

Oxidation Resistance of Hafnium Diboride Ceramics with Additions of Silicon Carbide and Tungsten Boride or Tungsten Carbide

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Dense samples of HfB₂–SiC, HfB₂–SiC–WC, and HfB₂–SiC–WB were prepared by field-assisted sintering. The WB and WC additives were incorporated by solid solution into the HfB₂ and the HfC that formed during sintering. Oxidation of the samples was studied using isothermal furnace oxidation between 1600° and 2000°C. Sample microstructure and chemistry before and after oxidation were analyzed by scanning electron microscopy and X-ray diffraction. The addition of WC and WB did not alter oxidation kinetics of the baseline HfB₂–SiC composition below 1800°C; however, at 2000°C, HfB₂–SiC–WC and HfB₂–SiC–WB had oxide scales that were 30% thinner than the oxide scale of HfB₂–SiC. It is believed that WC and WB promoted liquid-phase densification of the HfO₂ scale, thereby reducing the path of oxygen ingress, during oxidation.

I. Introduction

TRANSITION metal borides and carbides with melting temperatures exceeding 2700°C are commonly referred to as ultra-high-temperature ceramics (UHTCs). Of these materials, hafnium diboride (HfB₂) has shown the highest oxidation resistance.^{1–5} Although its density is higher than that of zirconium diboride (ZrB₂)^{1–4} (10.5 vs 6.09 g/cm³) its high melting point (>3100°C) and high thermal conductivity (~100 W/MK at room temperature) make it a leading candidate for extreme environment thermal protection systems such as those found at the sharp leading edges of hypersonic vehicles.^{6,7}

The oxidation of HfB₂ proceeds according to reaction (1) where the B₂O₃ liquid formed is volatile and expected to be removed through evaporation above 1100°C. Although HfO₂ is a stable refractory with a melting point of 2750°C the oxide formed on the surface of the diboride is porous and nonprotective from further oxygen penetration.³ As such, development of these materials in the 1960s led to the addition of 5–30 vol% of silicon carbide (SiC) to form a borosilicate glass upon oxidation.^{1,3–5} Above 1100°C, SiC will oxidize by reaction (2). Available B₂O₃ can dissolve in SiO₂ to form a protective borosilicate glass that covers or fills the pores of the HfO₂ scale. The SiO₂ glass has shown to improve oxidation resistance at moderate temperatures (<1700°C) when compared with the oxidation of pure HfB₂.^{3,6,7}

$$HfB_2(cr) + 5/2O_2(g) \rightarrow HfO_2(cr) + B_2O_3(l)$$
(1)

$$\operatorname{SiC}(cr) + 3/2\operatorname{O}_2(g) \to \operatorname{SiO}_2 + \operatorname{CO}(g)$$
 (2)

Manuscript No. 28917. Received November 19, 2010; approved January 21, 2011. This work was financially supported under Contract No. FA8650-10-D-5226. *Member, The American Ceramic Society. However, as these materials have been tested in environments that more closely simulate atmospheric reentry and hypersonic cruise applications that include higher temperatures (>1723°C) and flowing air^{8–13} it has become apparent that there is a point at which the protective SiO₂-based scale begins to fail. Above the melting point of SiO₂ (1723°C) it is observed that the less viscous SiO₂ will flow into the pores of the HfO₂ and even flow from the sample resulting in a less protective porous outer scale.¹² Recent research has focused on extending the oxidation resistance of HfB₂–SiC to these temperatures by adding additional phases.^{7,13–17} There are three strategies for selecting the appropriate additive that will accomplish one or more goals of (1) controlling the phase transformations of the HfO₂ scale, (2) increasing the viscosity of the SiO₂ scale, or (3) promoting densification of the HfO₂ scale.

Mixed results have been obtained with the addition of rareearth elements (Ta, La and Nd) and some transition metals (Ti, Cr, and Cr) with reduced oxidation being observed for oxidation temperatures below $1700^{\circ}C^{7,15-21}$ and increased oxidation above $1700^{\circ}C^{.12,15}$ Most recently, Zhang *et al.*^{17,21} have prepared ZrB₂based UHTCs with additions of WC to promote liquid-phase sintering in the oxide scale. It was shown that the sample containing WC had a denser ZrO₂ scale and the weight gain during oxidation was reduced at temperatures of $1600^{\circ}C$ and below.

The present paper focuses on the addition of tungsten (W) to an HfB2-based UHTC to promote improved oxidation resistance at temperatures >1600°C. The WO₃-HfO₂ phase diagram suggests a solid solution between the phases of at least 5 mol% WO_3 at temperatures up to and beyond 2000°C.²² Similar to ZrO₂-WO₃, HfO₂ will form a liquid phase with WO₃ at temperatures above 1280°C.²² In the present study, W was added in two phases: (1) WC and (2) WB. Samples with W-based additives are compared with a baseline composition of HfB₂-15 vol% SiC. SiC content was held constant in the samples to allow a direct comparison. Fifteen volume percent SiC was chosen based on internal experiments that showed it to provide oxidation scales of similar total lengths and comparable weight gains as 20 vol% SiC at the tested temperatures, but with a thinner SiO₂ scale. The samples were oxidized between 1600° and 2000°C. Because of the differences in weight between the formation of HfO₂ and WO₃ and the volatility of WO₃, scale thickness was used as a measure of oxidation resistance.

II. Experimental Procedure

(1) Powder Processing

Commercially available HfB₂, β -SiC, WC, and WB powders were used to prepare the samples. Table I is a list of the suppliers, purity, and starting particle sizes. Powders were used as received except for the HfB₂ which was premilled using Si₃N₄ grinding media in isopropanol for 60 h to reduce the grain size. The weight change of the grinding media was 0.07 g, which was 0.01 wt% of the total batch weight. Representative batches of milled HfB₂ were measured using a laser diffraction particle size

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	Table I. Starting Powder Size and Purity				
Powder	Supplier	Particle size [†]	Purity (%)	Impurities (wt%) [‡]	
HfB ₂ SiC	Cerac (Milwaukee, WI) Alfa Aesar (Ward Hill, MA)	-325 mesh (44 μm) <1 μm	99.5 99.8	Zr (0.2), Fe (0.02) C (1.39), O (0.5), N (0.13), Fe (0.0151)	
WC WB	Cerac Cerac	<1 μm -325 mesh (44 μm)	99.5 99.5	Cr (0.01), Fe (0.01) Mg (0.08)	

[†]As received. [‡]As reported for any impurity over 0.01%.

analyzer (LS230, Beckman Coulter, Brea, CA) and had an average particle size of 1.3 μ m ($D_{90} = 2.2 \mu$ m). The oxygen content of the premilled HfB₂ was 0.86 wt% compared with 0.58 wt% in the as received powder as measured by Leco Corporation (St. Joseph, MI). Compositions were chosen based on the HfO₂-WO₃ phase diagram. The prepared samples were HfB₂-15 vol% SiC (HS), HfB₂-15 vol% SiC-3 vol% WC (HSWC) and HfB₂-15 vol% SiC-3 vol% WB (HSWB). 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 the additives with HfB_2 was 0.2 mg (0.1 wt% of the total batch). The powders were sieved through an 80-mesh (177 µm) screen.

(2) Sintering and Sample Preparation

The milled powders were loaded into a 25-mm-diameter 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 20 MPa and loaded into the field-assisted sintering (FCT Systeme GmbH, Model HPD 25-1, Rauenstein, Germany) unit. The graphite die was wrapped in graphite felt to limit heat radiation from the die. Heating and cooling rates were 50°C/min. and 32 MPa was applied while heating up to 1600°C. The 32 MPa was held for the remainder of the sintering schedule and rereleased during the free cool (below 1000°C). The samples were held at 2100°C for times between 5 and 9 min. The temperature was measured by a pyrometer focused on the bottom of a bore hole in the upper punch \sim 5 mm from the surface of the powder. Densification was monitored by tracking the movement of the pistons.

Sintered samples were cut with a wire electron discharge machine into 2.5 mm \times 2.0 mm \times 9.0 mm rectangles and polished using diamond slurry to a 1 µm finish on all six sides using an autopolisher to ensure samples with parallel sides and uniform sizes.

(3) Oxidation Exposure and Sample Characterization

Polished samples were heated in a zirconia element furnace (ZrF-25: Shinagawa Refractories Co., Tokyo, Japan) to 1600°, 1800°, or 2000°C and held at temperature for 30 min. The heating and cooling rates were 5°C/min., which were limited by the furnace. Samples were placed on a concave ZrO₂ crucible to limit contact between the sample and ZrO2. Oxidized samples were polished in cross section perpendicular to the bottom $(2.5 \text{ mm} \times 9.0 \text{ mm} \text{ side facing the crucible})$ of the sample to a 1 µm finish using diamond slurry. Sintered samples were polished to 6 µm using diamond slurry and then polished to 1 µm using electrochemical-mechanical polishing^{23*} to reveal grain structure and reduce SiC pullout. The microstructures were characterized using scanning electron microcopy (SEM: Quanta, FEI, Hillsborough, OR) along with energy-dispersive spectroscopy (EDS: Pegasus 4000, EDAX, Mahwah, NJ) for elemental analysis. Samples were also prepared for transmission electron microscopy (TEM: Phillips CM200, FEI) using a focused ion beam microscope (FIB: FEI Dual Beam 235, FEI). The crystallographic analysis of the oxide was performed on an X-ray diffractometer with CuKa radiation (XRD: Rigaku 2500, Tokyo, Japan). Densities of the oxide scale and phase analysis were measured from SEM micrographs at \times 1000 magnification using a threshold and area measurement routine in Adobe Photoshop (Fovea Pro 4, Reindeer Graphics).

III. Results

(1) Processing and Sample Characteristics

Samples were heated to 2100°C and held for 5-9 min. allowing at least 4 min past the last observed piston movement change to ensure complete densification. Figure 1 is a plot of the relative piston motion for the heating portion of the program for each of the samples. The maximum piston motion was normalized so that the final piston motion values were equal for ease of comparison. The first sample to densify was HSWC followed by HSWB and finally HS. HSWC reached its maximum piston motion at 2000°C, while HSWB and HS did not reach full density until 2100°C. The more rapid densification of the samples containing W is as expected from previous data concerning densification of diborides containing WC additives.17,24 The densities of the HS, HSWC, and HSWB samples were measured to be 9.93, 10.14, and 10.30 g/cm³, while the theoretical values are 9.92, 9.99, and 9.91 g/cm³, respectively. The discrepancy between the measured densities and theoretical values for the Wcontaining samples is due to the formation of high-density phases such as HfC and offset by some lower density oxides as discussed below.

Figure 2 is a series of micrographs of the as-sintered HS (Fig. 2(a)), HSWC (Fig. 2(b)), and HSWB (Figs. 2(c) and (d)) samples. The micrographs in Figs. 2(a)-(c) were obtained after electrochemical polishing. The SiC is distinct and uniformly distributed throughout each of the samples. The SiC phase was defined by the presence of only Si and C in the EDS spectrum and is identified as the darkest phase in the images (labeled A in Fig. 2(d)). The backscattered electron images revealed the grain structure of the HfB₂ indicated by the presence of Hf-B in the EDS spectra (labeled B in Fig. 2(d)). The average grain size of HfB₂ in the HS, HSWC, and HSWB samples was 2.6, 1.8, and 1.7 µm, respectively. It was observed that the SiC morphology was changed upon addition of WC or WB so that 20%-30% of the SiC grains became rod-shaped with average aspect ratios of 2.9.



Fig. 1. Plot of relative piston motion versus time for the HS, HSWC, and HSWB samples. The onset of densification was more rapid for samples containing W. The vertical line indicates the time at which 2100°C was attained.



Fig. 2. SEM micrographs of the sintered (a) HS, (b) HSWC, and (c) HSWB samples. (d) Backscattered electron image of a region of HSWB highlighting the five phases in the sample: (A) SiC, (B) HfB₂, (C) W–C–O–B, (D) Hf–C–W, and (E) HfC.

Figure 2(d) is a backscattered electron SEM micrograph highlighting the minor phases found in both HSWB and HSWC. Grain pullout is evident in this sample as electrochemical-mechanical polishing was not used to prepare the specimen. Grains containing W were identified by EDS mapping conducted with a 20 keV beam. The grains highlighted in the W map (labeled C in Fig. 2(d)) were subsequently analyzed by point EDS analysis using a 10 keV beam. The 10 keV analyses of at least 15 distinct areas revealed the presence of B, C, and O in different concentrations with W. An additional phase composed of Hf and C was identified through point EDS analysis. In some instances (labeled D in Fig. 2(d)) the Hf-C phase contained W, while in others (labeled E in Fig. 2(d)) no W was found. Image analysis of five EDS maps taken at \times 2000 combined with backscattered electron images revealed that on average 0.5% of the sample was composed of the unidentified W-containing phase in both the HSWC and HSWB samples. Because HfC has a higher density (12.2 g/cm³) than HfB₂ (11.1 g/cm³) and WB (10.77 g/ cm³) its formation could contribute to the increase in the measured density of the HSWC and HSWB samples.

XRD patterns were taken of the sintered samples to determine the phases present (Fig. 3). Hexagonal HfB₂ and cubic SiC are readily identified and are the only phases present in the HS sample. In the HSWC and HSWB samples there is a shift in the HfB₂ peak attributable to a replacement of W on the Hf lattice. As expected, a replacement of the smaller W atom (1.41 Å) for the Hf atom (1.58 Å) on the hexagonal lattice shifts the peaks to higher 20 values with the (002) peak experiencing the greatest shift of all peaks within the observed angular range. Peaks matching the HfC pattern are found that are also shifted to higher 20 values confirming the EDS findings of a Hf–W–C phase. The peak shifts are shown in Table II. There is no evidence of a WC or WB phase remaining in the samples. At least one additional phase is suggested by small peaks unidentifiable by any combination of W, C, O, Si, Hf, or B in the database. The weak peaks near 2 θ values of 30° and 38° may be monoclinic HfO₂ or peaks of the unknown phase(s). A ternary rhombohedral HfW₄B₅ or hexagonal (Hf,W)₁₂B_{2-x} phase is possible, but not conclusively identified due to the low intensity of the peaks and variability in the lattice parameters reported for these phases.^{25,26}



Fig. 3. XRD of the sintered HS, HSWC, and HSWB samples showing peaks of SiC (3C), HfB₂, and HfC. The HfB₂ and HfC peaks are both shifted to higher 2θ values due to solid solutions formed with WC, WB, or W. The peaks marked with a plus symbol are unknown phase(s) which may include monoclinic HfO₂.

 Table II.
 Peak Shifts Observed for HfB2 and HfC in Samples

 HSWC and HSWB

	Peak shift in 20		
Peak	HSWC	HSWB	
HfB ₂ (001)	0.01	0.04	
$HfB_{2}(100)$	0.01	0.03	
$HfB_{2}(101)$	0.03	0.06	
$HfB_{2}(002)$	0.05	0.09	
$HfB_{2}(110)$	0.04	0.05	
HfC(111)	0.5	0.3	
HfC (200)	0.5	0.3	
HfC (220)	0.7	0.5	

(2) Oxidation

Oxidation was carried out at 1600°. 1800°, and 2000°C in a stagnant air atmosphere. The heating and cooling rates were 5° C/min, so that the samples experienced oxidizing temperatures before and after the 30-min hold at maximum temperature. Table III lists the average total oxide scale thickness as measured from at least 10 points on each sample. The average total scale thickness was measured by first performing EDS to determine the boundary between oxidized grains and the unaltered bulk. A measurement was then taken using the ruler tool in the xT microscope control software of the SEM. The oxide thickness values at 1600° and 1800°C are within one standard deviation of each other for all samples suggesting no improvement or detriment to oxidation resistance by adding W-containing phases at these temperatures. While at 2000°C both HSWC and HSWB had oxide scale thicknesses that were >30% thinner than the HS sample. As a comparison, samples of HfB2-20 vol% SiC-3 vol% WC heated to 1600° and 1800°C had average total scale thicknesses of 47 and 73 µm, respectively.

(A) Oxidation at $1600^{\circ}C$: HSWC and HSWB samples heated to 1600°C produced oxide scales with the same morphology and chemistry of the scale observed on the HS samples heated to 1600°C. The oxide scales were composed of an outer layer of SiO₂ and a porous HfO₂ layer underneath. EDS analysis of the SiO₂ scale in each of the samples revealed Al impurities whose concentration varied throughout the scale, but was never >1 mol% assuming Al as the only impurity in SiO₂. W-containing phases were observed as submicrometer spherical grains scattered throughout the HfO2 layer in the oxidized HSWC and HSWB samples. Additionally, a W-containing phase was found between the HfO_2 grains (Fig. 4) in areas where porosity or grain pullout due to polishing allowed its observation. Point EDS analysis of the features is limited by their size, but examination of at least 10 regions with the same features always showed the presence of W and O and sometimes Hf. The Hf signal may be from the background, while any potential small Si (K, 1.74 kV) peak may be obscured by the Hf (M, 1.645 kV) and W (M, 1.775 kV) peaks that bookend it in the energy spectra. Monoclinic HfO2 and hafnon (HfSiO4) are found by XRD analysis for each of the samples. HfSiO₄ is the reaction product from the combination of HfO2 and SiO2. Calculated HfO2- SiO_2 phase diagrams show that $HfSiO_4$ is stable up to ${\sim}1726^{\circ}C.^{27,28}$

Table III. Oxide Scale Thickness

	Oxide scale thickness (µm)			
Temperature (°C)	HS	HSWC	HSWB	
1600 1800 2000	35 ± 3.2 78 ± 5.5 826 ± 56.1	37 ± 5.3 67 ± 5.5 537 ± 28.1	$34\pm 2.3 \\ 76\pm 7.2 \\ 565\pm 23.8$	





Fig. 4. SEM micrograph of the W-containing phases that are found in the oxide scale after samples HSWC and HSWB are oxidized to 1600° C. Black arrows indicate the intergranular phase found between HfO₂ that is composed of W–O and possibly Hf, while the white arrow indicates spherical grains that are found throughout the oxide scale that also contain W–O and possibly Hf.

(B) Oxidation at 1800°C: Representative images of the oxide scales formed on the samples after exposure to 1800°C are found in Fig. 5. Point EDS analysis showed four layers that are labeled in Fig. 5: (I) dense SiO₂ outer layer with distributed HfO₂ grains, (II) porous HfO₂ penetrated by SiO₂, (III) porous HfO₂ with inclusions of varying concentrations of Si, O, and C, and (IV) porous HfB₂ with inclusions of varying concentrations of Si, O, and C. The average length of each layer was calculated using the same method as the total scale length to find that layers (I)–(III) of all samples were all within 3 μ m. The porosity of all the layers was also similar; in particular, layer (III) was calculated to be $90\% \pm 1\%$ dense for all samples. In measuring porosity by the thresholding method, the inside of the pores were taken as part of the matrix, so the actual density would be somewhat lower, but the same method was used for all samples. Layer (IV) is commonly known as the depleted layer and has been reported for ZrB_2 -SiC and HfB_2 -SiC systems.^{8,13–17,21} The average thickness of the depleted layer in the HS samples was 6 µm; however, samples HSWC and HSWB did not have a layer (IV); the entire porous interface between the bulk and the oxide is comprised of HfO₂. As in the 1600°C oxidized samples, the SiO₂ scale in each of the samples had Al impurities whose concentration varied throughout the scale, but was never >1 mol%assuming Al as the only impurity in SiO₂.

W-containing grains are present throughout all the layers in both HSWC and HSWB. Examples of the W-containing grains are indicated by arrows in Fig. 5(d). EDS of the larger $(1-2 \mu m)$ grains showed the presence of W and O. A third phase comprised of Hf, Si, and O is recognizable between HfO₂ grains and the amorphous SiO₂. The phase is likely HfSiO₂ (labeled in Fig. 5(d)) as evidenced by its presence at 1600°C and the increase in the peak intensity observed in the XRD patterns of all the samples after oxidation to 1800°C. Besides HfSiO₄, only monoclinic and tetragonal HfO₂ are present in the XRD patterns of all samples heated to 1800°C.

(C) Oxidation at $2000^{\circ}C$: Figure 6 is a series of combined micrographs taken of the oxide scale resulting from exposure to $2000^{\circ}C$. The layers of oxide scale for the HS sample heated to $2000^{\circ}C$ are: (I) a dense SiO₂ outer layer with distributed HfO₂ grains; (II) porous HfO₂ penetrated by SiO₂ (III) porous HfO₂ with inclusions of varying concentrations of Si, O, and C; and (IV) porous HfB₂ with inclusions of different concentrations of Si, O, and C. The total scale thickness (Table I)



Fig. 5. SEM micrographs of the (a) HS, (b) HSWC, and (c) HSWB samples after oxidation at 1800°C. The white arrows indicate the location of W containing grains in HSWC (d) while the HfSiO₄, HfO₂, and SiO₂ phases are labeled. HfSiO₄ was found in all three samples oxidized to 1800°C. The oxide scale layers are indicated in (a) as (I) dense SiO₂ outer layer with distributed HfO₂ grains, (II) porous HfO₂ penetrated by SiO₂, (III) porous HfO₂ with inclusions of varying concentrations of Si, O, and C, and (IV) porous HfB₂ with inclusions of varying concentrations of Si, O, and C.

was reduced by the addition of WC and WB while the SiO_2 penetration into the scale and the density increased. In the HSWC and HSWB samples the distinction between layer (I)

and layer (II) is blurred through the extensive formation of $HfSiO_4$. Layer (III) is reduced from an average thickness of 357 μ m in HS to 170 μ m in HSWC and 93 μ m in HSWB. In the



Fig. 6. SEM micrographs of the (a) HSWB, (b) HSWC, and (c) HS samples after oxidation at 2000°C. The layers: (I) a dense SiO₂ outer layer with distributed HfO₂ grains; (II) porous HfO₂ penetrated by SiO₂ and HfSiO₄; (III) porous HfO₂ with inclusions of varying concentrations of Si, O, and C; and (IV) porous HfB₂ with inclusions of varying concentrations of Si, O, and C are indicated in the images. The magnified image in (a) shows the SiO₂ and HfSiO₄/HfO₂ in layer (I) and (II), while the magnified image in (b) shows W-rich phases found in layer (III) as indicated by the arrows.



Fig. 7. (a) SEM micrograph showing three distinct glass phases of the HSWB sample oxidized to 2000° C: (A) W-rich, (B) SiO₂ with Al, Fe, Ca, and Ba, (C) SiO₂-rich, and (D) HfO₂. (b) A TEM section from layer (I). The dark phase is W-rich. (c) TEM micrograph of a section that was prepared after the surface glass had been removed. The inset is the SEM micrograph of the surface of the sample showing the Pt cap applied for FIB cutting. The HfO₂ (the light phase in the SEM and the dark phase in TEM) was monoclinic as determined by selected area electron diffraction (not shown). (d) TEM-EDS of the glass phase showing the composition of the light and dark glasses in (c).

HSWC (Fig. 6(b)) and HSWB (Fig. 6(a)) the average thickness of the depleted later (layer (IV)) is 22 μ m in HSWC and 32 μ m in HSWB compared with 90 μ m in HS. Image analysis calculated a layer (III) density of 87%, 96%, and 97% in HS, HSWC, and HSWB, respectively.

The SiO₂ in layer (I) of the HS sample had impurities of Al, Ca, Ba, and Fe whose concentration varied spatially. Additionally, the SiO₂ in the oxide scale contains the same impurities (Al, Ca, Fe, Ba) as were found in the HS sample but were also shown to form phases with W. Figure 6(a) is a magnified view of layers (I) and (II). Extensive HfSiO₄ formation is observed surrounding the lighter HfO₂ grains. The HfSiO₄ does not contain W, but small pockets (indicated by an arrow) of Hf–Si–W–O can be found in layer (II) of both the HSWC and HSWB samples. Figure 6(b) is a magnified image of layer (III) showing the Wcontaining spheres that were found scattered throughout in both the HSWC and HSWB samples.

SEM and TEM images of the W-containing phases in the glass are shown in Fig. 7. In Fig. 7(a) SEM-EDS suggests three distinct glass phases: (1) W-rich (labeled A), (2) SiO₂ with Al, Fe, Ca, and Ba (labeled B), and (3) SiO₂-rich (labeled C). A TEM section from layer (I) shows a similar microstructure for the multiphase glass with the black phase being W-rich. Figure 7(c) is an overview of a section that was prepared after the surface glass had been removed. The inset is the SEM micrograph of the surface of the sample showing the Pt cap applied for FIB cutting. The HfO₂ (the light phase in the SEM and the dark phase in TEM) was monoclinic as determined by selected area electron diffraction (not shown). TEM-EDS (Fig. 7(d)) were

taken of the glass phase. Fitting the EDS pattern under the assumption that all the impurities are oxides, the light glass contains <0.6 mol% of any impurity with HfO₂ having the highest concentration. The dark glass contained Si, O, Hf, W, Ca, Al, Ba, Fe, and possibly Mg. The low intensity of the MgK α peak and its overlap with an Hf M peak make Mg difficult to discern in this spectra. Selected area electron diffraction analysis revealed all phases in Fig. 7(b) and those in 7(c), exclusive of the HfO₂, to be amorphous.

The XRD patterns of the sample surfaces after oxidation at 2000°C reveal prominent $HfSiO_4$ peaks in the HSWB sample, which correlates well with the observed microstructure. Approximately 60% of the top surface of the 2000°C oxidized HSWB is comprised of the dense $HfSiO_4/Hf-Si-W-O$ phase while localized regions of dense $HfSiO_4/HfO_2$ comprise approximately 30% of the top surface observed in 2000°C oxidized HSWC. Although HfO_2 would be expected to transform to tetragonal at 2000°C, the slow cooling rate (5°C/min) would allow conversion to the monoclinic phase at lower temperatures and account for the small tetragonal peak (<15% of the height of the monoclinic (-111) peak) observed for all the samples.

IV. Discussion

After sintering, no pure WB or WC phases were observed in the HSWC and HSWB samples. The W was incorporated in the HfB₂ and HfC matrix as evidenced by their peak shifts in the XRD spectra. HfC can be formed by a reaction of HfO₂ and excess C. HfO_2 is present as oxygen contamination on the HfB_2 powders and oxidation during milling. Amorphous borides (B_2O_3) also exist at the surface. C can be introduced from wear of the high-density polyethylene bottles during milling or from the graphite dies used to sinter the powders. The oxides may be consumed at elevated temperatures through a reaction with free carbon by reactions (3) or (4) or with WC (reaction [5]).

$$HfO_{2}(s) + B_{2}O_{3}(l) + 5C(s) \to HfB_{2}(s) + 5CO(g)$$

$$\Delta G_{r}(2026.85^{\circ}C) = -8.6 \text{ KJ/mol}$$
(3)

$$\begin{aligned} &\text{HfO}_2(s) + 3\text{C}(s) \rightarrow \text{HfC}(s) + 2\text{CO}(g) \\ &\Delta G_r(2026.85^\circ\text{C}) = -111.5\,\text{KJ/mol} \end{aligned} \tag{4}$$

$$HfO_{2}(s) + 3WC(s) \rightarrow HfC(s) + 3W(s) + 2CO(g)$$

$$\Delta G_{r}(2026.85^{\circ}C) = -489.3 \text{ KJ/mol}$$
(5)

The presence of HfC after sintering diborides has been shown to be dependent on sintering temperature and additives.^{29,30}

The phase diagram of HfB_2 and $WB_{\sim 2}$ suggests a maximum W concentration of 23 mol% at $\sim 2365^{\circ}$ C and 10 mol% or above at temperatures above 1200°C,³¹ while melting experiments suggest that approximately 4 mol% W can be incorporated into the HfB₂ lattice.³² The same crystalline lattice and similar size allow 40 mol% of WC to be dissolved in HfC at 2027°C.³³ Limited literature exists for the HfC-WB system, but the similar XRD peak shift values of HSWC and HSWB suggest solubility of W in HfC in the HSWB sample. The W that is not incorporated into either HfC or HfB₂ can be found in grains shown to contain W, O, C, and B. The addition of W-containing phases increases the sinterability of the samples, results in smaller HfB2 grains, and promotes evolution of acicular SiC grains. A similar SiC microstructure was shown by Zhang et al.³⁴ for pressureless sintered ZrB_2 -SiC with B₄C additions and WC impurities. However, Chamberlain et al.24 do not show the same SiC microstructure for WC impurities in hot pressed ZrB₂-SiC. It is possible that excess B or C (from WB, WC, or B_4C^{34}) in the system can promote the β (cubic) to α (hexagonal) transformation at temperatures below 1800°C, with the α -SiC having acicular grain morphology.³⁵ Unfortunately the SiC XRD peak has a very low intensity and the main $\boldsymbol{\beta}$ and α -SiC peaks are within 0.07°, so phase identification is impractical. Engineering the microstructure may prove beneficial as it has been shown that the size and morphology of the SiC and HfB₂ grains can affect strength.^{29,35,36}

The oxidation of HS, HSWC, and HSWB samples resulted in oxide scales with comparable total thicknesses and scale morphologies at 1600° and 1800°C. The difference in the average thickness of the total oxide scale for each sample was within the spread measured for an individual sample. The oxide scales formed on the HSWC and HSWB samples at 2000°C were significantly different than the scale formed on HS. The HSWC and HSWB samples had less porous scales that were 30% thinner than the scale formed on the HS sample. The three methods by which W-additions may impact oxidation resistance are (1) controlling the phase transformations of the HfO₂ scale, (2) increasing the viscosity of the SiO₂ scale, or (3) promoting densification of the HfO₂ scale. The addition of W neither promoted nor delayed the monoclinic to tetragonal phase transformation, thus not affecting the density of the HfO₂ by this method.

Because no W was found in the SiO₂ at 1600° and 1800°C by SEM-EDS the addition of W-containing phases would not be expected to alter the viscosity or melting temperature of the SiO₂ glass and the SiO₂-rich layer would be expected to be protective at 1600° and 1800°C.^{3,4,18,21} A two-phase glass is not observed until above 1800°C which is above the melting temperature of pure SiO₂ (1723°C), so the two phase may form as the glass cools. Borate and silicate glasses with Group

IV–VI transition metal (Hf, Zr, Ti, Ta, W) oxides tend to exhibit microphase separation and crystallization upon cooling.^{15,37,38} Glass compositions that exhibit phase separation posses an increased viscosity in the two-phase region compared with a single-phase liquid.³⁸

Only a few phase diagrams for W and Hf in B_2O_3 or SiO₂ are reported. The most studied diagram, HfO₂-SiO₂, reveals that at 2000°C a single liquid phase exists for compositions with approximately 60 mol% (or greater) of SiO₂ and that at lower SiO₂ concentrations the Si-Hf-O liquid phase is found in equilibrium with HfO₂.^{27,37} In the WO₃– B_2O_3 system a single-phase liquid is formed at all compositions above 1430° C.³⁹ No phase diagram exists for HfO₂–B₂O₃ but a study of glass melts found that <1 mol% HfO₂ could be dissolved in B₂O₃.⁴⁰ However, the same study found that sodium borosilicate or aluminum borosilicate glasses can dissolve up to 17 mol% HfO2 with the allowable HfO2 concentration dependent on the concentration of the other glass species.³⁹ As evidenced by Fig. 7 the glass chemistry found in the 2000°C sample has spatial variances in chemistry. The presence of Al, Na, Ca, Ba, and Fe in the glass could originate from the impurities in the starting powders or be incorporated from the Ca-stabilized ZrO₂ crucible that holds the sample. Group I and Group II impurities have been observed in our previous experiments and also reported in the literature,¹⁶ but have not received much attention to date. However, as the development of new UHTC compositions seek to add elements in order to improve glass properties such as viscosity the presence of these impurities may play a crucial role in the outcome of these efforts.

The phase diagrams for WO₃ with SiO₂ or B₂O₃ are unavailable at the temperatures of interest, but inspection of other transition metal oxides with SiO₂ such as Nb₂O₅–SiO₂ and Cr₂O₃–SiO₂ suggest two-phase glasses above 1695° and 2200°C, respectively.^{41,42} Therefore the observed existence of a two-phase region in the WO₃–SiO₂ system seems logical. The two-phase glass may improve oxidation resistance by increasing the viscosity of the glass at 2000°C and/or during its slow cool down.

The impact of densification in the HfO_2 -based layers was examined in the HSWC and HSWB samples. The HfO_2 contained W both as individual grains and as a phase between HfO_2 grains. Reactions (6)–(8) describe the possible oxidation of WC and WB.^{43,44}

 $WC(cr) + 5/2O_2(g) \to WO_3(cr) + CO_2(g)$ (6)

$$2 \operatorname{WB}(cr) + 9/2 \operatorname{O}_2(g) \to 2 \operatorname{WO}_3(cr) + \operatorname{B}_2 \operatorname{O}_3(l)$$
(7)

$$WO_3(cr) \to WO_3(g)$$
 (8)

The HfO₂-WO₃ phase diagram shows a solubility of WO₃ of about 5 mol% at 1600°-2000°C, while above 5 mol% the HfO₂ solid solution will be accompanied by a liquid.²² The solubility of W in HfB₂ and HfC is between 4 and 40 mol% suggesting localized regions of W concentrations necessary for phase separation could exist. The resulting liquid has a melting point of 1473°C. The presence of this liquid can promote liquid-phase sintering of the HfO₂ resulting in the observed denser oxide scales for the HSWC and HSWB samples. The reduction in the length of the total SiC-depleted layer at 1800°C in the samples containing W can be explained by a reduction in oxygen penetration through the denser oxide scale. Upon cooling, the resulting crystalline phases are a HfO2 solid solution with <5 mol% WO₃ and WO₃ with no solid solubility for HfO₂. SEM-EDS confirmed the existence of W-rich phases between the HfO_2 grains in the postoxidation analysis.

In addition to the denser HfO_2 layer (layer (III)), layer (II) in the samples with W additions is composed of $HfSiO_4$ and HfO_2 . Although a dense $HfSiO_4$ would be expected to have a lower oxygen diffusion coefficient than the porous SiO_2 -filled HfO_2 found in the outermost regions of HS, the decomposition temperature of HfSiO₄ is $1726^{\circ}C^{27}$ so that the HfSiO₄ is likely formed on cooling and would not be responsible for the decrease in oxygen penetration at 2000°C.

The combined effect of the more viscous outer layer and denser inner layer promote oxidation resistance and provide for an overall thinner scale at exposure temperatures of 2000°C in HSWC and HSWB.

V. Conclusion

Dense HfB₂-SiC samples were prepared with additives of WC and WB. Both the WC and WB additives promoted sintering while reducing the grain size of HfB₂. Solid solutions of W-Hf-B and W-Hf-C were formed in both samples. The WC- and WB-containing HfB2-SiC samples oxidized to 1600° and 1800°C exhibited similar oxide scales as the HfB₂–SiC sample. However, the samples with WC and WB showed a 30% reduction in scale thickness when the samples were oxidized at 2000°C due to a more viscous phase separated glass found in the outermost regions of the scale and a denser inner HfO₂ that restricted oxygen penetration to the sample.

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