A Processing–Microstructure Correlation in ZrB_2 –SiC Composites Hot-pressed under a Load of 10 MPa

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Abstract Monolithic ZrB_2 ceramic and its composites, with 5 to 30 vol. % SiC, has been prepared by hot pressing at temperatures of 1700, 1850 and 2000 °C, for 30 minutes under relatively low pressure of 10 MPa. Densification behavior of ZrB_2 -based composites is improved by the addition of SiC particulates. The fracture surface of monolithic ZrB_2 ceramics shows a grained structure, with faceted ZrB_2 grains, as the fracture appears to spread prevalently along an intergranular path. The $\text{ZrB}_2/\text{ZrB}_2$ boundary interface is seemingly free of any secondary phases. The microstructure of ZrB_2 –30 vol. % SiC composite, hot-pressed at 1700 °C, is consistent with measured porosity for the sample that has ~8% open pores, nearly without closed pores. It seems that mechanical interlocking between ZrB_2 and SiC is an important mechanism for densification. In the microstructure of specimens consolidated at 1850 °C, neck formation between ZrB_2 particles is visible. In contrast, relatively fully dense samples are obtained by hot-pressing at 2000 °C. Intergranular SiC particles inside ZrB_2 grains show the occurrence of mass transfer among ZrB_2 particles, which in effect brings the elimination of pores to a fortunate ending. Efficient mixing of starting powders is very critical in order to achieve a fine-grained homogenous microstructure.

Keywords Hot Pressing, Zirconium Diboride, Silicon Carbide; Microstructure, Grain Growth, Powder Mixing

1. Introduction

Zirconium diboride is striking for its ultra-high melting temperature as well as its hardness, elastic modulus, low electrical resistivity, and resistance to chemical attack. As a result, this material has been proposed for a variety of structural applications at room and elevated temperature, including armor, cutting tools, molten metal containment, steel processing, and electrodes. Zirconium diboride is also considered to be an ultra-high-temperature ceramic and is a candidate to be used as leading edges and propulsion components in hypersonic aerospace vehicles and advanced reusable atmospheric reentry vehicles [1-3].

Because of strong covalent bonding and low self-diffusion coefficient, high temperature and external pressure is required to densify ZrB_2 . In early studies, nominally stoichiometric ZrB_2 without additives, had only been densified by hot press at 2000 °C or higher temperatures under pressures of 20-30 MPa, or at lower temperatures (1790-1840 °C) under much higher pressures (800-1500 MPa). Recent studies (listed in Table 1) have produced similar results. Nearly pure ZrB_2 with average starting particle sizes of 5-10 μm requires hot pressing above 2000 °C to achieve full density [1, 4]. Hot pressing of coarse ZrB_2 powder (20 μm) at 2000 °C under pressure of 20 MPa led to relative density of 73% [5]. Minimization of grain growth was attributed to lower sintering temperatures and reduced starting particle sizes. Recent research, using commercial ZrB_2 powders, has typically included non-reactive additives (e.g., SiC) to improve the densification. Using finer starting powder, high sintering temperature and pressure will not be necessary [1, 6-7]. Introduction of submicron α -SiC particulate (0.8 μm) was recognized as the key factor that enabled both control of ZrB_2 grain growth and achievement of full density (hot pressed at 1900 °C for 20 min under 50 MPa) [8]. Furthermore, addition of 22.4 vol. % nano-sized SiC, with average particles size ranging from 40 nm to 0.6 μm , sharply reduced the consolidating temperature necessary to achieve full density from 1900 to 1650 °C (pressed for 120 min under 60 MPa) [5]. ZrB_2 –SiC composites with relative densities over 95% were produced by reactive hot pressing at temperatures as low as 1650°C, and the ZrB_2 matrix was formed by reacting elemental zirconium and boron [4]. In addition, ZrB_2 containing 27 vol. % SiC with relative densities >99% was obtained by reactive hot pressing of ZrH_2 , B_4C and Si between temperatures 1600 and 1900 °C [9]. Analysis of polished sections of hot pressed samples, with starting particle size of 2 and 0.7 μm for respectively ZrB_2 and SiC, showed that SiC acts as a grain growth inhibitor [10]. Microstructure of ZrB_2 (with particle size of 2 and 6 μm), containing 30 vol. % SiC (with particle size of 0.7 μm), has been investigated at different hot pressing times and temperatures. The relative densities ranged from 97.2 to ~100%. The average grain size of ZrB_2 and SiC phases

varied from 2.2 to 4.7 μm and 1.2 to 2.7, respectively [11]. The effect of SiC particle size, ranging from 0.45 to 10 μm , on the microstructure of ZrB_2 -based composites, containing 30 vol. % SiC, was studied. Investigations showed that smaller starting SiC particles led to improved densification and finer microstructure [12]. A ZrB_2 -based composite containing 20 vol. % nano-sized β -SiC particles (30 nm) was hot pressed at 1900 $^{\circ}\text{C}$ for 30 min under 30 MPa. It was shown that the grain growth of ZrB_2 matrix was effectively suppressed by SiC particles [13]. Recently, the dominant densification mechanisms for hot pressing of ZrB_2 -20 vol. % SiC composite, at different sintering temperatures and pressures, was identified. For hot pressing at 1700 $^{\circ}\text{C}$, it was found to be only mechanically driven particle fragmentation and rearrangement, whereas at 1850 $^{\circ}\text{C}$ a plastic flow mechanism started to happen. At 2000 $^{\circ}\text{C}$, the dominant mechanism changed from plastic flow to grain boundary diffusion [14].

Although in recent years, ZrB_2 -based composites have been densified by other techniques such as pressureless sintering [6, 15-17], reactive hot pressing [4, 9, 18-24], and spark plasma sintering [25-28], but hot pressing is still the dominant method in research on consolidation. Table 1 lists the compositions, starting particle sizes, sintering conditions, and relative densities of the composites investigated by researchers, employing hot pressing as the sintering method.

The purpose of this paper is to describe the microstructural conduct of ZrB_2 -SiC composites, hot pressed under relatively low-pressure using mono-sized starting powders. X-ray diffraction analysis, optical microscopy and scanning electron microscopy micrographs are used to study the evolution of microstructure as a function of sintering temperature and SiC content. In addition, the densities and porosities of composites consolidated at 1700, 1850 and 2000 $^{\circ}\text{C}$ will be compared to deduce the effect of processing temperature.

Table 1. Hot pressing conditions and relative densities of ZrB_2 -SiC composites.

Composition (vol. %)		Particle size (μm)		Hot pressing conditions			Relative density (%)	References
ZrB_2	SiC	ZrB_2	SiC	Temperature ($^{\circ}\text{C}$)	Time (min)	Pressure (MPa)		
100	0	20	-	2000	20	20	73.0	5
100	0	5-10	-	1800	60	20	78.0	5
100	0	6	-	1900	30	30	86.5	1
100	0	2	-	1900	45	32	99.8	10
100	0	2	-	1650	20	60	71.6	5
94.3	5.7	2	1.7	1650	120	60	81.6	5
90	10	4-6	0.8	1900	20	50	100	8
90	10	2	0.7	1900	45	32	93.2	10
80	20	2	0.7	1900	45	32	99.7	10
80	20	-	-	-	-	-	100	2
77.6	22.4	2	1.7	1650	120	60	97.9	5
77.6	22.4	2	0.04	1650	120	60	99.6	5
70	30	6	10	1900	45	32	97.4	12
70	30	6	1.4	1900	45	32	98.9	12
70	30	6	0.7	2050	45	32	98.1	11
70	30	6	0.7	1950	45	32	98.2	11
70	30	6	0.7	1900	45	32	98.7	12
70	30	6	0.7	1850	45	32	99.5	11
70	30	2	0.7	2050	180	32	99.5	11
70	30	2	0.7	2050	90	32	99.0	11
70	30	2	0.7	2050	45	32	>99.9	11
70	30	2	0.7	1950	45	32	99.0	11
70	30	2	0.7	1900	45	32	99.4	10
70	30	2	0.7	1850	45	32	97.2	11
70	30	6	0.45	1900	45	32	99.8	12

2. Experimental Procedure

2.1. Processing

ZrB₂ (particle size ~2 μm , purity ~99.9%, Leung Hi-tech Co., China) and α -SiC (particle size ~2 μm , purity >99%, Carborundum Universal Limited, India) powders were the starting materials. Powder samples of ZrB₂ with 0, 5, 10, 15, 20, 25 and 30 vol. % SiC were mixed at 120 rpm for 1 hour in a zirconia cup with balls. To investigate the effect of mixing on final microstructure of the composites, some samples were prepared without efficient mixing. Then, samples were loaded into a graphite die and boron nitride spray was applied to all graphite surfaces. Hot pressing was completed in a graphite resistance-heated vacuum hot press furnace (made by Shenyang Weitai Science & Technology Development Co., Ltd., China). In each hot pressing experiment, 10 MPa pressure was applied as soon as the final isothermal temperature cycle started. Samples were initially heated at a rate of 12 $^{\circ}\text{C}/\text{min}$ up to 1000 $^{\circ}\text{C}$, given a dwell isotherm at 1000 $^{\circ}\text{C}$ for 30 min in order to remove volatile species from the powder batch, then heated again at a rate of 10 $^{\circ}\text{C}/\text{min}$ up to the designated temperatures. Above 1000 $^{\circ}\text{C}$, the temperature of the graphite die was monitored using an infrared temperature sensor (Model IT-6). Hot pressing was carried out at different temperatures (1700, 1850 and 2000 $^{\circ}\text{C}$), given a dwell isotherm for 30 min. Finally, the hot press furnace was cooled down naturally. One billet, with a diameter of 25 mm and thickness of 5 mm, was prepared for each experiment.

2.2. Characterization

X-ray diffraction (XRD) analysis (Cu lamp, $\lambda = 1.54 \text{ \AA}$, 40

kV, 30 mA, Siemens D5000 model) was carried out on the samples. Bulk density of samples was measured using the Archimedes' technique with distilled water as the immersing medium, and the relative density was calculated with respect to theoretical density. The theoretical density was estimated using rule of mixtures, based on starting compositions of the samples and pure component densities ZrB₂: 6.1 g/cm^3 and SiC: 3.2 g/cm^3 . Microstructure characterization was carried out by an optical microscopy (Nikon, Eclipse MA100, Japan), beside a scanning electron microscopy (Mira3 Tescan, Czech Republic). Chemical analysis was performed simultaneously with SEM, using energy dispersive spectroscopy (EDS). Samples were prepared for microscopy by a four-step mechanical polishing to 0.25 μm , using diamond abrasive. Some of the polished sections were thermally etched at 1600 $^{\circ}\text{C}$ for 30 min. The grain size was determined from optical microscopy images, using image analysis software (ImageJ 1.44p, Wayne Rasband, National Institute of Health, USA), after thermal etching in vacuum ($5 \times 10^{-2} \text{ Pa}$) at 1600 $^{\circ}\text{C}$ for 30 min.

3. Results and Discussion

Fig. 1 presents the SEM images of morphologies and the XRD of starting materials. As it seems, the only crystalline phases detected were ZrB₂ and SiC. As shown in Fig. 2, the densities decreased with increasing SiC content, due to lower density of SiC than ZrB₂ and/or decreasing hot pressing temperature and consequent incomplete densification. Based on this figure, it seems that by densification at 2000 $^{\circ}\text{C}$, the theoretical and experimental values are meeting each other in the ZrB₂–30 vol. % SiC composite.

Figure 1. SEM images of morphologies and XRD patterns of as-received powders; (a) ZrB₂ and (b) SiC.

Figure 2. Density of hot pressed ZrB_2 -SiC composites at different temperatures for 30 min under 10 MPa load.

Fig. 3 shows that the amount of porosity decreases as the sintering temperature or amount of SiC increases. Open pore is the dominant type of porosity in ZrB_2 -SiC composites, hot pressed at 1700 °C. But the type of pore changes completely to closed one at higher sintering temperatures. Since the progress of sintering process begins with elimination of open channels between starting powders, the nature of porosity changes gradually from open to closed form at final stages. Hence, no open pores exist at 1850 °C and higher temperatures.

Figure 3. Amount and type of porosities in hot pressed ZrB_2 -SiC composites at different temperatures.

Densification behavior of ZrB_2 -based composites were improved by adding SiC particulate. The monolithic ZrB_2 ceramic and the composites which have been reinforced using inadequate SiC particulates, demonstrated a sinterability lower than that of appropriate composite samples. Contamination of ZrB_2 powder by oxygen supports evaporation-condensation and grain coarsening mechanisms during hot pressing, which exacerbates the maximum reachable density. Achieving a denser composite with increasing additive content, manifestly confirmed the advantageous role of SiC in restricting such harmful mechanisms for densification. It seems that the cleaning of ZrB_2 powder surface from oxygen, through chemical interactions with SiC, is a key step to acquire fully dense materials.

The fracture surface of monolithic ZrB_2 ceramics, densified at 1850 and 2000 °C, were examined by SEM (Fig. 4). A grained structure with faceted ZrB_2 grains has been shown, as the fracture appeared to spread prevalently along an intergranular path. The $\text{ZrB}_2/\text{ZrB}_2$ boundary interfaces were seemingly free of secondary phases. Some pores were visible in the SEM micrographs of monolithic ZrB_2 ceramic, sintered at 1850 °C (Fig. 4-a), that had a relative density of ~89 %. On the other hand, since the relative density had been measured to be about 97 %, no discernible porosity was found in the hot pressed sample at 2000 °C (Fig. 4-b).

Figure 4. SEM micrographs of fracture surfaces of monolithic ZrB_2 ceramics, hot pressed at different temperatures; (a) 1850 °C, and (b) 2000 °C.

Examination of ZrB_2 -SiC composite by SEM showed that SiC particles were dispersed in the ZrB_2 matrix. The microstructure of ZrB_2 -30 vol. % SiC composite, hot pressed at 1700 °C, is shown in Fig. 5. It is consistent with

measured porosity value for the sample that has more than 8 percent open pores nearly without closed pores. It seems that mechanical interlocking between ZrB₂ and SiC is an important mechanism for densification at 1700 °C.

Figure 5. Micrographs of the ZrB₂–30 vol. % SiC, hot pressed at 1700 °C; (a) SEM image on a polished surface and elemental maps showing the distribution of (b) O, (c) Zr, and (d) Si.

In the microstructure of monolithic ZrB₂ and ZrB₂–30 vol. % SiC composite, after hot pressing at 1850 °C (Fig. 6), neck formation between ZrB₂ particles in both samples was observed. There were more obvious grain boundaries between ZrB₂ and SiC in the composite sample. It seems that the density of ZrB₂–30 vol. % SiC composite is higher than that of monolithic ceramic, hot pressed in the same condition. This is in agreement with the result of porosity curve versus SiC addition (Fig. 3), because the amount of porosity in the composite sample is three times less than the other one. However, by the formation of necks, the density increased after hot pressing at 1850 °C in all compositions in comparison with samples processed at 1700 °C (as shown in Fig. 2). A highly dense network of dislocations in ZrB₂ grain was found by Patel et al. [14] in TEM images of a sample hot pressed at 1850 °C under 25 MPa. Limited grain growth and a network of dislocations in the sample suggested that the dominant densification mechanism might be plastic deformation of ZrB₂ grains.

Figure 6. SEM micrographs of the samples hot pressed at 1850 °C; (a) monolithic ZrB₂ ceramic, and (b) ZrB₂–30 vol. % SiC composite.

In contrast, relatively fully dense samples were obtained by hot pressing at 2000 °C. SEM observations of the polished sections (Fig. 7) confirmed that residual porosity is not substantial.

The XRD analysis (not shown here) from fully dense composites, except ZrB₂ and SiC, did not detect any extra crystalline phases. Patel et al. have shown a considerable grain growth and extinction of dislocations in a sample hot pressed at 2000 °C, and therefore, grain boundary diffusion could be the dominant densification mechanism. The ruin of dislocations at interfaces may be due to the diffusion of

atoms through grain boundaries [14]. Intergranular SiC particles inside ZrB_2 grains (Fig. 8 and Fig. 10) prove a meaningful mass transfer among the ZrB_2 particles, which in effect brought the elimination of the pores to a fortunate ending.

Average ZrB_2 grain sizes in the samples (consolidated at 2000 °C) were measured from the polished and thermally etched surfaces (Fig. 8). As the results are shown in Fig. 9, largest grain sizes belonged to monolithic ZrB_2 ceramic (~15.4 μm). For the composite samples, average ZrB_2 grain size reached ~3.5 μm , when 30 vol. % SiC was added to the ZrB_2 powder under the same conditions. Hence, the effect of SiC as a ZrB_2 grain growth controller is demonstrated clearly.

The influence of inefficient mixing of the starting powders on the final microstructure of the composites has been revealed in Fig. 10. In the optical microscope images of the polished and thermally etched surfaces of nearly fully dense (but without proper mixing) ZrB_2 -based composites, there is a clear boundary that has divided the microstructure into two regions. In the region with relatively good distribution of SiC phase, the ZrB_2 grains seem to have normal size (based on Fig. 9), but on the other side, ZrB_2 grains grow dramatically due to lack of SiC phases, reaching a microstructure like monolithic ZrB_2 ceramic. Therefore, efficient mixing of the starting powders is very critical in order to achieve a fine-grained homogenous microstructure.

Figure 7. SEM micrographs of the composites hot pressed at 2000 °C; (a) ZrB_2 -20 vol. % SiC, and (b) ZrB_2 -30 vol. % SiC. Light grains are ZrB_2 and dark grains are SiC.

Figure 8. Optical microscope images of polished and thermally etched surfaces of ZrB_2 -based composites hot pressed at 2000 °C; (a) ZrB_2 -15 vol. % SiC, and (b) ZrB_2 -25 vol. % SiC (Light grains are ZrB_2 and dark grains are SiC).

Figure 9. Average ZrB_2 grain size in the ZrB_2 -SiC composites microstructure as a function of amount of SiC additive (hot pressed at 2000 °C for 30 min under 10 MPa load).

4. Conclusions

The effect of consolidating temperature and SiC content as a reinforcement on the microstructure of hot pressed ZrB_2 -SiC composites under 10 MPa was investigated. Increasing the amount of SiC particles and using higher sintering temperatures enhanced the densification of ZrB_2 -SiC composites, reaching a fully dense sample by hot pressing at 2000 °C for ZrB_2 -based composite, containing 30 vol. % SiC.

The microstructure of composites is consistent with measured values for porosity. Mechanical interlocking between ZrB₂ and SiC, neck formation between ZrB₂ particles alongside with more obvious grain boundaries between ZrB₂ and SiC, and Intergranular SiC particles inside ZrB₂ grains was observed in the microstructures of composites densified at 1700, 1850, and 2000 °C, respectively. Achieving a finely grained homogenous microstructure was strongly depended on an efficient mixing of the starting powders.

Figure 10. Optical microscope images of polished and thermally etched surfaces of ZrB₂-based composites, hot pressed at 2000 °C; (a) ZrB₂-20 vol. % SiC, and (b) ZrB₂-30 vol. % SiC (Light grains are ZrB₂ and dark grains are SiC).

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