Protective and High-temperature Coatings
Room Palm 5-6 - Session MA2-1-MoA

Thermal and Environmental Barrier Coatings
Moderator: Pantcho Stoyanov, Concordia University, Canada

1:40pm **MA2-1-MoA-1 Oxygen Permeability, Degradation and Failure Analysis Formulated by Artificial Intelligence of Environmental Barrier Coatings under Adverse Environments Environments*, Kuiying Chen (kuiying_chen@hotmail.ca)*,** National Research Council of Canada*; K. Lee,* NASA Glenn Research Center, USA **INVITED**

Environmental barrier coatings (EBCs) are typically used to protect ceramic matrix composites (CMCs) under harsh environmental attack such as water vapor-induced recession in aero-engines. Under adverse operations, the oxygen permeability of ytterbium disilicate (YbDS) topcoat and thermally grown oxide (TGO) silicon dioxide in EBCs plays a key role in determining EBCs durability and lifespan. Using physics-based model and thermodynamics along with defect reaction formulae, oxygen permeabilities under both dry oxygen and water vapor conditions, as well as different temperatures, partial pressures and topcoat modifiers, are investigated. Results show that oxygen permeability of YbDS is an order of magnitude larger than that for TGO, indicating TGO hinders the oxidant diffusion stronger, proving to be diffusion rate controlling layer while water vapor strongly increases oxidant permeation.

Solid particle erosion of EBCs was numerically evaluated using mechanics-based formulae where the model parameters are fitted to the test data. The cutting wear, the deformation wear and their relationship with erosion rate are elaborated, while possible mechanisms of erosion rate correlated with EBCs microstructures are explored. The failure mechanisms of EBCs under solid particle erosion processes are discussed combining microstructures, internal cracking within topcoat and external erosion on the topcoat surface. The kinetic behavior of erosion and its effect on life span in EBC are calculated based on the erosion rate obtained from the mechanics-based model.

A non-destructive technique based on convolution neural network (CNN) in deep learning is used to evaluate crack evolution in EBCs. The candidate crack region of interest (ROI) was identified by using Visual Geometry Group Network (VGG) as baseline network, and CNN detector was then used to refine the candidate regions which provide a comprehensive feature for better crack detection. With the information on crack evolution, a fusion lifetime prediction model was used to estimate the remaining lifetime of EBCs system. The performance of the used model on remaining life span was examined.

2:20pm **MA2-1-MoA-3 Effect of Thermal Barrier Coatings on the Thermal Management of a Jet Engine Combustion Chamber*, Rodrigue Beaini (rodrigue.beaini@polymtl.ca),*** Polytechnique Montréal, Canada

The aircraft engine industry depends extensively on the advancement of high-performance materials and protective coating systems to enable a continuous ascent in engine performance requirements. In this context, thermal barrier coatings (TBCs) play a key role by providing a protective layer between the hot gases generated by combustion and the underlying metallic components. This allows higher operating temperatures and pressures which results in higher engine efficiency, lower fuel consumption and reduced environmental impact.

TBCs have significant effects on the three primary heat transfer mechanisms, namely convection, conduction and radiation. Considerable efforts have been deployed over the past years to ensure that TBCs possess low thermal conductivity, however, the radiative component has been comparatively largely ignored mainly due to the complexity of the assessment techniques.

This research aims to understand and quantify the impact of high-performance TBCs on the heat management in engine combustion chamber. To accomplish this, a laboratory-scale combustion chamber rig, equipped with a kerosene burner, has been designed and built to mimic aircraft engine conditions. The burner has a tunable power level and can be operated under various flame equivalence ratios, ranging from fuel-lean to rich conditions. Multiple diagnostic tools have been integrated such as thermocouples, heat flux gardon gauges and a multispectral IR camera. A novel approach to solve for emissivity and temperature at high temperatures (> 900°C) using IR imaging was developed, accounting for the multiple reflections inside the combustion chamber and apparent emissivity of a surface in an enclosed cavity. TBCs with different porosities were compared under 5 flame conditions, and an evaluation of the CMAS (calcium-magnesium-alumina-silicate) infiltration inside the pores and its impact on the performance of the TBCs in the combustion chamber was studied. We show and quantify how higher porosity in a TBC leads to a lower temperature on the substrate and how CMAS infiltration increases the temperature locally on the contaminated surface.

Key words:

Thermal barrier coatings (TBC), high temperature, IR imaging, heat transfer, kerosene burner, CMAS

2:40pm **MA2-1-MoA-4 Elevated Temperature Micro-Scale Impact Testing of Thermal Barrier Coatings for Erosion Simulation*, Ben Beake (ben@micromaterials.co.uk)*,** *J. Roberts,* Micro Materials Ltd, UK*; L. Isern, C. Chalk, J. Nicholls,* Cranfield University, UK

Higher engine operating temperatures will increase the efficiency of gas turbines, saving fuel and reducing CO_2 emissions. However, it is challenging to develop TBC systems with required low thermal conductivity and high resistance to CMAS attack while maintaining or improving their resistance to high temperature impact and erosion. To speed up TBC development a high efficiency impact / erosion test method providing rapid data with small volumes of material is needed.

A novel nano-/micro-mechanical test technique has been developed to experimentally simulate the stochastic nature of the repetitive particulate impacts that occur in high temperature erosion by performing multiple impacts at different locations on the TBC surface [1]. In the randomised impact test, a specified number of individual impacts occur with defined energy and chosen statistical distribution within a set area. Analysis of instantaneous depth vs. time data from every impact shows how residual depth, coefficient of restitution and kinetic energy loss all vary throughout the test to provide evidence of changing damage mechanisms.

Single impacts, repetitive impact and randomised impact tests have been performed at room temperature on EB-PVD 7YSZ and Gadolinium Zirconate coating systems deposited on aluminised Nimonic 75 alloy coupons. Differences in erosion rate and some erosion mechanisms were well replicated in the shorter impact tests compared with erosion test data [2].

The experimental capability has recently been extended to higher temperatures. Tests were performed at 500 °C and 825 °C on the 7YSZ coating with a ~25 µm radius diamond indenter so that each impact only affected a few columns. The depth on initial impact increased with temperature due to the softening of the TBC. Although the final impact depths were greater at higher temperatures, the increase with continued impact was smaller than at room temperature. 7YSZ impact behaviour at 825 °C is compared to previously reported erosion data obtained with a high temperature erosion rig at Cranfield and in the literature [3].

For comparison repetitive impact tests were also performed on a bulk glass (fused silica) at 25, 250, 400, 650 and 825 °C. At higher temperature there was reduced cracking in the multiple impact tests. This was balanced by a gradual softening over the temperature range with the result that the maximum impact depths were found at intermediate temperatures.

[1]UK Patent Application #2217939.4. [2] BD Beake et al, ICMCTF, 2023. [3] RG Wellman, JR Nicholls, J Phys D: Appl Phys. 40 (2007) R293-R305 and Tribol. Int. 41 (2008) 657-662.

3:00pm **MA2-1-MoA-5 Influence of Coating Variables on the Steam Oxidation of Modified Si / $Yb_2Si_2O_7$ Environmental Barrier Coatings*, Kang Lee (ken.k.lee@nasa.gov)*,** *R. Webster, J. Stuckner, A. Garg, L. Wilson,* NASA Glenn Research Center, USA

Environmental barrier coatings (EBCs) have enabled the implementation of SiC/SiC ceramic matrix composites (CMCs) in gas turbines by protecting CMCs from H_2O. Improving the reliability of CMC components requires long-life EBCs and accurate EBC lifing. Steam oxidation-induced failure is one of the most critical EBC failure modes. NASA has developed modified Si / $Yb_2Si_2O_7$ EBCs by adding dopants such as Al_2O_3, mullite, and/or YAG ($Y_3Al_5O_{12}$) in the $Yb_2Si_2O_7$ topcoat, which reduce the parabolic oxidation rates by more than ten folds in steam. Modified EBCs have shown that oxidation kinetics are highly sensitive to the chemistry of SiO_2 oxide scale, which in turn is influenced by the chemistry of EBC and CMC. Plasma-sprayed silicate coatings contain a large amount of amorphous phase due the rapid quenching of molten droplets during the coating formation. Annealing is often employed to stabilize the EBC phase by crystalizing the amorphous phase prior to oxidation testing. Our study has shown that the effects of annealing on oxidation kinetics are influenced by the EBC chemistry. The current understanding of the complex relationship between selected EBC variables (EBC chemistry, CMC chemistry and annealing condition) and the EBC oxidation behavior will be discussed. Various analytical techniques such as scanning electron microscopy, x-ray diffractometry and transmission electron microscopy are used to help understand the relationship.

3:20pm **MA2-1-MoA-6 Effect of Pre-Oxidation on the Growth of Thermally Grown Oxide and High Temperature Durability of Thermal Barrier Coatings***, **Do Hyun Kim (dohyunkim@kims.re.kr)**, Y. Kang, H. Kwon, Y. Yoo, Y. Park, S. Lee,* Korea Institute of Materials Science, Republic of Korea

Thermal barrier coatings(TBCs) are widely applied in turbine components of modern jet engines and land base gas turbine to reduces the surface temperature of superalloy substrate. Typically, TBCs consist of a ceramic top coat with low thermal conductivity and an Al-rich and oxidation-resistant metallic bond coat. Upon exposure at high temperature over 1,000℃, a protective thermally grown oxide(TGO) layer, predominately α-Al_2O_3, is formed between the top coat and the bond coat, which is considered to be the most crucial factor that determine the durability and life of TBCs system. Therefore, to enhance the durability and reliability of turbine component in high temperature, the formation of a slow growing TGO is substantial.In this study, we performed the pre-oxidation of bond coat to improve the oxidation resistance of bond coat in TBCs. As coated bond coats were pre-oxidized with different heat treatment conditions of atmosphere, low oxygen, and vacuum for the initial formation of TGO, and then TBC samples were exposed to high temperature during isothermal oxidation. The results showed that the growth behavior of the TGO layer on the bond coat surface during isothermal oxidation was significantly changed by the pre-oxidation heat treatments. In order to explore the mechanism of the improved oxidation resistance of pre-oxidized bond coats, the chemical composition, phase constitutes and thickness of TGO(α-Al_2O_3 and spinel oxide), and microstructural changes of bond coat were characterized. Finally, furnace cycle test(FCT) were performed to evaluate the TBC lifetime.

4:00pm **MA2-1-MoA-8 Correlative Microscopy and AI-assisted Image Analysis Synergetic Approach on High Temperature Applications Coatings***, **Hugues Francois-Saint-Cyr (hugues.fsc@thermofisher.com)**,* Thermo Fisher Scientific, USA*; A. Scarpellini,* Thermo Fisher Scientific, Netherlands*; B. Winiarski,* Thermo Fisher Scientific, Czechia*; J. Yorston, R. Pelapur,* Thermo Fisher Scientific, USA

High-temperature applications coatings require the validation of a thorough checklist regarding their chemical and mechanical properties, as-deposited and within the environments they are designed for.

In order to gain a solid understanding of those complex structures, the use of correlative microscopy (CM) workflows provide a structured approach to integrating microscopy and analytical techniques, delivering a multi-dimensional and multi-modal view of the analyzed samples.

Beside the traditional CM approach where X-ray, Electron-beam, and Ion beam techniques complement each other, today engineers and scientists expect additional help from the image analysis (IA) linking those techniques. Namely, Artificial Intelligence (AI)-assisted IA has become a must-have, allowing specialists, and non-specialists alike, to quickly produce results.

Yet, the use of Deep-Learning (DL) as part of this process still requires setting up a meaningful ground truth, using a “human-in-the-loop” AI-assisted training steps to speed up time-to-results.

We illustrate the synergy between CM and AI-assisted IA by treating the example of a Thermal Barrier Coating (TBC) designed as an afterburner liner of a turboramjet engine.

This example was chosen because of its complexity where several ceramic layers (top coats, bond coats) together with metallic substrates were designed to maintain their efficiency at high temperatures and extremely oxidizing environments. Since their performance and durability are intimately linked to their microstructure and composition, the CM workflow encompasses broad ion beam (BIB) milling, Scanning electron microscopy (SEM) coupled with Energy Dispersive X-Ray Spectroscopy (EDS), as well as a cross-section using a Focused-Ion Beam (FIB) system.

A clean and easy to characterize cross-section has been automatically prepared by the CleanMill BIB, without user intervention. Combined and always-on SEM/EDS information, automatically delivered by ChemiSEM, has highlighted cracks, oxidation, interfaces, interphases and chemical variations within the various layers. With AI-assisted IA, as long as the specimen preparation is respectful of the sample integrity, researchers can now boost their CM efficiency level.

4:20pm **MA2-1-MoA-9 Characterization of SiO_2 Thermally Grown Oxide Kinetics and Stress Evolution of EBCs with Al-Containing Dopants***, **Michael Lance (lancem@ornl.gov)**, M. Ridley, B. Pint,* Oak Ridge National Laboratory, USA

SiC ceramic matrix composites (CMCs) are desirable for use in combustion environments to achieve higher turbine operating temperatures, although CMCs require environmental barrier coatings (EBCs) for protection from the gas environment. EBC systems are known to primarily fail through coating delamination via growth of a thermally grown oxide (TGO) at the EBC – silicon bond coat interface especially when exposed to steam, which accelerates the TGO growth rate. The TGO undergoes a phase transformation during thermal cycling, which results in stresses that may encourage EBC spallation. Yb-silicate EBCs with mullite and yttrium aluminum garnet (YAG) dopant additions were deposited on SiC substrates with a Si intermediate bond coating and exposed to thermal cycling in flowing steam.The impact of Al dopant additions on the TGO growth rate and the impact of the SiO_2 phase transformation were assessed. Photo-stimulated luminescence spectroscopy (PSLS) was used to characterize the Al-containing phases and to measure stress evolution in the EBC following exposure using the stress-induced peak shift of the R-lines of mullite and YAG. Raman microscopy was used to map the Yb-silicate phases in the EBC and the SiO_2 phases in the TGO following exposure. Wavelength dispersive x-ray spectroscopy (WDS) tracked the concentration of Al in the EBC and the TGO with exposure time. This research was funded by the Advanced Turbine Program, Office of Fossil Energy and Carbon Management, U.S. Department of Energy.

4:40pm **MA2-1-MoA-10 Promising SiOxNyCz Coatings for Glass Protection in Aggressive Chemical Media***, **Farah Inoubli (farah.inoubli@cnrs-orleans.fr)**, B. Diallo,* CNRS/Université D'Orleans, France*; K. Topka,* Air Liquide Laboratories, Japan*; T. Sauvage,* CNRS/Université D'Orleans, France*; R. Laloo, V. Turq,* CNRS-CIRIMAT, France*; B. Caussat,* CNRS, France*; N. Pellerin,* CNRS/Université D'Orleans, France

Despite of its high chemical inertia, Glass still interacts when exposed to aqueous solution. This reactivity could be problematic when it concerns particularly food and medicines containers. Thus, one of the biggest challenges that pharmaceutics and food industries are facing consist of limiting this interaction. But how?

In this work, we expose very promoting results on chemical vapour deposited silicon oxycarbonitride coatings in terms of chemical resistance in front of extremely aggressive aqueous solutions.

Different precursors were used leading to various film compositions with tunable properties. Pure silica films were obtained from tetraethylorthosilicate (TEOS) precursor. However, tris(dimethylsilyl)amine (TDMSA) and a novel proprietary trisilylamine-derivative precursor (TSAR) developed and provided by Air Liquide led to silicon oxycarbonitride films with different oxygen, nitrogen and carbon contents, depending on the deposition parameters (precursor, gas flow rates ratios and deposition temperatures td).

Films deposited on the two sides of a flat silicon monocrystalline substrate were subjected to moderately long alteration of one month in a citric acid aqueous solution with pH adjusted to 8 and under thermal conditions of 80°C. Their chemical resistance was assessed by tracking the structural evolution, the changes in the elemental composition and the calculation of the dissolved thickness if it exists. A wide range of characterization techniques were used for this purpose, namely ion beam analysis such as ERDA, RBS and NRA techniques, FTIR spectroscopy, XPS. SEM and AFM imaging techniques were also used to explore the changes occurring to surface state of our layers after exposure to the aqueous solution. Finally, nanoindentation tests have been done to verify any alteration happening to the hardness and the elasticity of the films. Very promising results were found especially for films both concentrated in N and C with a very high corrosion resistance even in such extreme chemical and thermal conditions.

To be closer to reality, pharmaceutical type I glass vials that have been successfully coated with SiOxNyCz thin layer, were tested according to the severe screening conditions of the United States Pharmacopeia USP<1660> chapter. They withstood to the test by preventing the degradation of the glass matrix with an average improvement factor of about 95% compared to a bare vial.

This excellent performance can make these materials a real key for the future of the pharmaceutical industry and can be transferable to multiple applications of surface coating by adaptation of the deposition conditions.

5:00pm **MA2-1-MoA-11 Influence of Gas Composition on the Growth Behavior of CVD Processed HfC Coatings for Ultra-high Temperature Application***, **Byung-Hyuk Jun (bhjun@kaeri.re.kr)**, J. Lee, D. Kim, H. Lee,* Korea Atomic Energy Research Institute, Republic of Korea

Refractory metal carbides for thermal protection under ultra-high temperature condition have attracted much attention due to their potential applications in field of advanced aerospace hypersonic vehicles, such as rocket and scramjet components. Hafnium carbide (HfC) has high melting point of 4163 K, low thermal conductivity, high mechanical properties, excellent resistance to oxidation and thermal corrosion, which make it very attractive for coating applications in improving the ablation resistance of carbon/carbon composites in extremely combustion environment. The deposition of coatings was performed in a hot-wall type low pressure CVD furnace under the working pressure of 50 Torr. $HfCl_4$-C_3H_6-H_2-Ar system was applied to deposit HfC coatings on graphite substrate. $HfCl_4$ powder (99.9%) was used as the hafnium source and C_3H_6 instead of CH_4 as the carbon source was used to lower the deposition temperature. H_2 and Ar were used as reducing gas and diluting gas, respectively. In this work, a special powder feeder was designed to supply $HfCl_4$ powder into the reaction zone constantly. The delivery rate of $HfCl_4$ powder was fixed to be about 1 g/min. The gas composition of $HfCl_4$-C_3H_6-H_2-Ar and deposition temperature were mainly varied to optimize the HfC deposition condition for the purpose of obtaining dense and superior oxidation resistant HfC coatings with high deposition rate. Phase, crystal structure and crystallinity of the HfC coating layers were investigated by X-ray diffraction, and the results showed good crystalline phase with different preferred orientations depending on the deposition condition. Surface morphology and microstructure for the plane and cross-section were observed by a scanning electron microscopy. Raman spectroscopy analysis was performed to find out the C-deficit/-excess of HfC coatings. Quantitative analysis of the HfC composition including impurities inside coating layer was performed using Rutherford backscattering spectrometry (RBS) and elastic recoil detection-time of flight (ERD-TOF) methods. Mechanical properties of the HfC coatings including hardness and Young's modulus were examined with nanoindentor. These results of the growth behavior depending on the deposition parameters including gas composition are described.

5:20pm **MA2-1-MoA-12 Tribological Insights of Nickel – and Cobalt – Based Alloys in Extreme Conditions***, **Pantcho Stoyanov (pantcho.stoyanov@concordia.ca)**,* Concordia University, Canada

Nickel- and cobalt – based alloys are widely used as structural components in demanding environments due to their excellent stability (i.e., resistance to mechanical and chemical degradation) at elevated temperatures. These superalloys were primarily developed to meet the demand of jet engine and industrial gas turbine engine blades operating at extreme temperature ranges. Unfortunately, while intensive alloy and process development activities for these high-temperature alloys have been performed over the last few decades, their tribological behavior (i.e., friction and wear) has received little attention. With the increasing demand in temperature and spread of application of these alloys to other static and dynamic components in the engine, there is a clear need for a better understanding of their tribological behavior.

The main purpose of this study was to critically investigate the friction and wear behavior of Co- and Ni- based materials under low and high temperature environmental conditions. The ultimate goal was to identify the underlying interfacial processes leading to the observed tribological behavior. Thus, a series of studies on the friction and wear behavior of Ni-based and Co-based superalloys was conducted using a custom build high temperature fretting wear apparatus.In addition, ex situ analysis was performed on the worn surfaces using XPS, AFM, and cross-sectional SEM imaging of the near-surface region. The results showed a clear correlation between the third body formation process (e.g. oxide layer formation, transferfilms) and the tribological behavior of the superalloys as a function of temperature. The low friction and wear of these material systems at elevated temperatures is attributed to the formation of a lubricious 'glaze layer'. Depending on the contact conditions, stable lubricous oxides will form above a critical temperature and provide sufficient wear resistance as long as the system continuously operates at these temperatures.

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