Preparation and Oxidation of ZrB2/SiC/Zr2Al4C5 Multi-phase Ceramics with Spark Plasma Sintering

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Abstract. The ZrB2/SiC/Zr2Al4C5 multi-phase ceramics were fabricated by spark plasma sintering (SPS) at 1800 °C for 3 min under 20 MPa in an vacuum. Oxidation behavior of multi-phase ceramics were investigated using thermo gravimetric analysis (TGA) from 20 °C to 1500 °C and muffle furnace in stagnant air at 1200 °C. Samples were analyzed after oxidation by X-ray diffraction (XRD), scanning electron microscopy (SEM) along with energy dispersive spectroscopy (EDS) to determine the reaction products and to observe the microstructure. The results showed that the aluminium borate and mullite crystallize on the surface in the samples oxidized. The effect of Zr2Al4C5 content on the oxidation resistance of the ZrB2 ceramics were discussed respectively, and oxidation mechanism was also analysed.

1. Introduction

Zirconium diboride (ZrB2) as a member of ultrahigh-temperature ceramics (UHTCs) is currently expected to be a potential candidate material for aerospace applications, owing to its high melting point, high thermal and electrical conductivity, low theoretical density and good chemical inertness [1, 2]. Based on these properties, ZrB2 ceramics are attracting more and more attention in ultra-high temperature applications where corrosion-wear-oxidation resistance is demanded [3].

However, oxidation resistance is a well-known bottleneck in the exploration of ZrB2-based ceramics. Many studies reported that the addition of SiC could improve the oxidation resistance and fracture strength of the ZrB2-based composites [4], and the oxidation of ZrB2 can be improved by adding SiC to promote the formation of a silica-rich scale on the exposed surface. Other development had been also achieved on the oxidation behavior of ZrB2-based ceramics with addition of MoSi2, LaB6, TaB2 and TaSi2 [5-7].
Our previous work has revealed [8] that addition of $\text{Zr}_2\text{Al}_4\text{C}_5$ was favorable to the densification and especially the toughness of $\text{ZrB}_2$-based ceramics. This paper focused on the oxidation behavior of $\text{Zr}_2\text{Al}_4\text{C}_5$-toughened $\text{ZrB}_2$ and $\text{ZrB}_2$-$\text{SiC}$ ceramics using muffle furnace in air. By means of the investigation of microstructure and mass change after oxidation, effect of $\text{Zr}_2\text{Al}_4\text{C}_5$ content on the oxidation resistance of $\text{ZrB}_2$/SiC/$\text{Zr}_2\text{Al}_4\text{C}_5$ ceramics was newly explored.

2. Experimental procedures

Commercially available $\text{ZrB}_2$ powders ( $\geq 99.5\%$, 2 $\mu$m), Zr powders ( $\geq 99.9\%$, 10 $\mu$m), Al powders ( $\geq 99.99\%$, 8 $\mu$m) and graphite powders ( $\geq 99.9\%$, 1 $\mu$m) powders were used as starting materials. $\text{Zr}_2\text{Al}_4\text{C}_5$ was prepared by the spark plasma sintering-reactive synthesis using Zr, Al, and C powders as sintering materials. The $\text{ZrB}_2$ and $\text{Zr}_2\text{Al}_4\text{C}_5$ powders were mixed in an agate mortar, and put into a graphite die with graphite foil and sintered using a SPS system.

The temperature was measured by an optical pyrometer focused on the surface of the graphite die. The samples were heated to 1800 °C at an average heating rate of 100 °C/min, and then the temperature holds constant for 3 min. The sample was cooled naturally after the sintering period finished. The bulk density of the sintered products was determined by Archimedes’ immersion method with water as the immersing medium. The phase compositions and microstructure were analyzed by XRD and SEM-EDS, respectively.

The oxidation test was carried out by two methods: TGA and Oxidation tests at a fixed temperature in air oven. Small specimens of either $\text{ZrB}_2$, $\text{ZrB}_2$/Zr$_2$Al$_4$C$_5$, and $\text{ZrB}_2$/SiC/ Zr$_2$Al$_4$C$_5$, having dimensions of approximately 0.5mm×2.0mm×1.5mm, were kept in alumina crucibles and then subjected to heating at the rate of 10 °C/min from 20 to 1500 °C in flowing air inside a thermogravimetric analyzer (TGA, Netzsch, STA449C, Germany). Oxidation tests were performed using an electronic furnace at 1200 °C for 30min in dry air. Specimens were heated to the designated temperature at a heating rate of 10 °C/min.

3. Results and discussion

![Figure 1. Backscattered electron images of $\text{ZrB}_2$/Zr$_2$Al$_4$C$_5$ composites surface (a) 0 vol.% (b) 10 vol.% (c) 20 vol.% (d) 30 vol.% and (e) 40 vol.%](image)

Figure 1 shows the microstructure of sintered $\text{ZrB}_2$/Zr$_2$Al$_4$C$_5$ composites. The light phase was $\text{ZrB}_2$ whereas the gray phase consists of Zr$_2$Al$_4$C$_5$, the large columnar or plate-like gray Zr$_2$Al$_4$C$_5$ grains dispersed homogenously in all these composites. Near-theoretical density of composite was achieved by spark plasma sintering for $\text{ZrB}_2$/Zr$_2$Al$_4$C$_5$ composites with
different content of Zr$_2$Al$_4$C$_5$. Our previous work has revealed [8] that addition of Zr$_2$Al$_4$C$_5$ can enhance the mechanical properties of ZrB$_2$-based ceramics.

Thermal gravimetric analysis studies on ZrB$_2$/Zr$_2$Al$_4$C$_5$ composites from 20 °C to 1500°C are presented in Figure 2. The weight did not change with the increased testing temperature for ZrB$_2$/Zr$_2$Al$_4$C$_5$ ceramics below 700 °C. The weight change of ZrB$_2$ ceramics occurred at 700 °C, such weight change indicated the presence of the oxidation of ZrB$_2$ according to reaction (1).

\[
\text{ZrB}_2(s) + \frac{5}{2} \text{O}_2(g) = \text{ZrO}_2 + \text{B}_2\text{O}_3(l)
\]

However, the weight of ZrB$_2$/Zr$_2$Al$_4$C$_5$ ceramics did not change, the inflection points of these ceramics at 1200 °C shown in Figure 2 imply that oxidation resistance have changed with the introduction of Zr$_2$Al$_4$C$_5$. The rapid increase in weight was observed in all the samples between 1200 and 1500 °C, which indicated that the rate of oxidation aggravated during the temperature. The overall weight gain observed in the ZrB$_2$ sample was larger than that of the ZrB$_2$/Zr$_2$Al$_4$C$_5$ samples at high temperature. In this case, the oxidation products were mainly B$_2$O$_3$, ZrO$_2$ and Al$_2$O$_3$, and a protective scale of glassy B$_2$O$_3$-Al$_2$O$_3$ phase formed, which was more viscous and stable [9].

In this study, the final increase in weight for the pure Zr$_2$Al$_4$C$_5$ and ZrB$_2$-30vol% Zr$_2$Al$_4$C$_5$ composites were 15.67% and 8.07%, respectively. It can be concluded that the introduction of Zr$_2$Al$_4$C$_5$ can improve oxidation property of ZrB$_2$ ceramic.

Figure 3 shows the typical XRD patterns of ZrB$_2$ and ZrB$_2$-30vol%Zr$_2$Al$_4$C$_5$ before and after oxidized at 1200 °C for 30min: (a) and (c) ZrB$_2$, (b) and (d) ZrB$_2$/30vol% Zr$_2$Al$_4$C$_5$. After oxidation, it was seen that the oxide layer on ZrB$_2$ contains significant ZrO$_2$ phases and a small amount of B$_2$O$_3$ phase. For the ZrB$_2$-30vol%Zr$_2$Al$_4$C$_5$ sample, the peaks of (Al$_2$O$_3$)$_2$(B$_2$O$_3$), B$_2$O$_3$ and AlBO$_3$ were detected.

In addition, the intensity of ZrO$_2$ phase peaks decreased with the amount of Zr$_2$Al$_4$C$_5$ added, showing improved oxidation resistance, due to a continuous and/or partially amorphous B$_2$O$_3$-Al$_2$O$_3$ glassy scale was produced on the surface of samples. The formation of the scale, in particular continuous scale, inhibited the inward diffusion of oxygen in air, therefore improvement of oxidation resistance[10].

The SEM images depicting the top surface of the oxide scales formed on ZrB$_2$ and
ZrB2-30vol% Zr2Al4C5 ceramics subjected to exposure at 1200 °C for 30min are shown in Figure 4(a) and (b), respectively. Some pores were found on the surface of ZrB2 ceramics, such pores appearing on the surface of ZrB2 ceramic provided more paths for the inward flow of oxygen, and therefore led to the severe oxidation. EDS spectrum from bulk of the oxide scale formed on exposure at 1200 °C for 30min showed the peaks of O, Zr and B, which was suggestive of the presence of ZrO2 and B2O3. The surface layers of the ZrB2/30vol%Zr2Al4C5 sample appeared compact and adherent, no macro-cracks or porous were observed. The bright phase was crystalline ZrO2 and dark phase was glassy phase. EDS analysis showed that the nubbles were rich in Zr, Al, O and B (Fig. 7d), which should be a mixture of zirconium oxide and Al-B-O glassy phase. Based on EDS and XRD results, the oxidation products should be amorphous zirconium oxide and Al-B-O glassy phases.

![Figure 4](image1)

**Figure 4.** The surface morphologies of the samples after oxidation: (a) ZrB2, (b) ZrB2-30vol% Zr2Al4C5.

![Figure 5](image2)

**Figure 5.** Cross-sectional morphologies and the corresponding EDS line scans of the samples after oxidation: (a) ZrB2 and (b) ZrB2-30vol%Zr2Al4C5.

Figure 5(a) shows the cross-sectional morphology and corresponding EDS line scans of ZrB2 oxidized at 1200 °C for 30min. The oxidized layer in the outer section was dominantly ZrO2, and evident directional growth had been achieved for ZrO2 grains. And obvious pores were further observed on the oxidized layer, which was favorable for the inward transport of oxygen. The dense oxide layer was about 200 μm thick. The cross-sectional morphology and corresponding EDS line scans of ZrB2-30vol% Zr2Al4C5 exposed to the same oxidizing environment is given in Figure 5(b). The dark phase was Al-B-O glassy phases, and the thickness of the oxide scale was only 150 μm, which was less than that for ZrB2 ceramics. Such layered structure along the cross-section could be testified by the line scanning with EDS in Figure 5. It could be found that the oxide scale had a monolayer structure mainly composed of dark and light grains, and was rich in Zr, Al, B and O. Based on EDS, XRD and Raman spectroscopy results, the oxidation products should be a mixture of ZrO2, Al2O3 and Al-B-O glassy phase.

The oxidation tests these composites have been used to analyze the effect of Zr2Al4C5 on the oxidation property of ZrB2-SiC ceramics. Thermal gravimetric analysis studies on ZrB2/SiC/ Zr2Al4C5 composites from 20 °C to 1500 °C in the air are presented in Figure 6. The weight did not change with the increased testing temperature for ZrB2/SiC/Zr2Al4C5 ceramics below 1200 °C. The inflection points of these ceramics at 1400 °C shown in Figure 6 imply that oxidation resistance have changed with the introduction of SiC. The weight change of ZrB2/SiC/Zr2Al4C5 ceramics first increased and then decreased with increase in the amount of SiC. The rapid increase in weight was observed in all the samples between 1400 and
1500°C, which indicated that the rate of oxidation aggravated during the temperature.

In this study, the final increase in weight for the ZrB\textsubscript{2}-30vol%Zr\textsubscript{2}Al\textsubscript{4}C\textsubscript{5} samples and ZrB\textsubscript{2}-20vol.%SiC-30vol%Zr\textsubscript{2}Al\textsubscript{4}C\textsubscript{5} composites were 8.07% and 4.19%, respectively. It can be concluded that the introduction of SiC can improve oxidation property of ZrB\textsubscript{2}/Zr\textsubscript{2}Al\textsubscript{4}C\textsubscript{5} ceramic. This was because that the oxidation products were mainly B\textsubscript{2}O\textsubscript{3}, ZrO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3}, and a protective scale of glassy B\textsubscript{2}O\textsubscript{3}-Al\textsubscript{2}O\textsubscript{3} phase, Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} phase, borosilicate glass and SiO\textsubscript{2} formed, which was more viscous and stable. Thus, oxidation resistance of ZrB\textsubscript{2}/SiC/Zr\textsubscript{2}Al\textsubscript{4}C\textsubscript{5} ceramics was achieved by the formation of silica and borosilicate glass layer with oxygen permeability produced by oxidation of SiC, which provided an effective protection for the ZrB\textsubscript{2}/SiC/Zr\textsubscript{2}Al\textsubscript{4}C\textsubscript{5} ceramics.

4. Conclusion

The ZrB\textsubscript{2}/SiC/Zr\textsubscript{2}Al\textsubscript{4}C\textsubscript{5} multi-phase ceramics were fabricated by spark plasma sintering (SPS) at 1800 °C for 3 min under 20 MPa in an vacuum. Near-theoretical density of composite was achieved, and the introduction of Zr\textsubscript{2}Al\textsubscript{4}C\textsubscript{5} in restricting the coarsening of ZrB\textsubscript{2}. Oxidation behavior of multi-phase ceramics were investigated using muffle furnace in stagnant air at 1200 °C and thermo gravimetric analysis (TGA) from 20 °C to 1500 °C. The results showed that oxidation protection had been attributed to the presence of a glassy Al-B-O phases, which acted as an oxygen diffusion barrier on the surface in the ZrB\textsubscript{2}/Zr\textsubscript{2}Al\textsubscript{4}C\textsubscript{5} samples oxidized. At the same time, the introduction of SiC can improve oxidation property of ZrB\textsubscript{2}/Zr\textsubscript{2}Al\textsubscript{4}C\textsubscript{5} ceramic, due to a fully dense protective layer with SiO\textsubscript{2}-rich glassy scale on the exposed surface.

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