Fabrication and properties of ZrB$_2$–SiC and ZrC–SiC composites by spark plasma sintering

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ZrB$_2$–SiC and ZrC–SiC composites were fabricated by spark plasma sintering at 1800°C for 5 min under a pressure of 40 MPa with ZrB$_2$ powder, ZrC powder and SiC powder as the starting materials, respectively. The phase compositions, microstructures, and mechanical properties were investigated. The results show ZrB$_2$–SiC composite is denser than ZrC–SiC composite. The relative density, an apparent porosity, and the bending strength of ZrB$_2$–SiC composite are 97.9%, 1.08%, and 310 MPa, respectively, whereas those of ZrC–SiC composite are 89.7%, 1.20%, and 257 MPa.

1. Introduction

Silicon carbide (SiC) is one of the promising candidate ceramics for high temperature structural components possessing superior mechanical and chemical properties, including high strength, high melting point, high corrosion, and oxidation resistance. With the increasing demand for applications, SiC is limited because of active oxidation over 1400°C. The extreme high melting points and good oxidation resistance of Ultra High Temperature Ceramics (UHTCs) aroused people’s wide concern. Introduction of UHTCs into SiC can improve the oxidation resistance at high temperature. Among them, zirconium diboride (ZrB$_2$) and zirconium carbide (ZrC) perform relative low density (<6.8 g/cm$^3$), high melting points (>3000°C), high hardness (>23 GPa), and high modulus of elasticity (>440 GPa). Thus, ZrB$_2$–SiC and ZrC–SiC composites were studied widely and applied in aerospace industry and other ultra high temperature applications.

At present, ZrB$_2$–SiC and ZrC–SiC composites were fabricated by pressureless sintering, hot-press sintering and spark plasma sintering (SPS). However, in order to obtain high density bodies, high sintering temperature and external pressure are required in sintering process and hot-press sintering, respectively. SPS makes it possible to fabricate dense ZrB$_2$–SiC and ZrC–SiC composites at a relative lower temperature for a short time. Therefore, the composites with fine and homogeneous microstructures can be obtained under the conditions of short sintering time and rapid heating rate of the SPS technique.

On the whole, most of the research mentioned above is focused on the preparation and properties of ZrB$_2$–SiC or ZrC–SiC composite. However, preparation and properties of ZrB$_2$–SiC and ZrC–SiC composites are rare on the same conditions. Thus, in the present work, ZrB$_2$–SiC and ZrC–SiC composites were fabricated, on the same conditions, by SPS at 1800°C for 5 min under a pressure of 40 MPa with the heating rate of 150°C/min, respectively. The properties of them were compared. The phase compositions and the microstructures were investigated. In addition, the mechanical properties including relative density, apparent porosity and bending strength of ZrB$_2$–SiC and ZrC–SiC composites were compared.

2. Experimental procedure

Experimental procedure for fabrication of ZrB$_2$–SiC and ZrC–SiC composites is shown in Fig. 1. ZrB$_2$ powder (<10μm, >90 wt% pure, Dandong Chemical Co. Ltd., Dandong, China) or ZrC powder (Kaier Nanometer Technology Development Co. Ltd., Hefei, China) and SiC (99.9 wt% pure, Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) were mixed in a proportion of 84:16 relatively and milled in ball mill (TENCAN powder Co. Ltd., Shanghai, China) with 150 r/min with ethyl alcohol as the milling medium. The ball-to-powder weight ratio was 10:1. Zirconium oxide balls with average size of about 8 mm were used, which can reduce the contamination of the starting powders.

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during the milling process. The slurry was produced after milling for 24 h and then dried at 80°C for 24 h in vacuum. The homogeneous mixture powders were granulated. Drying was made at about 100°C for 12 h. Polyvinyl alcohol (PVA) was added in the mixture powders to granulate to mold. In the next step, they were put into graphite die with compaction and sintered in spark plasma sintering furnace at 1800°C for 5 min under a pressure of 40 MPa. The pressure was progressive with the temperature increment. The obtained composites products were cut into three pieces of strip specimens with a size of 28 mm × 4 mm × 3 mm. The specimens were polished using SiC powders.

The density and porosity were determined based on the Archimedean principle. The theoretical density of the corresponding composite was calculated through rule of mixture.13) The phase compositions were characterized by X-ray diffraction (XRD) with CuKa radiation. The microstructures of the composites were characterized by Scanning Electron Microscope (SEM, FEI QUANTA FEG250, USA). The bending strength of the specimens was measured via electronic universal-testing machine (CMT5105 100 kN, China) with the span of 20 mm.

3. Results and discussion

The X-ray diffraction patterns of fabricated ZrB$_2$–SiC and ZrC–SiC composites are presented in Fig. 2. The peaks of ZrB$_2$, ZrC and SiC are identified and no product of chemical reaction between ZrB$_2$ and SiC or between ZrC and SiC is detected. The shapes of peaks are sharp because the process of milling and SPS don’t influence the compositions and the crystal forms of ZrB$_2$, ZrC and SiC obviously.

Figure 3 shows the SEM images of polished surfaces of ZrB$_2$–SiC and ZrC–SiC composites. There are a few pores in Fig. 3(a) while substantial pores in Fig. 3(b). The densification of ZrB$_2$–SiC composite is higher than that of ZrC–SiC composite fabricated under the same conditions. The coarseness in Fig. 3(b) may result from the incomplete sintering of ZrC–SiC composite. It can be conjectured that ZrC–SiC composite is harder to sinter than ZrB$_2$–SiC composite.

The SEM images of the fracture surfaces of ZrB$_2$–SiC and ZrC–SiC composites are shown in Fig. 4. It is obvious that the mean particle size of ZrB$_2$–SiC [Fig. 4(a)] is bigger than that of ZrC–SiC [Fig. 4(b)]. The densification of the former is a little higher without apparent pores while substantial pores and lamellar structure is present in Fig. 4(b). What’s more, ZrB$_2$–SiC composite showed transgranular fracture as shown in Fig. 4(a) whereas ZrC–SiC composite showed intergranular fracture in Fig. 4(b), which resulted from the difference of the ultra high temperature phase.

![Fig. 2. The X-ray diffraction patterns of fabricated ZrB$_2$–SiC and ZrC–SiC composites.](image1)

![Fig. 3. The SEM images of the polished surfaces of ZrB$_2$–SiC composite (a) and ZrC–SiC composite (b).](image2)

![Fig. 4. The SEM images of the fracture surfaces of ZrB$_2$–SiC composite (a) and ZrC–SiC composite (b).](image3)
As shown in Table 1, the relative density of ZrB$_2$–SiC composite is higher than that of ZrC–SiC composite, and the value of ZrB$_2$–SiC composite is 97.9%, which is corresponding to the SEM images of the polished surfaces in Fig. 3 and the cross-sections in Fig. 4. In addition, the apparent porosity of ZrB$_2$–SiC composite is relatively lower. That demonstrates that the SiC with introduction of ZrB$_2$ is easier to sinter than introduction of ZrC. This can be explained by the difference of covalent bonding character and self-diffusion coefficients of ZrB$_2$ and ZrC.\(^{14}\)

Correspondingly, the bending strength of ZrB$_2$–SiC composite is much higher than that of ZrC–SiC composite, as shown in Table 1.

### 4. Conclusions

ZrB$_2$–SiC and ZrC–SiC composites were successfully fabricated by SPS at a relatively low temperature (1800°C) for 5 min under a pressure of 40 MPa with ZrB$_2$, ZrC and SiC as the starting powders. The phase compositions, the microstructures, and the mechanical properties were investigated in the form of comparison. The results show ZrB$_2$–SiC composite is denser and represents better mechanical properties than ZrC–SiC composite.

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### Table 1. The mechanical properties of ZrB$_2$–SiC and ZrC–SiC composites

| Component | Theoretical density (g/cm$^3$) | Actual density (g/cm$^3$) | Relative density (%) | Apparent porosity (%) | Bending strength (MPa) |
|-----------|-------------------------------|--------------------------|----------------------|-----------------------|------------------------|
| ZrB$_2$–SiC | 5.636                         | 5.516                    | 97.9                 | 1.08                  | 310                    |
| ZrC–SiC   | 6.140                         | 5.508                    | 89.7                 | 1.20                  | 257                    |