Fracture mechanisms of ytterbium monosilicate environmental barrier coatings during cyclic thermal exposure

Bradley T. Richards a, Stephen Sehr b, Foucault de Franqueville c, Matthew R. Begley b, Haydn N.G. Wadley a,⁎

a Department of Materials Science and Engineering, University of Virginia, Charlottesville, VA 22903, USA
b Department of Mechanical Engineering and Materials, University of California, Santa Barbara, Santa Barbara, CA 93106, USA
c Département de Génie Mécanique, E.N.S. Cachan, 61 Avenue du Président Wilson, 94230 Cachan, France

A R T I C L E   I N F O

Article history:
Received 20 July 2015
Received in revised form 9 October 2015
Accepted 12 October 2015
Available online xxx

Keywords:
Environmental barrier coatings
Ytterbium silicates
Steam erosion
Channel cracking
Finite element analysis

A B S T R A C T

A recently optimized air plasma spray process has been used to deposit a model tri-layer Yb2SiO5/Al6Si2O13/Si environmental barrier coating (EBC) system on SiC substrates using low power deposition parameters to reduce silicon losses, improve interface adherence and decrease defect concentrations. During cooling, tensile stresses developed in the ytterbium monosilicate layer since its coefficient of thermal expansion exceeded that of the substrate. These stresses drove vertical mud cracks that underwent crack branching either within the Al6Si2O13 (mullite) layer or at one of its interfaces. Upon subsequent thermal cycling between temperatures of 1316 °C and 110 °C in a 90% H2O + 10% O2 environment, the branched mud cracks propagated into the Si bond coat and grew laterally along the midplane of this layer. The faces of the branched cracks were accessible to the steam environment resulting in the formation of a cristobalite surface layer, which mud cracked due to repeated β ↔ α cristobalite phase transformations during thermal cycling. After extended cycling, these cracks linked to cause partial spallation of the coating. The crack branching phenomenon was analyzed using finite element analysis, and the crack trajectory was assessed in terms of the crack driving force controlling kinking from the tip of the mud cracks. A comparison between the present optimized deposition process (performed at low deposition power) with a previous study of a non-optimized process (performed at high power) highlights the importance of reducing the crack driving force and controlling microstructural defects. Finite element simulations provided an effective means to quantify the susceptibility of coating design to failure by the various cracking modalities.

© 2015 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

1. Introduction

Substantial gains to the fuel efficiency and specific power output (thrust) of future gas turbine engines could be achieved by increasing the temperature within the engine core [1–4]. However, this requires the use of new materials with higher maximum use temperatures than current superalloys. The most promising candidates are ceramic matrix composites (CMCs) based on SiC matrices reinforced with BN-coated SiC fibers [5–11]. While their high temperature creep strength offers much promise, they are susceptible to fiber embrittling interactions (pesting) at temperatures between 700 and 900 °C [12–18]. In gas turbine environments, they also suffer rapid recession at temperatures of 1200 °C and above. This arises from water vapor reactions with the silica layer that forms on SiC, resulting in the formation of gaseous silicon hydroxides such as Si(OH)4 [19–23]. The use of SiC/SiC composites in engines therefore requires the development of a protective environmental barrier coating (EBC) system [24–31].

An EBC system should have a low recession rate and be thermochemically stable in engine environments. It must also provide complete surface protection from oxidizing species penetration (by either gas phase permeation through pinholes/cracks or solid-state diffusion through the coating), remain adherent to the substrate during prolonged thermal cyclic exposures and thermal shock loading. A tri-layer coating consisting of a silicon bond coat applied to the SiC substrate, a mullite (Al6Si2O13) intermediate layer, and an ytterbium monosilicate (Yb2SiO5, YbMS) topcoat has recently attracted significant interest [26,27,32–34]. The bond coat is
intended to impede transport of any oxygen or water vapor that penetrates the outer coating layers by forming a protective thermally grown oxide (TGO). This TGO reaction consumes oxidizing species that reach the bond coat, and creates a diffusion barrier to delay the transport of oxidizing species to the substrate. The intermediate $\text{Al}_6\text{Si}_2\text{O}_{13}$ (mullite) layer serves as an oxidizing element diffusion barrier while also preventing potential solid-state reactions between thermally grown silica on the bond coat and the topcoat. The YbMS topcoat serves as a low silica activity compound

EBC systems are usually deposited using an air plasma spray (APS) process. A recent study has used high deposition power and a large plasma torch standoff distance to deposit YbMS topcoat and mullite layers with a thickness of 75 $\mu$m and a highly porous silicon bond coat with a thickness of 100 $\mu$m, Fig. 1(a) [32]. Significant SiO loss from the YbMS layer (and mullite) was found to occur during plasma heating of the powder resulting in a topcoat that included a significant volume fraction of Yb$_2$O$_3$ (and the presence of excess Al$_2$O$_3$ platelets in the mullite). The coefficient of thermal expansion (CTE) of the YbMS and (to a lesser extent) mullite layers was significantly higher than that of the SiC substrate, and resulted in mud cracking of the ytterbium monosilicate and mullite layers after stabilization annealing at 1300 °C, Fig. 1(a). These mud cracks had an average spacing of 280 $\mu$m, and vertically penetrated both the YbMS and $\text{Al}_6\text{Si}_2\text{O}_{13}$ layers before arresting at the $\text{Al}_6\text{Si}_2\text{O}_{13} – $ Si interface.

During steam cycling, the presence of these mud cracks led to rapid localized oxidation (and local steam erosion) of the bond coat, Fig. 1(b), and its early delamination failure, in part due to the low adhesive strength of the Si–SiC and $\text{Al}_6\text{Si}_2\text{O}_{13} – $ Si interfaces (a result of bond coat oxidation during spray deposition in air) [32]. The rapid failure was strongly influenced by the formation of a $\beta$-cristobalite ($\text{SiO}_2$) thermally grown oxide (TGO) upon the surface of the Si bond coat, both at the tips of mud cracks and at the environment exposed side edges of the samples. During the cooling phase of each thermal cycle, the cristobalite TGO underwent a reversible $\beta \rightarrow $ $\alpha$ phase transformation at $\approx 220^\circ$C that was accompanied by a 4.5% decrease in volume during cooling [35–37]. The repetition of this reversible phase transformation during thermal cycling severely mud cracked the TGO layer itself and resulted in loss of its oxidation protective capability. Rapid thickening of the TGO was then observed, and was accompanied by development of high stresses that were relieved by delamination fracture initiated from the edge of the samples [32].

Recent studies have indicated that the plasma spray parameters used for application of the coating can significantly influence the composition and microstructure of the coating layers, as well as the defects incorporated within them, and this in turn could influence the failure mechanisms [32–34]. Here, the same YbMS/$\text{Al}_6\text{Si}_2\text{O}_{13}$/Si tri-layer EBC system studied previously [32] was APS deposited onto SiC substrates using lower power plasma spray parameters optimized to reduce the loss of SiO during deposition, decrease the porosity in the three layers and improve the $\text{Al}_6\text{Si}_2\text{O}_{13} – $ Si and Si–SiC interfacial adherences. The structure of the coatings and their failure mechanisms during steam-cycling are then explored both experimentally and via thermomechanical simulations, and compared with those observed previously for the same material system (but different layer thicknesses) deposited under different conditions.

2. Experimental approach

2.1. Coating deposition

Tri-layer Yb$_2$SiO$_3$/Al$_6$Si$_2$O$_{13}$/Si coatings were deposited onto the grit blast roughened, 25.4 mm $\times$ 12.7 mm surface of six 4.8 mm thick $\alpha$-SiC Hexoloy™ substrates (Saint Gobain Ceramics, Niagara Falls, NY) with the geometry shown in Fig. 2. The APS deposition system used a Praxair SG-100 torch with a model 02083-175 anode (implementing internal powder injection), a standard model 02083-120 cathode and a model 03083-112 gas injector. The deposition parameters used for each layers are given in Table 1, while Table 2 provides layer thickness (including those for the previous (high power) study) [32] and estimates for fully dense and typically porous moduli of APS coatings.

A recently optimized deposition process developed by Richards et al. [34] was used for the present study. For a full description of the tri-layer deposition process, the reader is referred to Richards et. al. [34]. Briefly, the corners of the $\alpha$-SiC test coupons were rounded, and the side edges of the coating deliberately extended to cover the sides of the test coupons to reduce the propensity for edge initiated delamination. The deposition of all layers was performed at 1200 °C with each layer requiring roughly 10 s to deposit. Most importantly, an Ar/H$_2$ reducing gas mixture was continuously flowed through the high temperature deposition furnace to reduce oxidation of the substrate during preheating, and of the Si bond coat during its deposition. After deposition of the Si layer, the reducing gas flow was stopped, and the other two layers promptly applied. These low plasma power coatings had a YbMS layer thickness of 125 $\mu$m (compared to 75 $\mu$m in the previously studied system) while that of the Al$_6$Si$_2$O$_{13}$ layer and the Si bond coat were each 75 $\mu$m, Fig. 2.
2.2. Coating stabilization and steam furnace cycling

The coated samples were annealed at 1300 °C in laboratory air for 20 h to transform metastable phases typically found in the as-deposited ytterbium monosilicate and mullite layers \[24,26,28,32,34,49\]. The coated substrates were then thermally cycled in a steam-cycling furnace between 110 and 1316 °C, following, atmospheric pressure gas mixture consisting of 90% H2O/10% O2 with a flow velocity of 4.4 cm/s in the test gage (a volumetric flow of 4.1 slm). The furnace and flow conditions were identical to those used in a previous steam-cycling study of the Yb2SiO5/Al6Si2O13/Si system \[32\]. The maximum temperature of 1316 °C was held for 1 h. The temperatures were periodically verified using a reference thermocouple inserted into the process tube. These testing conditions approximate the H2O partial pressure during lean hydrocarbon combustion at a pressure of ~10 atm. The samples were examined visually before testing and after every 25-steam cycles. Stress calculations for the Yb2SiO5/Al6Si2O13/Si EBC system, Table 2, indicate that the high CTEs of the Yb2SiO5 and Al6Si2O13 layers result in substantial tensile residual stresses, even when significantly reduced moduli (EAPS) consistent with APS processing are used. Note that a significant compressive stress in the Si layer is also predicted.

2.3. Coating characterization

The samples were sectioned and polished, and then examined with a scanning electron microscope (Quanta 650 FE-SEM, FEI, Hillsboro, OR) operating in the back-scattered electron (BSE) mode. All images were collected under low-vacuum conditions. A gamma correction was applied to raw images to enable contrast of Yb and non-Yb containing materials to be simultaneously observed. The imaging conditions and image processing are consistent with prior work \[32,34\]. Elemental mapping by Energy Dispersive Spectroscopy (EDS: X-MaxN SDD, Oxford Instruments, Concord, MA) was used to generate compositional maps. The EDS spectra used for elemental mapping were not standardized. Raman Spectroscopy was performed using an inVia (Renishaw, Hoffman Estates, IL) microscope to identify bond coat oxidation phases in the steam-cycled coatings. This technique has previously been used to identify bond coat oxidation phases in EBCs \[32\]. The Raman analyses were performed using a 50x lens with a numerical aperture of 0.5. An argon-ion laser (wavelength of 488 nm) was used as the light source. Approximately 99% of the Gaussian distributed incident light resided within a 1 μm diameter spot.

**Figure 2.** Schematic illustration of the tri-layer coated α-SiC substrate whose EBC was deposited using optimized low plasma power deposition conditions. Note the layer thicknesses are different to the system shown in Fig. 1(a).

**Table 1** Deposition parameters for low power plasma spray parameter EBC layers.

<table>
<thead>
<tr>
<th>APS Layer</th>
<th>Torch power (kW)</th>
<th>Arc current (A)</th>
<th>Primary Ar (slm)</th>
<th>Secondary H2 (slm)</th>
<th>Powder feed (g/min)</th>
<th>Carrier Ar (slm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yb2SiO5</td>
<td>11.2</td>
<td>275</td>
<td>85.0</td>
<td>0.9</td>
<td>41.5/upper</td>
<td>5.9</td>
</tr>
<tr>
<td>Al6Si2O13</td>
<td>15.2</td>
<td>375</td>
<td>77.9</td>
<td>0.9</td>
<td>18.9/upper</td>
<td>5.4</td>
</tr>
<tr>
<td>Si</td>
<td>14.0</td>
<td>350</td>
<td>77.9</td>
<td>0.9</td>
<td>31.0/upper</td>
<td>5.9</td>
</tr>
</tbody>
</table>

**Table 2** Thermomechanical properties and residual stress of the EBC system components. Quantities in italics corresponded to those estimated for the APS deposited structure.

<table>
<thead>
<tr>
<th>Material</th>
<th>CTE (\ast 10^{-6} \degree C^{-1})</th>
<th>Young’s Modulus (GPa)</th>
<th>Poisson ratio ν</th>
<th>Thermal residual stress (MPa)</th>
<th>Low power Layer thickness</th>
<th>High power Layer thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>YMS</td>
<td>7.5 [33]</td>
<td>172 [33]</td>
<td>0.27(^a)</td>
<td>820</td>
<td>125 μm</td>
<td>75 μm</td>
</tr>
<tr>
<td>E(_{APS})</td>
<td>80 (^c)</td>
<td>220 [39]</td>
<td>0.28 [40]</td>
<td>190</td>
<td>75 μm</td>
<td>75 μm</td>
</tr>
<tr>
<td>Mullite</td>
<td>5.3 [38]</td>
<td>65 [42]</td>
<td>−0.164 [43]</td>
<td>4350</td>
<td>0–40 μm</td>
<td>0–40 μm</td>
</tr>
<tr>
<td>E(_{APS})</td>
<td>30 (^d)</td>
<td>70 (^e)</td>
<td>−0.042 [44]</td>
<td>–194</td>
<td>75 μm</td>
<td>100 μm</td>
</tr>
<tr>
<td>Cristobalite-α</td>
<td>30 (^d)</td>
<td>109 (^d)</td>
<td>−0.164 [43]</td>
<td>4350</td>
<td>0–40 μm</td>
<td>0–40 μm</td>
</tr>
<tr>
<td>Cristobalite-β</td>
<td>3.1 [41]</td>
<td>163 [45]</td>
<td>0.223 [45]</td>
<td>–194</td>
<td>75 μm</td>
<td>100 μm</td>
</tr>
<tr>
<td>Si</td>
<td>4.1 [45]</td>
<td>82 (^e)</td>
<td>0.14</td>
<td>–90</td>
<td>4.76 mm</td>
<td>4.76 mm</td>
</tr>
<tr>
<td>SiC (α)</td>
<td>4.67</td>
<td>430</td>
<td>0.14</td>
<td>–90</td>
<td>4.76 mm</td>
<td>4.76 mm</td>
</tr>
</tbody>
</table>

\(^a\) 50% reduction in elastic modulus assumed for APS material.
\(^b\) Based on Y2Si2O7 [46].
\(^c\) Average of values reported on the 20–200 °C interval [37,47].
\(^d\) Based on Young’s modulus ratio of α and β quartz [48] and α cristobalite.
3. Stress and cracking analysis

To complement the experimental studies, a broad parameter study of the thermomechanical response of the system was performed using finite element software specifically designed to analyze multilayer cracking problems [50]. The software tool utilizes specialized mesh generation strategies that ensure accurate computation of crack tip parameters, notably energy release rates and the stress intensity factors needed to characterize mode-mixity. The meshing strategy is also designed to enable rapid and comprehensive studies of various cracking possibilities through parameterization of a model geometry.

The software was used to compute the energy release rate and mode-mixity associated with (i) steady-state delamination cracks at the interfaces between all the layers, (ii) vertical mud cracks, and (iii) putative double-sided kink cracks emerging from the tips of channeling cracks. The results were generated for cracks occurring at numerous depths throughout the EBC layer stack, and for putative kink orientations, \( \theta \), ranging from zero to \(-85^\circ\), Fig. 3(a). The software automated the generation of finite element models, requiring only specification of the dimensions of the specimen layers, the crack length and location. It then automatically placed an appropriate radial fan mesh at the crack tip, with appropriate grading of element size away from the highly refined mesh in the radial fan, Fig. 3(b) and (c). Care was taken to ensure accurate results for any given geometry, using convergence studies that ensured results were independent of the internal meshing parameters used to generate the model.

Following the computation of stresses and deformation via finite element analysis, the software computes energy release rates and stress intensity factors using the virtual crack extension technique described by Matos et al. [51], which has been proven highly efficient for the mesh densities required to yield accurate results. The analyses typically involved \(-10,000\) elements (with approximately \(-3000\) in the refined radial fan region near the crack tip and the remainder graded to a coarse mesh at the boundaries). A single model was generated in seconds, and analysis was typically completed within a few tens of seconds, implying that a thousand crack geometries could be analyzed overnight on a standard PC.

The materials were described using isotropic elasticity, subject to plane strain deformation, with isotropic thermal strains generated in each layer according to their coefficient of thermal expansion and prescribed temperature changes relative to a reference state. In all computations, the reference state corresponding to zero stress was taken as the elevated thermal cycling temperature \((1316 \, ^\circ C)\), under the reasonable presumption that rapid stress relaxation occurs at elevated temperatures [52]. The results are then presented for the stresses that develop upon cooling to room temperature.

Clearly, this approximation depends critically on the relative magnitudes of the hold time at elevated temperature and cooling time to the characteristic relaxation time of the layers. If the hold time is not much larger than the characteristic relaxation time(s) of the layers, residual stresses may exist at elevated temperature, which would reduce the driving force for delamination upon cooling. Similarly, if the cooling time is not sufficiently short, viscoplastic relaxation of stresses during cooling could also occur, again mitigating the driving force for delamination in the final cooled state. However, in order to account accurately for such behaviors, a quantitative (calibrated) viscoplastic constitutive law for all the coating layers is required. At the present time, such a law does not exist. Hence, we adopt the present idealization and recognize that it gives an upper bound (valid in the limit of long hold times and rapid cooling) estimate of stresses that can develop from CTE mismatches in the system.

Fig. 3. The low power coating system used for the thermomechanical analysis. (a) Shows a schematic of the double kink (bifurcated) crack configuration simulated with the relevant dimensions and scaling features indicated. (b) Part of the actual mesh simulated with (c) a higher magnification view of the putative double kink crack in the Al\(_2\)Si\(_2\)O\(_3\) layer. (b) and (c) are for a normalized bifurcation position of 0.8 (parent crack length of 140 \(\mu m\)) with a kink angle \(\theta = 45^\circ\) and a putative crack length of \(a = 1 \mu m\).

A list of the properties used in the analysis is given in Table 3. It should be noted that coating anisotropy can play a significant role in the development of stress and the cracking behaviors that develop in spray-coated systems. However, the present coatings were deposited under conditions that resulted in limited spherical droplet spreading during deposition. Furthermore, the coatings did not exhibit evidence of preferential texture when their X-ray pole figures were examined. This was also consistent with TEM, and high-resolution BSE (grain contrast) SEM analyses. While as-deposited inter-splat boundaries contained microporosity, the
stabilization annealing process resulted in substantial sintering and reduction in this porosity before testing. The propagation of cracks during coating failure did not therefore appear to follow splat boundaries.

Fig. 4(a) shows the computed energy release rate for delamination cracks as a function of the crack plane’s location within the tri-layer/substrate stack, for locations spanning the top three layers (ytterbium monosilicate, mullite and silicon) and the top portion of the SiC substrate. The results in Fig. 4(a) are for a delamination crack that is ten times larger than the parent-channeling crack. These results are within several percent of the values associated with steady-state, as computed using the idealized semi-infinite stack analysis found in many other works, but notably described in detail in that by Jackson et al. [53]. The close agreement between the finite element results and the semi-infinite crack approximation indicates that the outer dimensions of the specimen have no influence on the present calculations.

Due to the close agreement with steady-state conditions, the average stresses in the layers reported here are those obtained with a semi-infinite layer calculation, which avoids ambiguity associated with the choice of where finite element results are sampled. Results in Fig. 4(a) are shown for both the low power coatings studied here and the high power coatings of the previous study. Since plasma spray coatings have lower elastic moduli than the solid materials used to make them, results are shown for coating layers with bulk (fully dense) moduli and for layers with a modulus of one half the bulk value. Fig. 4(b) shows the mode-mixity of the delamination cracks analyzed in Fig. 4(a). These results cannot be obtained without recourse to the finite element computations. They indicate that in both coating systems the mixity undergoes a transition from a Mode II dominated response at the top of the stack to one with a much higher Mode I response near the SiC–Si interface. The implications of these results on likely failure modes in EBCs are discussed in concert with the experimental results described below.

Fig. 5 shows maps of the energy release rate associated with putative double-sided kink cracks at the tip of parent channeling cracks, again generated using the automatic model generation capability described above. Results are reported for the energy release rate (ERR) during extension of a double-sided kink crack (as shown in Fig. 3(a)), as a function of both crack tip position in the coating stack (defined by distanced from the top surface) and the bifurcation angle, \( \theta \). For putative kink cracks lying at the interface, the method of extracting ERR and stress intensity factors is still valid, as it incorporates the requisite bi-material fields as described in Matos et al. [40]. These results correspond to kink cracks of approximately 1 \( \mu \text{m} \) in length; the crack tip parameters are shown to exhibit a relatively weak dependence on crack length. For both cases, results are shown for coatings with and without a 5 \( \mu \text{m} \) thick TGO layer. Although results are only shown in Fig. 5 for the “fully dense” moduli estimates, additional analyses for the present EBC system have shown that the ERR results are effectively proportional to the moduli in the EBC layers (reducing the effective modulus by a factor of two reduces the ERR by a factor of two). Again, the implications of these results for interpreting the observations seen in the present experiments are discussed in the following sections.

4. Results

No delaminations were observed along any of the edges or at any corners of the six coated samples after deposition or after the 20-h, 1300 \( ^\circ \text{C} \) stabilization anneal in air. All four edges of the samples were confirmed to have been slightly over-sprayed. One of

<table>
<thead>
<tr>
<th>Coating Layer</th>
<th>Yb2SiO5 E(GPa)/Thickness (( \mu \text{m} ))</th>
<th>Al2Si2O5 E(GPa)/Thickness (( \mu \text{m} ))</th>
<th>Si E(GPa)/Thickness (( \mu \text{m} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low power APS moduli</td>
<td>172 GPa/125 ( \mu \text{m} )</td>
<td>220 GPa/75 ( \mu \text{m} )</td>
<td>82 GPa/75 ( \mu \text{m} )</td>
</tr>
<tr>
<td>High power APS moduli</td>
<td>86 GPa/125 ( \mu \text{m} )</td>
<td>110 GPa/75 ( \mu \text{m} )</td>
<td>82 GPa/75 ( \mu \text{m} )</td>
</tr>
<tr>
<td>Low power Bulk moduli</td>
<td>172 GPa/75 ( \mu \text{m} )</td>
<td>220 GPa/75 ( \mu \text{m} )</td>
<td>16 GPa/100 ( \mu \text{m} )</td>
</tr>
<tr>
<td>High power Bulk moduli</td>
<td>86 GPa/75 ( \mu \text{m} )</td>
<td>110 GPa/75 ( \mu \text{m} )</td>
<td>16 GPa/100 ( \mu \text{m} )</td>
</tr>
</tbody>
</table>

Table 3: Material properties of tri-layer Yb2SiO5/Al2Si2O5/Si EBC systems [33].
the coated samples was used for investigation of as-deposited and annealed microstructures, while the remaining five coated samples were thermally cycled in the steam-cycling apparatus.

4.1. Coating structure

BSE mode SEM micrographs of the coating-substrate system after stabilization annealing highlight the presence of periodically spaced mud cracks in the coating, Fig. 6. In Fig. 6(a), white arrows along the top of the coating indicate these mud cracks. By analyzing the number of mud cracks in a 25 mm span of the coating cross-section, the average mud crack spacing was determined to be 240 μm, and was similar to that of the high power deposited tri-layer Yb2SiO5/Al6Si2O13/Si EBC [32]. When measured by image analysis, the pore volume fraction was found to be ~1% in the ytterbium monosilicate layer and ~5% in the Al6Si2O13 and Si layers.

Mud cracks were observed to have penetrated the Yb2SiO5 and Al6Si2O13 layers, Fig. 6(b) and (c). Mud crack penetration of the oxide layers is consistent with channel cracking in several other rare earth silicate based tri-layer systems [26,27]. Thermal residual stress calculations for the Yb2SiO5/Al6Si2O13/Si EBC system, Table 2, indicate that the high CTE of the Yb2SiO5 and Al6Si2O13 layers relative to the SiC substrate result in substantial tensile residual stresses upon cooling from the annealing temperature. The calculations assume macroscopic (layer level) crystallographic isotropy, and the resulting stresses scale with the modulus of the layers and remain significant even when a 50% reduction of modulus (consistent with APS processing) is used. We note that this preliminary assessment has ignored the single crystal anisotropy present at the grain size scale within each splat of the outer coating layers. Table 2 shows that a substantial compressive stress in the Si layer is also predicted. The channel cracking observed in Fig. 6 is consistent with these stress calculations.

Light and dark contrast features are evident in the Yb2SiO5 layer, Fig. 6. The lighter contrast regions correspond to particles that are depleted in Si, and are a manifestation of SiO loss from the originally stoichiometric powder particles during plasma melting [33,34]. During their solidification, the modified composition droplet formed a two-phase Yb2SiO5 + Yb2O3 microstructure. The volume fraction of precipitated Yb2O3 was ~15 vol% for this low power deposited topcoat [34]. This is in contrast to ~40 vol% precipitated Yb2O3 previously measured in coatings deposited with high power conditions [33]. The precipitated Yb2O3 volume fraction, however, has only a small effect on the thermomechanical behavior of the system since the CTE and elastic modulus of Yb2SiO5 and Yb2O3 are similar.
The adherence of interfaces in the tri-layer coating is of particular interest due to the prevalence of interface delamination, particularly at the Si—SiC and Al$_6$Si$_2$O$_13$—Si interfaces in the previous high power study [32]. When examined using BSE imaging, adhesion of the low power Si—SiC interface, Fig. 7(a), appeared significantly improved compared to that of the previous high power interface, Fig. 7(b). The low power deposited Si—SiC interface had minimal interface porosity with no SiO$_2$ formation, Fig. 7(a). No delamination was observed at the Si—SiC interface in any of the low power EBCs and intra-splat oxidation and porosity appeared minimal. In high power coatings, insufficient and inconsistent adhesion of the EBC has been attributed to porosity and oxidation at the Si—SiC interface, Fig. 7(b), which resulted in delamination from coating edges or corners upon cooling from elevated temperature [32].

Adhesion at the Al$_6$Si$_2$O$_13$—Si interface was also improved in low power deposited tri-layers when compared to their high power counterparts, Fig. 8. Considerable surface connected porosity was observed at the Al$_6$Si$_2$O$_13$—Si interface in high power EBCs; this interface was found to suffer oxidation damage during annealing, Fig. 8(a) and (b). The same interface in low power tri-layers had limited porosity and the unconnected internal pore surfaces were not oxidized after annealing, Fig. 8(c) and (d). The differences in the two layers were consistent with the a tighter Si powder size distribution, optimized APS parameters and a reducing environment during elevated temperature deposition of silicon in the low power coatings.

Mud cracks in the tri-layer system frequently branched as they entered the Al$_6$Si$_2$O$_13$ layer of the low power system. Crack branching appeared at the majority of mud cracks observed in this study, particularly after annealing, and in many cases took the form of a bifurcation into two cracks. Bifurcation of mud cracks occurred at either the Yb$_2$SiO$_5$—Al$_6$Si$_2$O$_13$ interface, Fig. 9(a), within the Al$_6$Si$_2$O$_13$ layer, Fig. 9(b), or at the Al$_6$Si$_2$O$_13$—Si interface, Fig. 9(c). Bifurcation at these three locations was observed with equal frequency, and all bifurcation locations resulted in cracks that propagated along a trajectory towards or within the Si bond coat. The tendency for bifurcation in this system differed from previous observations of EBCs in the Yb$_2$SiO$_5$/Al$_6$Si$_2$O$_13$/Si system where mud cracks were found to terminate at the Al$_6$Si$_2$O$_13$—Si interface, as shown in Fig. 1(a). It is noted that the low power EBCs of the present study have a higher density (particularly in the Si bond coat) and a thicker Yb$_2$SiO$_5$ layer than for those previously studied [26,27,33].

4.2. Steam-cycling response

Five samples were thermally cycled in the H$_2$O/O$_2$ environment.
between 1316 °C and 110 °C. One coating partially spalled after 250 steam cycles while the other four survived much longer, with one sample visibly beginning to spall only after 725 steam cycles. The cumulative spallation probability is plotted against the number of steam cycles while the other four survived much longer, with one in Fig. 10. Insufficient statistical evidence exists, even at a significance level of 0.25, to indicate that either the average sample life or the variability in sample life differed between the two sets of samples.

No optically visible damage was evident in the annealed coatings, Fig. 11(a). Spallation of the coating during cycling, however, was readily observed optically, Fig. 11(b). Though some spallation was observed at the coating’s corners after 250 steam cycles, spallation also occurred from the middle of the specimens. This behavior was typical of all steam cycled low power EBCs, and markedly different to that observed for high power EBCs. There, spallation initiated at coating edges where oxidation damage was most severe, and the delamination propagated towards the center of the sample upon cycling [32]. In contrast, edge spallation of low power EBCs resulted from propagation of a delamination crack that had initiated internally at the nearest mud crack to the coating edge and then grown outward to the edge, Fig. 11(c).

A previously unobserved failure mode was found in all five low power steam cycled samples. Fig. 12 shows the propagation of delamination cracks within the bond coat. This failure mechanism was particularly evident in the coating that failed after 250 steam cycles and was observed across the entire specimen. Though this was the first of the five steam cycled samples to fail, it most clearly exhibited this new failure mode due to the reduced crack face oxidation damage associated with its short life. Examination of the serial cross-sections, Fig. 12(a) and (b), shows that propagation of the delamination cracks occurred through the mid-plane of the Si bond coat, and originated from bifurcated mud cracks. These mud cracks bifurcated within the Al6Si2O13 layer in Fig. 12(a) and at the Yb2SiO5 – Al6Si2O13 interface in Fig. 12(b), corresponding to the bifurcation locations indicated in Fig. 9(a) and (b), respectively.

A darker gray (lower atomic number) layer can be seen to have formed on the bifurcated crack faces within the Si bond coat, Figs. 12 and 13(a). An EDS analysis of this layer, Fig. 13(b) – (d), indicated it was composed of only Si and O, and was therefore a thermally grown silicon oxide. Further analysis using Raman spectroscopy identified the ambient temperature phase to be a (low) cristobalite (SiO2) based on the presence of only two spectral peaks not belonging to Si with wavenumbers of 230 cm⁻¹ and 416 cm⁻¹ that are typical of α-cristobalite [54–56]. Cristobalite has previously been identified to be the dominant TGO phase grown in the Yb2SiO5/Al6Si2O13/Si system using this Raman technique [32] and has also been identified as a dominant reaction product upon exposure to oxygen or water vapor at comparable temperatures [19,57].

The thickness of this TGO was measured to be less than 25 μm in all bifurcated ligaments of the specimen that failed after 250 steam cycles. The TGO layer on bifurcated crack faces had a constant thickness, indicating the crack had abruptly formed and then stopped propagating in the silicon layer. Close examination of the TGO, Fig. 13(a), shows that it had micro-mud cracked with the microcracks running normal to the crack face and arresting at the interface with silicon. Some oxidation of the Si bond coat at the Al6Si2O13 – Si interface was also observed, Fig. 12(a), but its thickness was less than 3 μm in all specimens (except very near to surface connected mud cracks). This again contrasted with the oxidation behavior of high power deposited tri-layers where severe oxidation was observed across the entirety of the Al6Si2O13 – Si interface in all samples as a consequence of the significant (often interconnected) porosity in the coating layers and their interfaces, Fig. 7(b) [32]. Fig. 13(a) also indicates that bifurcation began within the Al6Si2O13 layer and not within the thermally grown oxide located at the original Al6Si2O13 – Si interface. The micro-mud cracking of the TGO formed on the bifurcated crack faces, Fig. 12(a), also did not penetrate the Si upon which it had grown, consistent with previous observations of the cristobalite TGO formed upon Si in this EBC system [32]. However, it was clear that these micro-mud cracks had created diffusive short circuits for oxidizing species to reach the bond coat.
Fig. 9. Examples of mud crack bifurcation in stabilization annealed low power deposited Yb<sub>2</sub>SiO<sub>5</sub>/Al<sub>2</sub>Si<sub>2</sub>O<sub>13</sub>/Si EBCs. (a) Shows a bifurcation at the Yb<sub>2</sub>SiO<sub>5</sub> – Al<sub>2</sub>Si<sub>2</sub>O<sub>13</sub> interface, (b) shows a bifurcation within the Al<sub>2</sub>Si<sub>2</sub>O<sub>13</sub> layer, and (c) shows a bifurcation at the Al<sub>2</sub>Si<sub>2</sub>O<sub>13</sub> – Si interface. In all three cases, the resultant trajectory of the bifurcated crack ligaments was directed toward the silicon bond coat.

Fig. 10. Spallation failure probability of tri-layer coatings as a function of number of 60 min steam cycles at 1316 °C.

Fig. 11. (a) Shows an annealed tri-layer EBC deposited using low power plasma spray parameters. The same sample after 250 steam cycles at 1316 °C is imaged optically in (b) and its cross section near an edge in (c) using BSE mode SEM imaging. The red bar in (b) indicates the location of the section shown in (c). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 12. Cross sectional micrographs of the failed coating presented in Fig. 11 after 250 1-h steam cycles. The cross sections were (a) 1 mm and (b) 3 mm from the coating edge. Note the oxide layer that has formed on the bifurcated crack faces within the silicon bond coat.
large volume change during the observations. The high CTE of the TGO layer, combined with a very high power coating systems that is consistent with experimental up a powerful driving force for channel cracking in both the low and high power deposited systems provides a potent driving force for TGO microcracking, and for its delamination from both the low and high power deposited systems. The ERR values for delamination crack in the low power coatings had weaker SiC interface, suggesting that delamination crack growth is favorable at these locations. While the significantly improved interfaces in the low power coatings will have reduced their susceptibility to interfacial delamination (ostensibly by improving their effective toughness by eliminating interface porosity), these assessments do not explain the emergence of the branched crack failure mode observed in the coatings deposited under low power conditions. The ERR for bifurcation cracking was investigated using FEA simulations that included putative double-sided kink cracks at the tip of channeling cracks. The ERR associated with nearly all possible combinations of parent channeling crack depth and kink angle are illustrated in Fig. 5 for both the low power coatings investigated here and the earlier coatings deposited with higher torch power. The kink angle is defined as 0° for a crack that branches to form an inverted “T”, while a branched crack with kink angles of 85° forms a very sharp inverted “Y”.

The results are shown for the case with full elastic moduli of all layers. Additional calculations (not shown) demonstrate the ERR values in the maps in Fig. 5 can be scaled linearly with any changes to the moduli values. (In other words, the substrate is sufficiently thick that bending is negligible.) The results for the low power system indicate that the absolute ERR for bifurcation reaches a maximum of 1 kN/m just above the Yb2SiO5 topcoat from the SiC substrate has a similar ERR. Since the low power EBC had a greater topcoat thickness than the previous high power study, the ERR is greater for that system because of the associated increase in the total stored elastic energy. The predicted values of the ERR are significantly greater than the mode I toughness of typical oxide ceramics (\( G_c \sim 1\text{–}50 \text{ N/m}, \) which roughly equates to a fracture toughness of 0.1\text{–}10 \text{ MPa}\cdot\text{m}^{1/2} \) [64]. However, the high mode mixity values shown in Fig. 4(b) indicate a significant Mode II component which can result in a higher effective cracking resistance if there is frictional contact between non-planar crack faces. Interestingly, the Mode II component is smallest for delamination cracks within the silicon bond coat, and near zero around the SiC interface, suggesting that delamination crack growth is favorable at these locations.

The use of optimized low power APS conditions for the deposition of a model tri-layer EBC applied to a SiC substrate has resulted in a change in failure mode during steam cycling compared to a similar coating system deposited using higher power conditions, Fig. 14 [32]. The study has therefore exposed a significant dependency of the failure mechanism upon the parameters that differed between the two coating systems, Table 2. Recall that the high power coatings had weaker SiC and Al6Si2O13–Si interfaces, different layer thicknesses (a thinner YbMS layer) and a higher pore defect concentration.

The CTE, elastic moduli and calculated thermal residual stresses for the EBC system, Fig. 2, are presented in Table 2. The thermal residual stresses have been calculated using both elastic moduli appropriate for dense material and elastic moduli reduced by 50% (\( E_{APS} \) values) that are more appropriate for low porosity APS deposited materials [58–63]. The calculated residual stress values were tensile in the ytterbium monosilicate and mullite layers and compressive in the silicon bond coat. They are the same as those of the high power EBC system [32]. These biaxial tensile stresses set up a powerful driving force for channel cracking in both the low and high power coating systems that is consistent with experimental observations. The high CTE of the TGO layer, combined with a very large volume change during the \( \alpha \rightarrow \beta \) phase change resulted in an unrelaxed \( \beta \)-cristobalite tensile thermal residual stress (at 20 °C) that exceed 4 GPa. The stored elastic strain energy of cristobalite in both the low and high power deposited systems provides a potent driving force for TGO microcracking, and for its delamination from the silicon to which it is attached.

The energy release rates for delamination crack in the low power coating system before TGO formation have been calculated, and were plotted as a function of depth in the coating/substrate system in Fig. 4(a). The ERR values have been calculated assuming both bulk material elastic moduli 50% reduced (\( E_{APS} \)) elastic moduli as indicated in Table 2; the trends using these two bounding assumptions are similar with the magnitude of the residual stress reduced by a factor of ~1/2 for the lower moduli system. The high thermal residual stress in the Yb2SiO5 layer and significant strain energy dominates the ERR of the entire system: debonding at any location below Yb2SiO5 topcoat from the SiC substrate is a similar ERR. Since the low power EBC had a greater topcoat thickness than the previous high power study, the ERR is greater for that system because of the associated increase in the total stored elastic energy. The predicted values of the ERR are significantly greater than the mode I toughness of typical oxide ceramics (\( G_c \sim 1\text{–}50 \text{ N/m}, \) which roughly equates to a fracture toughness of 0.1\text{–}10 \text{ MPa}\cdot\text{m}^{1/2} \) [64]. However, the high mode mixity values shown in Fig. 4(b) indicate a significant Mode II component which can result in a higher effective cracking resistance if there is frictional contact between non-planar crack faces. Interestingly, the Mode II component is smallest for delamination cracks within the silicon bond coat, and near zero around the SiC interface, suggesting that delamination crack growth is favorable at these locations.
The ERR drops rapidly in the silicon layer which is under biaxial compression; interestingly, despite the compression in the silicon layer, the tips of all branched cracks reflected in Fig. 5 remain open with positive $K_I$ values (maps of $K_I$ and $K_II$ will be presented in a companion paper [39]). This is a consequence of significant tension in the upper layers; sufficient to always pull the crack open, despite the compression that exists in the silicon layer far from the crack tip. It should also be noted that the ERR associated with the tips of the double-sided kink are always lower than that of the parent channeling crack, ranging from ~25% (for 0° branches) to ~75% (for 60°–70° branches). This is entirely consistent with previous studies of crack deflection [65]. The fact that the parent-channeling crack has a larger ERR implies that the parent crack tip must interact with a defect (which serves as the putative kink crack) in order to bifurcate.

The simulations for the high power system, Fig. 5(c), show a much lower ERR exists for bifurcated crack extension at both locations. These results are generally consistent with the experimentally observed location of bifurcation initiation in the low power coatings and its absence in the previously deposited high power coatings. It is noted that the calculations do not address the role of stochastically distributed defects in the mullite layer which can initiate bifurcation in regions of high (but not maximal) ERR for a branched crack. The simulations of the low and high power coatings with a 5 µm thick TGO layer on the Si bond coat, Fig. 5(b) and (d) respectively, indicate that the energy release rate for bifurcated crack extension has been increased by about 25% in both cases.

Fig. 14 summarizes the failure mode of the low power deposited coatings during steam cycling and compares it to the high power case. In the low power deposited system, failure of the coating system resulted from the horizontal penetration of a bifurcated crack through the silicon bond coat. Since such cracks are exposed to the external oxidizing environment, TGO formation occurs on the freshly exposed crack faces. The strain energy resulting from crack face TGO thermal contraction and phase transformation therefore acts locally upon already debonded sections of the coating and is not expected to contribute to the ERR for adherent sections. In addition, since modest TGO growth was observed at the Al$_2$Si$_2$O$_5$–Si interface above the region of delamination crack propagation, it is reasonable to presume the ERR is primarily governed by that of the thicknesses and thermomechanical properties of the layered system.

It is also clear that the bifurcated cracks tended to propagate on a plane that was approximately midway through the silicon bond coat. Fig. 3(a) indicates that the ERR varies by only ~1% with depth in the bond coat, indicating that crack path selection will depend strongly upon other characteristics of the crack tip fields. For example, Fig. 3(b) indicates the mode II contribution to the ERR decreases for delamination cracks that occur deeper into the silicon bond coat. If there is any mode II dependence on the fracture toughness (e.g., due to frictional sliding arising during crack face contact), the delamination crack will seek a depth at which the mode II contribution is sufficiently small to lower the relevant mixed-mode toughness to the point that delamination occurs. In the absence of mode-dependent toughness, the ultimate delamination crack location is likely governed by the orientation of additional flaws encountered after bifurcation.

The propagation of cracks in the compressive silicon layer is controlled by the much larger tensile stress in the top layers; for all cases, the tensile stresses in the top layers are sufficient to generate tensile stresses at the crack tip ($K_I > 0$), despite the fact that far field stresses are compressive. After the channeling crack deflections and extends, the crack transitions to a delamination crack, driven by upward bending of the multilayer above the crack. In the limit of a fully formed, steady-state delamination crack, this upward bending again causes $K_I > 0$ even in the presence of compressive stress in the silicon layer. Intermediate states (between the initial crack deflection and steady state delamination crack) require further study with more sophisticated tools that are capable of predicting crack path evolution. However, the present predictions, combined with the observations of crack deflection, provide strong evidence that the tensile stresses in the top layers dominate the response.

Bifurcation of mud cracks was observed in low power EBMs, and was demonstrated to be favorable in Section 4, Fig. 5. Consequently, assessing the scenario that contributes to bifurcation in the low power EBM but not in the high power EBC [32] is of interest. In high power EBMs, Fig. 14(d), mud cracks penetrated the Yb$_2$Si$_2$O$_5$ and Al$_2$Si$_2$O$_5$ layers but terminated at pores in the porous Si bond coat, Fig. 8(a) and (b). In low power EBMs, Fig. 14(a), mud cracks penetrated the Yb$_2$Si$_2$O$_5$ and Al$_2$Si$_2$O$_5$ layers but also bifurcated. The higher YbMS thickness has increased the driving force for fracture and the likelihood for branching, as evidenced by the fact that this is the only change to the mechanics model used to predict driving force.

Fig. 14. Damage mechanisms contributing to failure of the tri-layer EBC deposited using optimized low power deposition conditions. (a) Shows the stresses in the post annealed coating system. (b) Illustrates the damage mechanisms active during high temperature exposure and (c) shows the mechanical damage that develops during cooling of the sample.
At 1316 °C the active damage mechanism in low power EBCs was environmental: even though mud cracks were mechanically closed (assuming the coating is stress free at the annealing temperature and no wedging effect occurs upon oxidation), O₂ and H₂O permeated through the bifurcated mud crack network and began to oxidize the Si bond coat, Fig. 14(b) and (e). The small-scale processes and mechanics of TGO growth upon Si in this system have already been examined in high power EBCs by Richards et al.[32], Fig. 14(e). The reaction products and growth of cristobalite are found to be similar in the low power EBC system: penetrating oxidizers reacted with the Si bond coat to form a β-cristobalite TGO along the bifurcated crack ligaments, Fig. 14(b). Transport along the crack path would have been different surface diffusion based or gas phase depending upon the degree of crack closure; in either case it would be rapid when compared to bulk diffusion through the coating. Gas path diffusion is supported by the observation of uniform oxidation along delamination faces in the bond coat, Fig 12(b).

Upon cooling, Fig. 14(c), the CTE mismatch-derived residual stresses began to develop and the bifurcated mud cracks began to re-open in the low power coating. During cooling, the thermally grown β cristobalite transformed to the α-phase at ~220 °C with a volume reduction of ~4.5% [32]. This volume change was constrained by adhesion to the crack faces, which resulted in micro-cracking of the TGO in an orientation normal to that of the primary crack ligament (micro-mud cracking). At the crack tip, the volumetric contraction had the effect of advancing the crack (at the minimum) through the oxide grown at the crack tip during the hot cycle.

During subsequent heating cycles, the growth of a TGO on crack faces and the accompanying ~100% volumetric expansion of Si oxidizing to SiO₂ [32] would have provided a wedging mechanism that caused a slight opening of mud cracks even at high temperatures. This opening would have allowed enhanced penetration of oxidizers through the TGO-microcrack network, resulting in an increased oxidation and steam volatilization rate along the bifurcated crack ligaments. Repeated thermal cycling resulted in incremental growth of the delaminations through the Si bond coat midplane with eventual linkage between the bifurcated ligaments of neighboring mud cracks. This linkage resulted in the spallation of a section of the EBC.

Ultimate failure in tri-layer Yb₂SiO₅/Al₆Si₂O₁₃/Si EBCs was controlled by the high stored elastic strain energy (high thermal residual stress) in this materials system at low temperature. The high residual stresses resulted in the formation of high diffusivity pathways for oxidizer access and chemical reaction via mud cracking. Based on the observation of failure mechanisms in tri-layer ytterbium monosilicate based EBC systems, minimization of stored elastic strain energy is critical for long-term EBC durability. The avoidance of coating structures that result in damage upon cooling from deposition (either in the form of mud cracking or bifurcated mud cracking) will also be critical for improved durability. Elimination of such high diffusivity paths would most readily be achieved by some combination of closer CTE matching constraint and reduced elastic modulus. The finite element modeling strategy implemented here provides a means for quantification of coating design variables, and identifies the stringent demands on the properties of candidate materials used for the environmental barrier (oxidizer impermeable) layer in EBC systems.

6. Conclusions

Tri-layer Yb₂SiO₅/Al₆Si₂O₁₃/Si EBCs have been deposited onto α-SiC substrates using a low power APS approach [34]. These coatings have been steam cycled to failure (defined as any observed spallation) in an atmospheric pressure, slowly flowing 90% H₂O/10% O₂ environment using 60 min hot (1316 °C) and 10 min cool (110 °C) cycles. The coating lifetime was controlled by interactions between mechanical damage resulting from thermal residual stresses and phase transformation with environmental damage and growth of oxide scales experienced during the hot cycle of testing. Specifically, it was found that:

a) Mud crack bifurcation in the low power EBC is an energetically favorable phenomenon that is reflective of the elastic moduli, stress states of the layers and coating thickness. Mud cracks penetrating the upper layers of the EBC bifurcated upon encountering flaws as opposed to continuing to propagate in the form of a single mud crack. The favorability of bifurcation in the low power EBC system as compared to the high power EBC system is supported by kinking analysis on both systems.

b) The difference in mud crack structure (bifurcation) when compared to other coatings using comparable macrostructure and materials [32] led to the occurrence of an additional, previously unreported failure mechanism wherein bifurcated cracks propagated through the mid-plane of the bond coat in the form of delamination cracks upon cycling. This terminal crack trajectory has been determined to be mechanically favored by analysis of steady-state delamination cracks.

c) Oxidizers penetrated the bifurcated crack structure and oxidized the Si bond coat. A high density bond coat and improved coating layer adhesion resulted in a singular oxidizer access route through the bifurcated mud crack network. Cristobalite was again confirmed to be the only oxidation product in this system.

d) The mean steam-cycling lifetime of low power Yb₂SiO₅/Al₆Si₂O₁₃/Si EBCs and variance in steam-cycling lifetime did not differ considerably from those reported for high power EBCs of the same materials system but different macrostructure [32].

e) Altering the deposition process to achieve higher density and increased layer adhesion did not overcome the fundamental thermomechanical limitations of the Yb₂SiO₅/Al₆Si₂O₁₃/Si EBC system. The intrinsically high strain energy release rates (ERRs) of this materials system that result from mismatched CTEs were not overcome by attempts to inhibit oxidation by increasing coating layer density and interface adhesion. Examination of coating cracking/spallation criteria will be critical in the design of future EBCs.

Acknowledgments

We thank Elizabeth Opila of the University of Virginia, Bryan Harder and Dongming Zhu of the NASA Glenn Research Center, and Kang Lee from Rolls Royce (Indianapolis) for helpful discussions. We would also like to thank Richard White from UVA for advice concerning coating characterization. This work was supported by the Office of Naval Research under grants N00014-11-1-0917 (BTR and HNGW) and N00014-13-1-0859 (SS, FF, and MRB) both managed by Dr. David Shiffer.

References


459