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Preparation and Microstructure of a ZrB_2–SiC Composite Fabricated by the Spark Plasma Sintering–Reactive Synthesis (SPS–RS) Method

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A mixture of Zr, B_4C, and Si powders was adopted to synthesize a ZrB_2–SiC composite using the spark plasma sintering–reactive synthesis (SPS–RS) method. SPS treatments were carried out in the temperature range of 1350°–1500°C under a varying pressure of 20–65 MPa with a 3-min holding time. A dense (~98.5%) ZrB_2–SiC composite was successfully fabricated at 1450°C for 3 min under 30 MPa. The microstructure of the composite was investigated. The *in situ* formed ZrB_2 and SiC phases dispersed homogeneously on the whole. The grain size of ZrB_2 and SiC was <5 and 1 μm, respectively. A number of *in situ* formed ultrafine SiC particles were observed entrapped in the ZrB_2 grains.

I. Introduction

Previous studies have shown that composites of ZrB_2 with SiC are candidates for ultra high-temperature applications. The addition of SiC can improve the oxidation resistance and may inhibit grain growth and improve strength.[1,2] Several methods have been utilized for the preparation of dense ZrB_2–SiC composites. For example, ZrB_2–SiC composites could be produced by hot pressing (HP) of mechanically mixed powders. Sometimes, ceramic additives are used to enhance the sinterability. The sintering temperature is typically above 1800°C.[3,4] Reactive hot pressing (RHP) is an alternative route to fabricate ceramic composites, and some attempts to synthesize ZrB_2–SiC composites have been made by RHP. ZrB_2–20 vol% SiC composites with a relative density in excess of 95% have been successfully fabricated at 1650°C by RHP.[5–8] Compared with HP, RHP could synthesize ZrB_2-based composites at a relatively low temperature without sintering aids, while in the above-mentioned methods, the typical duration of cycles is more than 2 h and the sintering temperature is above 1650°C.

Recently, we reported a simple one-step method, that is, a spark plasma sintering–reactive synthesis (SPS–RS) method. This novel fabrication process combines the advantages of an *in situ* process and an SPS process. In our previous work, dense composites such as Ti_5Si_3–TiC–Ti_3SiC_2, Ti_5Si_3–TiC, and Ti_3SiC_2–SiC with fine microstructures were successfully fabricated in about 20 min, and the sintering temperatures were 100°–200°C lower than that of RHP.[9–11]

Based on the above research, we used this new technique to synthesize a ZrB_2–SiC composite with Zr, Si, and B_4C as the starting powders. In this communication, the manufacturing process, microstructure, and mechanical properties of the composite are reported.

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, particle size <45 μm, Guoyao Chemicals Co. Ltd., Shanghai, China), Si (purity >99%, particle size <50 μm, Guoyao Chemicals Co. Ltd.), and B_4C (purity 99%, particle size about 2 μm, Jingangzhuan Boron Carbide Co. Ltd., Mudanjiang, China). Si was milled in an agate jar using absolute ethanol and agate balls beforehand. After being milled for 48 h, the particle size decreased to about 2 μm, as determined by scanning electron microscopy (SEM). The stoichiometic powders were ball milled in ethanol with ZrO_2 balls for 24 h, and then dried. The mixed powders were placed in a graphite die (15 mm in diameter) and sintered with the Dr. Sinter® 2040 spark plasma sintering system (Sumitomo Coal Mining Co., Tokyo, Japan) in vacuum (<6 Pa). The heating rate was controlled to about 80°C/min and the pressure was applied from 1250°C and maintained constant during the subsequent heating and holding period. The experiments were carried out in the temperature range of 1350°–1500°C under various pressures of 20–65 MPa for 3 min. The current was stopped and pressure was released as soon as the holding at the sintering temperature was over. The whole process took only 20–22 min.

After sintering, the surfaces of the samples were ground to remove the graphite layer. The bulk density was measured using the Archimedes method. According to reaction (1), the volume percents of ZrB_2 and SiC in the composite obtained are 74.85% and 25.15%, respectively. The theoretical density of the composite calculated according to the rule of mixtures is 5.37 g/cm^3, based on the densities of 6.09 and 3.21 g/cm^3 for ZrB_2 and SiC, respectively,

$$2Zr + Si + B_4C \rightarrow 2ZrB_2 + SiC \quad (1)$$

Phase composition was determined by X-ray diffraction (XRD; D/Max-2250V, Rigaku, Tokyo, Japan) using Cu$K\alpha$ radiation. The microstructure analyses of the samples were conducted using SEM (JXA-8100, JEOL, Tokyo, Japan). Vickers hardness (H_v) of the polished samples was measured by the indentation technique (Wilson-wolpert Tukon® 2100B, Instron, Boston, MA). The indentation parameters were made using a 10-kg load with a dwell of 15 s.

III. Results and Discussion

Figure 1 shows the XRD results of the raw powder and the samples sintered at different temperatures. From the XRD patterns, it appears that some ZrB_2 had formed at 900°C, but that SiC formation was not detected until 1000°C. Within the

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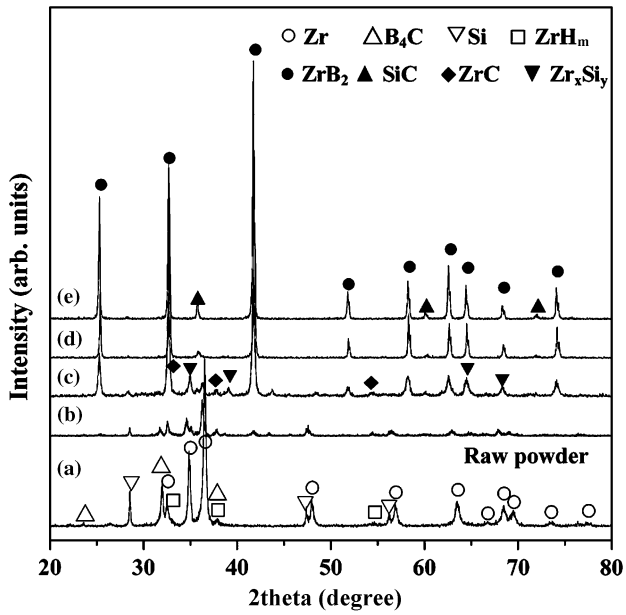

Fig. 1. X-ray diffractometry patterns of the Zr/Si/B_4C mixed powders heated at (b) 900°C, (c) 1000°C, (d) 1200°C, and (e) 1500°C.

temperature range 900°–1200°C, several chemical reactions take place. The emergence of intermediate phases such as ZrC and the mixture of zirconium silicides, most probably Zr_2Si and $ZrSi_2$, were ascertained.

In order to fabricate a composite with nearly fully dense composites, a much higher sintering temperature and pressure are needed, although reaction (1) is completed at 1200°C. According to Fig. 2, the relative densities of all samples increase with increasing pressure, but the trend is lowered with increasing temperature. A dense (~98.5%) ZrB_2–SiC composite could be fabricated at 1450°C under 30 MPa for 3 min. Although the relative density is considerably high, it is believed that the relative density can be improved through further optimization of the processing parameters. Compared with HP and RHP, a ZrB_2–SiC composite could be fabricated via SPS–RS at a relatively low temperature and a short time, and so we believe that the SPS–RS technique is considerably advantageous in the synthesis of a ZrB_2–SiC composite.

The microstructure of a composite synthesized at 1450°C under 30 MPa is shown in Fig. 3. On the whole, the distribution of the *in situ* formed ZrB_2 and SiC phases was homogeneous, although agglomeration existed. The phase distribution is related to the particle size of the staring powders, in agreement with

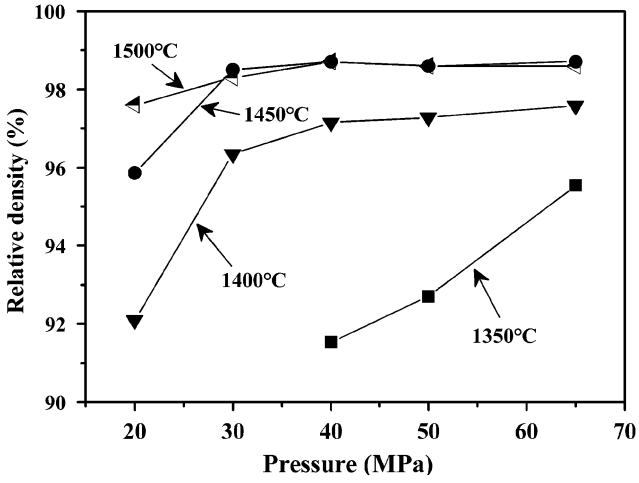

Fig. 2. Variation of relative density depending on the sintering temperature and pressure.

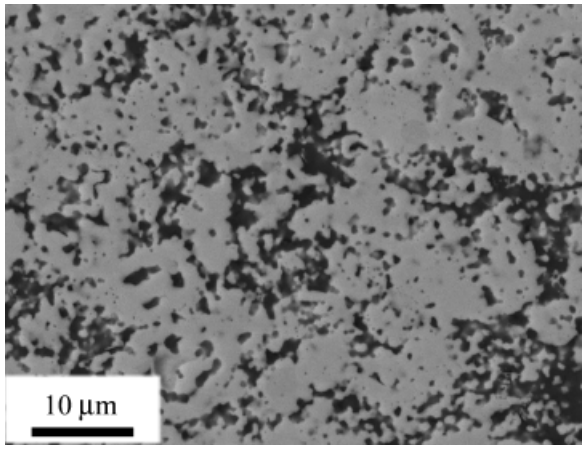

Fig. 3. Backscattered electron image of a polished surface of the as-sintered composite (the gray phase represents ZrB_2, and the dark phase represents SiC).

that reported for a ZrB_2—25 vol% SiC composite synthesized by RHP.[5,6]

Figure 4 shows the SEM micrograph from a fracture surface of this sample. The grain size of ZrB_2 and SiC is <5 and 1ím, respectively. Usually, the grain size depends on the sintering temperature, and the average grain size increases with the sintering temperature. HP of ZrB_2–SiC composites is typically conducted above 1800°C, and RHP needs a temperature above 1650°C. The SPS–RS process in this work is conducted at a markedly lower temperature with a shorter holding time. In addition, can easily be seen from Fig. 4 that the fracture mode is mainly intragranular.

Both intergranular and intragranular SiC grains are found in the micrographs of the composite, and a number of SiC grains (<0.5 μm) are entrapped within the ZrB_2 grains. The reason for the formation of this microstructure was possibly based on the following two factors: (i) some of the SiC grains may not form directly from the initial Si, but from intermediate phases. By analogy with a similar system,[12] the following chemical reactions (dG_{25}: Gibbs-free energy of reaction at 25°C) are proposed to occur.

$$3Zr + B_4C = 2ZrB_2 + ZrC \ (dG_{25} = -759\,kJ/mol) \quad (2)$$

$$xZr + ySi = Zr_xSi_y, \ x/y = 1/2, 2 \quad (3)$$

$$2ZrC + 3Si + B_4C = 2ZrB_2 + 3SiC \ (dG_{25} = -391\,kJ/mol) \quad (4)$$

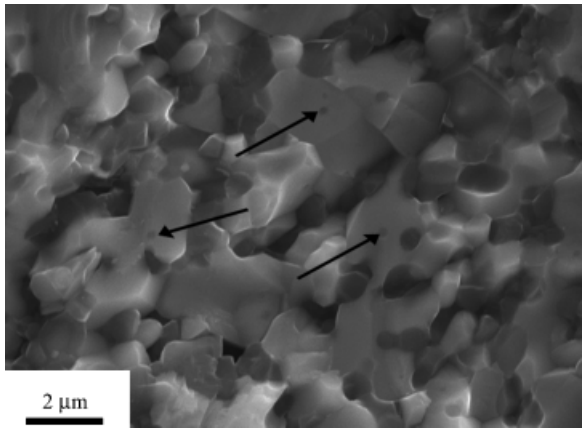

Fig. 4. Scanning electron micrograph from a fracture of the as-sintered composite (examples of intragranular SiC particulates are marked with black arrows).

$$ZrSi_2 + B_4C + ZrC = 2ZrB_2 + 2SiC \ (dG_{25} = -356\,kJ/mol) \quad (5)$$

$$Zr_2Si + B_4C = 2ZrB_2 + SiC \ (dG_{25} = -427\,kJ/mol) \quad (6)$$

$$ZrSi_2 + Zr_2Si + 3B_4C + 3Zr = 6ZrB_2 + 3SiC \ (dG_{25} = -1541\,kJ/mol) \quad (7)$$

Reactions (5)–(7) describe the delayed formation of SiC. (ii) the shortened sintering time and lowered sintering temperature, as a high sintering temperature and a long sintering time, could induce grain growth. With lowered sintering temperature and a shortened sintering time, the SiC nanophase can be retained. It is speculated that the reaction nucleation and grain growth rate of ZrB_2 is much faster than that of SiC. During sintering and consolidation processes, some of the SiC grains (<0.5 μm) remain located intragranularly. A similar structure was reported in a study of the beneficial effects of an ultrafine SiC on the sinterability and mechanical properties of ZrB_2.[13] The mechanism of this interesting structure formation needs to be further investigated.

The characteristics of the composite synthesized at 1450°C under 30 MPa were measured. The fracture toughness (K_{Ic}) value was 4.31 ± 0.20 MPa · $m^{1/2}$. For the composites of ZrB_2 with 20–30 vol% SiC prepared by HP and RHP, the fracture toughness values range from 3.9 to 5.5 MPa · $m^{1/2}$.[2,4,5,13,14] The Vickers hardness (H_v10) of the composite was 17.18 ± 0.26 GPa, compared with the hardness of 17.5–27 GPa reported by other authors, which is not high. The inhomogeneous distribution of SiC might result in a relatively low hardness.

IV. Conclusions

A combined SPS–RS approach was used to prepare a ZrB_2–25 vol% SiC composite using Zr, B_4C, and Si as the reactants. A dense (~98.5%) composite was obtained at 1450°C for a 3-min dwelling time under 30 MPa. The entire processing time applied to obtain a nearly full density through this method was much shorter (about 20–22 min) than that necessary for the HP or RHP. The microstructure was fine and homogeneous on the whole. The grain size of ZrB_2 was <5 μm, and that of SiC was <1 μm. The Vickers hardness was 17.18 ± 0.26 GPa, and the fracture toughness was 4.31 ± 0.20 MPa · $m^{1/2}$. The intrafracture mode dominated the fracture process.

References

[1]M. M. Opeka, I. G. Talmy, E. J. Wuchina, J. A. Zaykoski, and S. J. Causey, "Mechanical, Thermal, and Oxidation Properties of Hafnium and Zirconium Compounds," *J. Eur. Ceram. Soc.*, **19** [13–14] 2405–14 (1999).

[2]A. L. Chamberlain, W. G. Fahrenholtz, G. E. Hilma, and D. T. Ellerby, "High-Strength Zirconium Diboride-Based Ceramics," *J. Am. Ceram. Soc.*, **87** [6] 1170–2 (2004).

[3]F. Monteverde and L. Scatteia, "Resistance to Thermal Shock and to Oxidation of Metal Diborides–SiC Ceramics for Aerospace Application," *J. Am. Ceram. Soc.*, **90** [4] 1130–8 (2007).

[4]A. Rezaie, W. G. Fahrenholtz, and G. E. Hilmas, "Effect of Hot Pressing Time and Temperature on the Microstructure and Mechanical Properties of ZrB_2–SiC," *J. Mater. Sci.*, **42** [8] 2735–44 (2007).

[5]G. J. Zhang, Z. Y. Deng, N. Kondo, J. F. Yang, and T. Ohji, "Reactive Hot Pressing of ZrB_2–SiC Composites," *J. Am. Ceram. Soc.*, **83** [9] 2330–2 (2000).

[6]G. J. Zhang, M. Ando, J. F. Yang, T. Ohji, and S. Kanzaki, "Boron Carbide and Nitride as Reactants for In Situ Synthesis of Boride-Containing Ceramic Composites," *J. Eur. Ceram. Soc.*, **24**, 171–8 (2004).

[7]A. L. Chamberlain, W. G. Fahrenholtz, and G. E. Hilmas, "Low-Temperature Densification of Zirconium Diboride Ceramics by Reactive Hot Pressing," *J. Am. Ceram. Soc.*, **89** [12] 3638–45 (2006).

[8]J. W. Zimmermann, G. E. Hilmas, W. G. Fahrenholtz, F. Monteverde, and A. Bellosi, "Fabrication and Properties of Reactively Hot Pressed ZrB_2–SiC Ceramics," *J. Eur. Ceram. Soc.*, **27**, 2729–36 (2007).

[9]L. J. Wang, W. Jiang, L. D. Chen, and G. Z. Bai, "Microstructure of Ti_5Si_3–TiC–Ti_3SiC_2 and Ti_5Si_3–TiC Nanocomposites In Situ Synthesized by Spark Plasma Sintering," *J. Mater. Res.*, **19** [10] 3004–8 (2004).

[10]J. F. Zhang, L. J. Wang, L. Shi, W. Jiang, and L. D. Chen, "Rapid Fabrication of Ti_3SiC_2–SiC Nanocomposite Using the Spark Plasma Sintering–Reactive Synthesis (SPS–RS) Method," *Scr. Mater.*, **56** [3] 241–4 (2007).

[11]L. J. Wang, J. Wang, S. Q. Bai, G. Wang, and L. D. Chen, "Rapid Fabrication of Nano-Structured Ti_5Si_3–TiC Composites by Spark Plasma Sintering," *J. Inorg. Mater.*, **19** [6] 1436–40 (2004).

[12]F. Monteverde, "Progress in the Fabrication of Ultra-High-Temperature Ceramics: 'In Situ' Synthesis, Microstucture and Properties of a Reactive Hot-Pressed HfB_2–SiC Composite," *Compos. Sci. Technol.*, **65**, 1869–79 (2005).

[13]F. Monteverde, "Beneficial Effects of an Ultra-Fine α-SiC Incorporation on the Sinterability and Mechanical Properties of ZrB_2," *Appl. Phys. A*, **82** [2] 329–37 (2006).

[14]S. Zhu, W. G. Fahrenholtz, and G. E. Hilmas, "Influence of Silicon Carbide Particle Size on the Microstructure and Mechanical Properties of Zirconium Diboride–Silicon Carbide Ceramics," *J. Eur. Ceram. Soc.*, **27** [4] 2077–83 (2007). □