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Short Communication

Effect of holding time and pressure on properties of ZrB_2–SiC composite fabricated by the spark plasma sintering reactive synthesis method

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ABSTRACT

Structure-property relations of ZrB_2–SiC composites fabricated by spark plasma sintering reactive synthesis (SPS-RS) method were investigated. The effects of the holding time and pressure on the density, mechanical properties and microstructures were characterized. The results showed that the density increased with both holding time and pressure increased. Hardness was not affected much by the processing condition when the density was above 96.3%. However, fracture toughness values were found to depend on holding time. The value increased from 4.3 ± 0.2 MPa $m^{1/2}$ to 5.3 ± 0.3 MPa $m^{1/2}$ when the holding time prolonged from 9 min to 12 min for the grain size of ZrB_2 and SiC increased.

1. Introduction

Zirconium diboride (ZrB_2) displays a number of unique properties, including high melting point (3245 °C) and hardness (12–22 GPa), high electrical conductivity (10^7 S/m) and thermal conductivity (23–25 W/mK), superb thermal shock resistance and resistance to chemical attack. Therefore, the use of ZrB_2 composites can be expected to offer potential candidates for a variety of high-temperature structural applications [1–3]. However, the insufficient oxidation resistance of ZrB_2 composites limits their utility in high-temperature oxidizing environments. Previous studies show that the addition of silicon carbide (SiC) as a second phase could improve the oxidation resistance of ZrB_2, and the SiC particulates could also improve the mechanical properties of ZrB_2 composites [4–6].

Chamberlain et al. reported that uniform distribution of SiC and the maintaining of fine grain size could increase the strength of the composites [7]. Monteverde reported that the ultra-fine SiC could improve the sinterability and mechanical properties of ZrB_2 [8,9]. Subsequently, Hwang et al. studied the properties of ZrB_2–SiC composites as a function of SiC starting powder size with average particle sizes ranging from ~80 nm to 1.8 μm. They pointed out that the hardness increased with decreasing SiC grain size, whereas the dense ZrB_2–SiC composites with coarser SiC grains had the higher toughness [10].

In our previous study, we have successfully synthesized ZrB_2–SiC composites by spark plasma sintering reactive synthesis method (SPS-RS) [11]. In this paper, we focus on the effect of different holding time and pressure on microstructure and mechanical properties of ZrB_2–SiC composites. The density, microstructure, and mechanical properties were evaluated and compared.

2. Experimental

The raw materials used in this work were 95.82% pure Zr powder (<45 μm), 99% pure Si powder (<2 μm) and 99% pure B_4C powder (<2 μm). The powder mixtures were milled for 24 h in absolute ethanol using zirconia milling media and then dried.

SPS was carried out in vacuum (less than 6 Pa) using Dr. Sinter@ 2040 spark plasma sintering system (Sumitomo Coal Mining, Tokyo, Japan). After loading the powder into a 15 mm diameter graphite die, the furnace was heated at an average rate of ~80 °C/min to the sintering temperature at 1400 °C. Holding time and pressure were controlled following two protocols: (1) the holding time was 0, 3, 6, 9 and 12 min with a pressure of 30 MPa; (2) the applied pressure was 20, 30, 40, 50 and 65 MPa with 3 min holding time. In each case, pressure was applied from 1250 °C, and was immediately relaxed as soon as the holding at sintering temperature was over. The sintering sample was cooled

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to below 600 °C within 2–3 min. The temperature was measured by means of a pyrometer focused on to the graphite die surface, which centered on the sintering sample. In addition, with the aim of minimizing heat losses by thermal radiation, the die was covered with a layer of graphite felt.

After sintering, the surfaces of samples were ground for removing 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.

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

The microstructure observation of the samples was conducted using scanning electron microscopy (SEM). Vickers hardness (Hv) of the polished samples was measured by the indentation technique (Wilson-wolpert Tukon@ 2100B). The indentation parameters were made using a 5 kg load with a dwell of 15 s.

3. Results and discussion

All the properties are listed in Table 1. The measured bulk densities ranged from 4.64 to 5.28 g/cm^3, and the relative densities ranged from ~86.4% to ~98.3%. Density of these various pellets showed differences versus the applied process. Densities rose from 86.4% to 98.3% for specimens 1 to 5, and rose from 92.1% to 97.6% for specimens 6, 2, 7, 8, 9. A more significant difference (13.8%) was found in specimens 1 and specimens 5.

Hardness increased rapidly as porosity decreased. When the relative density above 96.3%, the value of hardness varied from 17.3 ± 0.3 to 18.6 ± 0.5 GPa. The value decreased slightly with the holding time increased from 9 min to 12 min.

Table 1
Characteristics of the obtained ZrB_2–SiC composites

Samples	Holding time (min)	Pressure (MPa)	Relative density (%TD)	Hv (GPa)	K_{IC} (MPa m$^{1/2}$)
1	0	30	86.4	10.8 ± 0.7	–
2	3	30	96.3	17.8 ± 0.5	4.0 ± 0.2
3	6	30	97.5	18.0 ± 0.5	4.5 ± 0.3
4	9	30	98.3	18.1 ± 0.4	4.3 ± 0.2
5	12	30	98.3	17.3 ± 0.3	5.3 ± 0.3
6	3	20	92.1	11.7 ± 1.0	–
2	3	30	96.3	17.8 ± 0.5	4.0 ± 0.2
7	3	40	97.2	18.5 ± 0.9	3.8 ± 0.4
8	3	50	97.3	18.6 ± 0.5	3.6 ± 0.3
9	3	65	97.6	18.6 ± 0.5	3.9 ± 0.3

The fracture toughness appeared to vary more obviously with the processing conditions. For specimens prepared under the same pressure (30 MPa), fracture toughness increased from 4.3 ± 0.2 to 5.3 ± 0.3 MPa m$^{1/2}$ when holding time increased from 9 min to 12 min. For these specimens prepared with the same holding time (3 min), the fracture toughness values were statistically identical to each other.

To understand how the variation fracture toughness related to microstructure, the specimen 4 with fracture toughness about 4.3 ± 0.2 MPa m$^{1/2}$ and specimen 5 with fracture toughness about 5.3 ± 0.3 MPa m$^{1/2}$ were indented using a load of 5 kg and the paths of the indentation cracks were observed. From the SEM images of polished sections shown in Fig. 1 the indentation crack path in specimen 5 appeared more tortuous than the crack path in specimen 1.

After the initial crack path observations, five specimens were selected for more detailed analysis. The specimens 1, 2, 4, 5 and 9 were investigated. The SEM pictures of fracture surfaces are shown in Fig. 2. The microstructure of specimen 1 shows that the grain size distribution of ZrB_2 was wide (from less than 1 μm to 3 μm). SiC particles basically dispersed within the diboride skeleton. Longer holding time (3 min) at the same temperature and pressure produced specimen 2 in which porosity decreased meanwhile some of SiC grains (<0.5 μm) were entrapped in the ZrB_2 matrix. Similar structure was reported in the study about the beneficial effects of an ultra-fine SiC on the sinterability and mechanical properties of ZrB_2 [8]. In the report, the SiC particulates were mainly distributed intergranularly and a limited fraction remains located intragranularly. Neither prolonging holding time from 3 min to 9 min nor increasing pressure from 30 MPa to 65 MPa changed the grain size obviously. But when prolonging the holding time from 9 min to 12 min, both of the grain sizes of ZrB_2 and SiC increase obviously. The largest ZrB_2 grains increased to about 5 μm and the largest SiC grains increased to about 1 μm.

At 1400 °C, density appears to be promoted by both holding time and pressure. But this is not achieved in the same manner. The grain size increased obviously when holding time was prolonged from 3 to 12 min under 30 MPa whereas for a 3 min holding time and pressure evolving from 30 MPa to 65 MPa, grain size changed not much. It appears that holding time plays a greater role in grain size than pressure. The hardness could be affected by both relative density and grain size. Pores in ceramics have no resistance to applied stress, so materials with more porosity have lower apparent hardness than the dense ones. In addition to the effects of porosity, the grain size also influences hardness. Smaller grain size increases the frequency with which dislocations encounter grain boundaries,

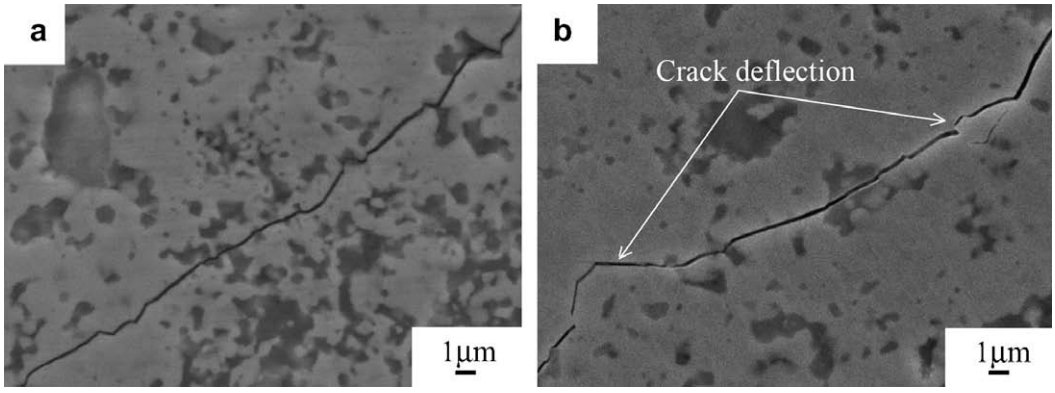

Fig. 1. Polished cross sections with indentation crack paths for the specimens with the fracture toughness value (a) 4.3 ± 0.2 MPa m$^{1/2}$ (specimen 4) and 5.3 ± 0.3 MPa m$^{1/2}$ (specimen 5).