SEPARATING TEST ARTIFACTS FROM MATERIAL BEHAVIOR IN THE OXIDATION STUDIES OF HfB$_2$-SiC AT 2000°C AND ABOVE (POSTPRINT)

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Introduction

Characterization of the oxide scale formed on ultra high temperature ceramics (UHTCs) has been a topic of intense study over the past decade. In particular, composite systems of diborides of hafnium or zirconium with SiC have been studied for their improved oxidation resistance compared with the diborides alone near 1600°C. At temperatures below 1800–2000°C, a refractory porous metal oxide scale is formed that is protected by a glassy silica scale. However, as temperatures are increased the protective silica becomes less viscous and thus less protective. Hypersonic flight will require leading edges and nose cone components to withstand rapid heating and cooling to temperatures in excess of 2000°C under shear stresses imparted by air flow. In addition, the environment within the boundary layer near the component...
will be comprised of a fraction of dissociated atoms depending on velocity, altitude, and other factors.\textsuperscript{4,5} Dissociated oxygen can alter the boundary between active and passive oxidation of SiC and thus influence oxidation kinetics.\textsuperscript{6} These temperatures and conditions are unattainable in traditional molybdenum disilicide element furnaces whereas conventionally accepted arc jet testing is expensive and the primary oxidant is dissociated oxygen, so new methods of testing have been developed. Methods such as oxyacetylene torch heating,\textsuperscript{7–9} laser heating,\textsuperscript{10} direct resistance heating of the sample itself,\textsuperscript{11–13} and scramjet simulators\textsuperscript{14} are being developed. The rapid heating profiles and higher temperatures attainable with these tests may lead to different oxide morphologies and performance than those observed with furnace-heated samples. It is imperative that a correlation between different testing methods is made so that samples prepared by different exposure methods may be compared. To this end, HfB$_2$–SiC samples were heated in air at 2000°C using a zirconia-resistance furnace and direct resistance heating of the sample and the resulting oxidation products were compared. In addition, the limits of resistance heating including multiple cycles and maximum temperatures were examined.

\textbf{Experimental Procedure}

Commercially available HfB$_2$ (Materion, Milwaukee, WI, 99.99%, 45 µm) and β-SiC (Materion, 99.99%, 1 µm) were used to prepare HfB$_2$-15 vol% SiC (HS). The powder mixtures were ball milled in isopropanol for 24 h with SiC grinding media, dried at room temperature, and subsequently dry milled for 12 h. Typical weight loss of the SiC grinding media after milling was 0.2 mg (0.2 wt% of the total batch). The powders were sieved through an 80-mesh (177 µm) screen.

A quantity of 150 g of the milled powders was loaded into a 60-mm diam. graphite die. A layer of BN and graphite foil separated the powder from the die with the powder in contact with the graphite foil. The powder-filled dies were cold pressed at approximately 50 MPa. The powders were sintered using field-assisted sintering (FAS: HPD 25-1, FCT Systems, Rauenstein, Germany) at 2000°C for 15 min under a 32 MPa load. The controlled heating and cooling rates were 50°C/min. The load was applied during heating to 1600°C and released on cooling to 1000°C.

Oxidation samples were cut with a wire electro-discharge machine (EDM) into 5 mm × 5 mm × 3 mm rectangles (furnace heating) and 53 mm × 3.5 mm × 5.0 mm rectangles with a centered 19–25 mm long 3 mm thick region of reduced area (resistance heating). The samples were polished using diamond slurry to a 1 µm finish.

Polished samples were heated by a zirconia-resistance furnace (ZrF-25: Shinagawa Refractories, Tokyo, Japan) and direct electrical resistance. Macrographs of the two tests and sample geometry are shown in Fig. 1. The furnace heating was accomplished by a molybdenum disilicide pre-heater to 1100°C and a zirconia element to 2000°C at a rate of 5°C/min. The samples were held at temperature for 30 min. Temperature measurements were performed using a single color pyrometer focused on the zirconia element. Samples were supported on a zirconia crucible. The zirconia crucibles were cut from a larger crucible (Advalue, Tuscon, AZ; 10 mL Ca-stabilized ZrO$_2$ crucible; 95% ZrO$_2$ and 4 ± 1% Ca). Direct electrical resistance heating was controlled by the power output of an AC power supply across the sample and temperature was read by a two-color pyrometer (FMP2; FAR Associates, Macedonia, OH) that was focused on the center of the reduced-thickness area. The samples were held in place between two graphite spacers by tightening set screws on the copper electrodes. Ag paint was used on the ends of the samples to improve electrical contact. Temperature, current, and voltage data were recorded using LabVIEW (National Instruments, Austin, TX). Table I lists the oxidized samples with their heating conditions.

Oxidized samples were mounted in epoxy and polished in cross section perpendicular to the bottom (side facing the crucible or notched side) of the sample to a 1 µm finish using diamond slurry. The microstructures were characterized using scanning electron microscopy (SEM, Quanta, FEI, Hillsborough, OR) along with energy dispersive spectroscopy (EDS, Pegasus 4000; EDAX, Mahwah, NJ)) for elemental analysis. All EDS analysis was done using 15 kV accelerating voltage and at least a 100 s live capture time.

\textbf{Results}

\textit{Single 2000°C Exposure}

The heating profiles of the HfB$_2$-15 vol% SiC zirconia-resistance furnace heated sample (HS-F) and
direct electrical resistance-heated (HS-R) sample are shown in Fig. 2a and b, respectively. The maximum observed temperature of the HS-R sample was 2027°C using 82.5 V and 20.3 A (averaged over the hold). The oxidized HS-F sample had a thicker oxide scale (Fig. 3a) compared to the HS-R sample (Fig. 3b). The HS-F sample was exposed to oxidizing temperatures for a greater length of time than the HS-R sample (6.5 h above 1100°C compared to ~4 min above 800°C). The oxide layers labeled in Fig. 3a (HS-F) and Fig. 3b (HS-R) are composed of (I) a SiO$_2$-based glass that penetrates a HfO$_2$-based skeleton; (II) a porous HfO$_2$ scale; and (III) a SiC-depleted layer. The SiC-depleted layer is defined as HfB$_2$ with a reduced SiC content (partially oxidized SiC). The average total oxide scale thickness measured from the top side of the HS-F sample is 660 ± 45 μm with the depleted layer comprising 53% of the scale. The thickest total oxide scale measured on the HS-R sample was 105 μm with 5% of the total scale consisting of the depleted layer.

The oxide scales of HS-F samples possess a distinct two-phase SiO$_2$-based glass with the less-pure (less viscous) impurity-laden glass rising to the surface of the oxide scale and the purer glass found deeper within the scale (Fig. 4a). A two-phase glass found in furnace heating has been described previously by the authors, which was shown to contain Al and Ca as major impurities.$^{15}$ In addition, HfSiO$_4$ (with a Ca impurity) is found in the HS-F sample, but not the HS-R sample. The existence and absence of HfSiO$_4$ was confirmed by XRD. Figure 4b is an EDS comparison of the purer (darker) and impure (lighter) glasses in the HS-F sample along with the HfSiO$_4$ and HfO$_2$ phases. In the HS-R sample Al impurities can be found randomly distributed throughout the glassy phase (inset Fig. 4c). Figure 4d is a representative EDS spectra of different locations within the HS-R glass. There is no hierarchy to the concentration of Al in the glass phase when comparing the chemistry of the glass along the length of the HS-R oxide scale.

**Repeated 2000°C Exposure**

An advantage of the direct electrical resistance heating test is that the sample can be exposed multiple times to the same or different heating profiles. A sample (HS-Rr) was heated to 2000°C twice using the same heating profile as HS-R. The maximum observed temperature was 2030°C. The heating profile and a
The oxide scale has a periodic structure consisting of layers of SiO2 and HfO2 penetrated by SiO2. For comparison, a sample (HS-R2) was heated to 2000 °C for 2 min. (Fig. 5c) with a maximum observed temperature of 2040 °C. The thickest measured oxide scale of the HS-R2 sample was double that found for the HS-R sample (217 vs 105 μm), and the oxide scale was not composed of periodic layers.

Table I. List of the Oxidized HfB2-15 vol% SiC Samples and their Heating Conditions

<table>
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<tr>
<th>Sample ID</th>
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<th>Max. observed temp. (°C)</th>
<th>Hold time (min)</th>
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<td>Furnace</td>
<td>2000</td>
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<td>—</td>
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<tr>
<td>HS-R</td>
<td>Self-heating</td>
<td>2027</td>
<td>1</td>
<td>—</td>
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<tr>
<td>HS-Rr</td>
<td>Self-heating</td>
<td>2030</td>
<td>1</td>
<td>Two 1 min holds</td>
</tr>
<tr>
<td>HS-R2</td>
<td>Self-heating</td>
<td>2041</td>
<td>2</td>
<td>—</td>
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<tr>
<td>HS-Rf</td>
<td>Self-heating</td>
<td>2325</td>
<td>0</td>
<td>Heated to failure</td>
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Fig. 2. Heating profiles of the (a) HS-F (calculated) and (b) HS-R (actual) samples.

Fig. 3. (a) Micrograph of the HS-F sample after oxidation at 2000 °C (b) Micrograph of the HS-R sample after oxidation at ~2000 °C. The oxide layers are (I) HfO2 penetrated by SiO2, (II) porous HfO2, and (III) depleted HfB2 layer. The approximate boundary between layers is shown by the dashed white lines.
oxide scale formed near the center of the reduced area on the HS-Rr and HS-R2 samples were nonadherent. Cracks were also observed within the depleted layer of the HS-F sample and at the interface between HfO$_2$ and the SiC-depleted layer (Fig. 3a). In the HS-R sample, fracture is observed between the depleted layer and the HfO$_2$ layer at the center of the sample (Fig. 3b), whereas adherent oxide scales exist near the end of the reduced area.

Temperatures Beyond 2000°C

The maximum temperature of the direct resistance test is limited only by the available power and the survivability of the sample. A sample (HS-Rf) was heated to failure, where failure was defined as the sample fracturing such that the electrical path was disrupted. The maximum observed temperature was 2325°C. A micrograph of the cross section of the HS-Rf sample (Fig. 6) reveals extensive internal damage. Large pores are found inside the sample whereas an oxide scale covers the surface. The bulk unoxidized material from the center of the sample (inset Fig. 6) was confirmed by EDS to be SiC and HfB$_2$. The microstructure suggests formation of a liquid phase, which is consistent with the calculated eutectic at 2347°C in the HfB$_2$–SiC system. The oxide scale (inset Fig. 6) is composed of HfO$_2$ penetrated by SiO$_2$. Meng et al. similarly showed the failure of a ZrB$_2$–SiC sample at temperatures above 2300°C (2207°C eutectic temperature), but did not show any micrographs of the interior microstructure.

Discussion

The direct comparison of the zirconia-resistance heated and direct electrical resistance-heated HfB$_2$–SiC samples at 2000°C provide insight to the limitations of furnace heating. Due to slower heating rates and contamination from contact between the sample and...
crucible, the HS-F total oxide scale thickness is greater than that observed in the HS-R sample. The difference in heating rates can also explain the observation of HfSiO₄ in the HS-F sample but not in the HS-R sample. HfSiO₄ is only stable below ~1726°C,¹⁷,¹⁸ therefore; its formation in the HS-F sample could occur during slow cooling. HfO₂ and SiO₂ form an incongruently melting silicate and thus require solid-state diffusion to form the silicate phase adding an extra kinetic limitation on its formation.¹⁷ The rapid heating and cooling rates of the HS-F sample presumably do not allow for the separation of glasses with different viscosities or for the formation of HfSiO₄.

Fig. 5. (a) Heating profile of sample HS-Rr. (b) Micrograph of the oxide found in hottest region of the oxidized HS-Rr sample heated to 2000°C for 1 min two times. (c) Micrograph of the oxide found in hottest region of the oxidized HS-R2 sample heated to 2000°C for two minutes. The layers are the same as those found in the HS-R sample: (I) HfO₂ penetrated by SiO₂, (II) porous HfO₂, and (III) depleted HfB₂.

Fig. 6. Micrograph of the HS-Rf sample heated to 2325°C. The white-outlined inset shows HfB₂ grains (labeled) and the eutectic SiC (dark)-HfB₂ (light) structure found in the interior of the sample. The black-outlined inset is the oxide scale composed of HfO₂ and SiO₂ found on the exterior of the HS-Rf sample.

Fig. 7. Micrograph showing a Si-Al-O impurity phase in the bulk of the HfB₂-15 vol% SiC sample. The C signal in the EDS (inset) is from the carbon coating applied to the sample.
In addition, the lack of Ca impurity in the resistance-heated sample suggests the source of the impurity to be the CaO-stabilized zirconia crucible or zirconia heating element, whereas the presence of Al in both samples implies that it is an inherent impurity in the starting powders. For comparison, a HfB2–SiC sample was heated in the zirconia-resistance furnace using a Y2O3-stabilized zirconia crucible. The glass near the contact region of the sample and crucible was found to contain Si, Al, Ca, Y, and O. Since the crucible was reported to only contain 0.001% Ca, the zirconia sample stand (Part A in Fig. 1) was the likely source of Ca in this test. The HfB2 and SiC powders are reported by the manufacturer to contain 0.03% and 0.01% Al, respectively. Figure 7 is a micrograph showing the SiC grains with a pocket of impurities in the as-processed material. These areas can be found throughout the sample adjacent to SiC grains and are shown by EDS (inset) to contain Si, Al, and O. The slow heating rates and contact contamination issues of the zirconia element furnace are not expected in hypersonic flight conditions and serve to complicate the analysis of UHTC oxidation resistance testing.

When a HfB2–SiC sample is heated by direct electrical resistance through multiple heating and cooling cycles, spallation of the oxide scale is suggested by the presence of the repeating SiO2–HfO2 layers. Such layered oxide structures have not been reported for furnace-heated samples and was not observed in a sample heated for the same time (HS-R2) with a single heating and cooling cycle. There are two sources of stress during oxidation that may lead to fracture during temperature changes: (i) thermal expansion mismatch and (ii) volume changes associated with phase transformations. The coefficient of thermal expansion (CTE) of HfO2 depends on the impurity content and phase, but typical values are 5 × 10⁻⁶ to 7 × 10⁻⁶ °C⁻¹ for room temperature to 1250°C with purer HfO2 having lower values. Gasch et al. measured the CTE of pure HfB2, pure SiC, and a combination of HfB2–20 vol% SiC to find that the CTE of HfB2–20 vol% SiC was ~5 × 10⁻⁶ °C⁻¹ at room temperature and ~7 × 10⁻⁶ °C⁻¹ at 1600°C and fell between the CTE values of pure HfB2 (higher) and SiC (lower) as expected by the rule of mixtures. The transformation of HfO2 from monoclinic to tetragonal upon heating (10% conversion at 1642°C) or tetragonal to monoclinic during cooling (10% conversion at 1710°C) is accompanied by a 3–3.5% volume contraction/expansion upon heating/cooling. This volume expansion could lead to spallation of the oxide scale.

As the absolute CTE and modulus of the multi-phase oxide scale are not known at elevated temperatures, the main contributing factor to oxide spallation cannot be identified definitively. However, it is assumed that the volume expansion upon phase transformation is isotropic then at minimum the linear expansion due to phase transformation would be 1%. To achieve greater than 1% linear expansion from 2000°C to room temperature when compared to the bulk, the difference in CTE of the oxide scale and bulk would need to surpass ~4 × 10⁻⁶ °C⁻¹. The reported range of CTE values for the bulk HfB2–SiC and HfO2 allow for a ~2 × 10⁻⁶ °C⁻¹ difference between the CTE values, but the difference could increase at higher temperatures. Therefore, it is possible that the phase transformation and CTE mismatch both contribute to spallation of the oxide scale. The role of CTE mismatch and HfO2 phase transformation on oxide scale adherence deserve further study.

The limitation of the resistance heater was explored as the sample was heated to failure above 2300°C. The entire sample was soaked at the elevated temperature allowing for the formation of the HfB2–SiC liquid phase inside the HS–Rf sample. Furthermore, the temperature may be greater in the interior because the oxide scale will not be electrically conductive and is an effective thermal insulator. Under flight conditions, only the outer regions of the sample would be heated and the high thermal conductivity of the diboride phase would lead to a temperature gradient through the thickness of the component. A temperature gradient is experienced along the length of the direct electrical resistance sample and can provide insight to oxide and bulk microstructures over a temperature range.

**Conclusion**

Temperatures up to 2000°C can be achieved in a laboratory furnace; however, these tests suffer from slow heating profiles and potential interactions between furnace materials and the sample being tested. The observation of Ca and HfSiO4 in the oxide scale affects the glass properties, but this is not expected in a flight environment. The use of resistance heating allows non-contact testing with a high heating profile. Features like fracture between the oxide scale and the depleted layer...
and Al impurities are universal observations between both heating tests and require further investigation. In addition, research to stabilize the tetragonal transformation may aid in a more adherent scale. Resistance heating may be further utilized to study multiple heating profiles and test materials for scale adherence. The resistance testing is limited by the uniform heating of the sample that would not be expected in a real flight environment. Further comparison of test methods such as laser heating, oxyacetylene torch testing, or scramjet testing would be beneficial to understanding material properties.

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References