Plasma spray deposition of tri-layer environmental barrier coatings

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Received 13 January 2014; received in revised form 15 April 2014; accepted 18 April 2014
Available online 14 May 2014

Abstract

An air plasma spray process has been used to deposit tri-layer environmental barrier coatings consisting of a silicon bond coat, a mullite inter-diffusion barrier, and a Yb2SiO5 top coat on SiC substrates. Solidified droplets in as-deposited Yb2SiO5 and mullite layers were discovered to be depleted in silicon. This led to the formation of an Yb2SiO5 + Yb2O3 two-phase top coat and 2:1 mullite (2Al2O3*SiO2) coat deposited from 3:2 mullite powder. The compositions were consistent with preferential silicon evaporation during transient plasma heating; a consequence of the high vapor pressure of silicon species at plasma temperatures. Annealing at 1300 °C resulted in internal bond coat oxidation of pore and splot surfaces, precipitation of Yb2O3 in the top coat, and transformation of 2:1 mullite to 3:2 mullite + Al2O3. Mud-cracks were found in the Yb2SiO5 layer and in precipitated Al2O3 due to the thermal expansion mismatch between these coating phases and the substrate.

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Keywords: Environmental barrier coatings; Ytterbium silicate

1. Introduction

Improvements to the fuel efficiency and specific thrust of future gas turbine engines will require advances in many areas including: (i) increasing the gas turbine inlet temperature, (ii) higher overall pressure ratios of engines, (iii) increasing the by-pass ratio and (iv) incorporation of more efficient thermodynamic cycles into novel engine core designs. 1-3 Developments will be paced by the emergence of new propulsion materials, protective coatings, thermal management concepts, and manufacturing tools for economical component fabrication. Arguably the most difficult materials challenge will be encountered in the engine’s hot core section. 2,4–6 Here, severely stressed rotating components will be subjected to ever increasing temperatures whose upper limit is set by stoichiometric combustion of the Jet-A fuel. At a combustor pressure of 1 MPa and an air temperature of 500 °C, the NASA CEA code 7 predicts this fuel burn temperature to be 2255 °C.

Recent increases to the turbine inlet temperature have been achieved by the use of internal air and surface film cooled superalloy components protected against oxidation and hot corrosion by thermal barrier coating (TBC) systems. Fig. 1. This strategy is approaching its limit because coating sintering leads to a loss of compliance and increased thermal conductivity, 9-13 the bond coat oxidation rate (and thus delamination risk) increase rapidly with temperature, 9,14-16 and calcium–magnesium–aluminum–silicate (CMAS) melting and infiltration cause premature coating failure.17-19 Even if these issues were resolved, TBCs can be eroded by fine (dust) particles19-22 or chipped away by larger foreign object damage (FOD).19,22,23

These considerations have stimulated the development of turbine components made from ceramic materials with much higher temperature capability.24-27 Monolithic ceramics have insufficient fracture toughness, so development has focused on damage tolerant fiber reinforced ceramic matrix composites (CMCs) with weak fiber/matrix interfaces.28-31 The most promising CMCs are based upon woven fabrics of BN coated SiC fibers (such as Hi-Nicalon S and Sylramic fibers) and SiC matrices incorporated by chemical vapor infiltration with residual pores filled by silicon slurry infiltration followed by carburization. While oxide–oxide CMC systems are chemically
Inert in oxidizing environments, the current fibers have insufficient creep rupture strengths at temperatures of interest, and are only used in lightly loaded applications. The most heavily stressed components in future engines are likely to utilize SiC fiber/SiC matrix CMC materials for robust mechanical performance.

When SiC is exposed to oxidizing environments a protective silica scale forms with a thickness that exhibits parabolic oxidation kinetics. Unfortunately, the protective scale reacts with water vapor in hydrocarbon combustion environments to create gaseous silicon hydroxides via several reaction pathways. The temperature, pressure, incident water vapor flux, and local flow conditions during exposure determine the observed parabolic oxidation kinetics. SiC recession rates significantly greater than 1 μm/h have been observed in the 1300–1350 °C range. Consequently, CMC components need to be protected by environmental barrier coatings (EBCs) to prevent component recession during operational lifetimes of tens of thousands of hours.

The first EBCs consisted of a 3:2 mullite (3Al2O3·2SiO2 or Al4Si2O7) coating applied directly to the substrate. During prolonged high temperature exposure, silica was volatilized from the mullite leaving an alumina scale that readily spalled, offering only short protection times. The next EBC development focused on bi-layer concepts in which an yttria-stabilized zirconia (YSZ) top coat was used to prevent volatilization and chemical attack of the underlying mullite. Thermal cycling tests in water vapor revealed that the coating quickly cracked and delaminated at either the YSZ/mullite or the mullite/SiC interfaces. The rapid failure was attributed to the substantial CTE mismatch between YSZ, the underlying mullite layer and the substrate. Subsequently, several alkaline earth and rare earth silicates were identified with well-matched CTE’s that exhibit little weight change during high temperature, high water vapor pressure environmental exposure.

Barium–strontium aluminosilicate (BSAS) has a low silica activity and a CTE that is well matched with substrates. However, BSAS EBCs react with thermally grown silica, necessitating a tri-layer BSAS/mullite/silicon EBC architecture to eliminate failure at the coating/substrate interface and increase EBC life. Unfortunately, low melting eutectics occur near 1300 °C and limit the useful lifetime to under 1000 h for higher temperatures, indicating the need for top coats with low volatility and high temperature phase stability. Ytterbium and lutetium silicates exhibit some of the lowest volatilities and are monomorphic. Ytterbium has monosilicate (Yb2SiO4) and disilicate (Yb2Si2O7) variants whereas lutetium has only a monosilicate variant. The reported CTE of these and other candidate materials are summarized in Table 1. The data for Yb2SiO4 is inconsistent. One report gives a value of 3.5–4.5 × 10⁻⁶ °C⁻¹ which is reasonably matched to SiC. However, a more recent report gives a higher value of 7–8 × 10⁻⁶ °C⁻¹. Like BSAS, the RE-silicates are unstable as single layer coatings and so a tri-layer RE-silicate/mullite/silicon coating approach analogous to the BSAS top coat EBC has been proposed.

There have been few studies of the tri-layer EBC deposition process or investigations of the relationships between coating deposition conditions, coating structure, and thermo-cyclic durability. To gain insight into these relationships, we describe an air plasma spray (APS) process to deposit tri-layer coatings on silicon carbide substrates with Yb2SiO4 top coats, and have used a variety of methods to characterize the coatings. We report the presence and identify the formation mechanism of previously unidentified phases in the Yb2SiO4 and mullite layers, and discuss the implications of their presence upon the propensity for cracking.

2. Experimental

2.1. Coating deposition

Three-layer Yb2SiO4/mullite/silicon EBCs were deposited onto SiC substrates using an APS approach. The general coating architecture is schematically illustrated in Fig. 2. Coatings were deposited on 2.54 cm × 1.27 cm × 0.32 cm α-SiC coupons obtained from Hexoloy™ (Saint Gobain Ceramics, Niagara Falls, NY). Prior to EBC deposition, the substrates were grit blasted using ~270 μm diameter SiC grit (Black SiC, White Abrasives, Niagara Falls, ON CA) resulting in an average surface roughness Ra = 1 μm, as measured by surface profilometry using a 500 μm sampling distance. The substrates were then ultrasonically cleaned in ethanol to remove surface contamination.

The silicon powder used for bond coat deposition was supplied by Micron Metals (Bergenfield, NJ) with a particle...
Table 1
Thermal expansion coefficients of EBC materials, adapted from Ref. 57.

<table>
<thead>
<tr>
<th>Material</th>
<th>CTE (×10⁻⁶ (C⁻¹))</th>
<th>Melting point (°C)</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y₂SiO₅</td>
<td>5–6</td>
<td>1980</td>
<td>Topcoat</td>
</tr>
<tr>
<td>Er₂SiO₅</td>
<td>5–7, 7–8</td>
<td>1980</td>
<td></td>
</tr>
<tr>
<td>Yb₂SiO₅</td>
<td>3.5–4.5, 7–8</td>
<td>1950</td>
<td></td>
</tr>
<tr>
<td>La₂Si₂O₇</td>
<td>3.8</td>
<td>Unknown</td>
<td></td>
</tr>
<tr>
<td>Sc₂Si₂O₇ + Sc₂O₃</td>
<td>5–6</td>
<td>1860</td>
<td>Topcoat</td>
</tr>
<tr>
<td>Yb₂Si₂O₇</td>
<td>4–6</td>
<td>1850</td>
<td>Intermediate coat</td>
</tr>
<tr>
<td>Yb₂O₃</td>
<td>6.8–8.4</td>
<td>2415</td>
<td>Bond coat</td>
</tr>
<tr>
<td>BSAS (monoclinic)</td>
<td>4–5</td>
<td>1300</td>
<td></td>
</tr>
<tr>
<td>BSAS (hexagonal)</td>
<td>7–8</td>
<td>1300</td>
<td></td>
</tr>
<tr>
<td>Mullite</td>
<td>5–6</td>
<td>1800</td>
<td>Substrate</td>
</tr>
<tr>
<td>Alumina (α)</td>
<td>6–0–8.4</td>
<td>2072</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>3.5–4.5</td>
<td>1400</td>
<td></td>
</tr>
<tr>
<td>SiC, SiC/SiC</td>
<td>4.5–5.5</td>
<td>2545</td>
<td></td>
</tr>
<tr>
<td>Si₃N₄</td>
<td>3–4</td>
<td>1875</td>
<td></td>
</tr>
</tbody>
</table>

a More recent value reported.
b Value determined in Section 3.1 of this article.
c Lower-melting eutectic at 1770 °C on Sc₂O₃-rich side and 1660 °C on SiO₂-rich side.d Undergoes pre-melt phase transformation at 2360 °C.

Table 2
Measured composition of received ytterbium monosilicate powder, and predictions for ytterbium silicates and ytterbia. Data is also shown from individual splats in an as-deposited coating.

<table>
<thead>
<tr>
<th>Spectrum location</th>
<th>Yb (at%)</th>
<th>Si (at%)</th>
<th>O (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder</td>
<td>21.0–22.1</td>
<td>13.3–13.6</td>
<td>64.4–65.6</td>
</tr>
<tr>
<td>Yb₂SiO₅</td>
<td>25</td>
<td>12.5</td>
<td>62.5</td>
</tr>
<tr>
<td>Yb₂Si₂O₇</td>
<td>18.2</td>
<td>18.2</td>
<td>63.6</td>
</tr>
<tr>
<td>Yb₂O₃</td>
<td>40</td>
<td>0</td>
<td>60</td>
</tr>
<tr>
<td>Point 1</td>
<td>37.3</td>
<td>4.0</td>
<td>58.7</td>
</tr>
<tr>
<td>Point 2</td>
<td>32.9</td>
<td>7.0</td>
<td>60.1</td>
</tr>
<tr>
<td>Point 3</td>
<td>31.6</td>
<td>8.4</td>
<td>60</td>
</tr>
<tr>
<td>Point 4</td>
<td>29.6</td>
<td>9.9</td>
<td>60.4</td>
</tr>
<tr>
<td>Point 5</td>
<td>27.4</td>
<td>12.5</td>
<td>60.1</td>
</tr>
<tr>
<td>Point 6</td>
<td>26.5</td>
<td>12.4</td>
<td>61.1</td>
</tr>
</tbody>
</table>

a 95% confidence interval.

diameter range of 10–44 μm. The mullite powder provided by Saint Gobain Ceramics (Worcester, MA) had a particle diameter of 16–53 μm. The Yb₂SiO₅ powder was supplied by Treibacher Industrie Inc. (Toronto, ON) with a particle diameter of 20–50 μm. The composition certified powders were identified by their respective manufacturers as fully reacted and phase pure, and confirmed by XRD prior to deposition. The composition of the Yb₂SiO₅ powder was also measured using EDS on polished cross sections. Using a PB-ZAF algorithm (Bruker Corporation, Ewing, NJ), the composition was found to be very close to that of Yb₂SiO₅ with variability of about ±0.5 at%, Table 2.

The coatings were deposited using two air plasma spray systems at the NASA Glenn Research Center. The silicon bond coat was deposited using an ambient substrate temperature APS system with a Sulzer Metco 9MB torch at a standoff distance of 100 mm. The two other coating layers were deposited at 1200 °C within a box furnace, using a plasma torch originally designed by Electro-Plasma Inc. (EPI) with a standoff distance of 190 mm, Fig. 3. Each spray system had a single Plasmatron Roto Feed Hopper (Model 1251) with standard powder feed wheel that was set to 2.2 rpm. Based on a similar powder feed system, we estimate the Yb₂SiO₅ feed rate was ~27 g/min and the mullite feed rate was ~13 g/min. The fineness of the silicon powder led to difficulties with catch can experiments, but we project (based on differently sized Si powder) that the feed rate was ~10 g/min. The silicon bond coat was deposited onto unheated substrates using a torch power of 50 kW. The plasma forming gas was a 2:1 mixture of Ar and N₂ with a flow rate of 3400SLM. The plasma plume was traversed 3 times across the sample at a speed of 1250 mm/s using six-axis robotic manipulation. For the mullite and Yb₂SiO₅ top coat deposition, the silicon coated substrates were heated to 1200 °C inside a box furnace containing a small aperture through which APS depositions were performed, Fig. 3. The mullite layer was deposited using a plasma power of 56 kW; the Yb₂SiO₅ was deposited at a lower power of 35 kW. Both coatings were deposited using a 2:1 mixture of Ar and He for the plasma forming gas and a flow rate of 763SLM. These coating layers were deposited by traversing the plasma plume twice across the samples at a speed of 950 mm/s. After fabrication,
some samples were stabilization annealed in air at 1300°C for 20 h.

2.2. Characterization

Both the as-fabricated and annealed samples were subjected to XRD analysis using a PANalytical X’Pert PRO MPD diffractometer (Westborough, MA) and Cu Kα radiation to identify top coat phases and volume fractions. Residual stress was calculated for the top coat from XRD measurements using the sin²ψ technique[35] with χ tilts of 0°, 18.43°, 26.56°, 33.21°, 39.23°, and 45° for diffraction peaks (2θ) between 55° and 65°. Diffraction peaks of this low angle reflection were used because neither Yb₂O₃ nor Yb₂SiO₅ had high angle peaks of measurable intensity. The low angle of the peaks prohibits precise measurements, but reported figures are reasonable approximations of the stress state. Peak center fitting was accomplished using a Gaussian fitting algorithm (Solver in Microsoft Excel) that included a slanting background fit. Additionally, both as-fabricated and annealed samples were sectioned and diamond polished to 0.25 μm finish, and in some cases vibrapolished using 0.02 μm silica colloid suspension. They were then examined by SEM in BSE mode, and with EDS.

The difference in electron backscattering coefficient η between regions of disparate composition was utilized during coating characterization. It relates the flux of backscattered electrons emitted from the sample to the flux of incident electrons in the probe. This factor can be calculated for a multicomponent mixture using a weighted sum: ηmix = Σηic i where ηi is the backscatter coefficient for the ith element in pure form, and Ci is the weight fraction for the ith element in the compound. The backscatter coefficient for each pure element may be estimated (for a broad range of accelerating voltages) using an empirical expression[36]:

\[
\eta_i = -0.0254 + (0.016)Z_i - (1.86 \times 10^{-4})Z_i^2 + (8.3 \times 10^{-7})Z_i^3
\]

where Z_i is the atomic number of the ith element. Contrast in BSE images was adjusted using gamma-correction over multiple ranges of the 16-bit spectrum to preserve detail of compositional variation within each coating layer.

The EDS spectra were standardized (except where noted) using an aggregate spectrum from the respective powders for calibration. To form the calibration standard, spectra were collected from a minimum of 20 randomly selected particles of the as-received powder with greater than 2.5 × 10⁵ total counts for each spectrum. The net integrated intensity under the respective peaks was summed to attain a total standard spectrum for the respective compound with greater than 5 million total counts. Crack and pore distributions were calculated by image analysis using an average from 3 different areas of the same sample where a 100 μm length of the layer was examined.

2.3. Dilatometry

We have measured the CTE of the ytterbium monosilicate using a Netzsch 402 C Dilatometer (Burlington, MA) calibrated with high purity alumina. The Yb₂SiO₅ sample was prepared by hot-pressing the as-received Yb₂SiO₅ powder for 3 h at 1650 °C with ~40 MPa load. The hot pressing resulted in a blank that was ~70% dense. The Yb₂SiO₅ dilatometry sample was cut from the blank with dimensions of 4 mm × 4 mm × 14 mm. The tests were performed between 20 °C and 1450 °C using heating and cooling rates of 3 °C/min. The expansion displacement data was recorded at 0.05 °C steps and used to compute the expansion strain and CTE. CTE curves have been smoothed whereas expansion curves have not.

3. Results and discussion

3.1. Yb₂SiO₅ thermal expansion coefficient

The thermal expansion strain versus temperature relationships during heating and cooling of hot pressed Yb₂SiO₅ are shown in Fig. 4. The hysteresis upon heating and cooling is similar to that previously reported for RE tungstate’s of low crystal symmetry, attributed to anisotropic thermal expansion. The CTE deduced from the strain data is also shown in Fig. 4. The CTE during heating ranged from 5.7 to 9.1 × 10⁻⁶ °C⁻¹, while during cooling it varied from 2.8 to 10.9 × 10⁻⁶ °C⁻¹. Standard convention is to report the CTE measured during the heating phase of the test, and we report an average CTE of 7.4 × 10⁻⁶ °C⁻¹, which supports the most recent value reported by Lee.⁵⁷ Table 1. While hysteresis of the thermal expansion strain was observed, no permanent change in length occurred, indicating that sintering did not contribute to the measured CTE.

3.2. Tri-layer EBC structure

A BSE image of an as-deposited tri-layered EBC system is shown in Fig. 5(a). Detailed measurements over the 1.27 cm
wide coating indicated a variation in silicon bond coat thickness of 75–150 μm, a mullite layer thickness variation of 25–100 μm, and an Yb2SiO5 top coat thickness between 25 and 100 μm. These variations resulted from fluctuations in the powder feed rate (“powder pulsing”, presumably due to low feed RPM) and temperature variation of the particles which impacted the surface: those that had not sufficiently melted did not adhere to the sample, and those that were too hot may have “splashed” off. Mud-cracking of the top coat was observed in the as-deposited coatings, Fig. 5(a). These mud-cracks were spaced several hundred micrometers apart, and frequently extended into the mullite layer during the stabilization annealing treatment, Fig. 5(b), but were arrested at the silicon bond coat confirming previous observations.38 All three layers contained porosity in the as-deposited condition; it was not removed by stabilization annealing.

Adhesion between the silicon bond coat and the SiC substrate appeared good, except in areas with high interfacial porosity, Fig. 5(a). Though the pores on the interface were small, they were numerous with 5–10 pores of 3–5 μm diameter intersecting each 100 μm length of interface. The interface between the silicon bond coat and mullite also contained isolated regions of weak bonding that appeared to result from incomplete flow of the liquid mullite droplets over the rough silicon bond coat, Fig. 5. The length of these regions ranged from a few to approximately 30 μm. On average these more weakly bonded regions were spaced 100 μm apart. The interface between the mullite and the Yb2SiO5 had very little porosity. The several micrometer long pores observed were typically located in areas where the radius of curvature of the underlying mullite coat was smallest.

3.3. Yb2SiO5 top coat

Splat-to-splat adherence in the ytterbium monosilicate coat appeared very good, though some spherical pores (with pore diameter of <0.5 μm) and more elongated porosity were seen at both splat-to-splat boundaries and within splats, Fig. 6(a). The planar density of these pores in cross-section was approximately 50 pores per 1000 μm² of coating. Pores of diameter <0.5 μm contributed about 0.2% to the total porosity while the contribution from larger spherical pores was around 0.7%. Filling defects (non-spherical/jagged pores) contributed roughly 0.6% to the total porosity, resulting in a total void volume fraction of about 1.5%.

Large vertical mud-cracks were present in as-deposited coatings, Fig. 5(a). These mud-cracks were not deflected by splat boundaries or pores, and were oriented nearly normal to the coating’s surface. The mud-cracks were periodically spaced several hundred micrometers apart. The cracks in as-deposited coatings generally terminated at the Yb2SiO5/mullite interface and had crack face opening widths (at ambient temperature) greater than a micrometer. Additional 1–10 μm long microcracks were also observed to originate at splat interfaces, Fig. 6(a). Some of the cracks were confined to a single solidified droplet while others had penetrated several solidified droplets. The cross-section planar density of these microcracks was roughly 5 cracks per 1000 μm² of top coat examined. Most were oriented normal to the coating surface, and therefore appear to be a micro-scale form of mud-cracking. While this population of micro-mud-cracks did not extend during stabilization annealing at 1300 °C, Fig. 6(b), a new population of equiaxed microcracks developed within many of the splats. These microcracks had lengths of 3–10 μm, and the combined planar density of all the microcracks after annealing had doubled to 10 cracks per 1000 μm² of top coat, Fig. 6(b). No delamination cracks were found in either the as-deposited or annealed Yb2SiO5 layer. When viewed at higher magnification, Fig. 7(a), many of the splats appear to have deposited with fine dendritic structures with intermediate spacing around 100 nm; these structures stabilized into a two-phase structure upon annealing similar to that expected for the slow cooling of eutectic phase structures, Fig. 7(b).

The presence of both circular (undeformed) and highly elongated splat shapes in the as-deposited coatings indicates both partially and fully melted particles were present during deposition of the layer, Fig. 6. This variation is consistent with a substantial spread in particle trajectories (and therefore
thermal profiles) through the plasma plume. BSE contrast differences between individual splats in Fig. 6(a) indicate compositional variations in the as deposited ytterbium silicate layer. The contrast is directly related to the electron backscatter coefficient $\eta$ of a composition. We calculate (using Eq. (1)) that for Yb$_2$O$_3$, $\eta = 0.75$. It is 0.67 for Yb$_2$SiO$_5$, and 0.61 for Yb$_2$Si$_2$O$_7$. The large differences in $\eta$ between these three phases indicate that small compositional differences in the Yb$_2$O$_3$–SiO$_2$ pseudo-binary system are readily observed by BSE imaging, and the differences in contrast of the various splats in Fig. 6(a) are due to variations of their composition.

To quantify the compositional differences of splats in the as-deposited coating, energy dispersive spectra were collected from the points indicated in Fig. 6(a). A summary of the composition data as well as that of the as-received powder was given in Table 2. EDS analysis indicated significant loss of silicon from the lightest contrast splats. A summary of the EDS analysis, Table 3, indicated some splats contained as little as 2 at% silicon. The deposited stoichiometry was on average 0.6 at% lower in Yb, 1.9 at% lower in Si and 2.5 at% higher in oxygen than the starting powder, indicating loss of Si with respect to Yb. We note that preferential loss of silicon during APS processing has also been suggested for the RE silicate apatite phase La$_9$SrSi$_6$O$_{26.5}$.

Table 3

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Composition (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Yb content</td>
<td>24.4 ± 2.7</td>
</tr>
<tr>
<td>Yb max/min</td>
<td>36.1/17.4</td>
</tr>
<tr>
<td>Average Si content</td>
<td>10.6 ± 2.3</td>
</tr>
<tr>
<td>Si max/min</td>
<td>14.3/1.6</td>
</tr>
<tr>
<td>Average O content</td>
<td>65.0 ± 0.9</td>
</tr>
<tr>
<td>O max/min</td>
<td>68.9/59.1</td>
</tr>
</tbody>
</table>

Upon stabilization annealing (1300 °C, 20 h, air), many of the solidified droplets appeared to have undergone a phase decomposition reaction with a light BSE contrast phase appearing on the grain boundaries. This can be clearly seen for the center top

Fig. 6. High magnification micrographs of the Yb$_2$SiO$_5$ topcoats from: (a) region I in as-deposited micrograph Fig. 5(a), and (b) region IV in the annealed condition micrograph Fig. 5(b).

Fig. 7. High magnification views of (a) region VII in the as-deposited coating shown in Fig. 6(a), and (b) annealed top coat near a splat boundary.
splat of Fig. 6(b). After stabilization annealing, the dendritic structure of the splats in Fig. 7(a) has been replaced with an equiaxed polycrystalline structure with extremely fine precipitates, Fig. 7(b). Again, the precipitate structure was too fine to analyze via EDS, but compositional fluctuations within the bulk structure after annealing were assessed using a line scan, Fig. 8. The variations in Si, Yb and O are shown together with the reference concentrations of these elements in Yb$_2$SiO$_5$. The results indicate that the darker contrast droplets had compositions close to that of Yb$_2$SiO$_5$ and precipitated a smaller volume fraction of the second phase than the silicon depleted droplets. The medium contrast splats had low silicon contents and decomposed into a two-phase mixture with approximately equal volume fractions of each phase. The lightest contrast splats precipitated small amounts of the gray phase in some instances (as can be seen in Fig. 7(b)), but remained largely free of gray phase precipitates. The composition of the lightest regions approached that of ytterbia (Yb$_2$O$_3$).

The silicon content of the solidified droplets in the as-deposited ytterbium monosilicate layer showed considerable variability, Table 2, but was almost always less than that of the powder used for its fabrication. Examination of Fig. 5 shows that while some of the larger diameter powder particles had retained a spherical shape, indicating they had barely melted in the plasma plume, others with much lighter BSE contrast (indicative of a higher fraction of high atomic number elements) had flowed significantly upon impingement with the depositing coating. This suggests they had been heated well above the melting point of ytterbium monosilicate ($T_m = 1950$ °C). The lighter BSE contrast and the EDS compositional characterization is consistent with preferential silicon evaporation from the most heated particles during the plasma spray process.

The partial pressure of the highest vapor pressure species in equilibrium with a mixture of Yb$_2$O$_3$ + SiO$_2$ and plasma forming gases at 1 MPa can be calculated using the FactSage software program. Assuming ideal interactions between Yb$_2$O$_3$ and SiO$_2$, and 80 g of Yb$_2$SiO$_5$ in 761 standard liters of an inert gas mixture with an Ar:He gas volume ratio of 2:1 containing 10 ppm of O$_2$, it is possible to calculate the partial pressure of the constituents as a function of temperature, Fig. 9. Recent thermal models of plasma spray processes predict temperatures of powder particles in plasma spray plumes in the 2000–3500 °C range for spray parameters similar to those used here.\cite{86-90} Particles heated into this temperature range have SiO activities (vapor partial pressures) that are many orders of magnitude above those of Yb or any of its oxides. We therefore conclude that during superheated molten particle transport through the plasma plume, the loss of SiO significantly exceeds that of Yb. This will be exacerbated for particles that are heated to the highest temperatures or for the longest times; i.e. smaller diameter particles or those entrained in the core of the plasma plume where temperatures are the highest.\cite{86-90}

The phases that form during solidification of silicon depleted droplets can be understood with the aid of the ytterbia-silica pseudo-binary phase diagram, Fig. 10.\cite{59} Silicon loss from Yb$_2$SiO$_3$ line compound shifts the composition into a two phase

Fig. 8. EDS line scan of annealed ytterbium silicate top coat. Dashed lines indicate atomic compositions for Yb$_2$SiO$_5$. Note 40 at% Yb–60 at% O is the composition of ytterbia. Location of scan line is indicated on accompanying micrograph.

Fig. 9. Calculated partial pressure versus temperature plot for primary gaseous species in the Yb–Si–O system. Curves are reported for an equilibrated system.

Fig. 10. Ytterbia-silica pseudo-binary phase diagram (redrawn from Ref. 59).
Yb$_2$O$_3$ + Yb$_2$SiO$_5$ region of the phase diagram. This region contains a eutectic point, and so the as-solidified structure that forms will be dependent upon a droplet’s composition. Examination of Table 3 shows that some particles contained only a tenth the silicon fraction of the original powder. Under equilibrium cooling conditions, these would nucleate solid proeutectic Yb$_2$O$_3$ dendrites, and a eutectic Yb$_2$SiO$_5$ + Yb$_2$O$_3$ inter-dendritic structure consistent with the result shown in Fig. 7(a). Liquid droplets with hypereutectic compositions would precipitate proeutectic Yb$_2$SiO$_5$ and an inter-dendritic eutectic structure. The rapid solidification rate of the droplets is likely to result in a very small dendrite spacing that would be difficult to resolve with the SEM; but on annealing, these two microstructures are expected to evolve to the two types of coarser structure seen in micrographs such as Figs. 6(b) and 7(b). The lightest contrast (most silicon depleted) regions consisted of a continuous Yb$_2$O$_3$ phase containing particles of Yb$_2$SiO$_5$, Fig. 7(b), whereas those with hyper-eutectic compositions consisted of equiaxed Yb$_2$SiO$_5$ polycrystals with grain boundary Yb$_2$O$_3$ particles as seen in the darker contrast splats in Fig. 6(b).

XRD patterns of both the as-deposited and annealed top coat are shown in Fig. 11. The reflection peaks in both patterns can be indexed using the diffraction patterns of monoclinic ytterbium monosilicate and cubic ytterbia. A hump in the diffraction pattern at low 2θ (below 20°, not shown) was present in the XRD patterns of as-deposited top coats indicating the presence of amorphous material. After the annealing, the absence of a low 2θ hump in the patterns indicated the coating had fully crystallized. A Rietveld analysis$^{83}$ of the annealed coating indicates the composition to be 85 vol% Yb$_2$SiO$_5$ and 15 vol% Yb$_2$O$_3$, Fig. 11(b). The as-deposited ytterbia exhibited peak shifts with respect to the ytterbia reference pattern; for example the ytterbia {2 2 2} peak was shifted +0.5°. This peak shift is not seen in annealed coatings and corresponds to a contraction in lattice
parameter in the out-of-plane (coating normal) direction with respect to the reference crystal lattice parameter. A XRD residual stress measurement of the as-deposited top coat was performed using the ytterbia \((6\,2\,2)\) peaks, and indicated the ytterbia in the top coat at room temperature to have a tensile residual stress of 425 MPa with a \(\sin^2 \psi\) correlation coefficient of \(R^2 = 0.74\). For the annealed top coat only ytterbium monosilicate peaks had high enough intensities for stress measurements. However, since \(\text{Yb}_2\text{SiO}_5\) is monoclinic,\(^{59}\) the room temperature stress state between individual grains is expected to vary widely, and the \(\sin^2 \psi\) measurement technique was inconclusive.

The observed mud-cracking is consistent with the substantial CTE difference between the top coat and the rest of the system, as suggested by a recently reported CTE measurement for \(\text{Yb}_2\text{SiO}_4\)\(^{57}\) and confirmed by our dilatometry measurements in Section 3.1, Table 1. To investigate the origin of cracking, we performed an elastic thermomechanical calculation of the stress state in the coating system using a previously described approach that used a thin film approximation.\(^{91}\) The thin film approximation assumes curvature of the composite system and a biaxial stress state in coating layers whose elastic moduli, Poisson’s ratio and CTE are different. It is also assumes that the interactions between coating layers are small in comparison to the interaction with the substrate, and the stress in each coating layer is therefore independent of that in adjacent layers. This approach leads to a thermal residual stress in the \(i\)th coating layer (prior to relaxation by cracking) given by:

\[
\sigma_i = \left(\frac{E_i}{(1 - \nu_i)}(\alpha_x - \alpha_i)\right) \Delta T
\]

where \(\sigma_i\) is the thermal stress in the \(i\)th layer, \(E_i\) is the elastic modulus of the \(i\)th layer, \(\nu_i\) is its Poisson’s ratio, \(\alpha_x\) and \(\alpha_i\) are the CTE of the substrate and \(i\)th layer respectively, and \(\Delta T\) is the difference in temperature between the stress free (deposition) temperature of the \(i\)th layer and the temperature of interest. We have verified the validity of this approach for our system using a more accurate solution formulated by Hsueh\(^{92}\) where the layer stresses are interdependent: the stresses calculated using the two methods were identical.

Residual thermal stresses have been calculated for all layers of the coating and secondary phases using the thermophysical properties of each layer and assuming the stress free temperature to be the annealing temperature \((1300\, ^\circ \text{C})\), Table 4. If we assume the top coat to be pure ytterbium monosilicate with a CTE of \(7.5 \times 10^{-6} \, ^\circ \text{C}^{-1}\) (as proposed by Lee\(^{57}\) and consistent with our measurements), we calculate that the top coat develops a biaxial tensile stress of 893 MPa upon cooling to ambient temperature. The stress calculated for an \(\text{Yb}_2\text{O}_3\) enriched \(\text{Yb}_2\text{SiO}_5/\text{Yb}_2\text{O}_3\) top coat would be somewhere between the values calculated for \(\text{Yb}_2\text{SiO}_3\) and \(\text{Yb}_2\text{O}_3\): the stress will increase moderately with increasing \(\text{Yb}_2\text{O}_3\) content, Table 4.

The mud-cracking observed in as-deposited and annealed coatings is consistent with the high tensile stress calculated for the top coat using Eq. (2). If such a tensile stress exists upon cooling from deposition, the lattice parameter of all phases should be slightly larger in the in-plane directions due to the biaxial tensile stress state, and slightly contracted in the out-of-plane directions (due to the Poisson effect). This is consistent with analysis of the diffraction pattern of Fig. 11(a). The measured residual tensile stress of 425 MPa in the \(\text{Yb}_2\text{O}_3\) phase of the as-deposited coating is about half that calculated in Table 4, presumably because mud-cracking had partially relaxed the strain in this layer. For annealed top coats, only diffraction from monoclinic ytterbium monosilicate could be measured. However, the anisotropic thermal expansion properties of this crystal class lead to angular distortions\(^{93}\) and a room-temperature stress state which is not biaxial at the grain size scale: accurate stress measurement using the \(\sin^2 \psi\) method was not possible, so stress evolution could not be monitored using this technique.

Micro-mud-cracking was observed in the most silicon depleted droplets, Fig. 6(a). If we assume a rule of mixtures for the CTE and elastic modulus of such splats, then the lightest contrast splats will have a slightly greater CTE and elastic modulus than dark contrast splats (Table 4). When the slightly higher CTE is combined with the increased elastic modulus of these predominantly ytterbia splats, the small, ytterbia rich splats will experience a state of triaxial tension (even in the mud-cracked coating) upon cooling due to their higher CTE. The strain energy may then be released by microcracking. We therefore conclude that in the most intensely heated, light contrast splats, evaporation of silicon in the molten state leads to the formation of \(\text{Yb}_2\text{O}_3\) which is susceptible to microcracking due to high macro and local tensile thermal residual stresses.

Upon annealing the top coat, additional “equiaxed” microcracking was observed in the darker BSE contrast droplets, Fig. 6(b). Increases in microcracking upon annealing have been...

---

Table 4

<table>
<thead>
<tr>
<th>Coating layer</th>
<th>Young’s modulus (GPa)</th>
<th>CTE ((\alpha \times 10^9) , ^\circ \text{C}^{-1})</th>
<th>Poisson ratio (\nu)</th>
<th>Thermal stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Yb}_2\text{SiO}_5) (monoclinic)</td>
<td>172(^a)</td>
<td>7.5 ((58, \text{Section 3.1}))</td>
<td>0.27(^b)</td>
<td>893 (tensile)</td>
</tr>
<tr>
<td>(\text{Yb}_2\text{SiO}_5) (monoclinic)</td>
<td>172(^a)</td>
<td>4.0(^b)</td>
<td>0.27(^b)</td>
<td>211 (compressive)</td>
</tr>
<tr>
<td>(\text{Yb}_2\text{O}_3) (cubic)</td>
<td>188(^b)</td>
<td>7.6(^d)</td>
<td>0.30(^e)</td>
<td>1013 (tensile)</td>
</tr>
<tr>
<td>3:2 Mullite (orthorhombic)</td>
<td>220(^f)</td>
<td>5.3(^g)</td>
<td>0.28(^h)</td>
<td>246 (tensile)</td>
</tr>
<tr>
<td>Alumina ((\alpha))</td>
<td>402(^i)</td>
<td>7.2(^j)</td>
<td>0.23(^k)</td>
<td>1693 (tensile)</td>
</tr>
<tr>
<td>Silicon ((\text{dcc}))</td>
<td>163(^l)</td>
<td>4.1(^m)</td>
<td>0.22(^n)</td>
<td>153 (compressive)</td>
</tr>
<tr>
<td>Silicon carbide ((\alpha))</td>
<td>430</td>
<td>4.67</td>
<td>0.14</td>
<td>N/A</td>
</tr>
</tbody>
</table>

\(^a\) Determined by nano-indentation.
\(^b\) Value taken for \(\text{Yb}_2\text{Si}_2\text{O}_7\).\(^{94}\)
\(^c\) Value taken for \(\text{Yb}_2\text{O}_3\).\(^{96}\)
observed previously in EBCs and have been linked to volume changes during phase transformation.\textsuperscript{50,65,99–101} We note that the droplets where microcracking was most prevalent consisted primarily of Yb\textsubscript{2}SiO\textsubscript{5}. If a substantial difference in CTE with crystallographic orientation exists as in Y\textsubscript{2}SiO\textsubscript{5}\textsuperscript{102} and other monoclinic structures,\textsuperscript{76} anisotropic thermal stresses will occur upon cooling between Yb\textsubscript{2}SiO\textsubscript{5} crystals that may have contributed to the observed cracking.

### 3.4. Mullite intermediate layer

A higher magnification micrograph of region II from Fig. 5(a) of the as-deposited mullite layer is shown in Fig. 12(a). The as-deposited mullite layer contained a variety of pore structures. Some larger, rounded pores had diameters of several micrometers while flattened pores existed at some inter-splat boundaries. Inter-splat pores have been reported to result from filling defects during plasma spray processing.\textsuperscript{84} We calculate that rounded and flattened pores contributed roughly 1% to total porosity of the coating layer. The majority of the mullite coat was nanoporous with a nanopore diameter of 10–100 nm and a cross-sectional pore density of approximately 7000 pores per 1000 \(\mu\)m\textsuperscript{2}, contributing 7% to total porosity of the layer. The total mullite coat porosity was \(\sim 8\%\). The as-deposited mullite structure was two-phase with a plate-like morphology second phase. After stabilization annealing, the number of plates had increased significantly and the spacing between plates decreased. Dense, recrystallized areas of the mullite matrix with columnar crystal growth were evident in the microstructure, Fig. 12(b).

EDS analysis of the as-deposited mullite coats indicates they were oxygen and silicon deficient, Table 5. The average deposited composition of the layer was 6.3 at% higher in Al, 1 at% higher in Si and 7.3 at% lower in O than the starting powder, indicating volatilization of Si and O. The deposited Al:Si ratio lies between 3:2 and 2:1 mullite, having a ratio of 3.5:1 (2:1 mullite is 4:1 Al:Si and 3:2 mullite is 3:1 Al:Si). The plate-like features seen in Fig. 12(a) were slightly rich in aluminum, having aluminum contents 1–3 at% higher than the surrounding matrix. An EDS line scan analysis of the annealed mullite layer, Fig. 13, indicates the stoichiometric difference between plate-like features and the surrounding matrix increased considerably during annealing. The EDS analysis indicated the plates to be composed of Al\textsubscript{2}O\textsubscript{3} containing 1–5 at% silicon, while the surrounding matrix composition approached 3Al:1Si corresponding to 3:2 mullite. Regions with no precipitated alumina yielded EDS compositions close to 3:2 mullite.

The presence of alumina plates in APS mullite is consistent with previous XRD and SEM observations.\textsuperscript{50} Higher resolution analysis showed the plates were composed of sub-plates of alumina with fine bands of a silicon-rich species interspersed, Fig. 14. Analysis of a single area at high magnification indicated that the plate region was composed of 76 vol% alumina platelets, 22 vol% silicon-rich species, and 2% porosity. The silicon-rich bands were too small to analyze with EDS in the SEM, having widths ranging from several nanometers to roughly 100 nanometers, but BSE imaging contrast indicates that these bands may be similar in composition to the surrounding mullite matrix. Several plates in the annealed coating were microracked, Figs. 12(b) and 13.

We have observed that the APS melting and deposition of initially stoichiometric 3:2 mullite powder resulted in an alumina rich, near 2:1 mullite coating, Table 5. The composition deposited here is similar to that of previous studies on melt processed mullite,\textsuperscript{66,103} but was less silicon deficient than the 3:1 stoichiometry coating previously reported for EBCs.\textsuperscript{50,104} The FactSage software\textsuperscript{85} can again be used to determine the

\begin{table}[h]
\centering
\begin{tabular}{|l|l|}
\hline
Parameter & Composition (at\%) \\
\hline
Average Al content & 34.9 \pm 1.6 \\
Al max/min & 39.9/27.1 \\
Average Si content & 10.5 \pm 1.6 \\
Si max/min & 19.2/5.2 \\
Average O content & 54.6 \pm 0.8 \\
O max/min & 56.9/51.4 \\
\hline
\end{tabular}
\caption{Atomic compositions for as-deposited mullite coat calculated from EDS point probe spectra at 550 rectangular grid points distributed over six different collection areas. All values are in at\%.}
\end{table}
equilibrium partial pressures of the gas species for a mixture of $3\text{Al}_2\text{O}_3 + 2\text{SiO}_2$ and the plasma forming gas assuming ideal interactions. Fig. 15 shows the calculated vapor pressure versus temperature relations for the components of a system consisting of $35\,\text{g}$ of $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$ (with a stoichiometry of $\text{Al}_6\text{Si}_2\text{O}_{13}$) and 761 standard liters of 2:1 $\text{Ar}:\text{He}$ volume fraction ratio gas containing 10 ppm O$_2$. The particle temperatures during plasma deposition lie in the 2000–3500 °C range where the vapor pressure of SiO is several orders of magnitude higher than those of any aluminum containing vapor species. This vapor pressure difference therefore results in preferential evaporation of SiO and formation of a compositionally modified mullite layer.

![Fig. 13. EDS line scan of annealed mullite layer. The initial $3\text{Al}_2\text{O}_3 + 2\text{SiO}_2$ molar mullite composition is indicated by dashed lines. Note that 40 at% Al–60 at% O is the composition of alumina. The location of the line scan is indicated on the micrograph.](image)

![Fig. 14. High magnification view of phase decomposition into alumina plate separated by silicon rich material in the annealed mullite coat.](image)

![Fig. 15. Calculated partial pressure vs. temperature plot for primary gaseous species in the Al–Si–O system. Data are reported for a fully equilibrated system.](image)

![Fig. 16. Alumina–silica pseudo-binary phase diagram. Dashed lines indicate the boundaries of metastable phases (modified and redrawn from Ref. 65).](image)

A phase diagram for the SiO$_2$–Al$_2$O$_3$ system is shown in Fig. 16. Dashed lines for 2:1 and 3:1 mullite indicate compositional boundaries for the formation of metastable mullites. The silicon deficient 2:1 mullite we have deposited lies in the alumina + mullite two-phase field of the equilibrium phase diagram. Examination of Fig. 12(a) indicates that a predominantly single-phase 2:1 composition mullite was deposited. This then transformed upon annealing at 1300 °C into a two-phase structure consisting of Al$_2$O$_3$ + mullite, consistent with the as-deposited composition and low temperature metastability of non-stoichiometric mullites. Afterannealing, areas in the mullite coat also have dense, columnar recrystallized grains with similar BSE contrast to the surrounding matrix. High aspect ratio columnar mullite grains have been previously observed in fine-grained (recrystallized) 3:2 mullite with growth textured along the “c” axis. These grains are interspersed with a very fine plate-morphology phase that appears similar in BSE contrast to alumina. The occurrence of such recrystallized regions is consistent with a phase transformation from metastable 2:1 mullite to equilibrium 3:2 mullite + alumina.

The as-deposited mullite layer had not mud-cracked. However, some areas of delamination between this layer and the silicon bond coat were observed, Fig. 12(a). During annealing 25–100 μm long intra-layer microcracking between solidified droplets was observed, as well as mud-crack extension from the top coat, Fig. 12(b). These observations are consistent with...
earlier findings of APS deposited mullite coatings.\textsuperscript{50,65} The overall crack density was low with roughly 1 crack per 1000 $\mu$m\textsuperscript{2} of cross section examined. Previous work in APS deposited mullite has suggested that mullite layers can microcrack as a result of second phase alumina or silica precipitation.\textsuperscript{51} The microcracking of the alumina plates after annealing, Figs. 12(b) and 13, appears to be a consequence of the CTE mismatch between alumina and mullite since $\alpha$-alumina has an average CTE of $7.2 \times 10^{-6}$ °C\textsuperscript{-1}, which is substantially higher than that reported for surrounding mullite ($5.5 \times 10^{-6}$ °C\textsuperscript{-1}, Table 1). Upon cooling to ambient temperature from the annealing temperature, this CTE difference would induce triaxial tensile stresses much higher than those experienced in the rest of the mullite coat (Table 4) that are conducive to alumina microcracking.

3.5. Silicon bond coat

The region marked as III in Fig. 5(a) of the as-deposited bond coat is shown at higher magnification in Fig. 17(a). The bond coat contained significant porosity located at splat boundaries. Typical pore diameter was 3–5 $\mu$m. There were approximately 5–10 pores per 100 $\mu$m of inter-splat interface. The many debonds and pores between the splats resulted in a network of interconnected pores and debonds within the bond coat.

Upon annealing in air, the interconnected pore-crack network became internally covered in a darker contrast phase. This appeared to be silica and was verified by EDS, Table 6. Oxidation of the pore surfaces resulted in an interconnected silica network throughout the bond coat, Fig. 17(b). The measured silica thickness was $\sim$500 nm throughout the majority of the bond coat, though greater thicknesses were observed near the coating edges. Mud-cracks that had extended from the top coat through the mullite layer had terminated at the silicon/mullite interface and did not show any sign of oxidation, Fig. 18, indicating that these cracks formed upon cooling after the stabilization anneal.

The presence of porosity both within the Si coating and at the SiC/Si interface resulted from several causes. The presence of inter-splat voids, Fig. 17(a), is consistent with both the temperature of some powder particles at impact being insufficient to allow complete liquid droplet flow over the coating surface and others being so hot that porous regions form due to droplet “splashing” that creates micrometer sized particles. Additionally, because the silicon bond coat was deposited in

---

**Table 6**

Atomic compositions reported by PB-ZAF (non-standardized) analysis of point probe spectra in Fig. 17(b).

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Si (at%)</th>
<th>O (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point 1</td>
<td>27.0</td>
<td>73.0</td>
</tr>
<tr>
<td>Point 2</td>
<td>26.5</td>
<td>73.5</td>
</tr>
<tr>
<td>Point 3</td>
<td>27.3</td>
<td>72.7</td>
</tr>
<tr>
<td>Point 4</td>
<td>93.7</td>
<td>6.3$^*$</td>
</tr>
<tr>
<td>Point 5</td>
<td>94.2</td>
<td>5.8$^*$</td>
</tr>
<tr>
<td>Point 6</td>
<td>93.8</td>
<td>6.2$^*$</td>
</tr>
<tr>
<td>Silica (SiO$_2$)</td>
<td>33.3</td>
<td>66.7</td>
</tr>
</tbody>
</table>

$^*$ Trace oxygen resulted from native oxide growth after sample preparation and oxygen detection inaccuracy in PB-ZAF analysis.
argon shrouded air, oxygen can be entrained in the plasma plume resulting in rapid formation of a native oxide on liquid particle surfaces that impedes inter-splat bonding. The combination of these effects has resulted in a less than ideal bond coat structure.

After annealing, the appearance of a roughly 500 nm thick silica layer was observed on the interior surface of many voids and inter-splat debonds within the silicon bond coat. Fig. 17(b). Regions closest to the edges of the sample coupon had silica scale thicknesses exceeding 600 nm. The growth of such silica scales is well documented and accepted to follow the Deal and Groves model. Using the Deal and Groves analysis, we have back-calculated the oxygen partial pressure during exposure to form a 500 nm silica scale in 20 h at 1300 °C. The oxygen partial pressure calculated is 0.13 atm, or 60% of the oxygen partial pressure found in dry air at atmospheric pressure (101 kPa); this partial pressure is too great to result from bulk diffusion through the coating. An oxygen partial pressure lower than the surrounding environment implies that oxygen was forced to follow a gas diffusion route as opposed to a convective route to the bond coat; the relatively high partial pressure back-calculated is reflective of the rapid gas diffusion kinetics of oxygen at high temperatures. The necessity of molecular diffusion transport combined with the long diffusion path through silica channels that are actively absorbing oxygen may have yielded lower O2 partial pressures in pores located far from coating edges and close to the substrate.

4. Conclusions

An APS process was used to deposit a tri-layer environmental barrier coating system consisting of a silicon bond coat, a mullite interdiffusion barrier, and an Yb2SiO5 top coat on monolithic α SiC substrates. We find that:

1. While the APS process is able to deposit tri-layer coatings, many defects are introduced during the process. These include micro and nanoscale porosity formed by incomplete molten droplet flow during splat impact, inter-splat delamination within the silicon bond coat forming an interconnected pore and crack network, and mud-crack formation in the Yb2SiO5 top coat resulting from in-plane biaxial thermal contraction during cooling.

2. The majority of the solidified droplets in the as-deposited Yb2SiO5 and mullite layers were depleted in silicon. This led to the formation of two-phase top coats consisting of a mixture of Yb2SiO5 and Yb2O3 as well as 2:1 mullite layers deposited from 3:2 mullite powders. The loss of silicon was consistent with preferential silicon evaporation from superheated powder particles; a consequence of the higher vapor pressure of silicon bearing species at the temperatures experienced during transient plasma heating.

3. Annealing in air at 1300 °C resulted in mud-crack extension from the top coat into the mullite layer and oxidation of the interconnected crack and pore network in the bond coat. The precipitation of Yb2O3 combined with the anisotropic thermal expansion of Yb2SiO5 in the top coat resulted in microcracking.

4. Upon annealing, the 2:1 as-deposited mullite transformed to a mixture of 3:2 mullite + alumina consistent with phase equilibria in this system. Additional microcracking occurred within the precipitated alumina plates due to significant CTE mismatch between alumina and the coating system.

Acknowledgements

We express our gratitude to Dennis Fox, Bryan Harder, and Michael Cuy at NASA Glenn who helped us to deposit the APS coatings described in this research. We are also grateful to Elizabeth Opila for advice on thermochemistry and Md Shamsujjohar for aid in residual stress measurement. Some imaging in this work was performed at ICTAS NCFL. Rolls Royce (Indianapolis) supported some aspects of this work and we are grateful to K. Lee of that organization for helpful discussions. The Office of Naval Research (ONR) also supported this study under grant N00014-11-1-0917 (program manager Dr. David Shifler).

References


Glossary

CTE: coefficient of thermal expansion
BSE: backscattered electron
EDS: energy dispersive X-ray spectroscopy
RE: rare earth
SEM: scanning electron microscope
XRD: X-ray diffraction