the coating.The compatibility of a given type of a coating with its base material substantially influences the performance of a coated material during service.Evaluation of the coating's high temperature behavior requires extensive experimental testing, but computational methods can substantially reduce these efforts required for coating evaluation and qualification.

In the current work,a coupled thermodynamic and kinetic computational model was employed to predict the microstructural evolution in nickel aluminide (NiAl) diffusion coatings on the Ni-base 31V alloy (UNS NO7032) and new recently developed high strength alloys during the coating (aluminising) process.Various heat treatment procedures were assessed to optimize the coating microstructure.The model was also used to predict the microstructural evolution of coated 31V coupons exposed at 800ºC for up to 5,000h.

Element concentrations and phase distribution were obtained by scanning electron microscopy (SEM).Phases were identified by energy/wavelength dispersive X-ray spectroscopy (EDX/WDX) and electron backscatter diffraction (EBSD). The model predicted the formation of sigma phase and carbides of the MC-type in the IDZ of the coating on 31V which was in agreement with experimental observations. The computational approach provides a general approach in predicting the IDZ microstructure during manufacturing and estimating the extent of microstructural changes in the coating as a function of alloy/coating composition, time and temperature.

8:20am **A1-1-TuM-2 Fabrication, Characterisation and Testing of Cr Coated Zr Alloy Nuclear Fuel Cladding for Enhanced Accident Tolerance***, A Evans,* Manchester Metropolitan University, UK*; D Goddard,* National Nuclear Laboratory, UK*; A Cole-Baker,* Wood plc, UK*; G Obasi, M Preuss,* Manchester University, UK*; E Vernon,* National Nuclear Laboratory, UK*;* ***Peter Kelly****,* Manchester Metropolitan University, UK

The deposition of an oxidation resistant Cr coating on Zr alloy nuclear fuel cladding is an advanced concept for deployment of an accident tolerant fuel, which is attracting considerable interest in the market. Improvements have been shown relative to uncoated Zr alloys in both operational conditions and when subjected to high temperature steam. Initial irradiation testing of this concept is also in progress. In the UK, a collaborative programme of research is investigating Cr deposition using magnetron sputtering. This research is examining how the integrity and microstructure of the coating is affected by deposition conditions and coating thickness for both flat coupons and short lengths of Zr alloy tube. Test coatings have been subjected to static autoclave tests under standard PWR operating conditions, as well as accelerated tests in air at 900ºC and in 400°C steam. The as-deposited and post-testing coatings have been characterised using SEM/EDX and XRD to determine structure, texture and residual stress and, in the latter case, damage arising from testing. Initial results have shown significant differences in the stress condition in the coatings as a function of deposition parameters. Furthermore, selected coatings have successfully undergone accelerated oxidation tests with little or no discernible detrimental effects.

8:40am **A1-1-TuM-3 High-temperature Oxidation Resistance and Self-healing Capability of HiPIMS Cr-Al-C Coating on Zr-based Alloy***, **Michaël Ougier**, A Michau, F Lomello,* CEA, Université Paris-Saclay, France*; F Schuster,* CEA Cross-Cutting Program on Materials and Processes Skills, France*; H Maskrot, M Schlegel,* CEA, Université Paris-Saclay, France

The development of nuclear accident-tolerant fuels (ATF) claddings has gained new momentum since Fukushima Daiichi accident. The primary goal of this study is to develop alternative fuel claddings which are more resilient to high-temperature steam oxidation to reduce hydrogen generation during loss-of-coolant-accident (LOCA). A promising solution is to protect the claddings by metallic or ceramic coatings, such as MAX phases. In order to resist such accidental conditions, the oxide coatings need to be physically and chemically stable in normal operating conditions and accidental (steam) situations; also, they should act as protectives barrier against oxygen diffusion. Al-containing MAX phases, as Cr_2AlC, possess excellent high-temperature oxidation resistance both in air and in humid atmosphere due to the formation of a dense and adherent alumina scale. In this work, Cr-Al-C thin films were synthesized as coatings on Zr-based alloy from a Cr_2AlC compound target by high-power magnetron sputtering (HiPIMS) and subsequent thermal annealing. The crystal structure, microstructure and oxidation behavior of these films were investigated in air. As-deposited coatings are dense and amorphous regardless the deposition temperature (between 25 to 450°C). The effect of the annealing post-treatment was studied by *in situ* X-ray diffraction from 550 to 650°C in helium for up to 12 h. In such conditions, HRTEM analysis demonstrated that the amorphous coating partially crystallized into Cr_2AlC nanocrystals above 600°C. Microcracks also appear on the surface for very thick films, due to the release of residual stresses originating from both the mismatch in thermal expansion coefficients of the coating and the substrate, and from internal stresses. Oxidation at temperatures up to 1200°C in air reveals no significant oxidation of the substrate thanks to the growth of a dense and protective Al_2O_3 layer fully covering residual Cr carbides. Voids also formed at the interface between oxide and Cr carbides. The relative weight gain of coated samples typically decreases by 80% compared with uncoated Zr-based alloy. Furthermore, coatings also possess a self-healing capability due to the formation of alumina within microcracks. In addition, water quenching tests prove that coatings demonstrate high adherence and thermal-shock resistance. As a comparison, the oxidation behavior of the crystalline film is also conducted. Results indicate that Cr-Al-C thin films grown by HiPIMS process are promising candidates for ATF cladding coatings.

Keywords : Accident-Tolerant Fuels, MAX phase coating, physical vapor deposition, oxidation resistance, self-healing

9:00am **A1-1-TuM-4 Ceramic Coatings for Protection of Ti and Zr Alloys at High Temperature***, **Ping Xiao**, Z Gao, X Zhang, H Liu,* University of Manchester, UK*; J Kulczyk-Malecka, P Kelly,* Manchester Metropolitan University, UK*; Z Zhang,* University of Manchester, UK **INVITED**

SiAlN coating have been produced with use of magnetron sputtering on both Ti and Zr alloy substrates for protection from oxidation in both air and steam environments. The coatings have demonstrated excellent oxidation resistance tested in both air and steam and the strong coating/substrate bonding, measured with use of scratch testing. Electron microscopy has been used to understand the oxidation mechanisms and the mechanisms controlling the coating/substrate adhesion. The study has presented that the coatings are very promising for protection of Ti and Zr alloys from oxidation in air and steam at high temperature.

9:40am **A1-1-TuM-6 Multi-functional AlZr-TiO_2 Bilayer Coatings Combining Anticorrosion and Antifouling Properties***, **Caroline Villardi de Oliveira**,* ICD-LASMIS, Université de Technologie de Troyes, France, Françe*; A Alhussein,* University of Technology of Troyes (UTT), France*; C Jiménez,* Univ. Grenoble Alpes, CNRS, France*; Z Dong,* School of Materials Science and Engineering, Nanyang Technological University, Singapore*; F Schuster,* CEA, PTCMP, France*; S Narasimalu,* School of Materials Science and Engineering, Nanyang Technological University, Singapore*; M Schlegel,* CEA, Université Paris-Saclay, France*; F Sanchette,* Nogent International Center for CVD Innovation, LRC CEA-ICD LASMIS UMR6281, UTT, Antenne de Nogent, France

Fouling in marine environment is a costly problem and can be described by the development of biofilms containing various types of micro and macro-organisms, which can enhance the processes and rates of steel corrosion in saline seawater. TiO_2 coating shows photocatalytic activity and hydrophilic behavior which can promote antifouling properties in order to minimize the biofouling process in the marine structures. Photocatalytic oxidation is a non-toxicity low cost promising technology to control fouling in submerged surfaces by generation of reactive oxygen species [1]. In this work we present a multi-functional coating made by an anticorrosion Al-Zr interlayer covered by an antibiofouling TiO_2 top layer. Al-Zr film is proposed as a potential candidate for affording sacrificial corrosion resistance of steels since it presents a good compromise between the mechanical reinforcement and the electrochemical properties[2].

Steel substrates were initially coated by magnetron sputtering with Al-Zr alloy (3 µm thick films) containing 5 at.% Zr. TiO_2 films were deposited on the top of the Al-Zr layer by atmospheric pressure Aerosol-Chemical Vapor Deposition (AACVD). The structure and morphology of the multi-functional coatings were analyzed by XRD and SEM. Photocatalytic activity using Orange G under UV light and electrochemical tests in saline solution were performed. The biofouling behavior and performance in natural seawater were also tested by in situ immersion tests.

Keywords: Al-Zr alloys, magnetron sputtering, steel protection, biofouling, TiO_2, AACVD, Photocatalysis.

References

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10:00am **A1-1-TuM-7 The Oxidation Behavior of ZrO_2-Coated Zircaloy-4 with ZrN Interlayer***, **I-Sheng Ting**, J Huang,* National Tsing Hua University, Taiwan

The purposes of this study were to investigate the oxidation behavior of ZrO_2-coated Zircaloy-4 (Zry-4) with different crystal structure and evaluate the effect of ZrN interlayer. Oxidation is a crucial problem for the Zry-4 fuel cladding in light water nuclear reactor. In general, when reacting with water, Zry-4 will naturally form a surface oxide layer that is composed of both tetragonal and monoclinic ZrO_2. Although ZrO_2 is a well-known protective material, the naturally formed oxide layer is only several nanometers, which is insufficient to protect the Zry-4 substrate from the severe water-corrosion environment in nuclear reactor. Several transition metal nitride coatings (TMeN), such as CrN, TiN, and TiAlN have been proposed to improve the oxidation resistance of Zry-4. Owing to the excellent thermal and chemical stability, TMeN can act as a diffusion barrier and prevent the substrate from further oxidation. In addition, TMeN possess superior mechanical properties that may enhance the service time of the Zry-4 claddings. Therefore, this study aimed to investigate the oxidation behavior of ZrO_2-coated Zry-4 with tetragonal, monoclinic, and yttria-stabilized cubic crystal structure, and evaluate whether the ZrN interlayer can act as an efficient diffusion barrier. ZrO_2 thin films with three different crystal structure and ZrN interlayer were deposited on both sides of the Zry-4 plate by unbalanced magnetron sputtering (UBMS). After the deposition of ZrO_2 thin films, the crystal structure was characterized by X-ray diffraction (XRD), and the chemical composition was measured using X-ray photoelectron spectroscopy (XPS). Thermogravimetric analysis (TGA) was carried out at 700, 800 and 900°C in argon atmosphere for 1 h. After the TGA oxidation, the uniformity of the multi-phases ZrO_2 oxide layer was examined using azimuthal $\cos^2\alpha\sin^2\psi$ technique, which combines $\cos^2\alpha\sin^2\psi$ XRD method [1] with average X-ray strain (AXS) method [2]. The surface morphology of the ZrO_2 thin films and the precipitation of nonuniform surface oxides after TGA oxidation were observed by SEM equipped with EDX.

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10:20am **A1-1-TuM-8 Novel HIPIMS Deposited Nanostructured CrN/NbN Coatings for Environmental Protection of Steam Turbine Components.***, **Papken Hovsepian**, A Ehiasarian, Y Purandare,* Sheffield Hallam University, UK*; P Mayr, K Abstoss,* Technische Universitat Chemnitz, Germany*; M Mosquera, W Schulz, A Kranzmann,* Federal Institute for Materials Research and Testing, Germany*; M Lasanta Carrasco, J Trujillo,* Universdad Complutense de Madrid, Spain

A significant reduction of CO_2 emissions is expected by increasing the efficiencies of the steam turbines to $\eta > 50\%$ which can be achieved by moving from subcritical low pressure/ low temperatures, to high pressure/high temperature, ultra-supercritical regime of operation. The main challenges faced by different steel components of the power plant with this approach however, consist of material failure due to high temperature oxidation, and phenomenon such as creep, erosion and descaling after a stipulated period of time.

In the current work, 4 µm thick CrN/NbN coating utilising nanoscale multilayer structure with bi-layer thickness of Δ = 3.4 nm has been used to protect low Cr content P92 steel widely used in steam power plants. The novel High Power Impulse Magnetron Sputtering (HIPIMS) deposition technology has been used to deposit CrN/NbN with enhanced adhesion (critical scratch adhesion value of Lc= 80N) and very dense microstructure as demonstrated by XTEM imaging.

P92 coated samples were oxidised at 600°C in 100% high pressure, 50 bar steam atmosphere up to 1500 h. The gas-flow velocity through the reaction zone of the test rig was 0.0133 m/s. In these conditions CrN/NbN provided reliable protection of the P92 steel.

This research also revealed that unlike other state-of -the-art PVD technologies, HIPIMS does not have an adverse effect on the mechanical properties of the substrate material, which is of paramount importance in case of turbine blade applications. In high temperature (650^{o}C) tensile strength test uncoated P92 steel showed Ultimate Tensile Strength (UTS) values of 229 MPa and Yield Strength, (YS) values of 222 MPa compared to UTS = 307 MPa and YS = 291 MPa measured for CrN/NbN coated P92 steel. Similarly in strain controlled, (0.4% strain) Low Cycle Fatigue tests at 650^{o}C both uncoated and coated specimens failed after similar number of cycles, N_f = 1700 and N_f= 1712 respectively and showed similar half-life stress drop of -37% and -43% respectively. Finally high temperature creep tests at 650^{o}C, tensile stress of 120 MPa revealed that the HIPIMS coating improved the creep lifetime by almost factor of two from 564 hours to 908 hours whereas the creep rate was decreased from 17.6 10^{-6} s^{-1} to 13.5 10^{-6} s^{-1}.

The protection properties of the coating against water droplet erosion attack were tested using specialized test rig. The coating shows high resistance against water droplet erosion. After 2.4E^6 impacts no measurable weight loss was detected.

10:40am **A1-1-TuM-9 NiAl Coatings Deposited on Inconel 600 by Using an Arc Ion Plating Process***, **Yinan Li**,* University of Manchester, UK*; Y Hung,* Feng Chia University, Taiwan*; M Lin, A Matthews,* University of Manchester, UK*; J He,* Feng Chia University, Taiwan

To protect against the most demanding environments in gas turbines, thermal barrier coatings (TBCs) made of a ceramic top coat and an intermetallic bond coat are applied throughout the hot sections. In a TBC system, a top coat of partially yttria stabilized zirconia (PYSZ) presently offers the main thermal insulation, whilst a bond coat of Ni(Pt),Al or MCrAlY provides the vital oxidation resistance. Currently, these coatings are typically deposited by electron beam physical vapour deposition (EB-PVD). A potential alternative processing route is to deposit both top coat and bond coat by an arc PVD method in a single coating cycle. Little work has been carried out on arc PVD NiAl and PYSZ coatings, which may offer benefits (e.g. in the degree of ionisation achieved, and therefore coating structure and uniformity improvements) compared to other methods.

In this study, the arc ion plating (AIP) method is used to deposit NiAl films on nickel-based alloy (Inconel 600) and AISI 304 stainless steel substrates. The composition of the cathode target is $Ni_{50}Al_{50}$. In order to study the influence of processing conditions on microstructure and phase composition, the parameters of substrate bias voltage and current, target pulse current and working pressure are controlled during the deposition. Thermal cyclic oxidation testing is carried out to evaluate the cyclic oxidation resistance. The results demonstrate the benefits of the process in terms of improved morphology and performance.

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