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LETTER

Effect of SiC particle dispersion on thermal properties of SiC particle-dispersed ZrB_2 matrix composites

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ZrB_2 ceramics have been developed for various structural and functional applications in ultra-high temperature environments [1–5]. The addition of SiC has been shown to be effective in enhancing the sinterability, mechanical properties and oxidation resistance of ZrB_2 [5–8]. Although some experimental results [9–11] reported that the addition of SiC particle also improves the thermal conductivity of ZrB_2, no systematic study has been conducted to prove the effectiveness of SiC dispersion on the thermal properties of SiC particle-dispersed ZrB_2 matrix composites (hereafter denotes as SiC/ZrB_2 composites). In this study, SiC/ZrB_2 composites with different SiC particle volume fraction were fabricated and effect of the SiC particle volume fraction on thermal properties of SiC/ZrB_2 composites were examined.

SiC/ZrB_2 composites were fabricated by spark plasma sintering (SPS) process using a mixture of SiC and ZrB_2 powders. The starting powder of ZrB_2 (Grade F, Japan New Metal, Tokyo, Japan) had an average particle size of 2.1 μm and a purity of 98.0 wt%. The starting powder of α-SiC (GC#800, Showa Denko, Tokyo) had an average particle size of ~22 μm and a purity of 99.0 wt%. SiC particle volume fraction in ZrB_2 matrix was set to be $f_p = 0.1$, 0.2, and 0.3, which was controlled by changing the weight ratio of the powders before mixing the powders. Here, the densities of ZrB_2 and α-SiC are 6.12 [10] and 3.22 g/cm^3 [11], respectively. The powder mixtures were fully wet-milled using SiC jar with ethyl-alcohol at 150 rpm for 3 h, and then, dried in ambient air, using an electric resistance heater. Thereafter, the dried mixtures were sieved with 250-screen size mesh.

The sieved powder mixture was put into a graphite die and sintered using SPS system (SPS-1030, Sumitomo Coal Mining Co. Ltd., Tokyo). Sintering was conducted at 2,173 K for 1.8 ks under Ar gas atmosphere. A uniaxial pressure of 40 MPa was applied to powder mixture during entire SPS process. Sintered specimens had a disk-shape with a diameter of ~10 mm and a thickness of ~3 mm. For comparison purpose, monolithic ZrB_2 was also sintered using the same SPS process, although wet-milling time was 24 h and sintering time was 180 s.

Densities of the composites were measured at room temperature (298 K), by the Archimedes method with ethyl-alcohol as the immersion medium. X-ray diffraction was used for identification of crystalline phase in the composites using Cu-Kα radiation with a scanning rate of 0.03 deg/s. Microstructure of the composites was examined by scanning electron microscope (SEM). Grain sizes of sintered ZrB_2 matrix, d_m, and SiC particle, d_p, were determined from SEM micrographs using "Feret diameter" [12] from a minimum 100 measurements.

Parallel surfaces, i.e., perpendicular to applied load direction, of as-sintered composites were progressively polished to a thickness of ~2 mm, and used for measurements of thermal properties. Final polishing was done using 0.5 μm diamond paste. Thermal diffusivity of the composites, α_c, was measured, using the laser-flash method (LFA447/2-4N, NETZSCH-Geratebau GmbH, Postfach,

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Germany), according to ASTM E 1461 [13]. Detailed measurement procedure was the same as the previous reports [11, 14]. The flash source was a Xenon flash lamp operating in the output wavelength range of 0.15–2 μm. This high-power Xenon flash lamp, which was surrounded by a parabolic mirror, was able to supply radiant pulse energy up to ~10 J. Before measurements, the surfaces of polished composites were coated with a colloidal graphite spray in order to enhance the absorption of the Xenon light pulse energy and the emission of infrared radiation to a temperature detector. Also, heat capacity, C_c, and thermal conductivity, κ_c, were determined with polycrystalline Al_2O_3 as a reference material. All the measurements were performed in ambient air at room temperature (296 K). The nominal accuracy of the thermal diffusivity measurements was less than ±3%, and that of the specific heat was less than ±5%.

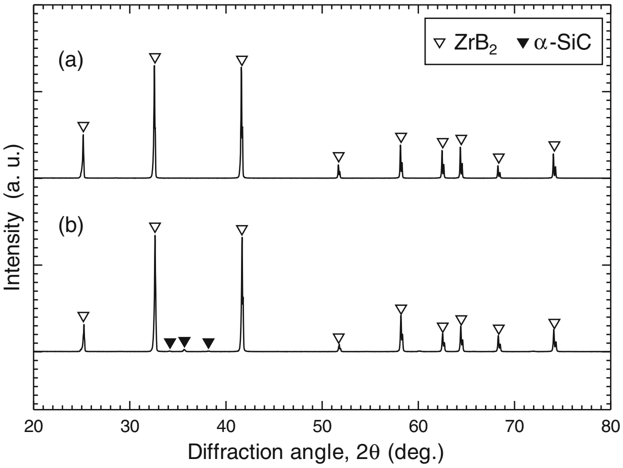

Fig. 1 X-ray diffraction patterns of monolithic ZrB_2 (**a**), SiC particle-dispersed ZrB_2 matrix composite ($f_p = 0.3$) (**b**)

Figure 1 shows X-ray diffraction profiles of a monolithic ZrB_2 (a) and SiC/ZrB_2 composite with SiC particle volume fraction of 0.3 (b). Only hexagonal ZrB_2 and α-SiC were detected from the composite. This result shows that no new phases are formed during SPS process, within the sensitivity of XRD. The result is the same independent of SiC particle volume fraction. Figure 2 shows typical microstructures of monolithic ZrB_2 and SiC/ZrB_2 composites. Dispersed SiC particles, residual pores and ZrB_2 matrix are clearly observed in the composites. The bright-grey regions are ZrB_2 grains, the dark-grey regions are SiC particles, and the black-regions are pores. It should be noted that some of SiC particles are removed from the surface during polishing process, however, easily distinguished from initially existed pores. Most of pores are located at a junction of adjacent grains and interface between SiC particle and ZrB_2 matrix. The pore contents of used composites are less than 0.006, and that of the monolithic ZrB_2 matrix is 0.044. Table 1 lists some

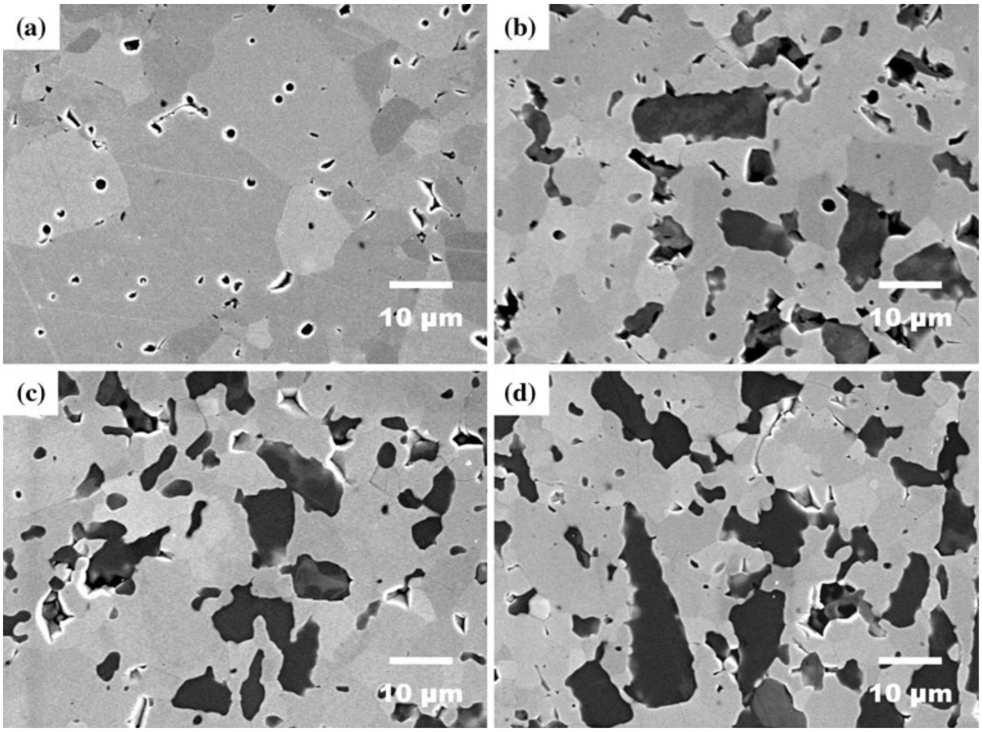

Fig. 2 Typical backscattering electron field-emission scanning electron microscopy images of monolithic ZrB_2 (**a**), SiC particle-dispersed ZrB_2 matrix composites, $f_p = 0.1$ (**b**), $f_p = 0.2$ (**c**), and $f_p = 0.3$ (**d**)

Table 1 Compositions, relative densities, and average diameters and deviations of ZrB_2 and SiC grain using Feret diameter method

Volume fraction of SiC, f_p	Relative density (%)	Average grain size of matrix (μm)	Average size of particle (μm)
0	95.6	3.0	
0.1	99.4	3.5	8.9
0.2	99.6	3.4	8.9
0.3	99.6	3.2	8.9

characteristics of the monolithic ZrB_2 and SiC/ZrB_2 composites. The average SiC particle size is determined to be ≈8.9 μm, which is independent of SiC content. In contrast, the average grain size of ZrB_2 matrix in the composite tends to decrease slightly with the increase of SiC content. For example, the average grain size of ZrB_2 at $f_p = 0.1$ is ≈3.5 μm, and it slightly decreases to ≈3.2 μm at $f_p = 0.3$. This indicates that addition of SiC particles have tendency to inhibit grain growth of ZrB_2 matrix during SPS process. Similar behaviors were reported in the same material systems sintered by hot-press process [5, 7].

The measured thermal diffusivities and heat capacities of monolithic ZrB_2 and SiC/ZrB_2 composites are summarized in Figs. 3 and 4, respectively. Thermal diffusivity of the composites was measured to be in the range of 35.05–45.54 mm^2/s, and the heat capacity was in the range of 0.53–0.58 J/g K. Figure 5 shows plots of thermal conductivity of composites, κ_c, at room temperature versus volume fraction of SiC particle. Thermal conductivity of the composites was found to increase with the increase of SiC content. The maximum thermal conductivity of SiC/ZrB_2 composite obtained in this study is $\kappa_c \approx 138.2$ W/m K at a volume fraction $f_p = 0.3$. The enhancement of thermal conductivity measured in SiC/ZrB_2 composite seems reasonable since the thermal conductivity of SiC is higher than that of ZrB_2. For example, thermal conductivity of SiC is reported to be ~125 W/m K [14] for polycrystalline and ~490 W/m K [9] for single crystal, respectively, and the thermal conductivity of single crystal ZrB_2 is reported to be ~100 W/m K along *c*-axis and ~140 W/m K along a-axis [15] at room temperature.

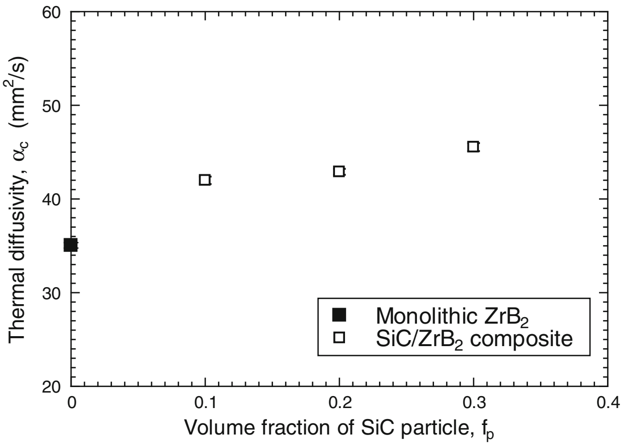

Fig. 3 SiC volume fraction dependence of the thermal diffusivity of SiC particle-dispersed ZrB_2 matrix composites

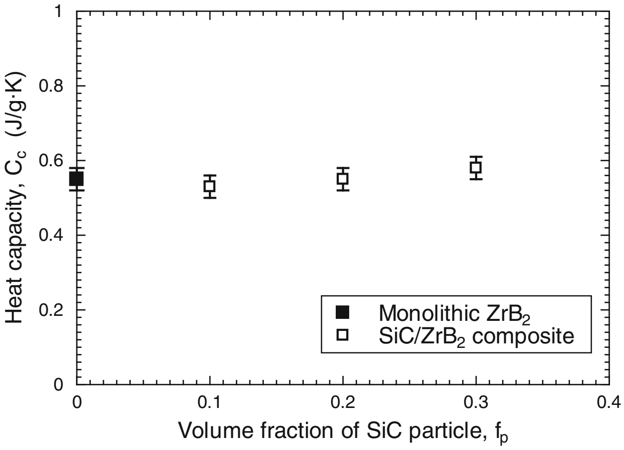

Fig. 4 SiC volume fraction dependence of the heat capacity of SiC particle-dispersed ZrB_2 matrix composites

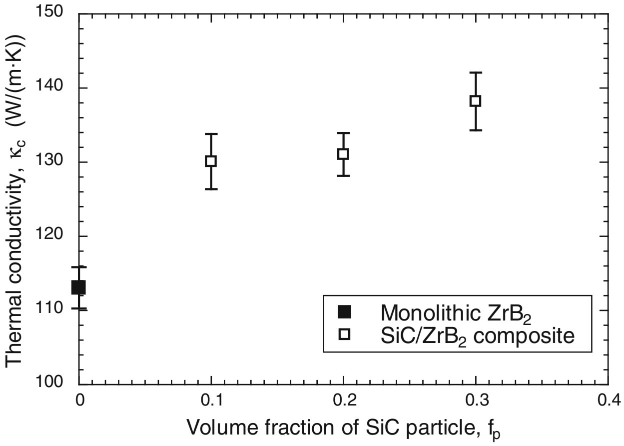

Fig. 5 SiC volume fraction of the thermal conductivity of SiC particle-dispersed ZrB_2 matrix composites

The highest values of thermal conductivity of SiC/ZrB_2 composite with volume fraction $f_p = 0.2$ were reported to be ~98.7 W/m K at a temperature of 373 K [16], and to be ~103.8 W/m K at a temperature of 298 K [17]. Recent report by Zimmermann et al. [9] showed that thermal conductivity at room temperature of monolithic ZrB_2 and SiC/ZrB_2 composite with $f_p = 0.3$ was ~53 and ~62 W/m K, respectively. Zimmermann et al. [9] has also shown that the thermal conductivity tends to increase with the increase of grain size. For example, the thermal conductivity of ZrB_2 with grain sizes of 6 and 15 μm was determined to be ~53 and ~85 W/m K, respectively. These reports suggest that ZrB_2 with larger grain size leads to higher thermal conductivity [9]. The large size SiC particle dispersion is another factor for improvement of thermal conductivity of ZrB_2 composites, because the total area between SiC particle and ZrB_2 matrix tends to decrease with the increase of SiC particle size. Further systematic study is needed to further prove the effectiveness of SiC particle dispersion on the thermal properties of SiC/ZrB_2 composites.

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