

High-Temperature Oxidation at 1900°C of ZrB₂–xSiC Ultrahigh-Temperature Ceramic Composites

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Oxidation of ZrB₂-based ultrahigh-temperature ceramic composites containing 10, 20, and 30 vol% SiC was performed at 1900°C for 1 h in air. ZrB₂-20 vol% SiC exhibited the highest oxidation resistance at this temperature and formed a dense coherent oxide scale after oxidation, whereas a strong degradation was observed for both ZrB₂-10 vol% SiC and ZrB₂-30 vol% SiC. In addition, cracks and spallation in the oxide scale were also detected for the latter materials. The oxidation behaviors of ZrB₂-SiC composites were investigated. The effect of SiC content was analyzed and oxidation models were proposed to describe the observed microstructures.

I. Introduction

THE ZrB_2 - and HfB_2 -based ultrahigh-temperature ceramics (UHTCs) are potential candidates for thermal protection materials in both re-entry and hypersonic vehicles because of their excellent and unique combination of high melting points, good thermal shock resistance, and good ablation/oxidation resistance.^{1–12} These properties make UHTCs attractive for the design of future hypersonic aerospace vehicles with features like sharp leading edges and sharp nose cones. Such design features could produce more agile vehicles that would open up a greater range of hypersonic flight paths and re-entry trajectories. Reentry and hypersonic vehicles, regardless of their specific designs, require control surfaces with sharp leading edges if they are to be maneuverable at hypersonic velocities. Low-radius leading edges are subject to much greater aerothermal heating than blunt edges, such as those on the space shuttle orbiter, and these edges will reach temperatures that may exceed 2000°C during reentry.^{13,14} The currently available thermal protection materials will not survive under such extreme temperatures and new materials are required for use in advanced thermal protection systems.

Oxidation resistance is a major issue in the development of UHTCs for aero-propulsion and hypersonic flight applications. The introduction of second phases (i.e., SiC, MoSi₂) has succeeded in improving both the oxidation/ablation resistance and the mechanical properties of UHTCs.^{3–6,8,11,15} In particular, the addition of Ta compounds significantly improves the oxidation resistance of ZrB₂–SiC below 1800°C, whereas it is detrimental to the performance of ZrB₂–SiC at a higher temperature.^{16,17} In accordance to the previously reported results, a diboride matrix composite that includes only SiC as a second phase is one of the most promising compositions. However, the oxidation mechanisms of these materials are still not well understood, especially for temperatures above 1900°C. In addition, the oxidation

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behavior of the ZrB_2 -SiC composites is significantly different from that at lower temperature. The purpose of this paper is to investigate the oxidation behaviors of ZrB_2 -SiC UHTC composites at 1900°C in air. The effect of SiC content on the oxidation resistance of the materials was investigated, and the proposed model was also discussed.

II. Experimental Procedure

The samples used here for oxidation testing were fabricated from commercial ZrB_2 (Northwest Institute for Non-ferrous Metal Research, Xi'an, China) and SiC (Weifang Kaihua Micro-powder Co. Ltd., Shandong, China) powders. The powder mixtures of ZrB_2+10 vol% SiC (ZS1), ZrB_2+20 vol% SiC (ZS2), and ZrB_2+30 vol% SiC (ZS3) were ball milled in ethanol for 8 h and dried in a rotating evaporator. Milled powders were then uniaxially hot pressed in a boron nitride-coated graphite die at 2000°C for 60 min under vacuum and 30 MPa of applied pressure.

Bulk density and theoretical density were evaluated using the Archimedes method and the rule of mixtures, respectively. Sample coupons in the size of 2.0 cm \times 1.0 cm \times 0.35 cm were cut from the hot-pressed materials, and all surfaces were diamond polished to a 1-µm finish. Coupons were ultrasonically cleaned successively in detergent, deionized water, acetone, and alcohol before exposure. All samples were loaded into a slotted ZrO₂ refractory brick and then exposed to 1-h oxidation in stagnant air at 1900°C using a bottom-loading furnace with zirconia heating elements, and the results are repeatable. The experiments were carried out with a Pt-Rh thermocouple and a two-color Raytek pyrometer (RAY-MR1SCSF, Raytek Corp. Santa Cruz, CA), which covers a temperature range of 1000°-3000°C. MoSi2 elements were used to heat before the operation of the zirconia heating elements, and the temperature was measured by the Pt-Rh thermocouple. The twocolor Raytek pyrometer was used to measure the temperature of the samples.

X-ray diffraction (Rigaku, Dmax-rb, Tokyo, Japan) was used to identify oxide phases present after exposure. Scanning electron microscopy (SEM; FEI Sirion, Eindhoven, Holland) along with energy-dispersive spectroscopy (EDAX, Mahwah, NJ) was used to characterize the composition and microstructure of the surface and cross section of the samples after oxidation. The different oxide layers were also investigated after removing the surface layers by polishing parallel to the original surface. The material removal was monitored using optical microscopy so that the desired region was reached.

III. Results and Discussion

(1) Density and Microstructure

Dense ZrB₂–SiC composites were obtained. The bulk densities of the sintered ZS1, ZS2, and ZS3 billets were 5.80, 5.41, and 5.22 g/cm³, which correspond to relative densities of 100%, 98%, and 100%, respectively. Figure 1 shows SEM micrographs of the polished surfaces of the ZrB₂–SiC UHTC composites. The darker phase is SiC, and it appears to be uniformly dispersed in the lighter ZrB₂ matrix. The microstructures of the

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Fig. 1. Scanning electron micrographs of the surfaces of the ZrB2-SiC ultrahigh-temperature ceramics: (a) ZS1, (b) ZS2, and (c) ZS3.

composites are regular, and little porosity was observed in the polished surfaces. Based on the high relative density and the lack of any open porosity, porosity should not have a significant effect on oxidation behavior.

(2) Microstructure Changes and Oxidation Properties

Figure 2 shows the micrographs of ZrB_2 -based UHTCs containing 10, 20, and 30 vol% SiC after oxidation at 1900°C for 1 h. The bright phase is ZrO_2 and the dark phase is SiO₂, as





shown in Fig. 2. A continuous SiO_2 layer was found to form on the surface of the oxide scale for ZS2, while a discontinuous SiO_2 layer was formed at the outside scale for ZS1 and ZS3. A number of holes were also observed on the surface of ZS1 and ZS3. The formation of the holes was attributed to the formation of large amounts of high-pressure gaseous oxidation products (i.e., B_2O_3 , CO, and SiO). Moreover, the oxide scale was flaky and brittle to the touch. No boron was detected in the surface layer of all the samples in the present situation.

Cross-sectional SEM micrographs of ZS3 oxidized at 1900°C in air for 1 h are shown in Fig. 3. There are four distinct layers in the oxide scale: (1) a silica-rich outer layer, (2) a subscale of crystalline zirconia, containing little silicate, (3) a partially depleted zirconium diboride layer along with a completely depleted layer in SiC grains, and (4) an unaltered material. The thickness of the first and second layer is far thinner than the third one. Apparently, the present condition is favorable for the active oxidation of SiC, which accounts for the generation of this layer with a relatively high thickness. Further analysis shows that the initial continuous ZrB_2 matrix was transformed into discrete structure (Fig. 3b), which has not been reported in the previous literature.^{3,6,8,18,19} Examination by EDS (not shown) indicated the presence of zirconium and boron as the primary elements that corresponded to ZrB_2 .

Figure 4 shows SEM micrographs of the subside scale of ZS3 after successfully removing the outside scale. This is an interface between layer 2 and layer 3, which contains two distinctive structures, namely, an intact oxide scale and a separate oxide scale as shown in Fig. 4(a). A discrete ZrO_2/ZrB_2 boundary was observed in Figs. 4(a) and (c). As can be seen, the ZrB_2 particles were partially consumed and ZrB_2 structure, initially connected, did not exist (Fig. 4(b)), which is consistent with the morphology of the oxide scale in Fig. 3(b). The oxide products did not adhere to the unaltered material in this region (Fig. 4(b)). However, the oxide products in the other region were adhered to the unreacted material (Fig. 4). The dark silica-containing phases were embedded in bright phases, which were identified as ZrO_2 (Fig. 4(d)). The ZrO_2 was sintered into an integrated structure at this temperature.

A number of pores were detected in the oxide scale of ZS1 after oxidation at 1900°C, as shown in Fig. 5(a). However, no SiC-depleted zone was detected in this material at this temper-



Fig. 3. Cross-sectional scanning electron micrographs of ZS3 oxidized at 1900°C in air for 1 h (a), and a detail of the SiC-depleted layer (b).

ature (Fig. 5(b)). The formation of the SiC-depleted layer in the ZrB_2 -SiC system depends not only on the surrounding conditions of pressure and temperature but also on the structure distribution of SiC in the ZrB_2 matrix. SiC particles were dispersed in the ZrB_2 matrix and the SiC content was too low to form interconnectivity in ZS1. Therefore, no SiC-depleted layer was formed because the diffusion of oxygen in ZrB_2 was very low.

Figure 6 shows the cross-sectional micrographs of oxidized ZS2 at 1900°C for 1 h. Thicknesses of the scale of ZS1, ZS2, and ZS3 after oxidation at 1900°C in air for 1 h are 1100, 600, and 800 µm, respectively. The thickness of the oxide scale of ZS2 is lower than ZS1 and ZS3. Interestingly, ZS2 is more resistant to oxidation than ZS3, which is contrary to the results at lower temperature.²⁰ The scale for ZS2 remains coherent and attached to the unreacted material despite the formation of voids in the SiC-depleted region. Furthermore, the microstructure of the subscale for ZS2 was remarkably different from ZS3. The subscale of ZS2 shows an oriented growth. The crystalline zirconia exhibited a columnar structure in the oxidized ZS2 sample (Fig. 6(c)), whereas this phenomenon was not observed in ZS3 after oxidation in the same condition. The oriented growth of the scale is most likely due to the evolution of the gaseous byproducts, which promoted growth of zirconia in the direction parallel to the discharge of the gaseous products. The preferential active oxidation of SiC at 1900°C did not provide enough SiO₂ for passive oxidation of ZrB₂-SiC composites. In addition, high SiC content would promote the formation of a large SiCdepleted zone and the transport of the oxide products of ZrB₂, which are detrimental to the oxidation of ZrB₂-SiC. Figure 7 shows the enlarged view of the cross sections for ZS1, ZS2, and ZS3 after oxidation at 1900°C. Cracks and spallation were detected at the interface between unreacted material and the oxide scale for ZS1. A dense adherent oxide scale composed of ZrO₂ and SiO2 was formed for ZS2, whereas a loose porous structure was generated for ZS3. Moreover, cracks and spallation beneath the surface layer were also observed. The images of the cross sections further revealed a strong degradation of ZS1 and ZS3 relative to ZS2. It should be noted that the failure modes and mechanisms of the ZrB_2 -SiC composites with low (e.g., ZS1) and high (e.g., ZS3) SiC content are different.

Thermodynamically, both ZrB2 and SiC should be significantly oxidized in the present case. The oxide products of SiC would either escape as gas phases or be transported to the surface layer through liquid convection. Consequently, SiC has been entirely removed from the partially depleted zirconium diboride layer. The oxide products of ZrB₂ are ZrO₂ and B₂O₃. In fact, the last compound has an unusually low melting point (450°C) and a high vapor pressure. Therefore, at high-temperature B_2O_3 quickly vaporizes. Most likely, if there is a channel for the transport of ZrO_2 , then the formed ZrO_2 would not adhere to the unreacted ZrB_2 at 1900°C, which is significantly different from the oxidation behavior of the ZrB2-based UHTC at lower temperature. The formation and migration of the liquid ZrO₂ oxides at lower temperature can be neglected. However, this phenomenon must be taken into account when the oxidation temperature is very high (e.g., 1900°C). ZrO₂ can form liquid oxides with SiO₂ at high temperature, and this can be quantitatively analyzed from the phase diagram of the binary ZrO_2 -SiO₂ system.²¹ Therefore, ZrO_2 can be transported to the surface layer by convection in the liquid silica, as well as dissolution in and recrystallization from the liquid silica. In fact, when the system is above the boiling point of B_2O_3 (1860°C), oxidation resistance of ZrB2 decreases remarkably, and the formed oxidation products will not be adhered to the unaltered ZrB₂. The consumption of SiC would leave behind channels for the transport of the formed ZrO₂. Moreover, the formation of high-pressure gaseous products would also accelerate the transport of ZrO₂, resulting in the generation of a discrete structure as shown in Figs. 3 and 4. However, this phenomenon was not observed in ZS2 (Figs. 6(a) and (d)). The structure in the SiCdepleted region was also continuous for ZS2, which is attributed to the difference of SiC content.



Fig. 4. Scanning electron micrographs of the subside scale of ZS3 after successfully removing the outside scale.



Fig. 5. Cross-sectional scanning electron micrographs of ZS1 oxidized at 1900°C in air for 1 h.

(3) Effect of SiC Content on the Oxidation Resistance

Theoretically, ZrB₂-SiC consists of a ZrB₂ matrix and dispersed SiC particles. No significant solid solution is expected between ZrB2 and SiC, which are stable when in contact with each other.¹⁹ A schematic oxidation model of ZrB₂ containing low (e.g., 10 vol%), medium (e.g., 20 vol%), and high (e.g., 30 vol%) SiC content is shown in Fig. 8. This paper represents the first attempt to use a model to interpret the effect of SiC content on the oxidation resistance of ZrB2-SiC UHTC composites. Thermodynamically, both ZrB2 and SiC should be oxidized when exposed to air. The dominant chemical process at 1900°C for ZrB₂ is the oxidation according to reaction (1), which produces an oxide layer that mainly consists of ZrO2. The expected main reactions for SiC are reactions (2) and (3). At 1900°C, reaction (3) is favored. In fact, SiC formed a network in both ZS2 and ZS3, which was interconnected in three dimensions, although it was discontinuous in two dimensions. The degree of SiC interconnectivity in the matrix increases with increasing SiC content. Kinetically, the oxidation of SiC is more rapid than the oxidation of ZrB₂ at this temperature, as evidenced by ZrB_2 inclusions present in the scale.

$$\operatorname{ZrB}_2(s) + \tfrac{5}{2}\operatorname{O}_2(g) \to \operatorname{ZrO}_2(s) + \operatorname{B}_2\operatorname{O}_3(g) \tag{1}$$

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

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

SiC exhibits preferential oxidation in the present system of ZrB_2 -SiC, leading to the formation of the layer depleted in SiC grains. At the same time, ZrB_2 grains that are in contact with depleted SiC grains are directly exposed to oxygen. Thus, the oxidation occurs from the boundary between ZrB_2 and SiC to inner ZrB_2 grains, which leads to the development of a structure similar to that shown schematically in Fig. 8. It should be noted that SiC particles are assumed to be of the same size and homogenously dispersed within the matrix. Apparently, the degree of SiC interconnectivity in the matrix increases with increasing SiC content. A high degree of SiC interconnectivity



Fig. 6. Cross-sectional scanning electron micrographs of ZS2 oxidized at 1900°C in air for 1 h (a); (b), (c), and (d) are the details of the silica-rich layer, zirconia-rich layer, and SiC-depleted layer, respectively.

causes the rapid active oxidation of SiC. Consequently, the thickness of the SiC-depleted layer for ZS3 is much higher than that for ZS2 under the same conditions, as shown in Figs. 3 and 6.

Based on the relative oxidation rates of ZrB_2 and SiC, SiC should be consumed first through the rapid active oxidation. On the one hand, the SiC consumption left behind channels for the transport of the formed ZrO_2 . On the other hand, the SiC con-



Fig. 7. Enlarged view of the cross sections for (a) ZS1, (b) ZS2, and (c) ZS3 after oxidation at 1900°C in air for 1 h.





Fig. 8. Oxidation models of the present SiC reinforced ZrB_2 matrix ultrahigh-temperature ceramics at 1900°C: (a) low SiC content (ZS1), (b) medium SiC content (ZS2), and (c) high SiC content (ZS3); white color represents holes.

sumption left behind space for the volume expansion resulting from the oxidation of ZrB₂. Cracks or spallation would occur when the vacant space cannot satisfy the volume expansion upon the conversion of ZrB_2 to ZrO_2 (Fig. 7(a)). The boiling of B₂O₃ and continuous evolution of CO and SiO would make the formed ZrO₂ phase nonadherent. ZrO₂ is not stationary in the present case and will be moved to the external oxide scale through the initially formed, connected pores. Apparently, if the oxidized regimes of the ZrB₂ matrix are interconnected within the SiC-depleted region and their oxidation products are transported to the external oxide scale, the solid skeleton will not interconnect with itself when the holes meet together (see Fig. 8(c)). Consequently, the scale for this material is visually nonadherent and some oxide is spallated (Figs. 3 and 8(c)). On the other hand, the rupture of the scale may not occur (Fig. 6) when the holes in the ZrB_2 matrix are not interconnected in the SiC-depleted region, as shown in Fig. 8(b). Whether the oxidized regimes of the ZrB₂ matrix in the SiC-depleted region are interconnected or not mostly depends on the content of SiC in the matrix (see Figs. 7 and 8). A SiC-depleted layer would not be formed when the SiC content is too low to form interconnectivity (see Fig. 8(a)). The average thickness of ZrB_2 matrix between two adjacent SiC particles for high SiC content (ZS3) is lower than that of medium SiC content (ZS2), as shown in Fig. 8. Therefore, the oxidized regimes of the ZrB_2 matrix in high SiC content (ZS3) are more liable to meet together in comparison with those of low SiC content (ZS2).

ZS2 exhibited superior oxidation resistance at 1900°C in air for 1 h. However, the oxidation behavior of ZS1 and ZS3 under the same conditions demonstrated the unsuitability of this material for ultrahigh-temperature applications. Comparison of the oxidation results between ZS1, ZS2, and ZS3 indicates that SiC content significantly affected the oxide structure and performance of ZrB₂–SiC at 1900°C. Neither high (e.g., 30 vol% SiC) nor low (e.g., 10 vol% SiC) content of SiC is appropriate for ultrahigh-temperature applications. With the assumption that oxidation products have theoretical density, 1 unit volume of ZrB₂ upon oxidation produces 1.19 unit volumes of solid oxide (ZrO₂). For ZrB₂ containing 10% SiC composite, the volume increase of the solid oxide during oxidation is 7%, leading to the cracks or spallation (B2O3 and SiO2 were not taken into account). In addition, the amount of the silica is lower than the high-SiC-content materials (i.e., ZS2 and ZS3). Obviously, a small amount of silica glass cannot provide an effective barrier for oxygen ingress. Similarly, ZrB2 containing 30% SiC composite is likely to crack and spall due to the failure of the SiCdepleted layer. However, the resulting structure of both the SiCdepleted layer and the ZrO₂-rich layer in ZS2 is less likely to crack and spall and remains more adherent. With respect to ZS2, the fraction of the formed solid is 95%, which will not lead to the cracks or spallation as a result of volume expansion during oxidation. The other fraction will be filled with liquid silica glass, which provides an effective obstacle against the inward diffusion of oxygen along short-circuit paths (i.e., residual porosity, cracks, and grain boundary) and it is helpful in forming a dense coherent oxide scale at the same time. Moreover, cracks and spallation would not occur in the SiC-depleted layer under the present condition, which was significantly affected by the SiC content. How to obtain a dense adherent oxide scale becomes a major issue for the applications of these materials at ultrahigh temperature, especially for temperatures above 1900°C. According to the previous study, high SiC content is beneficial to the oxidation resistance of the material below 1800°C, whereas it is detrimental at higher temperature. Therefore, we should optimize the SiC content and microstructure to meet the requirements of the practical application.

IV. Conclusions

Dense ZrB₂-SiC UHTC composites were prepared by hot pressing. ZrB₂ containing 20 vol% SiC particulates exhibited the highest oxidation resistance at 1900°C in air compared with ZrB2-10 vol% SiC and ZrB2-30 vol% SiC composites. ZrO2 is not stationary at high temperature and can be transported directly or by liquid convection to the surface layer, which is significantly different from that at lower temperature. The resulting structure of both the SiC-depleted layer and the ZrO₂-rich layer in ZrB₂-20 vol% SiC is less likely to crack and spall and remains more adherent. SiC content significantly affected the formation of the oxide structure and the performance of the UHTC at this temperature. These UHTC materials with low or high SiC content are inappropriate for ultrahigh-temperature applications. The SiC content and microstructure in the ZrB2 matrix should be optimized according to the requirements of the practical application.

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