Effect of Oxidation Exposure on Flexural Strength of Hot-Pressed ZrB₂-SiC Composites with Cr₃C₂ Additives

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Abstract. In this study, the effect of oxidation exposure on room temperature flexural strength was examined in 3 and 5 wt% Cr₃C₂-containing ZrB₂-20 vol% SiC composites exposed to air at different temperatures between 1100°C and 1300°C, for up to 100 h. The oxidation products determined by X-ray diffraction consisted of ZrO₂, SiO₂, Cr₂O₃ and ZrSiO₄. After 100 h of oxidation, the flexural strength of the two compositions was evaluated at room temperature by four-point bending test. The results show that the strength retention displayed by the two compositions depended on the amount of Cr₃C₂ additives. For 3 wt% Cr₃C₂ composition, the flexural strength slightly increased after 100 h of oxidation at 1100°C, however, the strength substantially degraded after 100 h oxidation at 1200°C and 1300°C. For 5 wt% Cr₃C₂ composition, on the other hand, the flexural strength decreased after 100 h of oxidation between 1100°C and 1300°C. Additionally, the flexural strength was higher for 3 wt% Cr₃C₂ composition than for 5 wt% Cr₃C₂ one in the oxidation temperature range 1100°C to 1300°C. The strength decrease was associated with the formation and coarsening of defects in the oxidized layer and the delamination of the outermost thinner dense oxide layer.

1. Introduction
Zirconium diboride (ZrB₂) is a refractory transition-metal diboride composed of the fourth to sixth groups of the periodic table. Many of these types of diborides have melting points greater than 3000°C, high thermal and electrical conductivities, great strength and better ablation resistance, making them potential candidates for several high-temperature structural applications.[1−3] The major problems associated with ZrB₂ ceramic materials include densification and high-temperature oxidation.[1−6] Because of strong covalent bonds and low self-diffusivity, the densification of ZrB₂ powder requires very high temperatures (>2100°C) and external pressure (≥20 MPa).[4] In addition, single-phase ZrB₂ ceramics are easily oxidized in air to form ZrO₂ and B₂O₃ at temperatures greater than ~800°C.[5],[6]

On the other hand, the composite approach has been successfully adopted to improve the densification and the oxidation resistance of single-phase ZrB₂ ceramics. It is known that the addition of SiC to ZrB₂ results in a composite with improved sinterability, great strength and better oxidation resistance,[7−12] and recently this composite has become a strong potential candidate for a variety of high-temperature structural applications.[1−3] However, sintering temperatures of equal to or above 1900°C are still required to obtain highly-dense ZrB₂-SiC composites. To further improve sinterability of ZrB₂-SiC composites, MoSi₂ has been added to aid the densification of the composites.[13],[14] Densities exceeding 97% were obtained for 20 vol% MoSi₂-containing ZrB₂-5 and 10 vol% SiC powders by hot-pressing at 1800°C and 30 MPa for 30 min in vacuum.[13],[14] In addition, Grigoriev
et al.[15] showed the hot-pressing temperature of ZrB$_2$ was lowered from 2200°C to 1500°C–1750°C when Cr$_3$C$_2$ is used as a sintering activator. Very recently, our study has showed that 3–10 wt% Cr$_3$C$_2$ additions substantially lowered densification temperature of ZrB$_2$-20 vol% SiC composites, with densities exceeding 95% after the hot-pressing at 1650°C and 20 MPa for 1 h in vacuum.[16] Furthermore, the resulting composites exhibited the good mechanical properties. However, the effect of oxidation on the flexural strength is not well known. Strength retention after oxidation at elevated temperatures is an important high-temperature property, because ZrB$_2$-SiC composites currently are being considered for use as structural components in high-temperature oxidizing environments. The aim of this study was to examine the effect of oxidation exposure at elevated temperatures on the room temperature flexural strength of ZrB$_2$-20 vol% SiC composites with Cr$_3$C$_2$ additives.

2. Experimental procedure

The ZrB$_2$-20 vol% SiC composites used in this study were hot-pressed from ball-milled mixtures of ZrB$_2$, α-SiC and Cr$_3$C$_2$ powders at 1700°C for 1 h under a uniaxial pressure of 20 MPa in vacuum. The starting powders were ZrB$_2$, α-SiC and Cr$_3$C$_2$. To examine the effect of Cr$_3$C$_2$ content on oxidation resistance, two ZrB$_2$-20 vol% SiC composites with 3 and 5 wt% Cr$_3$C$_2$ additives were prepared. Hereafter, the ZrB$_2$-SiC composites with 3 and 5 wt% Cr$_3$C$_2$ additives are denoted as ZSCRC3 and ZSCRC5, respectively. The detailed sintering process has been reported elsewhere.[16] Densities exceeding 99% were obtained for the two composition powders after the sintering. X-ray diffractometry confirmed the presence of the extensive crystalline ZrB$_2$, α-SiC, ZrC and CrB phases in the two composition composites. Backscattered field-emission scanning electron microscopy (FE-SEM) observations show that the two composites consisted of the equiaxed ZrB$_2$ (grey contrast), α-SiC (dark contrast), ZrC (white-grey contrast) and CrB (dark-grey contrast) grains (Figure 1).

![Figure 1. Typical backscattered FE-SEM image of the microstructure of ZSCRC3.](image)

Specimens, averaging 25 mm × 2.5 mm × 2 mm, in size were cut from the composite plates. The surfaces of the specimens were ground with an 800-grit diamond wheel. Subsequently, the specimens were ultrasonically cleaned in acetone and then kept in an oven at a constant temperature of 100°C prior to oxidation. Oxidation tests were performed at 1100°C, 1200°C and 1300°C in air over a period of 100 h. The specimens were supported on porous Al$_2$O$_3$ knife-edged fixtures in an electron furnace. Before and after oxidation, the specimens were weighed using an analytical balance with an accuracy of ± 0.01mg. The oxidized surfaces of specimens were examined using X-ray diffraction (XRD) to determine the oxidation products produced during the exposure at elevated temperatures.
The flexural strength of the pristine and post-oxidized specimens was determined by fracture at room temperature, using four-point fixture (inner span 10 mm, outer span 20 mm). The bending test was performed using an Autograph testing system, with a crosshead speed of 0.5 mm/min. A minimum of ten specimens were used for each measurement. After the bending test, the fracture surface was examined by FE-SEM.

![Figure 2. Plots of specific weight gain as a function of time for the two compositions oxidized between 1100°C and 1300°C.](image)

Table 1. Weight gain and XRD of the specimen surfaces for the two composition composites after 100 h of oxidation exposure at different temperatures between 1100°C and 1300°C.

| Materials | Average total weight gain (mg/cm²) | Oxidized surfaces |
|-----------|------------------------------------|-------------------|
|           | 1100°C | 1200°C | 1300°C | 1100°C | 1200°C | 1300°C |
| ZSCRC3    | 1.43 ± 0.09 | 11.0 ± 3.5 | 17.6 ± 2.8 | ZrB₂ | ZrO₂ | ZrO₂ |
|           |        |        |        | SiO₂ | SiO₂ | SiO₂ |
|           |        |        |        | Cr₂O₃ | Cr₂O₃ | Cr₂O₃ |
|           |        |        |        | ZrSiO₄ | ZrSiO₄ | ZrSiO₄ |
| ZSCRC5    | 1.78 ± 0.09 | 8.56 ± 1.67 | 15.4 ± 1.4 | ZrB₂ | ZrO₂ | ZrO₂ |
|           |        |        |        | SiO₂ | SiO₂ | SiO₂ |
|           |        |        |        | Cr₂O₃ | Cr₂O₃ | Cr₂O₃ |
|           |        |        |        | ZrSiO₄ | ZrSiO₄ | ZrSiO₄ |

3. Results and discussion

3.1 Oxidation behavior

Figure 2 shows plots of the weight gain as a function of exposure time for the two composition composites oxidized at different temperatures between 1100°C and 1300°C. It is found that the specific weight gain in composite increases rapidly within initial 10 h of exposure and then the specific weight gain increases gradually with further increasing exposure time, independent on the amount of Cr₃C₂ additives. Similar time dependency of the weight gain was previously reported in ZrB₂-SiC-MoSi₂ composites exposed to air at 1500°C.[17] The total specific weight gain data for the two compositions after 100 h of oxidation are summarized in Table 1. It is found that the average total specific weight
gains after 100 h of oxidation at 1100°C was lower for ZSCRC3 than for ZSCRC5. However, the specific weight gain after 100 h of oxidation at 1200°C and 1300°C was higher for ZSCRC3 than for ZSCRC5. The two compositions had specific weight gain on the order of 1.43–17.6 mg/cm² after 100 h of oxidation exposure between 1100°C and 1300°C.

The phases identified by XRD (not shown) in the oxidized surfaces of the two composition composites between 1100°C and 1300°C for 100 h are summarized in Table 1. The XRD patterns of the oxidized surfaces for the two compositions show that oxidation products did not depend on the amount of Cr₃C₂ additives, but depended on the oxidation temperature. For the specimens oxidized at 1100°C for 100 h, the XRD patterns identified that the crystalline ZrO₂ phase was the major oxidation product. Additionally, ZrB₂ and a trace amount of SiO₂ (α-cristobalite), ZrSiO₄ and Cr₂O₃ phases were present as well. Similar oxidation products were identified by XRD in the oxidized specimens at 1200°C for 100 h, with no ZrB₂ phase. Unlike the specimens oxidized at 1100°C and 1200°C, for the specimens oxidized at 1300°C for 100 h, it is found that the SiO₂, ZrO₂ and ZrSiO₄ phases were the major oxidation products in addition to a trace amount of Cr₂O₃. On the other hand, it was seen that the intensities of ZrB₂ peaks were substantially higher for the pristine samples than for the post-tested ones and the peak of ZrB₂ phase disappeared after 100 h of oxidation at 1200°C and 1300°C, presumably, the signals of ZrB₂ phase are from the bulk ceramic beneath the oxidized surface layer.

Moreover, FE-SEM observations of the oxidized surfaces were carried out to examine the morphologies of the two composition composites after 100 h of oxidation between 1100°C and 1300°C. Examples of FE-SEM images of the oxidized surfaces are shown in Figure 3. Under FE-SEM, similar morphologies of the oxidized surfaces were observed in the specimens surfaces of the two compositions after 100 h of oxidation between 1100°C and 1300°C, regardless of the amount of Cr₃C₂ additives. For the sample oxidized at 1100°C (Figure 3a), the spherical ZrO₂ particles (white contrast) were embedded into the glassy layer. With increase of temperature, the ZrO₂ particles increased and coarsened. For the sample oxidized at 1200°C (Figure 3b), the larger ZrO₂ particles were observed and their content at the top of the surface covered a wide area. Unlike the samples oxidized at 1100°C and 1200°C, for the sample oxidized at 1300°C (Figure 3c), large platelet-like ZrSiO₄ grains were observed in the glassy layer in addition to the ZrO₂ particles.

Oxidation behavior of ZrB₂-SiC-based composites in air at elevated temperatures had been previously reported in literatures.[5−7], [12], [18] Based on the previous studies, it is known that ZrB₂, SiC, ZrC and CrB phases oxidized to form ZrO₂, B₂O₃, SiO₂ and Cr₂O₃ when they are exposed to air at elevated temperatures, according to the following reactions:

\[
\text{ZrB}_2(s) + 2.5\text{O}_2(g) = \text{ZrO}_2(s) + \text{B}_2\text{O}_3(s) \tag{1}
\]

\[
\text{SiC}(s) + 1.5\text{O}_2(g) = \text{SiO}_2(s) + \text{CO}(g) \tag{2}
\]

\[
\text{ZrC}(s) + 1.5\text{O}_2(g) = \text{ZrO}_2(s) + \text{CO}(g) \tag{3}
\]
2CrB(s) + 3O₂(g) = Cr₂O₃(s) + B₂O₃(s)  \quad (4)

Subsequently, the ZrO₂ phase reacted with SiO₂ phase (the oxidation product of SiC) to form ZrSiO₄ phase as follows:

\[ \text{ZrO}_2(s) + \text{SiO}_2(s) = \text{ZrSiO}_4(s) \quad (5) \]

Similar ZrSiO₄ phase has been reported in the ZrB₂-SiC-MoSi₂ composites oxidized at 1500°C in air for 10 h[17] as well as in the ZrB₂-SiC composite thermally-cycling tested at 1200°C and 1400°C in air for up to 1000 cycles[19]. In the present study, XRD analysis clearly showed the presence of ZrO₂, ZrSiO₄, SiO₂ and Cr₂O₃ phases in the two composition composites oxidized between 1100°C and 1300°C in air for 100 h (Table 1). Thereby, it could be expected that similar oxidation reactions occurred during the exposure between 1100°C and 1300°C in air for the ZrB₂-SiC composites with Cr₃C₂ additives investigated in this study.

**Figure 4.** Effect of oxidation temperature on room temperature flexural strength of the composites after 100 h of oxidation.

### 3.2. Effect of oxidation on flexural strength

Figure 4 shows the effect of oxidation temperature on the room temperature flexural strength of the two compositions after 100 h of oxidation at different temperatures between 1100°C and 1300°C. It is found that the flexural strength before and after oxidation is always higher for ZSCRC3 than for ZSCRC5. However, degradation of strength due to exposure at elevated temperatures was related to the amount of Cr₃C₂ additives. For ZSCRC3, the flexural strength slightly increased from 760 MPa before oxidation to 770 MPa after 100 h of oxidation at 1100°C. For ZSCRC5, on the other hand, the flexural strength decreased from 730 MPa before oxidation to 680 MPa after 100 h of oxidation at 1100°C, with strength loss of ~7%. Unlike the samples exposed at 1100°C, the flexural strength of the two composition composites decreased after 100 h of oxidation at 1200°C and 1300°C, with no increase of strength. After 100 h of oxidation, the reduction in the strength from that before the oxidation is ~29% at 1200°C and ~26% at 1300°C for ZSCRC3 while is ~30% at 1200°C and ~36% at 1300°C for ZSCRC5. It is evident that the strength retentions of the composites after 100 h of oxidation depended on the amount of Cr₃C₂ additive as well as on the oxidation temperature. The strength retention of the two composition composites after 100 h of oxidation at 1200°C were almost the same, however, the strength retention after 100 h of oxidation at 1300°C was higher for ZSCRC3 than for ZSCRC5 although the weight gain in ZSCRC5 was lower than that in ZSCRC3 (Table 1).
Figure 5 shows FE-SEM micrographs of the fracture surfaces of ZSCRC3 after 100 h of oxidation between 1100ºC and 1300ºC. It is found that an oxidized layer was formed after 100 h of oxidation and its thickness increased with increasing temperature. The thickness of the oxidized layer was determined to be approximately 14 μm at 1100ºC, 22 μm at 1200ºC and 200 μm at 1300ºC. In addition, a thinner dense glassy layer was observed on the outermost surfaces of the oxidized layer. For the sample oxidized at 1100ºC (Figure 5a), the outermost dense glassy layer did not delaminate from the oxidized layer. The presence of the dense glassy layer can heal the surface flaws without creating new defects in the oxidized layer, therefore increase of strength. However, the dense glassy layer delaminated from the oxidized layer for the samples oxidized at 1200ºC and 1300ºC (indicated by arrows in Figure 5b and c). Presumably, the delamination of the outermost thinner glassy layer led to degeneration of strength after 100 h of oxidation at 1200ºC and 1300ºC. Similar oxidized layer was also observed for ZSCRC5 specimens oxidized between 1100ºC and 1300ºC for 100 h (Figure 6). The thickness of the oxidized layer was determined to be approximately 27 μm at 1100ºC, 63 μm at 1200ºC and 295 μm at 1300ºC. Clearly, the thickness of the oxidized layer is larger for ZSCRC5 than for ZSCRC3. Unlike ZSCRC3, the strength of ZSCRC5 significantly degraded after 100 h of oxidation at
1100°C although the delamination of the outermost dense glassy layer was not observed (Figure 6a). The strength decrease after 100 h of oxidation at 1100°C seems to be associated with the presence of the thicker oxidized layer for ZSCRC5 than for ZSCRC3 as a result of the excessive oxidation (Figures 5a and 6a). For the sample oxidized at 1200°C, although the delamination of the dense glassy layer was not clearly observed as well (Figure 6b), under higher-magnification FE-SEM, several pores were observed beneath the dense glassy layer and a transverse crack was present in the dense layer (indicated by arrows in Figure 6c). For the sample oxidized at 1300°C, the delamination of the dense glassy layer was clearly observed in addition to the transverse cracks (Figure 6d). Thereby, the presence of these defects resulted in the significant degeneration of strength after 100 h of oxidation at 1200°C and 1300°C. Additionally, for the specimens oxidized at 1300°C, ZSCRC5 had higher strength degeneration compared to ZSCRC3, as a result of its excessive oxidation occurred during the exposure at 1300°C (Figure 5c and Figure 6d). Thus, the substantial strength decrease for the two compositions after 100 h of oxidation at 1200°C and 1300°C should be attributed to the formation and coarsening of new defects in the oxidized layer and the delamination of the outermost thinner dense glassy layer.

4. Summary

In conclusion, the specific weight gain after oxidation depended on the amount of Cr$_3$C$_2$ additives. The specific weight gain after 100 h of oxidation at 1100°C was lower for ZSCRC3 than for ZSCRC5. However, the specific weight gain after 100 h of oxidation at 1200°C and 1300°C was larger for ZSCRC3 than for ZSCRC5. The oxidation products consisted of ZrO$_2$, SiO$_2$ ($\alpha$-cristobalite), Cr$_2$O$_3$ and ZrSiO$_4$ for the two compositions. The room temperature flexural strength of the two compositions degraded after oxidation and this degradation varied with the amount of Cr$_3$C$_2$ additives and the oxidation temperature. For 3 wt% Cr$_3$C$_2$ composition, the flexural strength slightly increased after 100 h of oxidation at 1100°C. However, the strength substantially degraded after 100 h of oxidation at 1200°C and 1300°C and the strength decreases were approximately 29% and 26%, respectively. For 5 wt% Cr$_3$C$_2$ composition, the flexural strength significantly decreased after 100 h of oxidation between 1100°C and 1300°C, the strength decreases were approximately 7% at 1100°C, 30% at 1200°C and 36% at 1300°C. The strength decrease was attributed to the formation and coarsening of new defects in the oxidized layer and delamination of the outermost thinner dense oxide layer.

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