Coatings for Use at High Temperatures
Room On Demand - Session A2
Thermal and Environmental Barrier Coatings

A2-1 Improvement of TBC Coating Resistance to Simultaneous Attacksby Sulfur and Vanadium Compounds, ***Jianhong He (Jianhong.He@Oerlikon.com)***, Oerlikon Metco , USA; *T. Sharobem, G. Dwivedi,* Oerlikon Metco, USA

Hot corrosion attacks of various TBC systems by sulfur and vanadium compounds have been tested at 1050ºC for 2 hours and 4 hours in the presence of 60% V_2O_5 and 40% Na_2SO_4. The results are summarized as follows.

(A) Sulfur and vanadium compounds at high temperature aggressively attacked the conventional 7YSZ TBC, the coating has been damaged at 1050ºC for only 2 hours in the presence of 60% V_2O_5 and 40% Na_2SO_4.

(B) High density of coarse YVO_4 crystals are quickly formed on coating surface, removal of Y_2O_3 stabilizer from zirconia leads t'-ZrO_2 to m-ZrO_2 phase transformation and thusdramatic increase in volume. There is no evidence showing fair metallurgical bonds among YVO_4 crystal and YVO_4 crystal, and matrix, therefore, integrity of the coating is totally destroyed by sulfur and vanadium compounds.At the same time, molten salt infiltrate into entire top coat and seal splat boundaries and pores similar to molten silicate deposits to reduce strain tolerance, finally causing top coat delamination.

(C) Hot corrosion resistance of TiO_2 and Y_2O_3 co-stabilized zirconia has doubled compared to a standard 7 YSZ TBC, while single stabilizer TBCs with high Y_2O_3 ratios do not increase hot corrosion resistance in the presence of 60 % V_2O_5 and 40 % Na_2SO_4.

(D) TBC sprayed using mixture of 50% Metco 143 and 50% 48YSZ and Metco143/ A204NS-1/bi-layer TBC had the highest resistance to simultaneous attacks by sulfur and vanadium compounds, although the microstructures on the surface and cross-section of these two TBCs are totally different.

A2-2 High-Temperature Corrosion of Sintered $Er_2Si_2O_7$ With CMAS for Environmental Barrier Coatings, ***Seung-Hyeon Kim (kim.seung.hyeon.726@s.kyushu-u.ac.jp)***, Kyushu University, Japan; *N. Nagashima, Y. Matsushita,* National Institute for Materials Science, Japan; *B. Jang,* Kyushu University, Japan

Environmental barrier coatings (EBCs) is an element that protects silicon-based ceramic matrix composites (CMCs) from high temperatures. CMCs has high temperature performance and low density, which can greatly improve fuel consumption. CMCs low density can reduce weight by up to 30% compared to Ni-based super alloys. In addition, for the purpose of EBCs, insulation properties are important as the temperature change of the hardware inside the engine occurs at high temperatures. In addition, the demand for thermal protection of CMCs is increasing in higher temperature applications. Research and development are being conducted to investigate the effect of calcium-magnesium-aluminosilicate (CMAS) during high temperature operation. A composition similar to volcanic ash is being studied for the high temperature interaction between CMAS.

EBCs must be resistant to minimize the resistance to decomposition by molten actual volcanic ash (dust and sand) deposits. With increasing high-temperature corrosion requirements, EBCs based on rare earth (RE) monosilicates ($RESi_2O_5$), disilicates ($RE_2Si_2O_7$) and their variants are being developed. Disilicate ($RE_2Si_2O_7$) shows safety because SiC and CTE are better matched than monosilicate ($RESi_2O_5$). The process of preparing a hot corrosion specimen is as follows. The synthesized Er_2O_3-$2SiO_2$ powder was prepared to fabricate a sintered $Er_2Si_2O_7$ by the spark plasma sintering (SPS) at 1400°C for 20 min. CMAS was sprinkled on the sintered $Er_2Si_2O_7$ surface and exposed for 2, 12, and 48 h at 1400°C by isothermal heat treatment.

However, reaction layer for sintered $Er_2Si_2O_7$ by CMAS has not yet been reported. The purpose of the present work is to investigate the influence of CMAS corrosion properties at high temperatures on sintered $Er_2Si_2O_7$ fabricated by SPS. As time increases, it is a phenomenon that appears as $Er_2Si_2O_7$ particles are dissolved in molten CMAS by penetrating into grain boundaries. In addition, it was observed that some crystallization occurred at the boundary of the sintered $Er_2Si_2O_7$ molten CMAS.

Keywords: $Er_2Si_2O_7$; Corrosion behavior; CMAS; Environmental barrier coatings; Spark plasma sintering

A2-3 Experimental and Modelling Analysis of the Driving Force for TBC Damage During Thermal Cycling With Consideration of Temperature Gradients, ***Lara Mahfouz (lara.mahfouz@mines-paristech.fr)***, *V. Maurel , V. Guipont, B. Marchand,* Mines ParisTech, PSL Research University, France; *F. Coudon,* Safran Tech, Safran SA, France

The addition of Thermal Barrier systems to hot section components of gas turbines requires understanding of its degradation and failure modes, and its resulting impact on the components' lifetime. The spallation (total or partial) of the top coat will result in thermal protection loss, and hence an important reduction of the component's lifetime. The studied Thermal Barrier system is composed of EB-PDV YSZ ceramic top coat and (Ni, Al)-Pt metallic bond coat deposited on a AM1 substrate, a Ni-based superalloy. A first α-alumina layer is deposited on the substrate and grows in service (TGO).

Different approaches have been developed to asses TBC lifetime [1,2]. The main objective of this study is to provide a robust modeling of the damage and lifetime to spallation of Thermal Barrier systems, for thermo-mechanical stress conditions accounting for thermal gradients. The proposed approach is based on the analysis of the evolution of an interfacial crack. It has been widely observed for such systems, that thermal cycling induces damage at the TC/TGO interface leading to interfacial cracking and finally spallation of the TC. Laser shock test has been used to initiate a crack at the interface. The evolution of the crack is monitored during thermal cycling on a burner rig, with temperature gradients as close as possible to in-service conditions. This technique has been used and analyzed in previous studies [2,3] for furnace cycling tests. A numerical modeling of the energy evolution in a blister under thermal cycling is proposed. It relies on the evaluation of the energy release rate within the system at different cycling stages as the blister propagates. A sensitivity analysis has been achieved considering the influence of components' mechanical behaviors, as well as that of loading, ageing, and geometrical parameters.

1. J.-R. Vaunois. Modélisation de la durée de vie des barrières thermiques par le développement et l'exploitation d'essais d'adhérence. PhD thesis, Université de Grenoble, 2013.
2. R. Soulignac. Prévision de la durée de vie à l'écaillage des barrières thermiques. PhD thesis, Mines ParisTech, 2014.
3. V. Maurel, V. Guipont, M. Theveneau, B. Marchand, F. Coudon. Thermal cycling damage monitoring of thermal barrier coating assisted wth LASAT (Laser Shock Adhesion Test). Surface and Coatings Technology, Vol 380, 2019.
4. V. Guipont, G. Begue, G. Fabre, V. Maurel. Buckling and interface strength Analysis of EB-PVD TBC combining Laser Shock Adhesion Test (LASAT) to thermal cycling. Surface and Coatings Technology, Vol 378, 2019.

A2-4 Effect of Varying APS Flash Bond Coating Thickness on Furnace Cycle Lifetime, ***Michael Lance (lancem@ornl.gov)***, *K. Kane, J. Haynes, B. Pint,* Oak Ridge National Laboratory, USA; *E. Gildersleeve, S. Sampath,* Stony Brook University, USA

The addition of an air plasma sprayed (APS) "flash" bond coating layer on top of a high velocity oxy-fuel (HVOF) bond coating has been found to significantly extend the lifetime of APS yttria stabilized zirconia (YSZ) top coatings on rod and disk specimens. In order to test the hypothesis that the flash coating forms a crack-inhibiting mixed metal-oxide zone and the HVOF layer acts as an Al reservoir, a set of superalloy 247 disks were coated with 0, 25, 50 and 100% APS layers using NiCoCrAlY powder. Groups of five specimens of each coating type were cycled to failure using 1-h cycles in air+10%H_2O at 1100°C. Residual stress in the thermally-grown Al_2O_3 scale was measured using photo-luminescence piezospectroscopy (PLPS) as a function of time for one specimen of each coating variation. Principal component analysis (PCA) of both Raman and x-ray spectroscopy maps were conducted to determine the phases present within the oxide and the bond coating. The results of furnace cycling testing and analysis of the compositions and microstructures will be presented.

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A2-5 Electrodeposited Thin La_2O_3 Based Chromium Barrier Coating for Interconnectors in Solid Oxide Electrolysis*, Vladislav Kolarik (vladislav.kolarik@ict.fraunhofer.de), M. Juez Lorenzo, E. Walschburger,* Fraunhofer Institute for Chemical Technology ICT, Germany

Solid oxide steam electrolysis (SOE) using electric power from renewable sources is a promising technology to produce hydrogen for energy storage or for industrial purposes. Ferritic stainless steels are used for interconnectors between the SOE cells offering good mechanical properties and forming at high temperatures an electrically conductive Cr_2O_3 scale. In presence of water vapor however, the highly volatile and toxic $CrO_2(OH)_2$ is formed poisoning the SOE cell. To mitigate the Cr(VI) evaporation protective coatings are used.

To reduce the costs of an SOE stack, cost efficient coating processes are required. Electroplating was applied to deposit a $La(OH)_3$ layer on a Crofer 22 APU substrate with a subsequent heat treatment to transform the $La(OH)_3$ to a La_2O_3 coating. The coating thickness and morphology is controlled directly by the electroplating parameters. The electrodeposited layers are well adherent and exhibit thicknesses around 1 µm and a needle-like nano-crystalline structure. With higher layer thickness a network of thin cracks is observed. The heat treatment was followed is situ by high temperature X-ray diffraction both on heating as well as isothermally in order to adjust the parameters.

For investigating the chromium evaporation rate the coated samples as well as an uncoated reference sample were subjected in a closed furnace system to humid air with a mass flow of 2000 ml/min and a water content of 130 g/m^3 at 850°C for 500 h. On the furnace outlet the humid air was cooled to condense the water. The chromium content in the condensed water was detected by a colorimetric quick test as well as by ICP-OES analysis. The evaporation rate as a function of time was determined in time intervals of 24 h. Samples were taken out of the furnace for SEM analysis after 100 h, 200 h, 300 h and 500 h.

Chromium evaporation was found in all time intervals during the whole exposure duration. At the beginning lower chromium evaporation rates were measured with the coated samples than without coating. With longer exposure times the evaporation rate values are closer to those for uncoated steel. Areas with partial coating spallation were observed in the micrographs after longer exposure periods, probably originating from cracks that formed due to the thermal expansion mismatch. An oxide scale consisting of Cr_2O_3 and Cr-Mn-spinel formed beneath the coating as well as in the areas with coating spallation. Electrodeposition is a possible cost efficient method to produce chromium barrier coatings on interconnector steels. The process parameters however, need to be further investigated.

A2-6 Effects of Mo Interlayer on the Oxidation Behaviour and Degradation Mechanism of Amorphous SiAlN Coating at 1000 °C in Steam Environment*, Zhaohe Gao (zhaohe.gao@manchester.ac.uk),* The University of Manchester, UK*; J. Malecka, P. Kelly,* Manchester Metropolitan University, UK*; P. Xiao,* The University of Manchester, UK

Loss-of-Coolant Accident (LOCA) in a Light Water Reactor, such as occurred in the Fukushima Daiichi Power Plant, could be potentially mitigated by applying an oxidation-resistant coating onto the surface of the Zr alloy fuel rod as accident tolerant fuel cladding. In this study, 1.1 µm thick SiAlN amorphous coatings, consisting of AlN nanoparticles dispersed in an amorphous Si_3N_4 matrix, have been deposited on Zr alloys with 300 nm or 750 nm Mo interlayers and studied in a steam environment at 1000°C. The SiAlN coating with a 750 nm Mo exhibits excellent oxidation resistance without observable oxide scale after up to 4 hours at 1000°C, while the coating with a 300 nm Mo forms a thin oxide scale in an identical atmosphere after 1 h. The downward diffusion of Si into underlying Zr alloy, followed by relatively faster outward diffusion of N, generates excessive Si and lean N in the outmost surface of SiAlN, thereby resulting in the oxidation of the amorphous coating. A critical composition content of N below which oxidation can happen is predicted and verified. The sluggish effect of Mo on the downward diffusion of Si has also been discussed and this study provides a new insight into the degradation mechanism of this amorphous coating.

A2-7 Laser Processing of Freeze Casted Yttria Stabilized Zirconia / Gadolinia Thermal Barrier Coatings to Mitigate CMAS Attack*, Said Bakkar (SaidBakkar@my.unt.edu), E. Cairns, M. Vu, M. Young, D. Berman,* University of North Texas, USA*; T. Hossain,* Ceriumlabs, USA*; J. Moldenhauer, E. Steinmiller, W. Flanagan,* University of Dallas, USA*; S. Aouadi,* University of North Texas, USA

Yttria-stabilizedzirconia and Gadolinia blend (YSZ/Gd_2O_3) ceramics with unidirectionally-aligned pore channels were created using the freeze-casting method. Preforms were prepared by freezing 70 wt% YSZ and 30 wt % Gd_2O_3 after ball milling for 15 hours /distilled water/polyvinyl alcohol (PVA) slurry under a freezing temperature of -196 °C. The frozen preform was sublimated using a freeze-drying system in vacuum (0.05 mTorr) at -85 °C. The sublimated preforms were subsequently sintered at 1600°C for 9 h in air. The surface of the sintered samples was modified using a laser process to seal its surface tomitigateCMAS (calcium–magnesium–aluminum–silicon oxide) attack. Scanning electron microscopy (SEM) revealed that the pore channels consisted of columns, which act to decrease the thermal conductivity of the (YSZ/Gd_2O_3) blend. Also, SEM confirmed that the surface treatment successfully sealed the surface. The performance of the different surface treatment systems was compared by conducting CMAS infiltration studies. Deposit of Si_3N_4 as a sacrificial layer on the top of single crystal YSZ provides a perfect seal to cover the defects on the surface.The newly designed fabrication process that combines freeze casting with laser modification and using a sacrificial layer of Si_3N_4 was shown to be a viable technique to significantly reduce CMAS infiltration in porous thermalbarriercoatings.

A2-8 Corrosion Resistance and Fatigue Behavior of Bare and Coated Ni-based Superalloys*, Sebastien Dryepondt (dryepondtsn@ornl.gov), R. Pillai, J. Kurley,* Oak Ridge National Laboratory, USA

Rising temperature in land-based gas turbines has led to an increase of corrosion degradation of turbine blades operating at ~700-750º C. MCrAlY overlay bond coatings with or without a thermal barrier coatings (TBC) can provide some protection against this type 2 low temperature hot corrosion attack, but the coating impact on the blade mechanical performance needs to be evaluated. Hot corrosion testing in O_2+0.1%SO_2 environment with NA_2SO_4 salt deposition at the sample surface was conducted on bare CM247, Rene 80 and IN738 at 700º C for up to 100h. Systematic image analysis of the corroded specimens revealed a deeper metal loss for the IN738 alloy compared to the CM247 and Rene 80 alloys. Coupons of Rene 80 coated with two different types of MCrAlY coatings or MCrAlY + TBC were also exposed. Significant reduction of mass losses was observed for the MCrAlY coated samples, but the coatings were heavily oxidized after 60h of exposure. On the contrary, the MCrAlY + TBC coating was very protective with very limited corrosion attacks. Finally, low cycle oxidation testing was initiated on bare and coated CM247 specimens at 750º C in air and first results with a total deformation of 0.8% showed no impact of the coating on the number of cycles to failure. The next step is to conduct similar fatigue tests in a corrosive environment.

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