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Effects of SiC or $MoSi_2$ second phase on the oxide layers structure of HfB_2 -based composites



Sadjad Mashayekh¹, Hamid Reza Baharvandi

Faculty of Materials and Manufacturing Technology, Malek-Ashtar University of Technology, Tehran, Iran

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ABSTRACT

Monolithic HfB₂, HfB₂-30 vol% SiC and HfB₂-10 vol% MoSi₂ composites were prepared by SPS and oxidized in stagnant air at 1500 °C for 70 min. The microstructure of the oxide layer cross-sections showed that the oxidation extents were as follow: monolithic HfB₂ > HfB₂-30 vol%SiC > HfB₂-10 vol% MoSi₂.According to the EDS Line-scan, only one porous oxide layer containing a minor amount of B₂O₃was found on the HfB₂ oxidized surface whereas a thick silicate glass layer and a porous oxide layer below that existed on the surface of HfB₂-30 vol% SiC. After oxidation, the surface of HfB₂-10 vol% MoSi₂ had a narrow silicate-oxide compact layer covered by a very thin glass layer. X-ray diff raction patterns of the oxidized surfaces showed the monolithic HfB₂-10 vol% MoSi₂ contain, upon oxidation, only m-HfO₂ phase, mainly m-HfO₂ with a minor amount of HfSiO₄ and mainly HfSiO₄ with a minor amount of m-HfO₂ phases, respectively. Based on the observations in this study, it is suggested that the elimination of the porous layer and subsequent increase of the HfSiO₄ phase are the main reasons for the better oxidation resistance of HfB₂-10 vol% MoSi₂.

1. Introduction

The most important peculiarity that distinguishes ultra-high temperature ceramics (ceramics with melting temperatures above 3000 °C) from other refractory materials like graphite or refractory metals is their high oxidation and ablation resistance at extreme temperatures as described in detail by Opeka [1]. Previous studies suggest that HfB₂-SiC composites off er the best resistance to oxidation among UHTCs, due to the formation of a glass layer preventing oxygen diffusion at two temperature intervals, 800–1100 °C and 1200–1700 °C, and the absence of destructive phase transformations at low temperatures in the oxide layer [2]. Given these characteristics, many studies concentrated on the optimization of this composite as the base composite for the development of components and coatings [1]. HfB₂-SiC composite undergoes reaction (1) at low temperatures (below 1100 °C) and B₂O₃ glass layer is formed [3].

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

The presence of this glass layer at temperatures up to 1100 °C provides the composite with protection against the oxidation. However, given the high evaporation rate of B_2O_3 at temperatures above 1100 °C the glass can no longer prevent the oxidation [4,5]. Increasing temperature above 1200 °C, SiC oxidation starts according to reaction

¹ Corresponding author. *E-mail address:* sadjad mash@yahoo.com (S. Mashayekh).

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(2) and forms a SiO₂ glass layer.

$$\operatorname{SiC}(s) + 3/2O_2(g) \to \operatorname{SiO}_2(l) + \operatorname{CO}(g) \tag{2}$$

By forming a continuous glass layer on the surface, oxygen activity decreases at the interface of the oxide layer with the base composite and active SiC oxidation progresses in the sub-scales according to reaction (3) at $1500 \,^{\circ}C$ [6].

$$SiC(s) + O_2(g) \rightarrow SiO(g) + CO(g)$$
(3)

Formation of SiO gas beneath the surface glass layer makes the oxide surface layers to be composed of a glass layer on top and a porous layer depleted of SiC below the glass layer [6].

When examining mechanical properties, the SiC-depleted layer was found to be the origin of cracks [7-9]. In order to prevent the plunge of mechanical properties caused by the SiC-depleted layer, other glass-forming compounds such as MoSi₂ were used [7,10-16].

Unlike SiC, oxidation of $MoSi_2$ under high oxygen vapor pressure yields the volatile MoO_3 oxide. Under such circumstances, $MoSi_2$ is oxidized according to reaction (4) [17].

$$2\text{MoSi}_2(s) + 7\text{O}_2(g) \rightarrow 2\text{MoO}_3(g) + 4\text{SiO}_2(l)$$
(4)

However, after the formation of a SiO₂ protective layer and the reduction of oxygen vapor pressure at the oxide layer/base composite

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interface, the oxidation of $MoSi_2$ advances as stated in reaction (5) [17].

$$5\text{MoSi}_2(s) + 7\text{O}_2(g) \rightarrow \text{Mo}_5\text{Si}_3(g) + 7\text{SiO}_2(l)$$
(5)

Unlike SiC oxidation again, in a low oxygen vapor pressure, no gas is produced by the reaction (5) and hence no porous layer below the glass layer is expected in HfB_2 -MoSi₂ composites upon oxidation [12]. Additionally, the presence of molybdenum improves the surface glass protection by stabilizing the B_2O_3 glass and preventing its evaporation [18].

The main goal of this research is to compare the oxide layer structures of the monolithic HfB_2 ceramic with that of the HfB_2 -30 vol% SiC and HfB_2 -10 vol% $MoSi_2$ composites in an isothermal oxidation at 1500 °C. Microstructures before the oxidation and structure of oxide layers after the oxidation were examined. Elements distribution in the oxide layers was studied using line-scan analysis and oxidation products were determined by XRD. Finally, all these data were used to delineate a better understanding of the oxidation inhibition mechanisms in these UHTCs.

2. Experimental procedure

A 98% pure, 5 μ m (D90 = 9.5 μ m)HfB₂powder was obtained from Beijing Cerametek Materials Co. Ltd. The main impurity of the starting powder was oxygen, as obtained by X-ray diff raction, which resulted in about 9 wt% HfO2. α -SiC and MoSi₂ powders (provided by Goodfellow and Aldrich respectively) with purities above 99% and grain sizes below 5 μ m were used for this study.

After weighing, according to the equivalent weight percent of HfB₂-30 vol% SiC and HfB₂-10 vol% MoSi₂, powders were mixed for three hours at 170 rpm using a planetary ball mill. The amount of second phases are chosen based on the optimum amount reported in literature [1,19]. The jar and balls that were used, were made of WC-Co and the balls were 5 mm in diameter. Ball milling was performed under semiwet conditions, in order to prevent preferential precipitation of constituents with different densities, using ethanol in argon atmo-

sphere, for every 20 g powder batch, 4 ml ethanol was added and 200 g milling media were used.

Sintering was performed using a Spark Plasma Sintering device, manufactured by KPF,¹ in a graphite mold with an internal diameter of 26 mm in vacuum, under an applied pressure of 40 MPa. Samples were surrounded with a 0.2 mm-thick graphite foil to prevent the powder from sticking to the mold and the punches. Temperature was measured by a pyrometer focused at the end of an axial hole prepared in the upper punch. The sintering temperature was 1800 °C and the samples were kept at the maximum temperature for about 15 min.

The sintered pellets were ground using cubic boron nitride coated plate and then the surface polished by 60, 150, 220 and 400 sand papers, respectively upon perfect removal of the graphite foil. After the surface preparation, densities of the sintered samples were measured by Archimedes' method.

Isothermal oxidation was done in a furnace with $MoSi_2$ heating elements, capable of sample charging from the furnace bottom, in stagnant air, and at 1500 °C, for 70 min. It's noteworthy that the samples were put into the furnace when the temperature achieved 1500 °C and removed from the furnace just after being kept in it for the intended time.

The microstructures of as-sintered samples and the cross-section of the oxidized samples were examined by a TESCAN Mira3 field emission scanning electron microscope equipped with a SamX EDS detector. Using this Fe-SEM, line-scan diagrams are plotted using variations of K_{α} peak intensity corresponding to Si, B and O and L_{α} peak intensity corresponding to Mo and Hf. Optical images are taken with a Leica MEF4A optical microscope. X-ray diff raction patterns of oxidized samples were extracted using an Inel Equinox 6000.

3. Results

3.1. As-sintered materials

Using Archimedes' method, the relative density was measured to be 95%, 98.8% and 96.5% for HfB₂, HfB₂-30 vol% SiC and HfB₂-10 vol% MoSi₂samples, respectively (assuming 11.1, 3.22 and 6.26 g/cm³ theoretical densities for HfB₂, SiC and MoSi₂ respectively). Electron microscope images taken from polished surfaces of these samples are presented in Fig. 1. Some porosity is visible in all three microstructures. Given the large difference between HfB₂ and second phases densities, the darker phase in Fig. 1b,c can be attributed to SiC or MoSi₂ and the brighter phase to HfB₂.

3.2. Oxidized materials

After the oxidation, a relatively thick white oxide layer formed on the monolithic ceramic. Electron microscope image of the layer is presented in Fig. 2a. The oxidation front is marked by a dashed line and the thickness of the oxide layer is about 270 μ m. Considering that the layer was formed in 70 min the oxide layer does not seem to be protecting the substrate from oxidation. The layer affected by oxygen diffusion was investigated using Line-Scan EDS analysis. The peak intensity variations in the depth of the monolithic HfB₂ oxide layer can be found in Fig. 2b.

Despite the EDS questionable precision in quantitative examinations of light elements, the intensity changes of the elements peaks and comparing them to the microscope images can be useful in the identification of the oxide layer structure. Considering this limitation, the manner of boron peak changes in the surface oxide can be regarded. The variation of boron amount in the oxide layer from the surface to 280-290 µm depths is in accordance with the oxygen level. Therefore, it seems plausible that boron can be found as its oxide B $_{2}O$.

in this region. To note that Fig. 2b and all the other line-scans are plotted on a logarithmic scale, so little variations of the elements amounts are faded.

Due to the high vapor pressure of B_2O_3 at temperatures above 1200 °C, the evaporation rate of B_2O_3 is high in the outermost layer and the boron decreasing gradient toward the surface can be attributed to its intensified evaporation near the surface [20]. The harmony between boron and oxygen distribution varies at a depth around 300 µm by significantly reducing the oxygen level thus marking the interface between oxide scale and unoxidized bulk.

After oxidation, a glaze-like layer is observed on the surface of HfB_2 -30 vol% SiC composite. This layer seems to be the oxidation product of SiC. As shown in Fig. 3, this glass layer evenly spreads over the surface of the HfB_2 -30 vol% SiC composite except some bubbles. Two kinds of bubbles within the glass layer are clearly identifiable on the surface of the HfB_2 -30 vol% SiC composite. Some of these bubbles have grown so much that they reached the surface, indicated by white arrows in Fig. 3, but some have not opened a way to the surface (black arrows). The composite surface has been exposed to oxidation again as a result of bubbles breaking. Subsequently, a protective glass layer seems to have formed on the surface again. Moreover, possibly due to its very high viscosity, the glass layer has not flowed from the neighboring regions and does not cover beneath the bubble.

Fig. 4a shows the cross-section of the oxide layer formed in the HfB_2 -30 vol% SiC composite. Two layers produced by oxidation on the composite surface can be clearly seen in the image. According to the previous studies on HfB_2 -SiC oxide layers, it seems that the external layer is a silicate glass and the interlayer (brighter layer) is a SiC-depleted porous layer [21,22]. Line-scan EDS was employed to ascertain this hypothesis. Using the silicon variation profile, shown in

¹ KhalaPooshanFelez Co., Ahmad Abad Mostofi, Tehran, Iran.



Fig. 1. Microstructures of samples sintered by SPS at 1800 °C, 40 MPa and 15 min dwell, a) monolithic HfB2, b) HfB2-30 vol% SiC and c) HfB2-10 vol% MoSi2.



Fig. 2. a) Back-scattered electron image of monolithic HfB₂ cross-section upon oxidation at 1500 °C, 70 min, b) EDS line-scan across the oxide layer of monolithic HfB₂, Line-scan is done along the line shown on (a).

Fig. 4e, a SiC-depleted layer can be clearly identified at a 210–290 μ m distance from the surface. This region exactly matches the white layer. Besides, boron variation shows a clear coordination with hafnium variations. This coordination extends from the composite inner side up to nearly 250 μ m distance from the surface. Additionally, matching with microscope images, the point where the analysis was carried out is located in the white layer. Therefore, it can be claimed that hafnium is in oxide form 220–250 μ m far from the surface. The white layer thickness is around 75 μ m while the oxide layer thickness in the

monolithic HfB_2 ceramic was about 290 $\mu m.$ This reduction can be attributed to the glass layer formation which prevents further oxidation.

Exploring the surface glass layer in a closer view, white discrete particles can be seen in the glassy phase. A higher magnification image is presented in Fig. 4b. Using EDS analysis (Fig. 4c), it was found that the atomic concentration of hafnium and silicon is equal in these particles. In addition, the glass matrix is mainly composed of Si and O (Fig. 4d). Considering these facts, these particles are probably made of



Fig. 3. Optical image of the HfB $_{2}$ -30 vol% SiC surface after oxidation; white and black arrows indicate open and subsurface bubbles respectively.

perfectly smooth surface to cover all irregularities of the surface.

The structure of layers obtained from oxidation of the HfB_{2} -10 vol% $MoSi_{2}$ composite is presented in Fig. 5a. In the cross-section, similar to HfB_{2} -30 vol% SiC, the glass phase can be observed on the surface. But there are two major differences between these two structures. First, no porous layer can be seen beneath the glass. The second difference is in the thickness of the glassy layer. Given the scale of Figs. 4a and 6a, it is clear that the glass layer formed from HfB_{2} -10 vol% $MoSi_{2}$ is much thinner than HfB_{2} -30 vol% SiC.

The variation in the boron level, shown in Fig. 5b, can be used to identify the oxide layers for this sample as before. Moving from center to the surface, coordination between boron and hafnium is maintained up to a 15 μ m distance from the surface. The distance between this point and the point corresponding to the sudden drop in both hafnium and boron is about 3 μ m depicting the narrow oxide layer developed on the HfB₂-10 vol% MoSi₂ composite.



Fig. 4. a) The oxide layer cross-section of the HfB₂-30 vol% SiC composite upon oxidation at 1500 °C, 70 min (the line on the right image depicts line-scan pathway),b)High magnification image of precipitates in the middle of the surface glass, c) EDS spectrum of the precipitate pointed on (b), d) EDS spectrum of the glass, e) EDS line-scan across the oxide layer of the HfB₂-30 vol% SiC composite. Line-scan is done along the line shown on (a).

hafnium silicate (HfSiO $_4$) that given their ordered geometry, seems to have crystallized in the silicate glass.

A bubble-free glassy layer covering the surface was observed when exploring the oxidized surface of the HfB_{2} -10 vol% MoSi₂ composite. This layer does not seem to have sufficient thickness in order to form a

On the other hand, Fig. 5b shows a rise in molybdenum content right beneath the glass layer. This is conceivable given that products of $MoSi_2$ oxidation are not volatile in a low oxygen partial pressure [17]. Given the low solubility of molybdenum oxide in silicate glasses [23,24], the phase accumulates beneath the glass layer. Finally, a glass



Fig. 5. a) Back-scattered electron images of cross-section and b) line-scan EDS across the oxide layer of HfB₂-10 vol% MoSi₂ composite upon oxidation at 1500 °C, 70 min, Line-scan is done along the line shown on (a).



Fig. 6. Equilibrium oxidation products of 10 mol MoSi $_2$ (a) or SiC (b) at 1500 °C varying the oxygen partial pressure calculated by HSC software.

phase along with a molybdenum-rich phase seems to have formed with oxidation of HfB_{2} -10 vol% $MoSi_{2}$.

Comparing the equilibrium phases resulted from oxidation of SiC and MoSi₂ with variations of oxygen partial pressure is helpful for a better understanding of thermodynamic aspects of oxidation. Fig. 6, obtained through HSC Chemistry software [25], compares thermodynamic products of 10 mol SiC or MoSi₂ oxidized at 1500 °C with the

variation of oxygen level (phases below 1 mol were neglected). At very low levels of oxygen, the only gaseous product of $MoSi_2$ oxidation is SiO. On the contrary, in SiC oxidation, a great amount of CO gas is also produced in addition to the larger amount of SiO compared to $MoSi_2$ oxidation. Consequently, SiC oxidation beneath the SiO₂ glass to player continues with the formation of gaseous phases, finally creating a porous SiC-depleted layer. This explains the high bubbles production in SiC-containing composite. It should be noted that this simulation does not include the effects of HfB₂ matrix oxidation that notably influences the nature of the oxidation products.

The crystalline phases formed upon oxidation of the two samples are displayed in the X-ray diffraction of the oxidized samples (Fig. 7). The higher background intensity at around 20° seems to be due to the presence of the glass phase on the surface of HfB2-30 vol% SiC and HfB₂-10 vol% MoSi₂. Moreover, as it was seen in electron microscope images, the higher intensity of the HfO₂phase in HfB₂-30 vol% SiC composite, and on the other hand, the higher intensity of the HfB₂ phase in HfB2-10 vol% MoSi2 composite after the oxidation can be a sign of a thicker oxide layer and more severe oxidation of the HfB2-30 vol% SiC composite compared with the HfB2-10 vol% MoSi2 composite at the same oxidation time and temperature. Based upon the intensity of XRD peaks, the main phase obtained from oxidation in HfB₂-30 vol% SiC composite was monoclinic-HfO₂. Beside that phase, a small amount of HfSiO4 can also be found. This ratio was reversed for the oxidation of HfB₂-10 vol% MoSi₂ composite and the main phase obtained from oxidation was HfSiO4 with small amount of monoclinic-HfO2. MoB phase was also found in the HfB2-10 vol% MoSi2 composite which seems to be the reaction product between Mo species and B₂O₃ [15,26].

4. Discussion

Considering the line-scan spectra, the thickness of the SiO₂-based glass layer seems to have reduced from 180 μ m in the HfB₂-30 vol% SiC composite to about 12 μ m in the HfB₂-10 vol% MoSi₂ composite. This reduction of thickness can only result from the reduction of oxygen or silicon diffusion coefficients in the oxide layer.

According to the literature, addition of a polyvalent element, molybdenum in this case, leads to a more severe phase separation in boro-silicate glass and the viscosity of the glass rises subsequently [1–27]. Based on Stokes-Einstein law this increase in viscosity can reduce oxygen diffusion rate. Despite this claim, Rezaie et al. [28] have found boron to exist in a negligible amount in the surface glass



Fig. 7. X-ray diff raction patterns of samples after oxidation at 1500 °C, peaks indicated by 1, 2, 3, 4, and 5 belongs to HfB₂, monoclinic-HfO₂, HfSiO₄, MoB, and tetragonal-HfO₂ phases respectively.

obtained from the oxidation of ZrB_2 -30 vol% SiC without the presence of polyvalent elements therefore there could be no phase separation in such a glass. In the present study too, the boron amount in the glass was negligible and no intense variation suggesting phase separation, similar to what Karlsdottir and Halloran [29] have reported, was observed by Line-Scan in neither of the composites for boron or silicon. In addition, the formation of phase separation zones in Karlsdottir's research was accompanied with convection which seems to be accelerating oxygen diffusion below the glass layer [29]. Also, according to the very small thickness of the glass layer formed on the HfB₂-10 vol% MoSi₂ composite in Fig. 5a, it can be deduced that improved inhibition properties of the glass layer could not be the main reason for the oxidation reduction due to the replacement of SiC with MoSi₂, but it could rather concern the characteristics of the oxide layer beneath the glass.

Indeed, comparing the layers obtained from the oxidation of the two composites, elimination of the porous oxide layer in HfB₂-10 vol% MoSi₂ composite could be of major importance. The reduction of oxygen diffusion depth is very clear considering the oxygen profiles corresponding to the two composites. If the reference point is assumed to be right after the silica scale moving to the ceramic core, oxygen diffusion has continued at least down to a depth of 40 µm beneath the surface in the HfB₂-30 vol% SiC composite while only 8 µm far from the surface in the HfB2-10 vol% MoSi2 composite the oxygen amount reaches such a low intensity. Moreover, as Dehdashti et al. [18] reported, the addition of molybdenum and niobium could stabilize the B₂O₃ liquid by lowering its activity and improve the oxidation resistance of ZrB₂effectively. On the other hand, SiC oxidation in low oxygen vapor pressures creates SiO gas in addition to CO while Mo₃Si₅ with melting temperatures above 2000 °C [30], is formed instead of MoO₃ gas during oxidation of MoSi₂ in low oxygen vapor pressures (Fig. 6). Furthermore, consumption of B_2O_3 to form MoB [26], with a melting point over 2500 °C [31], could decrease volatile species even more. Therefore, MoSi₂ oxidation produces much less volatile phases than SiC in low oxygen vapor pressures and consequently less or no bubbling phenomena at 1500 °C. This prevents the porous layer to form beneath the glass layer. It is noteworthy that even in the Arc-Jet test that was performed by Savino et al. [12] on HfB2-5 vol% MoSi2 composite in which surface temperature reached 1950 °C, no porous layer formed beneath the glass. Accordingly, SiC replacement by MoSi₂ leads to the elimination of subsurface porosities that could be

unconstrained pathways for oxygen penetration.

Another phase obtained from oxidation of two composite samples is HfSiO₄. In the study carried out by Sciti et al. in which an HfB₂-20 vol% MoSi2 sample was oxidized above 1400 °C for 30 min under isothermal conditions, the HfSiO₄ phase was identified in the oxidized surface. Formation of HfSiO4 was attributed to the diffusion of Si from the glass into the HfO2 network and precipitation of HfSiO4 due to Si saturation in HfO2. Sciti et al. showed that crystallization of HfSiO₄alters weight increasing curve from parabolic to logarithmic one [15]. Carney, also proposed the same mechanism for HfSiO₄ formation during oxidation of HfB2-20 vol% SiC but considering the discontinuity of this phase, as it is depicted in Fig. 4b, no relation was deduced between its formation and the level of oxidation [32]. Given that less or no bubbling occurred in the HfB2-10 vol% MoSi2 composite, no porous layer exists and hence the interface between the glass and the oxide phase stretches over the entire surface and consequently a more continuous HfSiO₄ can precipitate. On the contrary in composites that contain SiC, considering the presence of a porous Si-depleted layer, the interfaces between the glass and the oxide have a less integrity leading to a non-contiguous silicate layer.

Moreover, previous studies showed that the temperature required for reacting SiO_2 and ZrO_2 in order to develop $ZrSiO_4$ is lowered from 1400 °C to 1100 °C in the presence of additives [33,34]. Although no study has addressed the effect of molybdenum in lowering this temperature, it is likely for molybdenum to decrease this reaction temperature.

5. Conclusion

Monolithic HfB₂, HfB₂-30 vol% SiC and HfB₂-10 vol% MoSi₂ samples were oxidized at 1500 °C for 70 min. The oxide layer thicknesses of the monolithic HfB₂, the HfB₂-30 vol% SiC and the HfB₂-10 vol% MoSi₂ composites decreased following this order. The improved resistance in the composite samples was attributed to the SiO₂-based glass phase which prevents oxygen diffusion. Comparing two composite samples, substantial decrease in gaseous products during oxidation of HfB₂-10 vol% MoSi₂ in low oxygen vapor pressures lead to the porous layer elimination. With porosities eliminated, oxygen penetration pathways are obstructed. Additionally, the elimination of the porous layer and possibly the presence of molybdenum resulted in a wider and more continuous development of HfSiO₄.

Therefore, replacement of SiC with MoSi₂ results in altered morphology and chemical composition of the subsurface oxide layer which improves oxidation resistance of the HfB₂ composite.

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