

The dominant densification mechanisms of ZrB_2 -SiC composites were identified at different hot pressing temperatures. For the samples hot pressed at 1700, 1850 and 2000 °C, liquid phase sintering/particle fragmentation/rearrangement, plastic deformation and atomic diffusion were determined as the dominant densification mechanisms, respectively [13,22]. The density of hot pressed TiB_2 ceramic increases rapidly at the initial sintering stage, but raises slowly at the final stage. Hence, the densification mechanisms of TiB_2 ceramics are not the same at different hot pressing stages. The plastic flow and diffusion creep are the dominant densification mechanisms at initial and final sintering stages, respectively [11]. The TiB_2 -SiC ceramics with different SiC contents were in-situ synthesized recently by the reactive hot pressing process at 1700 °C under 32 MPa. The amount of SiC and the sintering time were found to have significant influences on the microstructure and mechanical properties of the mentioned composites [23,24]. On the other hand, the applied pressure was identified as the most effective factor on the densification and hardness of hot pressed ZrB_2 -SiC composites [25].

In this work, the monolithic ZrB_2 and TiB_2 ceramics as well as ZrB_2 -SiC and TiB_2 -SiC ceramic composites with different SiC contents (15 vol% and 30 vol%) were densified by the hot pressing process at 1850 °C for 60 min under 20 MPa. The effects of SiC on the microstructure and sinterability of the ceramics were studied. The microstructure and sintering behavior of the hot pressed samples were investigated by scanning electron microscope, energy dispersive spectrometer and X-ray diffractometer.

2. Experimental procedure

2.1. Materials and process

Commercially available ZrB_2 powder (particle size $\sim 5 \mu m$, purity $> 99\%$, Leung Hi-tech Co., China), TiB_2 powder (particle size $\sim 5 \mu m$, purity $> 99\%$, Xuzhou Hongwu Nanometer Material Co., China) and α -SiC powder (particle size $\sim 5 \mu m$, purity $> 98\%$, Carborundum Universal Limited, India) were used as raw materials. The powder samples of ZrB_2 and TiB_2 with 0 vol%, 15 vol% and 30 vol% SiC were ball-mixed for 120 min in a polyethylene cup with SiC balls and ethanol as mediums. Then the mixed slurries were dried in a rotating heater and sieved by a 100-mesh sieve. After that, the powder mixtures were put into a graphite die coated with boron nitride and lined with a flexible graphite foil. The hot pressing process was conducted in a graphite resistance-heated furnace (Shenyang Weitai Science & Technology Development Co., Ltd., China) with a vacuum atmosphere of $< 0.05 Pa$, hot pressing temperature of 1850 °C, dwell time of 60 min, and applied pressure of 20 MPa. Each sample was heated at a rate of 15 °C/min up to 1000 °C, then was given a dwell isotherm at 1000 °C for 20 min in order to eliminate volatile gases, and finally was heated again at a rate of 15 °C/min up to 1850 °C. Above 1000 °C, the die temperature was monitored using an infrared thermometer (Dikai IT-6, China) through a sapphire window. Finally, the hot press chamber was cooled down naturally at an average rate of 10 °C/min. Three billets, with a diameter of 24 mm and a thickness of $\sim 5 mm$, were fabricated for each composition.

2.2. Characterization

Scanning electronic microscopy (SEM: Mira3 Tescan, Czech Republic), energy dispersive spectroscopy (EDS: DXP-X10P Digital X-Ray Processor) and high resolution X-ray diffraction analysis (HRXRD: Bruker D8 Advance, Germany) were used to evaluate the microstructure, chemical analysis, and phase identification of the hot pressed samples, respectively. The relative density of the samples was calculated as the bulk density was divided by the theoretical density. The bulk density was measured by the Archimedes' method using distilled water as the immersing medium. The theoretical density was estimated by the rule of mixtures assuming the true densities of 6.1 g/cm³ for ZrB_2 , 4.5 g/cm³ for TiB_2 , and 3.2 g/cm³ for SiC. Image analysis method (ImageJ 1.44p software, Wayne Rasband, National Institute of Health, USA) was used to determine the grain size. In this way, the samples were mechanically polished using diamond abrasive and then thermally etched at 1600 °C for 30 min in vacuum atmosphere ($5 \times 10^{-2} Pa$). Thermodynamic calculations were performed with the HSC Chemistry software (ver. 5.11, Outokumpu Research Oy, Pori, Finland).

3. Results and discussion

3.1. Densification and grain growth

Fig. 1 shows the relation between the SiC content and relative density of ZrB_2 and TiB_2 based ceramics. Without adding SiC, the relative densities of monolithic ZrB_2 and TiB_2 ceramics after hot pressing at 1850 °C were $94.0 \pm 0.2\%$ and $95.2 \pm 0.4\%$, respectively.

The relative density of ZrB_2 ceramic reached $98 \pm 0.4\%$ with adding 15 vol% SiC, and $97 \pm 0.5\%$ with adding 30 vol% SiC. This observation suggests that SiC can improve the densification of ZrB_2 -based ceramics when SiC content is about 15 vol%. However, if the reinforcement content reaches 30 vol%, the relative density decreases slightly, which may be a result of the pores formation caused by excessive SiC. Our group has already reported that the relative density of ZrB_2 -SiC composites rose

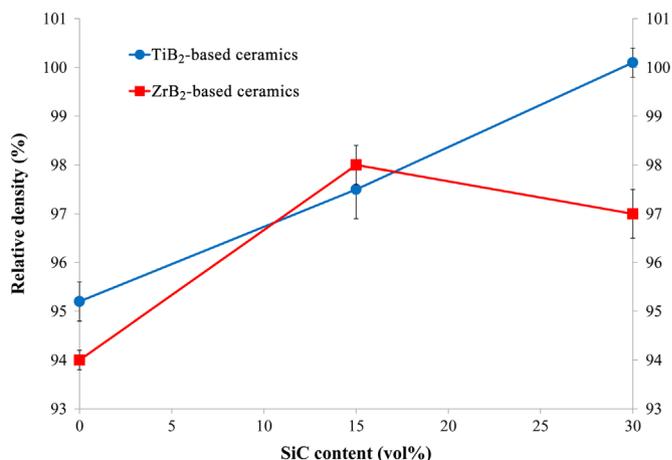


Fig. 1. Relative density of hot pressed ZrB_2 and TiB_2 based ceramics with different SiC additions.

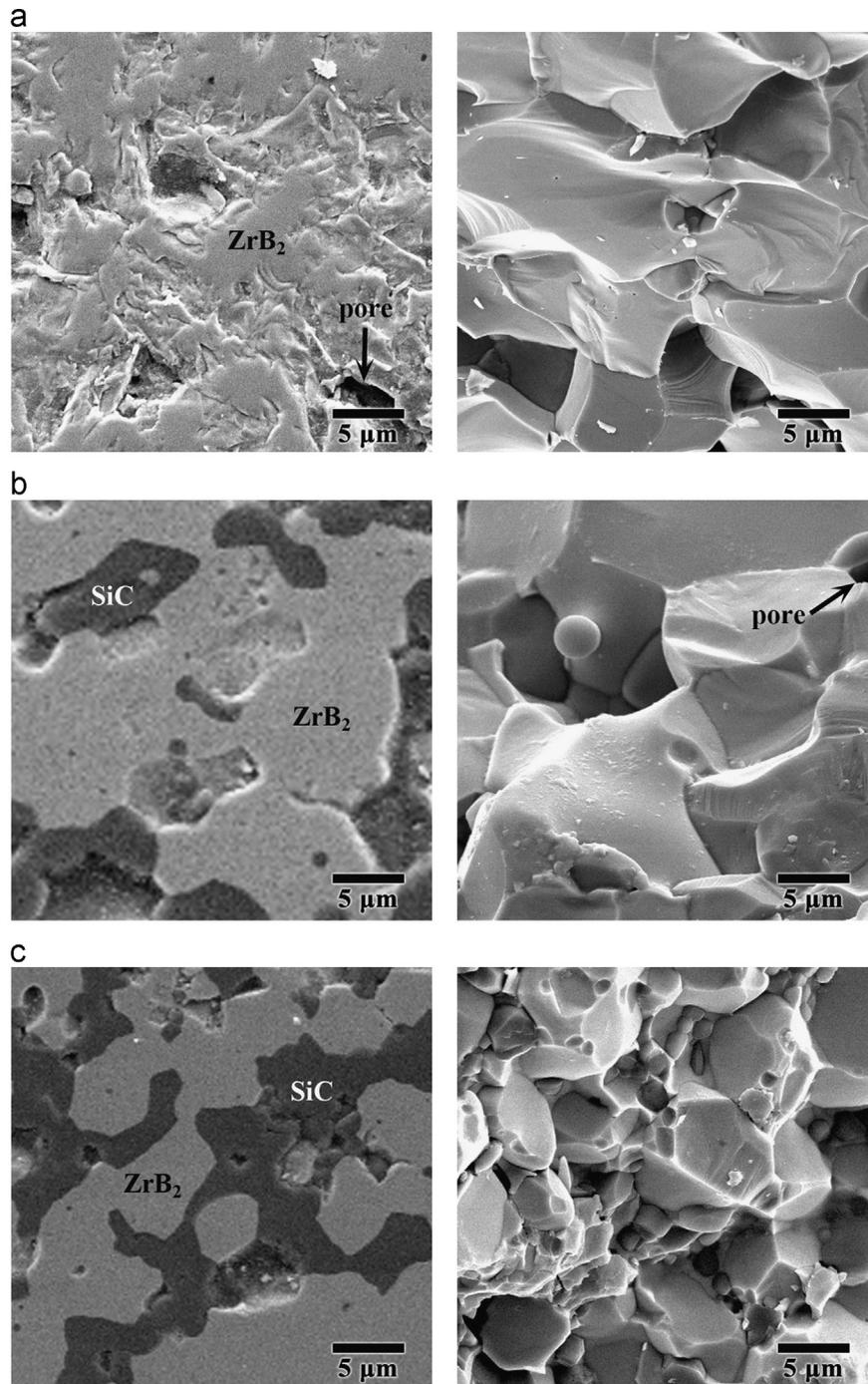


Fig. 3. SEM micrographs of the polished and fracture surfaces of hot pressed (a) ZrB_2 , (b) ZrB_2 -15 vol% SiC and (c) ZrB_2 -30 vol% SiC ceramics.

addition to the anticipated TiB_2 and SiC phases, TiC phase is also detected after hot pressing (Fig. 5b). Titanium carbide was not a part of the starting powders; then, it seems to form during the hot pressing process. The height of TiC peaks is higher than that of SiC which can be attributed to its greater volume fraction than that of SiC in the final microstructure of the hot pressed composite. This outcome is also consistent with the SEM micrograph of the polished surface of TiB_2 -30 vol% SiC composite (Fig. 4c).

Torizuka et al. [12] proved that the B_2O_3 surface layer of TiB_2 powder evaporates before the densification, but the TiO_2

surface layer remains in the batch. They showed that the TiO_2 can react with SiC which leads to the formation of TiC and amorphous SiO_2 (Eq. (1)):



The phase identification by HRXRD analysis (Fig. 5b) verifies the formation of TiC in the sintered TiB_2 -30 vol% SiC composite. This observation indicates that reaction Eq. (1) has occurred. Similar to Eq. (1) for the TiB_2 -SiC composites, a hypothetical reaction can be expressed by Eq. (2) for the ZrO_2 surface layer of ZrB_2 -SiC composites:

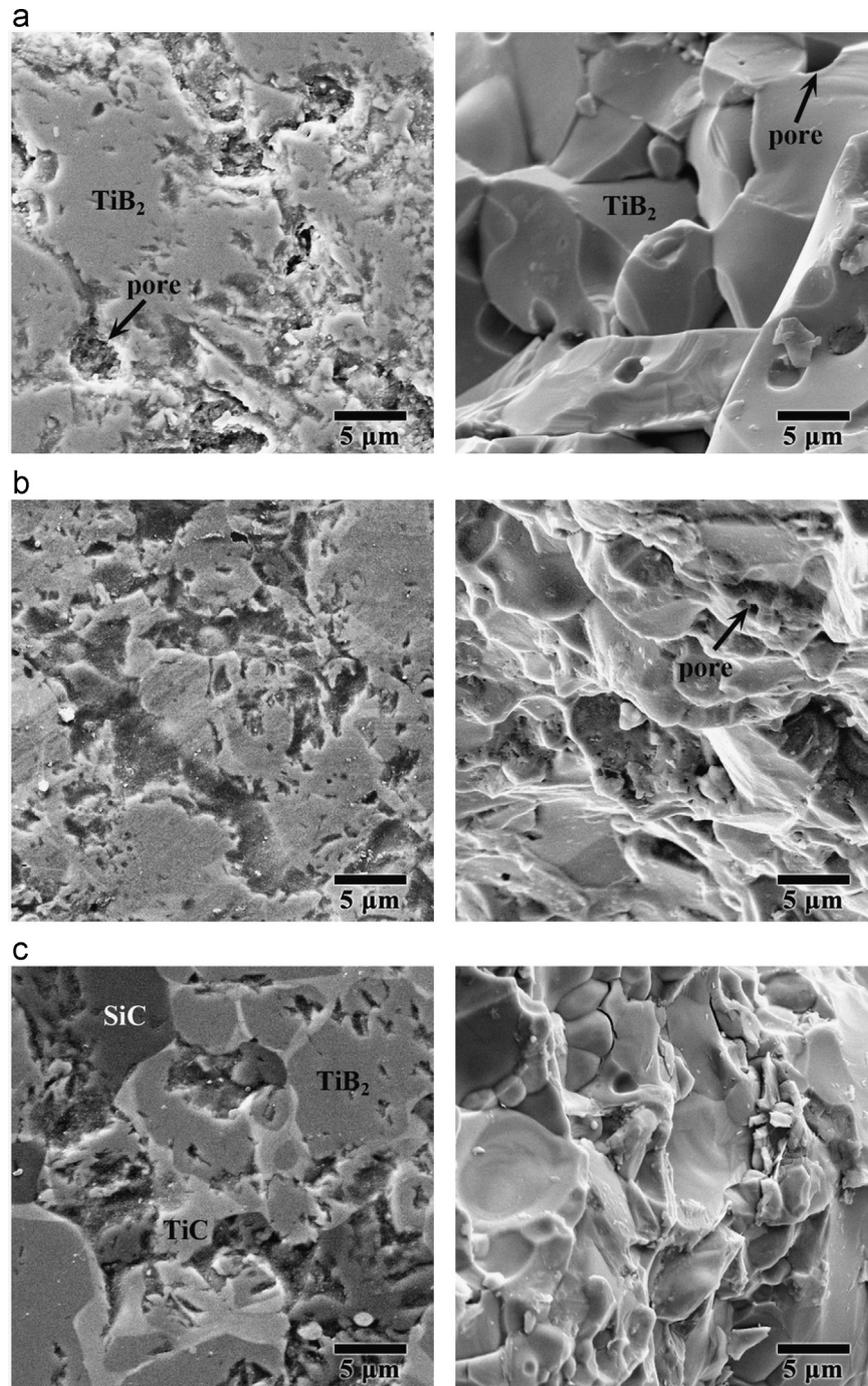


Fig. 4. SEM micrographs of the polished and fracture surfaces of hot pressed (a) TiB_2 , (b) TiB_2 -15 vol% SiC and (c) TiB_2 -30 vol% SiC ceramics.



On the other hand, the formation of ZrC in the hot pressed ZrB_2 -30 vol% SiC ceramic was not detected in its HRXRD pattern (Fig. 5a) which is against the occurrence of Eq. (2). Fig. 6 shows the Gibbs free energy values as a function of temperature which were obtained by the thermodynamic calculations of reactions Eqs. (1) and (2). The Gibbs free energy values of reaction Eqs. (1) and (2) from the room temperature to the sintering temperature are negative and positive, respectively. Hence, regarding the thermodynamics,

Eq. (1) occurs during the hot pressing process but Eq. (2) does not happen. However, our group has previously reported the formation of ZrC in the ZrB_2 -SiC composites when a tertiary component (such as graphene nano-platelets [36], graphite nano-flakes [37], carbon nanotubes [38], carbon fibers [39] or nano- ZrO_2 [40,41]) was being added to the powder mixture.

The amorphous SiO_2 melts during the hot pressing at 1850°C ; therefore, it improves the sinterability of TiB_2 particles by the liquid phase sintering mechanism which also results in the rearrangement of particles. However, Torizuka et al. [12] observed that only the liquid phase sintering is not enough to

