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Reactive Hot Pressing of ZrB_2–SiC–ZrC Ultra High-Temperature Ceramics at 1800°C

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A ZrB_2–SiC–ZrC composite was prepared from a mixture of zirconium, silicon, and B_4C via reactive hot pressing at a relatively low temperature (1800°C) for 60 min under 20 MPa in an argon atmosphere. The relative density was 96.8%, the micro-hardness (Hv10) was 16.7 GPa, and the fracture toughness was 5.1 $MPa \cdot m^{1/2}$. The presence of ZrC was helpful for the densification process and improved the mechanical properties of the composite. A model of the microstructure development of the composite was proposed to explain the phase distribution.

I. Introduction

Zirconium diboride (ZrB_2) and hafnium diboride (HfB_2) are ultra high-temperature ceramics (UHTCs) that have a number of unique properties, including extremely high melting temperature and hardness, low volatility, and high thermal and electrical conductivity.[1] Studies have shown that composites of diborides with silicon carbide (ZrB_2/SiC and HfB_2/SiC) are candidates for ultra high-temperature applications, because the addition of SiC can improve the oxidation resistance.[2,3] The presence of SiC can also increase the strength of the materials by acting as a grain-growth inhibitor.[4]

For most of the reported studies, ceramic composites have been fabricated simply by hot pressing from commercially available powders. Reactive hot pressing (RHP) is an alternative route. It can produce materials with novel and controlled microstructures, with high chemical compatibility of the *in situ*-formed individual phases, and phase distribution uniformity.[5] In boride-containing composites, for example, TiB_2–SiC binary composites and TiB_2–Ti(C,N)–SiC ternary composites have been prepared from a mixture of TiH_2, Si, and B_4C.[6–8]

For zirconium boride-containing UHTCs, a high-strength ZrB_2–SiC composite has been prepared by RHP at 1900°C for 60 min under 30 MPa pressure from a mixture of Zr, Si, and B_4C according to reaction (1).[9] The relative density of this composite is 97.67% with a Vickers hardness of 21.0 GPa and a facture toughness of 4.0 $MPa \cdot m^{1/2}$.

$$2Zr + Si + B_4C = 2ZrB_2 + SiC \tag{1}$$

The addition of ZrC to ZrB_2–SiC to form a ternary composite of ZrB_2–SiC–ZrC can tailor the microstructure and properties of ZrB_2–SiC, especially the superior resistance to oblation at a high temperature.[10] In the current work, a composite in the ZrB_2–SiC–ZrC system was prepared by RHP, using Zr, Si, and B_4C as starting powders according to reaction (2):

$$\begin{aligned}&(2+x)Zr + (1-x)Si + B_4C\\ &\quad = 2ZrB_2 + (1-x)SiC + xZrC\end{aligned} \tag{2}$$

When $x = 0$, reaction (2) reduces to reaction (1). In the present work, we took $x = 0.20$ based on calculations for maintaining the content of SiC at 20 vol%. The calculated volumetric composition is (vol%) $73.6ZrB_2+20SiC+6.4ZrC$. The theoretical density of the composite calculated according to the rule of mixtures is 5.55 g/cm^3, based on the densities of 6.09, 3.21, and 6.44 g/cm^3 for ZrB_2, SiC, and ZrC, respectively. The true density should be lower than the calculated one due to the impurities (mainly Ti). For comparison, a ZrB_2–SiC composite without ZrC (when $x = 0$) was also prepared. Reactions (1) and (2) are thermodynamically favorable and exothermic. In this communication, the samples were produced under relatively mild conditions (1800°C), and the manufacturing process, mechanical properties, and microstructure of the composites are reported, and the effect of ZrC on sintering is discussed.

II. Experimental Procedure

The starting powders were Zr (purity 95.82%, impurities include Ti 2.34, Hf 0.52, Fe 0.24, W 0.08, Cr 0.06, Ni 0.03, O 1.09, particle size <25 μm, Guoyao Chemicals Co. Ltd., Shanghai, China), Si (purity$>$99%, particle size <50 μm, Yinfeng Silcon Co. Ltd., Jinan, China), and B_4C (purity 99%, particle size about 2 μm, Jingangzuan Boron Carbide Co., Ltd, Mudanjiang, China). The stoichiometric powders were mixed and ground in ethanol in an agate mortar until all of the ethanol was evaporated. The grinding process was repeated once for a total grinding time of about 1 h. The mixed powder was then dried and placed in a graphite die with a BN coating. The composite was then RHPed at a temperature of 1800°C for 60 min under a pressure of 20 MPa in an argon atmosphere. A slow heating rate (10°C/min) was adopted to prevent the reaction from becoming self-sustaining. The application of pressure was initiated at 1550°C. The reacted disk had dimensions of 20 mm (diameter) and 5 mm (thickness).

After removing the surface layer from the hot-pressed disk by grinding, the bulk density was measured using the Archimedes method. Phase composition was determined by X-ray diffractometry (XRD) using Cu*K*α radiation. The disk was ground with SiC abrasives and then polished using a diamond pastor of 1 μm. The hardness and fracture toughness were measured by the indentation method, using a load of 10 kg for 10 s on a

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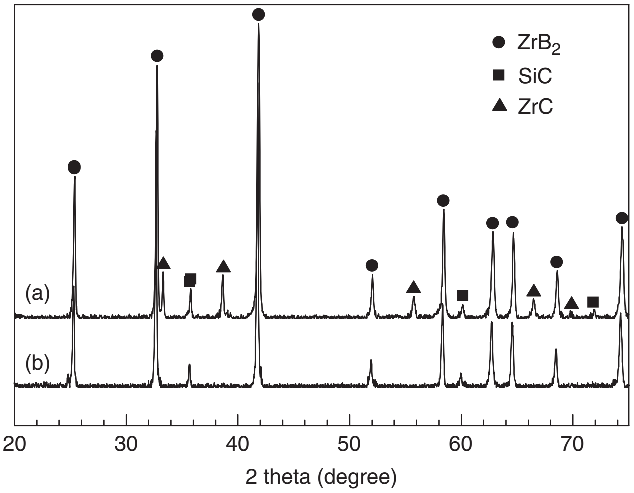

Fig. 1. X-ray diffractometry patterns of the reactive hot-pressed composites: (a) ZrB_2–SiC–ZrC; (b) ZrB_2–SiC.

polished surface; the reported value was an average of five measurements. Scanning electron microscopy (SEM) was performed to observe the microstructure of the composite.

III. Results and Discussion

According to the XRD patterns shown in Fig. 1, phases present in the composites agree with those predicted from reactions (1) and (2). This observation means that either ZrB_2–SiC or ZrB_2–SiC–ZrC can be produced by *in situ* reaction.

The experimental values of some properties of both composites are compared in Table I. The relative density (96.8%) of the ZrB_2–SiC–ZrC composite was higher than that of the ZrC-free composite. This indicates that the presence of ZrC improves the densification of the material, even though the reactants of the two systems are similar.

Compared with the hardness of 21.0 GPa of the composite we mentioned above,[9] the micro-hardness (Hv10) of the composite is not high as listed in Table I. The main reasons for this may be the inhomogeneous microstructure and the porosity in the composites. The regions that are rich in SiC will have a higher hardness than the other regions according to a similar system of TiB_2–SiC–TiC.[12] The fracture toughness of the composite ZrB_2–SiC–ZrC is 5.1 $MPa \cdot m^{1/2}$, which was higher than that measured for ZrB_2–SiC (4.5 $MPa \cdot m^{1/2}$); the formation of ZrC as the third phase improved the fracture toughness of the composite. It is the same case in the TiB_2–SiC–TiC system.[12] The authors of this study concluded that toughness was lower for ZrB_2–SiC because of little interaction between the phases, but the presence of ZrC induces strong bonds with both ZrB_2 and SiC.

Table I. Characteristics of the Obtained Composites

Property	Density (g/cm^3)	Relative density (%TD)	Hardness (GPa)	Fracture toughness ($MPa \cdot m^{1/2}$)
ZrB_2–SiC	5.09	94.8	13.8	4.5
ZrB_2–SiC–ZrC	5.37	96.8	16.7	5.1

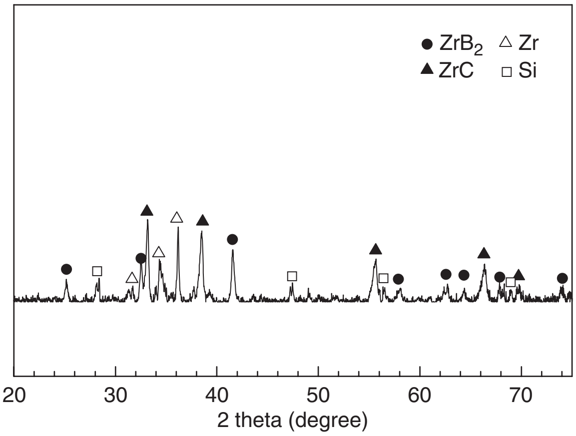

Fig. 2. X-ray diffractometry pattern of the mixed powder for preparing a ZrB_2–SiC–ZrC composite after heat treatment at 800°C for 60 min in an argon atmosphere.

Figure 2 shows the XRD pattern of the intermediate products in the ZrB_2–ZrC–SiC system heat treated at 800°C for 60 min in an argon atmosphere. It can be found that ZrC formed at a relatively low temperature of 800°C. As the temperature increased, ZrB_2 became the main phase; in addition, SiC appeared and the amount of ZrC decreased, based on the peak intensity in the XRD patterns. By analyzing the reaction process,[6,11] reactions (1) and (2) may take place in steps as follows:

$$3Zr + B_4C = 2ZrB_2 + ZrC \tag{3}$$

$$2ZrC + B_4C + 3Si = 2ZrB_2 + 3SiC \tag{4}$$

The above reactions have large negative Gibbs free energies (ΔG_{298} (3) = −767.641, ΔG_{1800} (3) = −703.078, ΔG_{298} (4) = −395.212, ΔG_{1800} (4) = −320.257 kJ/mol), showing that the reactions are all thermodynamically favorable.

The microstructure of ZrB_2–SiC–ZrC composite is shown in Fig. 3. This picture indicates that the distributions of the *in situ*-formed ZrB_2, SiC, and ZrC phases in the composite are not homogenous. The particle size of SiC and ZrC is similar and generally small, about 1–3 μm, whereas that of ZrB_2 is large, which is about 3–10 μm. SiC and ZrC are mainly located at the ZrB_2/ZrB_2 grain boundaries, but the phases do not appear in the same region. Namely, regions rich in SiC are poor in ZrC. This supports the conclusion that the SiC phase is formed from ZrC. Figure 4 shows a schematic of a possible formation sequence during RHP. For the model, it is assumed that B and C atoms from B_4C diffuse faster than Zr and Si.[9,13] Also, Si has a lower reactivity than Zr, so ZrB_2 and ZrC formed before any Si compounds. At higher temperatures, SiC formed *in situ* as a result of the reaction between Si, ZrC, and the residual B_4C. Owing to the large particle sizes of the Zr starting powder and its agglomeration, the size of the resulting ZrB_2 grains are large

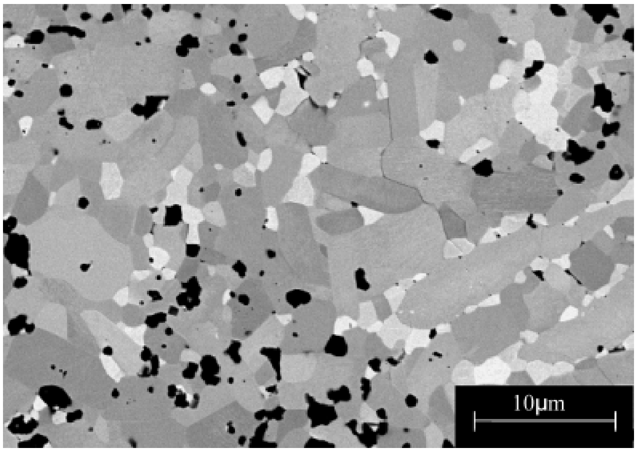

Fig. 3. Backscattered electron images of a polished surface of the reactive hot-pressed composite. The gray phase is ZrB_2, the dark phase is SiC, and the white phase is ZrC.

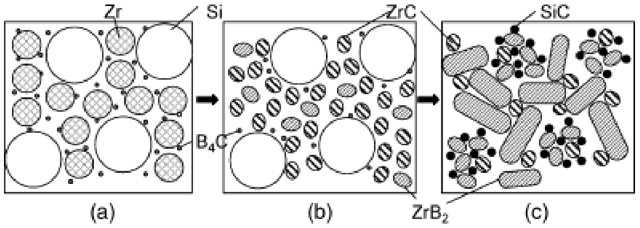

Fig. 4. Microstructure formation mechanism of the ZrB_2–ZrC–SiC composite in the reaction-synthesis process, depicting the conversion from (a) the powder compact to (b) the intermediate state, and (c) the final microstructure of the composite.

in the RHPed composite. In addition, the regions where SiC is concentrated are about the same size as the starting Si powders. Accordingly, using starting powders with a finer particle size and improving the uniformity of mixing should promote formation of a more homogeneous material.

From Fig. 3, it can be seen that the ZrB_2 grains surrounded by SiC are finer than those not surrounded by SiC. This supports the conclusion that SiC can reduce grain growth in ZrB_2.[3,14] This will be useful in ultra high-temperature applications, as a grain-growth inhibitor would improve the material's stability at elevated temperature. On the other hand, the existence of ZrC seems to promote the growth of the ZrB_2 platelets, and this should have improved the fracture toughness of the composite.

IV. Summary

A ZrB_2–SiC–ZrC composite was prepared by the RHP of a mixture of zirconium, silicon, and B_4C powders. The hardness and the fracture toughness of the product measured were 16.7 GPa and 5.1 $MPa \cdot m^{1/2}$. The presence of ZrC improves the densification process and fracture toughness of the composite. The microstructure of the composite was not homogeneous owning to the coarse particle size of the starting powders. The reaction took place in steps. First, B_4C reacted with Zr to form ZrB_2 and ZrC at a very low temperature. At a higher temperature, SiC was formed *in situ* by the reaction of Si with ZrC and the residual B_4C.

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