Effect of rare-earth dopant (Sm) concentration on total hemispherical emissivity and ablation resistance of ZrB₂/SiC coatings

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The temperature of leading edges during hypersonic flight can be reduced by maximizing the emissivity of their surface. In this study, the concentration of a known emissivity modifier (Sm) has been varied (3, 5, and 8 mol% Sm in ZrB₂/SiC coatings) and the total hemispherical emissivity and ablation resistance of the coatings has been evaluated. Maximum emissivity was observed to occur for the 5 mol% Sm ZrB₂/SiC coating, with a value of 0.9 measured at 1600°C. All the ablated Sm-doped coatings have an oxide scale consisting of m-ZrO₂ and c₁-Sm₂(Zr₀.₉O₁.₉)₂O₇, and/or Sm₂Zr₂O₇ depending on the Sm concentration. Large amounts of porosity were observed in the oxide scale of the ablated 8 mol% Sm ZrB₂/SiC coating. This was attributed to viscosity reduction of the B₂O₃ and SiO₂ glassy phases by the Sm⁺³ and their subsequent vaporization. The 5 mol% Sm-doped ZrB₂/SiC demonstrated the optimal emissivity properties and dense oxide scale formation.

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1. Introduction

The stagnation region of nose cones and leading edges of hypersonic vehicles have a large heat flux impinging their structure that leads to surface temperatures approaching 2000°C [1]. Zirconium diboride (ZrB₂), with 20–30 vol% SiC additions, is being considered for hypersonic applications because of its relative resistance to these extreme environments. The operating temperature of ZrB₂ with SiC additions, however, is still limited by the active evaporation of SiO₂ at 1600°C [2,3].

There are at least two heat transfer strategies to mitigate the temperature extremes that occur on the leading edges. These strategies point to a specific properties of the leading edge material to optimize. First, a high thermal conductivity lead edge material is desired to mitigate the effect of local hot spots and improve thermal shock resistance via conduction of the heat to thicker regions of the leading edge. The thermal conductivity of 30 vol% SiC/ZrB₂ has been reported as ranges between 44–64 W/mK at 400–1200°C [4]. Second, the emissivity of the surface should be maximized to be as close to that of a black body, ε ≈ 1, as possible. The radiation component of heat transfer has been shown to significantly cool the surface during hypersonic flight via re-radiation of the absorbed heat [2,5].

Previous studies by Guazzoni and McMahon et al. demonstrated the unique high emissivity properties of several rare-earth oxides, including Sm₂O₃ and Tm₂O₃ [6,7]. The unique optical properties of Sm₂O₃ arise from the strongly localized f-shell states of the samarium, which is independent of the details of the chemical bonding between the samarium and oxygen [8]. Based on Wien’s Displacement Law, at 1500–2000°C the maximum spectral emissivity occurs between 0.76–0.97 eV (1.27–1.62 μm). The absorption spectrum of Sm⁺³ [Xe]⁴f [5] is localized at 0.74–1.24 eV.

Preliminary work has indicated that emissivity modification is possible by doping samarium into ZrB₂/SiC coatings via a chemical infiltration approach [9–11]. At 1200°C, the total hemispherical emissivity increased from 0.8 to 0.93 when 10.3 mol% Sm was incorporated into the ZrB₂/SiC coating [9]. Furthermore, the ablation product of the samarium-doped ZrB₂/SiC coatings was c₁-Sm₁₋ₓBₓO₁.₉. This oxide has a melting temperature exceeding 2000°C [10], and remained protective after a 60 s exposure to a 2000°C oxyacetylene torch [12]. As maintaining sharp leading edges is crucial for performing flight maneuvers, the samarium-
modified ZrB$_2$/SiC system shows promise as a potential extreme condition coating for hypersonic flight.

The purpose of the current work was to determine the optimum concentration of samarium dopant required for ZrB$_2$/SiC coatings to maximize total hemispherical emissivity at temperatures up to 1500 °C. In addition, the effect of the amount of samarium on the microstructural development of the oxide ablation scale was studied. Thus, ZrB$_2$/SiC coatings were doped with 3, 5, and 8 mol% Sm as emissivity modifiers. The as-sprayed microstructure and phase analysis were investigated using several techniques including transmission electron microscopy (TEM).

2. Experimental procedure

2.1. Powder preparation and formulation

Spray-dried powders were prepared from a suspension with 58% powder loading. The suspension consisted of 80 vol% ZrB$_2$ (3–5 μm, Grade A, HC Starck, Munich, Germany), 20 vol% α-SiC (1.4 μm, Grade UF-05, HC Starck, Munich, Germany), 0.4 wt% dispersant (Darvan 821A, R.T. Vanderbilt Company, Inc., Norwalk, USA), 2 wt% PVA binder (Celvol 203, Celanese Corporation, Dallas, USA) and DI water. The average spray dried particle size was approximately 38 μm.

Samarium dopant was added to the spray dried ZrB$_2$/SiC powders via a chemical infiltration method [9,13]. In this process, 5, 10, and 15 mol% samarium nitrate hexahydrate (99.9% pure Sm(NO$_3$)$_3$·6H$_2$O, Sigma-Aldrich, St. Louis, USA) were dissolved in 200-proof ethanol and the resulting solution was then infiltrated into the porous spray-dried ZrB$_2$/SiC powder. Next, the solvent was removed via a rotary evaporator (BM 200, Yamato Scientific America Inc., Santa Clara, USA) at 100 °C. This powder was heated at 400 °C in air for an hour to remove residual moisture and nitrates. Subsequently, the dried mixture was sieved using a 60-mesh (250 μm aperture) to eliminate large agglomerates. Fumed silica (0.02 wt%, Cab-O-Sil®, Cabot Corporation, Boston, USA) was added to all the powders as a flowing agent for feeding the powders during the plasma spray process. The four different coatings studied are listed in Table 1.

The amount of samarium and silicon incorporated into the coatings was measured by mass spectroscopy on pulverized coatings (NSI Analytical Services Inc., Cleveland, USA). The actual concentrations of samarium in each coating are listed in Table 1. To help simplify discussion, the naming convention based on the actual samarium molar concentration will be used. For instance, the 3SmZBS coating contains ~3 mol% Sm in the ZrB$_2$/SiC matrix.

2.2. Plasma spray process

The coatings were prepared at Praxair Surface Technologies (Indianapolis, USA) using a shrouded plasma spray process, which limits oxidation of ZrB$_2$ and SiC [14]. Specifically, the shroud is flooded with argon during spraying. The coatings were sprayed on aluminum panels, ~99% dense sintered ZrB$_2$/SiC substrates, and tungsten rods for coating analysis, ablation testing, and total hemispherical emissivity testing, respectively. The average coating thickness ranged between 50–350 μm, depending on the test geometry. Stand-alone coatings were obtained by dissolving the coated aluminum panels in 5 M NaOH at 70 °C for 1 h.

2.3. Microstructural and phase analysis

The density of each coating, off the substrate, was determined using Archimedes’ methodology as described in the ASTM C373-88 standard [15]. The theoretical density was calculated using the rule of mixtures based on final coating compositions, where the density of ZrB$_2$, SiC, and Sm are 6.09 g/cm$^3$, 3.21 g/cm$^3$, and 7.52 g/cm$^3$, respectively. The surface roughness ($R_s$) of the coatings was quantified with a profilometer (AS0200 AlphaStep, Tencor Corporation, Milpitas, USA) at a scan speed of 10 μm/second. A total length of 300 μm was measured for each coating.

X-ray diffraction (XRD) using CuKα radiation (D8 Focus, Bruker Corporation, Billerica, USA) was performed on as-sprayed and oxidized coatings over 20 values of 20–70°. A step size of 0.05° and a scan rate of 5°/min were used. Coating topography, cross section, and element analysis were observed using a scanning electron microscope (SEM) equipped with energy dispersive x-ray spectroscopy (EDS) (Phillips XL-40, FEI Co., Hillsboro, USA). The non-conductive ceramic coatings were coated with a thin layer of Au/Pd prior to imaging. All post-ablative test samples were stored in a desiccator and the polishing process was performed with non-aqueous solutions.

TEM specimens were prepared with a focused ion beam (FIB) equipped with a gallium ion beam (FEI Quanta 3D FEG, Oregon, USA). Using a manipulator, the FIB specimens were lifted out and attached to a copper grid. Bright field (BF) images, electron energy loss spectroscopy (EELS), and EDS were acquired using a FEI Titan Environmental Electron Microscope (Oregon, USA).

2.4. Total hemispherical emissivity

Emissivity tests were performed by TPRL Inc. (West Lafayette, IN, USA) using the ASTM C835-06 standard as a guide [16]. A ~20 μm thick coating of ZrB$_2$/SiC was applied on the electrically conductive tungsten rod (3.8 mm outer diameter) before applying 50 μm of one of the samarium-doped ZrB$_2$/SiC coatings currently investigated. Prior to the start of the emissivity test, two pairs of type-K thermocouples and a pair of platinum electrodes were spot welded onto the center region of the sample to obtain temperature and voltage readings, respectively. The emissivity as a function of temperature, $\varepsilon(T)$, was calculated according to Stefan-Boltzmann law:

$$\varepsilon(T) = \frac{i\Delta V}{P_{Lr}(T^4 - T_s^4)}$$  

where $i$ is the electric current in amperes, $\Delta V$ is the voltage drop measured across the rod in volts, $P$ and $L$ are the perimeter and length of the rod, respectively, in meters, $\sigma$ is the Stefan-Boltzmann constant (W/m$^2$K$^4$), and $T_s$ and $T$ are the sample and ambient temperatures, respectively, in Kelvin. This test was performed in a vacuum (~1.3 mPa) to ensure radiation was the sole heat transfer mechanism. All emissivity values reported and discussed in this study are total hemispherical emissivity.

2.5. Oxyacetylene ablation test

The ablation resistance of the coatings in high heat flux conditions was evaluated by an oxyacetylene torch rig. The oxyacetylene ablative test setup was constructed using the ASTM 285-08 [17] standard as a guide. A two-color pyrometer (OS3750, Omega Engineering Inc., Stamford, CT, USA) was used to measure the front sample face temperatures and was connected to a data logger to record real time temperatures as a function of time. The coatings were deposited on sintered ZrB$_2$/SiC substrates and sectioned into 12 mm by 12 mm square samples. Each sample was held in place by a graphite fixture during testing. The ablation torch (Victor Technologies, St. Louis, USA) had a 3 mm orifice and the separation distance between the sample surface and torch was held constant at 20 mm. An oxygen-rich flame with a 10:12 slpm acetylene to oxygen ratio was used to simulate the oxidizing operating environment. Specimens were tested for 60 s, starting from when the
Table 1
Samarium-dopant concentration and as-sprayed coating properties.

<table>
<thead>
<tr>
<th>Sm(NO₃)₃ (mol%)</th>
<th>Actual Sm Incorporated (mol%)</th>
<th>Bulk Density* (g/cm³)</th>
<th>Total Porosity* (%)</th>
<th>Surface Roughness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZBS</td>
<td>0</td>
<td>4.5</td>
<td>18.2</td>
<td>3.47</td>
</tr>
<tr>
<td>3SmZBS</td>
<td>5</td>
<td>4.1</td>
<td>26.1</td>
<td>8.58</td>
</tr>
<tr>
<td>5SmZBS</td>
<td>10</td>
<td>3.7</td>
<td>32.0</td>
<td>16.07</td>
</tr>
<tr>
<td>8SmZBS</td>
<td>15</td>
<td>3.5</td>
<td>35.7</td>
<td>21.10</td>
</tr>
</tbody>
</table>

* All coatings nominally contained ZrB₂-20 vol% SiC. The porosity calculation is based on final coating composition.

Fig. 1. As-sprayed microstructure of a) ZBS, b) 3SmZBS, c) 5SmZBS, and d) 8SmZBS coatings. Microstructural features to include (1) lamellae, (2) melted and re-solidified spherical particles, and (3) angular unmelted particles were observed. SiC particles are labeled as A.

flame first hits the specimen surface. The test fixture was also modified to perform ablation testing on a coated tungsten rod, rastering the torch along the length of the rod while it rotated.

3. Results

3.1. As-sprayed microstructure and phase analysis

The density, porosity, and surface roughness of the as-sprayed coatings are listed in Table 1. The total porosity increases from 18.2% to 35.7% as the amount of Sm dopant is increased, and is likely associated with the flow properties of the powder feedstock, which diminished with increasing Sm dopant concentration. The cross-sectional micrographs of the as-sprayed coatings are shown in Fig. 1. The three distinctive microstructures observed in the coatings are (1) melted and solidified lamellae (2) melted and re-solidified spherical particles, and (3) unmelted particles that are angular. The ZBS coating has the lowest porosity and consists mainly of stacked lamellae. The volume of the spherical and angular particles was observed to increase with dopant concentration. The 8SmZBS coating consisted mainly of angular particles and had the highest coating porosity compared to the other three coatings.

XRD analysis of the as-sprayed coatings is shown in Fig. 2. ZrB₂ was the major phase observed in all as-sprayed coatings, and the highest intensity peak of α-SiC (2θ = 35.5°) was not observed, likely due to the small penetration depth of the X-rays. The mass spectroscopy results, however, indicated that ∼20 vol% of SiC was present in the coatings. Also, SiC particles were clearly observed in all coatings investigated as shown in Fig. 1a–d. Even though no distinctive peaks were observed for Sm, SmO, and Sm₂O₃, the broad hump observed between 2θ of 26–35° in the 5SmZBS and 8SmZBS coatings coincide with the samarium metal and samarium oxide diffraction.
The location of Sm species in the as-sprayed 5SmZBS coating was further identified using TEM and EELS mapping (Fig. 3). Lamellae and spherical particles, similar to those observed in SEM cross-section microscopy, were observed. The EELS maps show ZrB$_2$ is the major phase in the 5SmZBS coating as evidenced by the large areal Zr and B concentrations. A region comprised of nanometer-sized grains observed in Area I was identified as primarily ZrB$_2$ with up to 2.9 at.% Sm detected via individual EDS point scans. Area II contains regions of boron-deficient non-stoichiometric ZrB$_2$. Finally, Area III has the highest samarium content in the scanned area. Evaluation of the samarium areas suggests several conclusions. First, there are regions where the Sm is clearly concentrated (i.e. Area III). Within the same region the oxygen map suggests oxygen is present, presumably forming samarium oxide(s). Second, oxygen appears to be manifest in long narrow continuous regions. This manifestation of oxygen would be consistent with partial oxidation of the powders during plasma spray, i.e. affecting only the outer shell of the melted particle, prior to its collision with the substrate. Finally, there are regions where Sm appears to be co-located with Zr and B, and it appears that it is not confined to single lamella.

3.2. Total hemispherical emissivity of samarium-doped ZrB$_2$/SiC

The total hemispherical emissivity of the as-sprayed coatings is plotted in Fig. 4 as a function of temperature. Total hemispherical emissivity close to unity ($\varepsilon \approx 1$) is desired to maximize radiation heat transfer. The baseline ZBS coating has the lowest $\varepsilon$ at the tested temperature range. At 1500 °C, emissivity increases from $\varepsilon = 0.69$ for ZBS coating to $\varepsilon = 0.81$ for the 3SmZBS coating and $\varepsilon = 0.87$ for 5SmZBS coating. There is no clear difference in emissivity for the 5SmZBS and 8SmZBS coatings between 500 °C–1300 °C. However, beginning at 1300 °C, the $\varepsilon$ of 5SmZBS and 8SmZBS coatings diverge. The 5SmZBS coating has higher $\varepsilon$ compared to 8SmZBS coatings up to 1600 °C.

The effect of emissivity versus Sm dopant concentration is plotted at 900 °C, 1200 °C, and 1500 °C as shown in Fig. 5. The baseline ZBS coating demonstrated the lowest emissivity relative to the Sm-doped coatings at all temperatures. The emissivity increases

![Fig. 3](image_url) Bright field TEM image and EELS maps were used to identify the location of the elements of interest in a 5SmZBS coating. Area I is a nanometer-sized polycrystalline region, Area II is a non-stoichiometric ZrB$_2$ region and Area III appears to be rich in Sm, with varying amounts of oxygen detected suggesting an oxygen deficient Sm$_2$O$_3$ phase.

![Fig. 4](image_url) The Sm-modified ZrB$_2$/SiC coatings have higher total hemispherical emissivity, $\varepsilon$, compared to the ZBS coating, up to 1600 °C. The 5SmZBS and 8SmZBS coatings have the highest $\varepsilon$. 
significantly as dopant concentration increases from 3 to 5 mol% at all three temperatures, particularly at 1200 °C. At 1500 °C, the emissivity increased linearly with samarium dopant concentration up to 5 mol%, with a slight decrease in ε noted for the 8 mol% Sm-doped coating. The emissivity incremental increase was less significant when the Sm concentration was increased from 5 to 8 mol%.

It should be noted that in Tan et al., [9] a Sm-doped ZrB2/SiC coating demonstrated an ε of 0.93, which is higher than the emissivity for the similarly doped coating, i.e., 8SmZBS with ε = 0.82) studied currently. This difference is mainly attributed to the presence of ~20 vol% SiC in coatings reported here, where SiC has an average emissivity of 0.6–0.71 at temperatures between 841 and 1144 °C [18].

### 3.3. Post-ablation properties of samarium-doped ZrB2/SiC coatings

The post-ablation surface and cross-sectional micrographs of the coatings are shown in Fig. 6. The 8SmZBS coating (Fig. 6c) has a higher surface roughness after ablation testing perhaps due to it having a rougher as-sprayed surface (see Table 1). The microstructure observed in the cross-sectional micrographs of the ablated coatings (Fig. 6d–f), however, revealed more significant differences as a function of Sm-dopant concentration.

The 3SmZBS oxide scale was relatively dense compared to the 8SmZBS oxide scale, with only small pores observed. The scale formed in the 8SmZBS coating contained large 10–50 μm diameter pores distributed throughout. These pores appear larger near the ablated surface. The post-ablative 5SmZBS oxide scale inherited the features from both the 3SmZBS and 8SmZBS coatings with 1.5–15 μm diameter pores observed primarily in the scale closest to the exposed surface.

The phases present in the as-sprayed and post-ablation coating surfaces were identified via XRD and are presented in Table 2. In the 3SmZBS coating, C12Sm2Zr0.8O1.9 was the majority phase. As the Sm-dopant concentration increased to 5 mol%, the majority product was still C12Sm2Zr0.8O1.9, but a minor phase of samarium zirconate or Sm2Zr2O7 was detected. Finally, in the post-ablated 8SmZBS coating, Sm2Zr2O7 was the major phase detected and C12Sm2Zr0.8O1.9 was the minor phase. Small amounts of m-ZrO2 were detected in 3SmZBS, 5SmZBS, and 8SmZBS coatings.

Fig. 7 is the EDS point-to-point line scan taken across the 8SmZBS coating, starting from the substrate-coating interface (x = 0 μm) to the exposed surface (x = 320 μm). The concentration of samarium increased from ~6.8 mol% at x = 150 μm to ~20 mol% at x = 300 μm. All coatings demonstrated a similar feature with samarium concentration higher close to the ablated surface relative to the regions below it.

The maximum surface temperature during ablation testing as a function of Sm-dopant is presented in Table 3. The maximum surface temperature was highest for the 3SmZBS coating and approximately equal (1630–1660 °C) for 5SmZBS and 8SmZBS coating. This is consistent with the 3SmZBS coating having a lower emissivity than the higher Sm-doped coatings (see Figs. 4 and 5). Also presented in Table 3 is the mass increase after the ablation test for each coating type. The mass gain is primarily the result of ZrB2 oxidation to ZrO2. The mass gain increases with increasing Sm-dopant concentration, indicating a higher oxidation rate in the 8SmZBS. However, it should be remembered that mass is also lost due to the evaporation of a glass species from the surface, i.e., B2O3 and SiO2 [19,20]. As evidence of this, a thin vitreous transparent film was observed on the ablation test fixture after the test, apparently due to the evaporation and re-deposition of a B2O3 and/or SiO2 glassy phase.

The effect of an oxidized surface on total emissivity of ablated 5SmZBS coatings was investigated and compared to the as-sprayed 5SmZBS and ZBS coatings as shown in Fig. 8. It is clear that the ablated ZBS coating (Fig. 8a) did not remain adhered to the substrate whilst the 5SmZBS coating did (Fig. 8b). Delamination of the ablated ZBS coating exposed the underlying tungsten substrate, making an accurate emissivity measurement difficult, and thus no emissivity values are reported for this coating. The post-ablation 5SmZBS coating and as-sprayed ZBS coating emissivity ranges from 0.69–0.78 between 600 and 750 °C. Beyond these temperatures, the emissivity of the ablated SmZBS sample increases to ~0.73 and remains fairly constant between 850 and 1000 °C. Note that the values of emissivity for the post-ablated 5SmZBS sample are lower than for the as-sprayed 5SmZBS sample. The emissivity test on the ablated 5SmZBS sample was terminated early because the glassy phase on the ablated coating surface began to evaporate and condense on cooler parts of the test apparatus. Scattia et al. recorded emissivity values of 0.77–0.72 for temperatures 1037 °C–1681 °C respectively for oxidized ZBS coatings [24]. They obtained these emissivity values by increasing the total air pressure to 200 Pa in the emissivity chamber where we used an ablation method where air flow is also an important factor both for the test and for real situations.
**Fig. 6.** Surface morphology and the corresponding cross sectional micrographs of the 3SmZBS, 5SmZBS, and 8SmZBS coatings after a 60 s ablative test.

**Fig. 7.** The molar concentration of major elements in the ablated 8SmZBS coating across the coating thickness. The coating-substrate interface begins at $x=0 \mu m$ and the outermost scale corresponds to $x=320 \mu m$. 
4. Discussion

4.1. The effects of rare-earth dopant and dopant concentration on emissivity

In this study, the Sm-dopant was incorporated into spray-dried ZrB₂/SiC powder feedstock via a chemical-doping method and the coatings were prepared via shrouded plasma spray. The gas-filled shroud shielded the plasma plume from the oxygen-rich atmosphere to prevent most of the oxidation of the ZrB₂, SiC, and samarium during the thermal spray process. Samarium metal is metastable with a melting temperature of 1072°C and will oxidize readily to Sm₂O₃ in an oxygen-rich environment [21]. The EELS maps in Fig. 3 revealed the presence of some non-stoichiometric samarium oxides in the region labeled Area III of the as-sprayed 5SmZBS coating, despite the fact that all the samarium was added in non-oxide form. The outline of oxygen concentration around a lamellae (see oxygen map in Fig. 3) is indicative of the partial oxidation that would occur in the plasma plume. It should be noted that non-stoichiometric compounds are observed regularly in thermal spray coatings [22].

The total hemispherical emissivity results in Figs. 4 and 5 demonstrate the benefits of the Sm-doping. The 5SmZBS and 8SmZBS coatings have ε = 0.87 and ε = 0.83, respectively at T = 1500°C. Furthermore, the emissivity of 5SmZBS coating continues to increase with temperature to a maximum of 0.9 at 1600°C. There are two contributions to the increase in emissivity observed as the concentration of Sm dopant was increased. First, due to the intrinsic electronic structure of Sm increased amounts of this rare-earth atom should increase emissivity as observed presently [6]. Second, the improved emissivity in the Sm-doped coatings can be further understood by the density function theory (DFT) simulations performed by Advoshenko and Strachan [8]. In their simulation, the total emissivity of defect free and oxygen deficient of ZrO₂ and Sm₂O₃ were investigated. Advoshenko and Strachan [8] found that static disorders such as oxygen vacancies, a result of each compound being oxygen deficient, play an important role in emissivity. The presence of oxygen vacancies in the non-stoichiometric Sm₂O₃ and ZrO₂ lattice leads to localization of electronic states within the materials band gap, which affects their electronic structure significantly. This subsequently provides additional transitions and enhances the overall dielectric response with an increase total emissivity observed. In the case of oxygen deficient Sm₂O₃, the creation of acceptor states provides additional transitions to increase the emissivity from ε_defect-free = 0.7 to ε_oxygen-deficient = 0.78 [8].

Previous studies on ZrB₂/SiC coatings demonstrated that the method in which the rare-earth atoms were incorporated into the coating had a significant impact on emissivity [9]. The chemically-doped Sm ZrB₂/SiC coatings demonstrated a higher ε compared to when Sm₂O₃ powder was dry-mixed into ZrB₂/SiC powders prior to plasma spraying. This could possibly be due to the presence of oxygen-deficient Sm₂O₃ in the chemically doped coatings, while the dry-mixed Sm₂O₃ remained stoichiometric in the coating, as evidenced by the Sm₂O₃ crystal phase detected by XRD [9].

There are two microstructural features that varied slightly in the coatings presently studied, surface roughness and porosity, that can influence emissivity. In 2014, Wang et al. [23] investigated the effect of both microstructural features on the emissivity of C/SiC composites. While they did not quantify surface roughness, they did show that increasing the surface roughness increased the total emissivity. As shown in Table 1, surface roughness increased as more Sm dopant was added, as did the emissivity for the ZBS, 3SmZBS, and 5SmZBS coatings. This trend is consistent with the Wang et al. observations. However, the 8SmZBS coating was the...
roughest coating but had a similar emissivity to the 5SmZBS coating, at least up to 1200 °C. This trend is inconsistent with the trends observed by Wang et al. in that the 8SmZBS coating would be expected to have the highest emissivity. Thus, while the total porosity may affect the current emissivity values, there are clearly other influences suggesting the Sm is increasing the emissivity.

Furthermore, Wang et al. [23] noted an increase in emissivity as samples were processed to be less porous. This case was also consistent with alumina ceramics with more than 5% porosity [25]. With respect to current data, this is exactly the opposite of what was observed. In other words, the very porous 5 SmZBS and 8SmZBS coatings should have the lowest emissivity. Clearly from Fig. 4 they possessed the highest emissivities. This result suggests that the compositional differences between the Sm-doped coatings and the undoped or ZBS coating are responsible for the emissivity differences measured. In fact, making the 8SmZBS coating less porous would likely increase its emissivity further. While we do have not the precise relationships between coating roughness and porosity, and emissivity, it is clear that the Sm-dopant is influencing emissivity.

4.2. Post-ablation microstructure of samarium-doped ZrB2/SiC coatings

As shown in Table 2, c1Sm0.3Zr0.9O1.9, Sm2Zr2O7, and m-ZrO2 were detected in all the ablated Sm-doped coatings except for the 3SmZBS oxide scale, which only consisted of c1Sm0.3Zr0.9O1.9 and m-ZrO2. The c1Sm0.3Zr0.9O1.9 can be beneficial in protecting the underlying coating from exposure to oxidation [9]. This cubic fluoride (c1) compound has a melting temperature range between 2500 and 2700 °C, depending on the concentration of the samarium in the ZrO2 matrix. When the Sm-dopant concentration increased from 5 mol% to 8 mol%, Sm2Zr2O7 appears to be the majority phase of the oxide scale. Sm2Zr2O7 with a lower melting temperature range of 2190-2500 °C as compared to c1Sm0.3Zr0.9O1.9 is less desirable.

Based on the EDS line-scan of the ablated 8SmZBS coating (Fig. 7), the Sm concentration is much higher at the ablated surface as compared to the Sm concentration in the original coating. It is worth noting that the c1Sm0.3Zr0.9O1.9 and Sm2Zr2O7 phases require 6.6 and 18.2 at% Sm, respectively. The average Sm concentration between x = 275-320 µm (within the oxide scale), as shown in Fig. 7, is ~32.1 mol% Sm. It is believed that the overall samarium concentration in the coating is higher than the as-sprayed composition because of the oxidation of SiC to SiO2 and its subsequent evaporation at temperatures >1600 °C [20]. Thus, the high concentration of Sm on the ablated surface of the 8SmZBS coating makes the formation of Sm2Zr2O7 possible. Furthermore, the absence of the Sm2Zr2O7 in the ablated 3SmZBS coating (see Table 2) indicates that the concentration of Sm did not reach the necessary value to form Sm2Zr2O7, consistent with the low starting concentration of Sm in the as-sprayed coating.

The weight gain results in Table 3 indicated that the 8SmZBS coating oxidized more readily than the other two coatings. There are two possible reasons for this. First, this coating was much more porous (see Table 1) than the other two doped coatings. Second, it is well established that solvated ions added to a ZrO2 matrix can cause the formation of oxygen vacancies. For example, two Y3+ ions substituted on Zr2+ sites create one oxygen vacancy. As Sm3+ substitutes into the ZrO2 matrix there should also be an increase in the oxygen vacancy concentration. These oxygen vacancies provide very rapid transport of oxygen atoms which would lead to increased oxidation.

As shown in Fig. 6d-f, the porosity in the oxide scales of the three coatings increases as Sm dopant concentration increases. As shown in Table 2, post ablation XRD results indicated c1Sm0.3Zr0.9O1.9 was present in all three coatings investigated, and Sm2Zr2O7 phases in the 5SmZBS and 8SmZBS coatings. Conversion of ZrO2 and Sm2O3 to c1Sm0.3Zr0.9O1.9 or Sm2Zr2O7 results in a volume contraction of 4.7% and 2.0%, respectively. This contraction alone would not be enough to account for an amount of porosity observed in the 8SmZBS coating. It is also worth noting the spherical shape of the porosity in the 8SmZBS coating suggests it likely contained a liquid phase prior to its vaporization. In static oxidation tests, Tan et al. [9] showed that a boria-rich glass with samarium would form at temperatures as low as 900 °C. Also, increased weight loss associated with glass vaporization was observed in Sm-doped ZrB2/SiC coatings compared to ZrB2/SiC coatings, suggesting that the dopant was modifying the glass and lowering its viscosity. Thus, the observed porosity in Fig. 6 is likely the result of the oxidation of ZrB2 and SiC into their respective oxides, modification of these glasses by the Sm dopant, and the subsequent increased volatility of the modified B2O3 and SiO2 glassy phases as the local temperature exceeds the evaporation temperature of each. This transformation is likely enhanced by the large amounts of porosity in the 8SmZBS coating, providing easier access to the microstructure.

5. Conclusion

Three samarium dopant concentrations were incorporated into spray-dried ZrB2/SiC powders via chemical infiltration and prepared by shrouded air plasma spray. The actual Sm-dopant concentration in the ZrB2/SiC coatings were approximately 3, 5, and 8 mol%. The total hemispherical emissivity of the as-sprayed coatings were reported. Both 5SmZBS and 8SmZBS have the highest emissivity (ε8SmZBS = 0.87 and ε5SmZBS = 0.83, respectively) compared to the ZBS (ε=0.69) and 3SmZBS (ε=0.81) at 1500 °C. The highest emissivity measured was 0.9 for the 8SmZBS coating at 1600 °C. The emissivity increase observed with increasing Sm content was explained by both there being more of the high emissivity rare earth atom and/or the increase in vacancy concentration expected with Sm additions. The ablation resistance of the coatings was evaluated by heating the surface with an oxyacetylene torch for 60 s, with a maximum test temperature of ~1700 °C. All the ablated Sm-doped coatings have an oxide scale consisting of c1Sm0.3Zr0.9O1.9; however, Sm2Zr2O7 became the majority phase in 8SmZBS. The 8SmZBS coating exhibited significant amounts of porosity consistent with the vaporization of a glassy phase. It is proposed that the increased amount of Sm dopant modified the B2O3/SiO2 glass, lowering its viscosity and increasing its rate of vaporization. Considering both the total hemispherical emissivity and ablative properties of all the Sm-doped coatings investigated presently, the 5 mol% Sm doped ZrB2/SiC coating has the highest emissivity values with a sufficiently dense oxide scale formed and should be pursued in the future for high emissivity coatings for hypersonic applications.

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