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VERIFICATION OF AN EBC'S PROTECTIVE CAPABILITY BY FIRST-STAGE EVALUATION IN A HIGH TEMPERATURE, HIGH-PRESSURE FURNACE

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ABSTRACT

High-temperature, high-pressure exposure furnaces (commonly referred to as Keiser Rigs) have been used successfully to evaluate the ability of environmental barrier coatings (EBCs) on continuous fiber-reinforced ceramic matrix composites and monolithic Si_3N_4 to protect the underlying substrate at high temperatures and H_2O pressures. The ORNL rig provides for a relatively inexpensive way to conduct high sample throughput, first-stage evaluation of an EBCs protective capability on small ceramic specimens under a range of temperatures, pressures, and H_2O contents. The exposure of the EBCs in the Keiser Rig is coupled with extensive microstructural analysis to evaluate EBC failure and degradation mechanisms.

INTRODUCTION

There has been a significant amount of research during the past several years in the area of environmental barrier coating (EBC) development for the protection of Si-based ceramic composite and monolithic materials used in combustion environments. The exposure of such materials to the high temperature and high water-vapor pressures (>1atm) typical of gas turbine combustion environments results in rapid oxidation [1,2] and surface recession due to SiO_2 volatilization.[3,4] For example, continuous fiber-reinforced ceramic composite (CFCC) combustor liners were field-tested in a Solar Turbines Centaur 50S SoLoNOx engine at the Chevron, Bakersfield, CA test site as part of the U.S. Department of Energy's Ceramics for Stationary Gas Turbines (CSGT) Program. The first four field tests were conducted using uncoated SiC/SiC CFCC inner and outer liners.[5-7] Excessive composite damage was observed on the liners after each of the first four engine tests and high surface recession rates were measured for the uncoated SiC/SiC liner materials.[8,9] These results were consistent with published values for the recession of SiC materials at elevated water-vapor pressures.[2-4,10] As a result of excessive microstructural damage and high recession rates, none of the uncoated SiC/SiC composite liners were used in an engine for more than ~5000 h. It was determined that an EBC would be necessary to protect the SiC/SiC CFCC liners so as to achieve the required lifetimes in an engine.

More recently, inner and outer SiC/SiC liners having protective oxide-based EBCs (based on the barium strontium aluminosilicate (BSAS) + mullite system, which has been described in greater detail elsewhere [11,12]) were run in the same engine at the Bakersfield, CA test site and in another Centaur 50S engine located at the Malden Mills co-generation site in Lawrence, MA. The liners were in these engine tests for 13,937 h [13,14] and 15,144 h,[15] respectively, before being removed to evaluate environmental damage. In both cases, the engine test was stopped due to the formation of small holes or extended cracks, which were observed during routine boroscope inspections of the liners. Although holes and cracks formed, most of the gas-path surface on both the inner and outer liner were still coated with intact EBC and no loss of substrate (SiC/SiC composite) material due to recession occurred in these areas. The presence of the EBC on the gas-path surfaces clearly protected the CFCC liners from the detrimental effects of water-vapor, formed during the combustion process, for much greater times. Without an EBC, the projected lifetimes for the SiC/SiC combustor liners (100% material consumption or recession) would not have exceeded ~10,000 h. However, there are still some problems with the current state-of-the-art EBCs, such as constituent phase stability and volatilization, as described in detail in Ref. 13. The development and implementation of improved EBCs for use in high water-vapor-containing environments has become a critical need in order for ceramic materials to be considered for extended use as hot-section components in gas turbines or microturbines.

In order for a material to be an effective EBC for use in combustor environments for extended time periods (>25,000 h), the EBC material must (1) not interact with the underlying substrate, (2) be thermally stable at the expected use temperature (1100°C-1350°C), (3) provide an effective diffusion barrier to oxidizing species (primarily water), and (4) be volatilization-resistant. Because of the low gas-flow velocities in the Keiser Rig (3-20 cm/min.), volatility cannot be fully

assessed. However, factors (1)-(3) can be readily evaluated via cross-sectional microstructural examination after exposure in the Keiser Rig. To demonstrate the viability of the Keiser Rig exposures for simulating combustor-like environments, characterization results from the exposures of various EBC/substrate systems for thousands of hours at temperatures ranging from 1200-1315°C and high water-vapor pressures, 0.3-2.0 atm, will be presented here.

EXPERIMENTAL PROCEDURES

All laboratory exposures were conducted in ORNL's high-temperature, high-pressure facility. These Keiser Rigs primarily consisted of a large box furnace containing several ceramic (SiC) pressure vessels and a multiple-flow gas-supply/manifold system, as shown in Figure 1.[16] Sample size varied (depending on planned post-exposure evaluation), but the preferred size was 2.5 cm X 5 cm with a small hole drilled near one end such that each sample could be hung on the outside of a slotted alumina tube using Pt wire.[8] A typical EBC/Si_3N_4 coupon is shown in Figure 2. Exposures were conducted under a variety of conditions which best simulated the temperature, pressure, and principal reactive gas species of the combustor environments for each potential application. For example, to evaluate materials for use in a Solar Turbines Centaur 50S engine, all Keiser Rig exposures of EBC/SiC-SiC CFCCs were conducted at 1204°C (2200°F), 1.5 atm H_2O (balance air), and 10 atm total system pressure. With increased interest in higher temperature capability for some EBC formulations, exposures of EBC/CFCC coupons were also conducted at temperatures of 1250°C and 1315°C. Silicon nitride is currently being evaluated for use in hot-section components; specimens were typically exposed in the temperature range 1150°C-1315°C and water-vapor pressures ranging from 0.3-2.0 atm. The ORNL furnace holds up to six vertically-loaded 9 cm dia. X 122 cm SiC tubes. A slow-flow gas supply system (3-20 cm/min) can provide a pressurized mixture of steam and premixed gas independently to each SiC tube and each tube can hold up to 10 hanging specimens. Exposures were normally conducted for 500 h, after which time the specimens were carefully removed and sectioned for microstructural analysis. Selected specimens were then placed back in the furnace for additional exposure under the same conditions. If an EBC was ineffective, 500 h was usually a sufficient exposure time in a Keiser Rig to fully evaluate its lack of potential.

All EBC/CFCC or EBC/Si_3N_4 materials to be exposed in an ORNL furnace were microstructurally characterized in the as-processed condition for comparison with the same material after exposure. A ~0.3 cm section was cut from the bottom (end away from the hole) of representative as-processed coupons. The cut pieces were polished in cross-section in order to image the interface between the EBC and ceramic substrate. Pre- and post-exposure specimens were imaged in a scanning electron microscope (SEM) equipped with a backscatter detector and compositionally analyzed using an electron probe microanalyzer (EPMA). In this way, reaction products (or lack thereof) that formed within the EBC or at the EBC/ceramic interface during exposure, as well as any other microstructural changes, were identified, measured with respect to their spatial dimensions, and compared to as-processed EBCs or other exposed EBCs. An advantage of using the coupon size specified above is that a 2.5 cm X 5 cm coupon can readily be sectioned into three four-point-bend bars to test the EBC surface in flexure so as to evaluate the effects of these environmental exposures on mechanical properties.

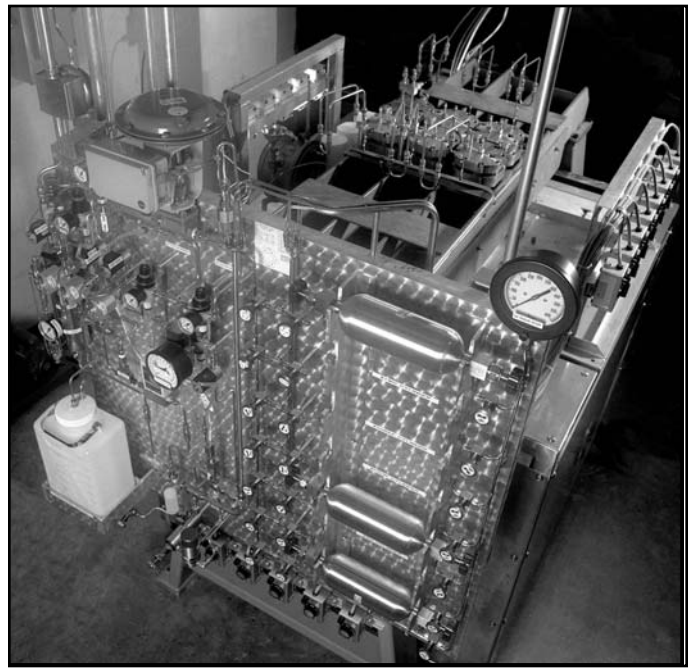

Fig. 1. ORNL's Keiser Rig consists of a large box furnace and independent gas supply systems for each SiC tube.

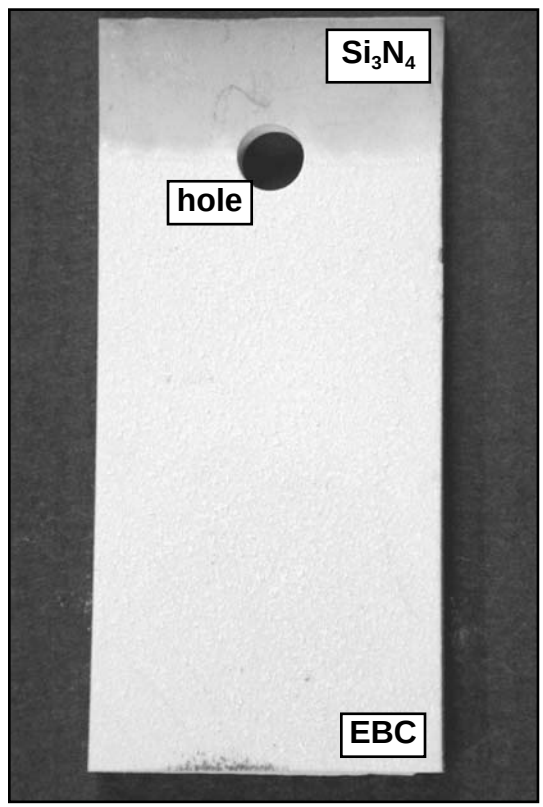

Fig. 2. Typical 2.5 cm X 5 cm EBC/Si_3N_4 coupon used for Keiser Rig exposures.

RESULTS AND DISCUSSION

While exposures in the slowly-flowing gas of a Keiser Rig cannot be used to *directly* reproduce intermediate- and high-velocity gas turbine or microturbine operating conditions, the high H_2O pressures have been used to reproduce the microstructural damage and accelerated recession rates observed during engine testing of SiC and SiC/SiC composites.[1,2,10,13] In fact, exposures in the Keiser Rig are ideally suited for evaluating damage accumulation below an EBC (i.e., evaluating the effectiveness of the EBC) since gas velocity is not a factor away from the surface in contact with the gas-flow path. Slow-flow conditions obviously exist at the EBC/substrate interface.

The BSAS (top coat)/(mullite+BSAS) or mullite (intermediate layer)/Si (bond coat) EBC system, which were optimized by United Technologies Research Center for the Solar Turbines CFCC combustor liner application,[11] were some of the first EBC/CFCCs exposed in the Keiser Rig. Two different EBC formulations were characterized after long-term exposure at 1200°C (>6500 h) for comparison with similarly-processed EBCs applied to combustor liners for testing at the Chevron engine-test site in Bakersfield, CA.[13,14] To evaluate the BSAS/mullite/Si EBC effectiveness as a diffusion barrier to water-vapor, cross-sections of the exposed EBC/CFCC were taken following sequential 500 h exposures in the Keiser Rig. As shown by the pre- and post-exposure images of the interfaces in Figures 3a and 3b, respectively, significant oxidation of the Si bond coat was observed after only 500 h and a layer of silica had formed (designated by arrows in Figure 3b). When the formulation of the EBC was changed to BSAS/(BSAS+mullite)/Si, much less oxidation of the Si bond coat below the EBC was observed, as shown in Figures 4a and 4b. Under these conditions, a silica layer thickness <<1 μm was observed (shown by arrows in Figure 4b). These results clearly showed that the "mixed layer" EBC in Figure 4a was a superior barrier to oxidant diffusion with respect to the "dual layer" EBC shown in Figure 3a. The observed differences between the two EBC formulations described above were due to (1) processing improvements that increased the density of the EBC layers (especially the BSAS top coat) for the BSAS/(BSAS+mullite)/Si system and (2) significant reduction in the density and extent of processing-induced cracks and microcracks for this system compared to the one with the mullite intermediate layer. The composite nature of the mixed intermediate layer can also act to reduce crack extension.

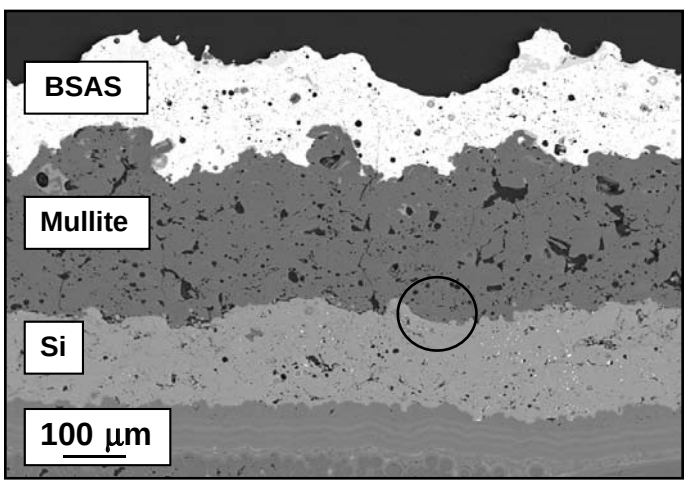

Fig. 3a. Typical as-processed BSAS/mullite/Si EBC. The circle denotes sub-surface interface of interest.

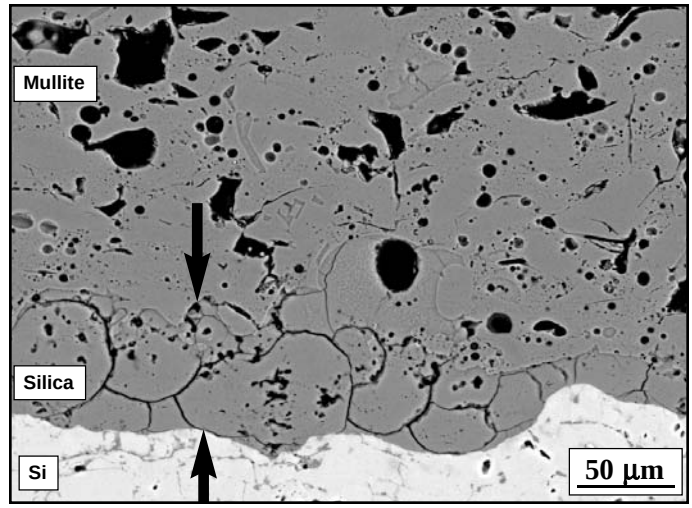

Fig. 3b. SEM image of SiO_2 formed at Si/mullite interface (~50μm thick) in BSAS/mullite EBC after 1500h at 1200°C and 1.5atm H_2O.

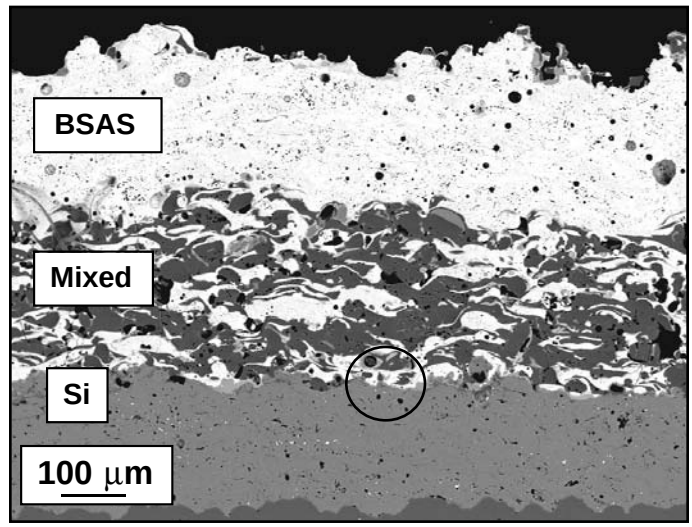

Fig. 4a. Typical as-processed BSAS/(mullite+BSAS)/Si EBC. The circle denotes sub-surface interface of interest.

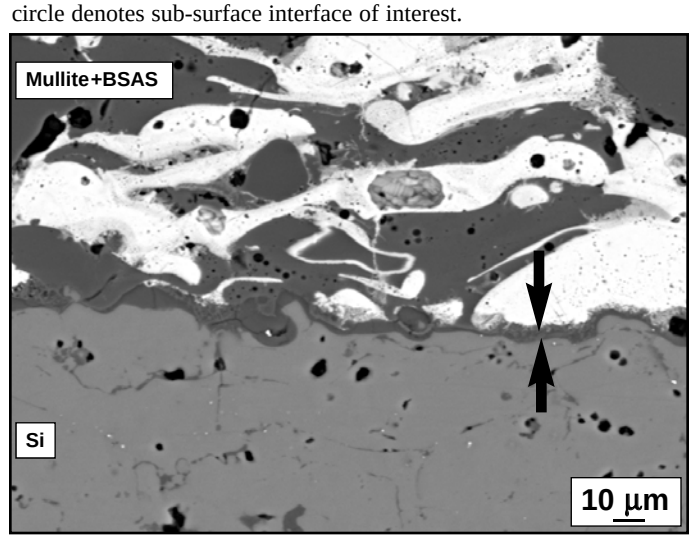

Fig. 4b. SEM image of SiO_2 formed at Si/(mullite+BSAS) interface (<10μm) in EBC after 1500h at 1200°C and 1.5atm H_2O.

Imaging of the EBC/substrate interface in cross-section following Keiser Rig exposure can be used to evaluate the effect of EBC processing defects on the ability of an EBC to provide protection to the underlying substrate. As shown in Figure 5, when defects, such as excessive interconnected porosity or through-thickness cracks, were present in one or more layers of an as-processed EBC, a rapid path for oxidant transport to the substrate was provided. In these localized areas, much thicker silica formed during exposure, as shown by arrows in Figure 5. High defect densities in the EBC will cause accelerated degradation below the surface, with degradation and material recession rates approaching those of uncoated ceramics. Minimizing processing defects such as interconnected porosity and cracks is crucial for enhancing an EBC's ability to protect a ceramic surface.

Silicon nitride is a leading ceramic material for hot-section components in microturbines. However, Si_3N_4 also exhibits accelerated oxidation in the presence of water-vapor [17,18] and, thus, an EBC is required to prevent the oxidation and silica volatilization that would result in excessive and rapid Si_3N_4 recession during operation of advanced, high-efficiency microturbines at high temperatures and pressure ratios.

The thermal stability of EBCs on Si_3N_4, as well as subsurface damage accunulation, were evaluated for several EBC systems at a temperature of 1315°C and an H_2O pressure of 2 atm (representing maximum expected temperatures and H_2O pressures for a microturbine.) For part of this work, a proprietary coating was applied to AS800 Si_3N_4 coupons (AS800 is manufactured by Honeywell Ceramic Components, Inc.) by either physical vapor deposition (PVD) or air plasma spraying (APS). A typical as-processed PVD EBC on Si_3N_4 is shown in Figure 6a. The columnar growth of the EBC grains was typical of that observed for PVD processed coatings. While the coating was relatively dense near the EBC/Si_3N_4 interface, a significant amount of porosity was observed between the columns away from the interface. After exposure in the Keiser Rig for 500 h, severe thermal degradation of the EBC was observed, as shown in Figure 6b. Extensive sintering of the columnar grains occurred and large gaps formed between the sintered columns. Clearly, the open structure of the sintered coating rendered it non-protective. Evidence for the ineffectiveness of this particular EBC on Si_3N_4 was found below the EBC surface at the EBC/Si_3N_4 interface where a 15-20 μm layer of silica formed during exposure. In fact, the thickness of the silica layer formed below the EBC was nearly identical to the thickness of the silica layer formed on uncoated AS800 Si_3N_4 exposed under the same Keiser Rig conditions, as shown in Figures 7a and 7b for exposed EBC/Si_3N_4 and uncoated Si_3N_4, respectively.

When the same proprietary EBC was plasma sprayed on AS800 Si_3N_4, the resulting EBC appeared denser and was relatively uniform in thickness, as shown in Figure 8a. However, after exposure in the Keiser Rig for 500 h under the same exposure conditions used for the PVD-coated Si_3N_4, similar microstructural changes took place. Sintering and extensive pore generation occurred during exposure at 1315°C, as shown in Figure 8b, and a ~20 μm silica layer formed below the EBC at the EBC/Si_3N_4 interface. These observations indicated that the proprietary formulation of this particular EBC was not only thermally unstable at the proposed use temperature of 1315°C, but was also ineffective as a diffusion barrier to oxidizing species. This EBC formulation is currently being evaluated for use at lower temperatures.

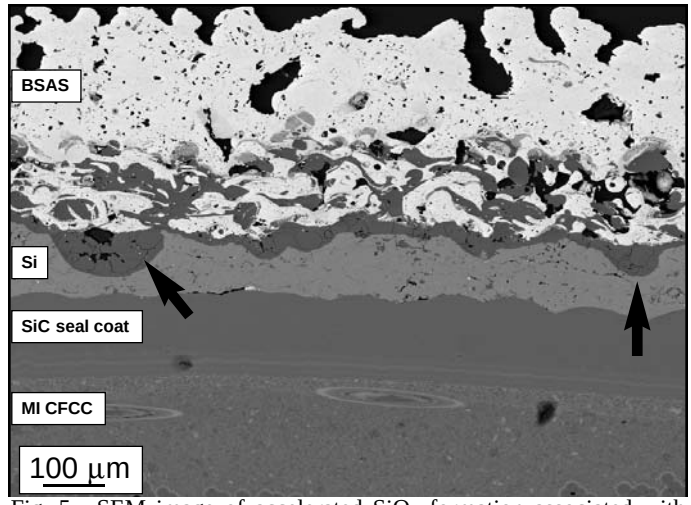

Fig. 5. SEM image of accelerated SiO_2 formation associated with defects (porosity) in BSAS EBC (5000 h at 1200°C and 1.5atm H_2O.)

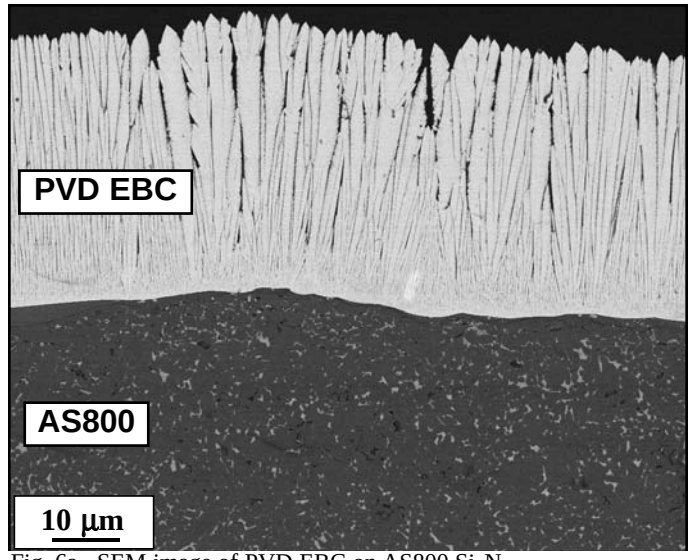

Fig. 6a. SEM image of PVD EBC on AS800 Si_3N_4.

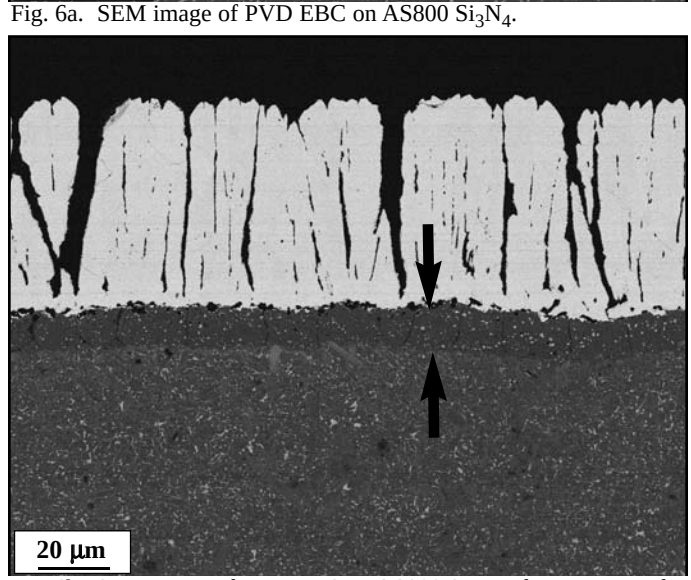

Fig. 6b. SEM image of PVD EBC on AS800 Si_3N_4 after exposure for 500 h at 1315°C and 2.0 atm H_2O. Arrows denote silica layer.

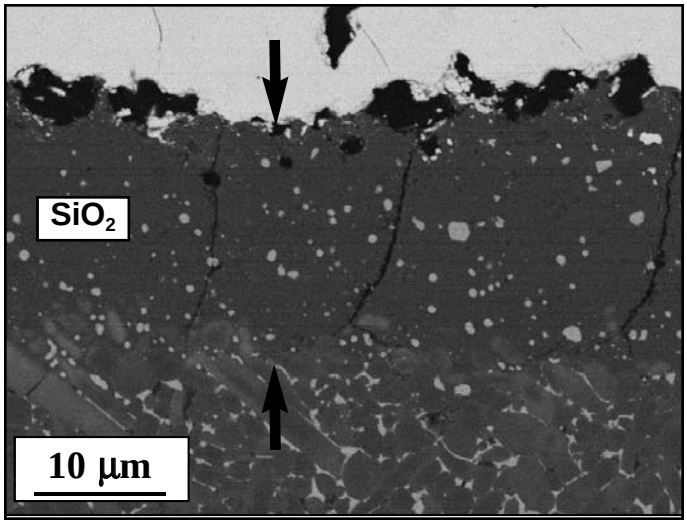

Fig. 7a. Silica formed beneath PVD EBC on AS800 Si_3N_4 after exposure in Keiser Rig for 500 h at 1315°C and 2.0 atm H_2O.

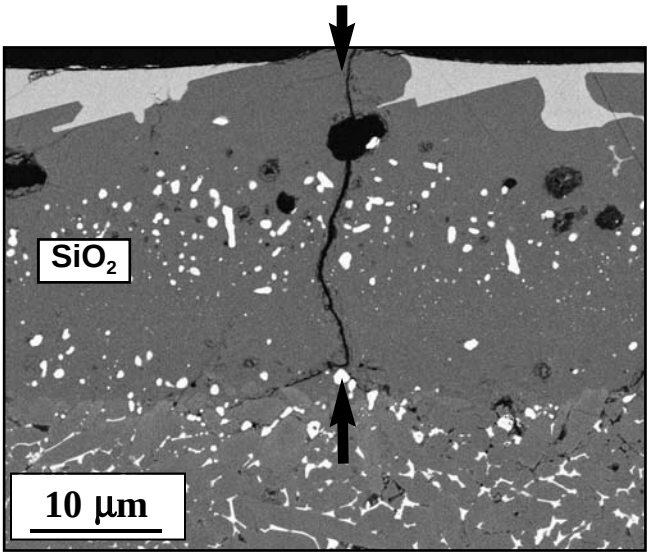

Fig. 7b. Silica formed on surface of uncoated AS800 Si_3N_4 after exposure in Keiser Rig for 500 h at 1315°C and 2.0 atm H_2O.

Recently, the BSAS/(BSAS+mullite)/Si layered EBC discussed above was plasma sprayed onto AS800 Si_3N_4. An EBC/Si_3N_4 coupon was exposed for ~3500 h in the Keiser Rig at 1200°C and 1.5 atm H_2O and exhibited little evidence of any sub-surface oxidation, as shown in Figure 9a. Most of the Si bond coat experienced minimal oxidation, as evidenced by the fact that <<10 μm of silica formed on the Si during exposure for the extended time at 1200°C. The only areas of the Si that exhibited enhanced oxidation were those areas associated with through-thickness cracks in the EBC, as shown in Figure 9b. In these areas, significant Si oxidation occurred at the base of the cracks (compare area A on Figure 9b with area B). However, minimizing the cracks has proved to be difficult because of the coefficient of thermal expansion mismatch between the EBC constituents and Si_3N_4.

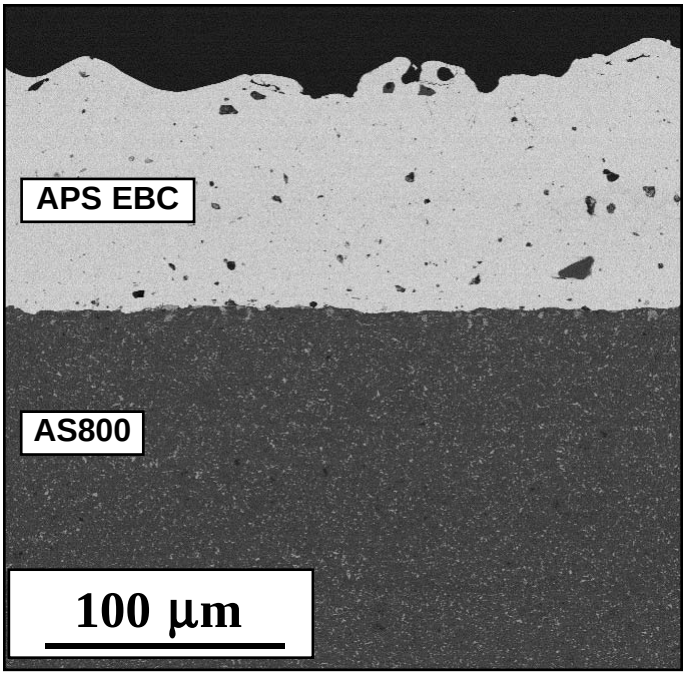

Fig. 8a. SEM image of a plasma sprayed EBC on AS800 Si_3N_4.

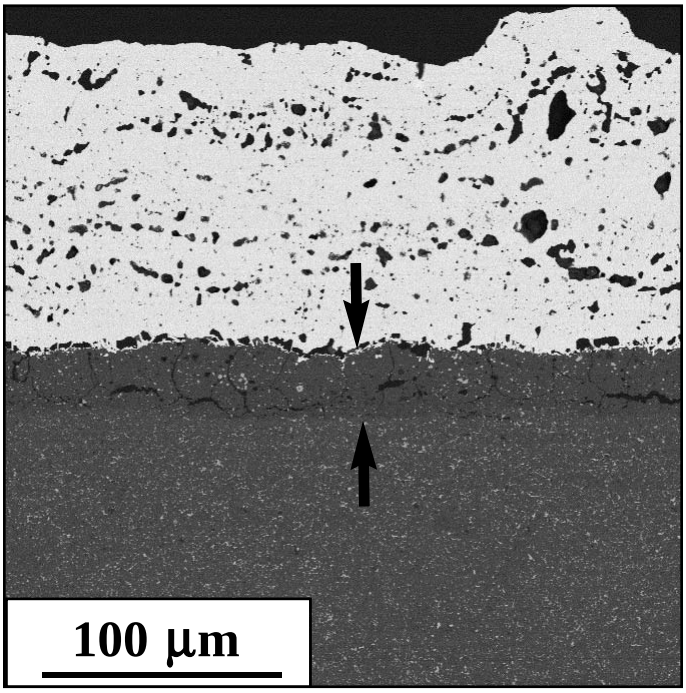

Fig. 8b. SEM image of a plasma sprayed EBC on AS800 Si_3N_4 after exposure in Keiser Rig for 500 h at 1315°C and 2.0 atm H_2O. Arrows denote silica layer.

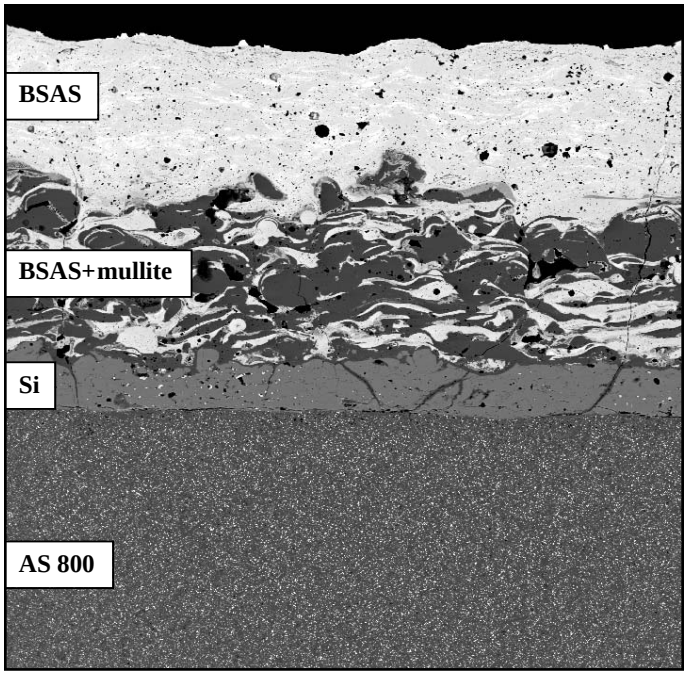

Fig. 9a. SEM image of BSAS/(BSAS+mullite)/Si EBC on AS800 Si_3N_4 after 2000 h at 1200°C and 1.5 atm H_2O.

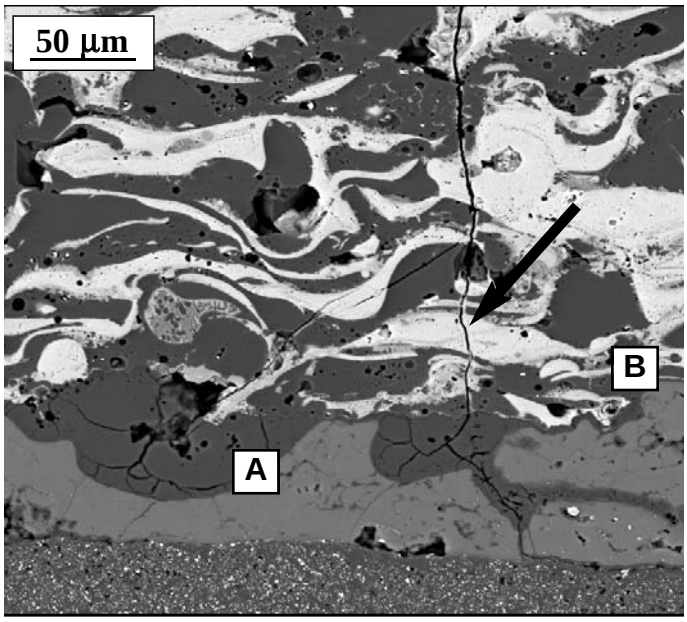

Fig. 9b. SEM image of BSAS/(BSAS+mullite)/Si EBC on AS800 Si_3N_4 after 2000 h at 1200°C and 1.5 atm H_2O. Through-thickness cracks in the EBC lead to localized enhanced oxidation of Si.

CONCLUSIONS

A high-temperature, high-pressure furnace (the Keiser Rig) has been shown to be an effective facility for exposing candidate EBCs to simulated gas turbine and microturbine combustor environments. While the Keiser Rig cannot directly reproduce the effects of high gas-velocity on EBC volatilization in a turbine engine, exposures in the furnace at high water-vapor pressures have accurately reproduced the microstructural damage and recession rates observed when extended defects in EBCs allow ingress of oxidants to the substrate. Thus, Keiser Rig-type exposures can effectively assess the ability of EBCs to provide a barrier to oxidant transport as well as their inherent thermal stability (in the absence of volatility.) To date, EBC formulations have been evaluated on several CFCC and Si_3N_4 substrates at temperatures ranging from 1100°C-1350°C and water-vapor pressures of 0.3-2.0 atm.

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