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# SiC–$B_4C$ composites for synergistic enhancement of thermoelectric property

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**Abstract**

SiC–$B_4C$ composites were fabricated by hot pressing of β-SiC and $B_4C$ powder mixture. The Seebeck coefficient was determined at 300–900 °C in air. The SiC–$B_4C$ composites exhibited very high value. Especially, the Seebeck coefficient of SiC–30wt.%$B_4C$ composite was about 700 μ/K at 900 °C. Such a high Seebeck coefficient is very attractive. Monolithic SiC and $B_4C$ had the Seebeck coefficient of 100–400 μV/K, respectively. In SiC–$B_4C$ composite system, the Seebeck coefficient had been increased by the combination of SiC and $B_4C$. In TEM observation, many stacking faults were observed in SiC–$B_4C$ composites. The presence of stacking faults may be one reason for the high Seebeck coefficient of SiC–$B_4C$ composite.

*Keywords:* $B_4C$; Composites; Grain size; Seebeck coefficient; SiC

## 1. Introduction

Thermoelectric material is useful for direct conversion between thermal and electric energy. For this application, high-temperature semiconductors have been receiving an attention. Boron carbide is semiconductors, having a good stability in high temperatures.[1] We noticed the possibility of SiC–$B_4C$ composite as a thermoelectric material. It was reported that, in SiC–70wt.%$B_4C$ eutectic composite fabricated by arc melting method, the Seebeck coefficient was very high 750 μV/K around 800 °C.[2] However, the eutectic point is too high as about 2300 °C[3] to produce the melt and the fine control of microstructure is difficult by the melting method.

In this work, SiC–$B_4C$ composites were fabricated by hot pressing of powder mixture, and the sinterabilities, mechanical properties and thermoelctric properties were investigated.

## 2. Experimental procedure

β-SiC powder (Ibiden Co. Ltd., particle size 0.3 μm) and $B_4C$ powder (Rare Metallic Co. Ltd., particle size 1.3 μm) were mixed in a agate mortar. $Al_2O_3$ powder (Nippon Aerosil, particle size 0.02 μm) was used as sintering aid. The mixed powder was hot-pressed using graphite mold for 0.5 h at 1800–2100 °C under uniaxial pressure of 50 MPa in Ar atmosphere. The hot-pressed bodies were polished with diamond abrasive. The bulk density was measured by the Archimedes method. The crystalline phases were identified by X-ray diffraction (XRD). The surface microstructure was observed by scanning electron microscopy (SEM) after etching with $K_3Fe(CN)_6$–NaOH aqueous solution. Thinned specimens were observed by transmission electron microscopy (TEM). The hardness and fracture toughness were determined by the Vickers indentation method at room temperature (load 10 kg), in which the Niihara's equation[4] was used for calculation. The Seebeck coefficient was determined from the voltage generated by temperature gradient of about 10 °C at 300–900 °C in air.

## 3. Results and discussion

### 3.1. Sintering behavior

Fig. 1 shows the relative densities of SiC–30wt.%$B_4C$ and SiC–70wt.%$B_4C$ as a function of hot-pressing temperature. The relative density reached up to 99% at 2000 °C in SiC–70wt.%$B_4C$ without additive. SiC–30wt.%$B_4C$ was densified at a lower temperature of 1900 °C. The sintering aid was not necessarily

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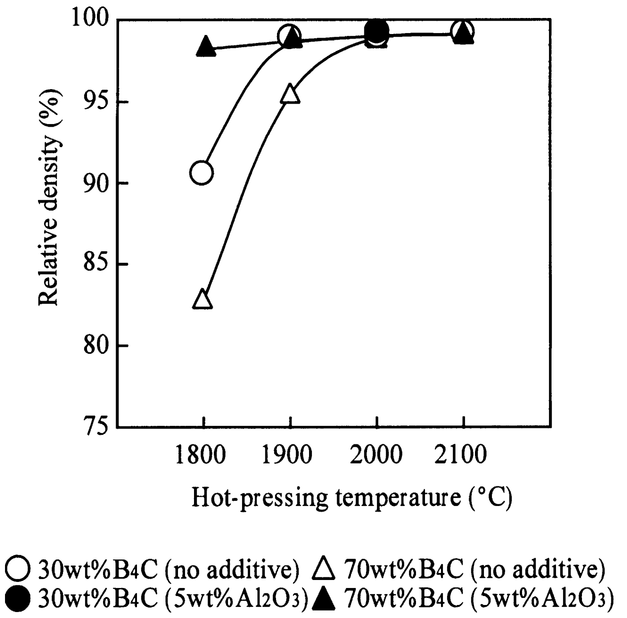

Fig. 1. Change in relative density of SiC–$B_4C$ composite with sintering temperature.

required because $B_4C$ works as sintering aid for SiC and $B_4C$ itself is sinterable without additive. The densification was promoted by addition of 5 wt.% $Al_2O_3$, and the relative density of SiC–30wt.%$B_4C$ reached about 99% at 1800 °C. This may be due to a liquid phase sintering mechanism caused by the oxide additive.

### 3.2. Microstructure

Fig. 2 shows the SEM images of surface microstructure after chemical etching. The white region is assinged to SiC phase and the black region to $B_4C$ phase. In SiC–30wt.%$B_4C$, SiC formed the network structure and $B_4C$ was isolated in SiC matrix. In SiC–70wt.%$B_4C$, SiC was isolated in $B_4C$ matrix. When $Al_2O_3$ was added, β-SiC was partially transformed into α-SiC, and rod-like SiC grains were observed. The rod-like grain growth may be due to the β-α transformation during liquid phase sintering. Fig. 3 shows the TEM image of thinned specimen. The more plane defects like as grain boundary and stacking fault were observed in SiC–30wt.%$B_4C$ than 70 wt.%$B_4C$.

### 3.3. Mechanical properties

Fig. 4 shows the change in hardness and fracture toughness by addition of $B_4C$ to SiC. The hot-pressing temperature was 2000 °C. Compared with monolithic SiC, the hardness was high in SiC–$B_4C$ composites because $B_4C$ has a higher hardness than SiC. However, the fracture toughness slightly decreased. The addition of $Al_2O_3$ increased the hardness of the composites, reaching about 30GPa, but the fracture toughness was not increased. These results indicate that $B_4C$ inclusions are not effective to improve the fracture toughness of SiC. The increase in hardness by $Al_2O_3$ addition may be due to the bonding strength between grains of SiC and $B_4C$. With $Al_2O_3$ additive, rod-like SiC grains were formed, but gave no effect on the fracture toughness. In all samples, the crack deflection was not observed.

### 3.4. Thermoelectric properties

Fig. 5 shows the Seebeck coefficient of SiC–$B_4C$ composites as a function of temperature. $B_4C$ and B-doped SiC are known to be P-type semiconductors. The composites also had the P-type of semiconductivity. In 30 wt.%$B_4C$ without additive, the Seebeck coefficient was the highest as about 700 μV/K at 900 °C. Monolithic SiC sintered with $Al_2O_3$ additive had the Seebeck coefficient of 100–400 μV/K. The Seebeck coefficient of $B_4C$ (non-additive) was the same level. Compared with these data, the Seebeck coefficient had been increased by the combination of SiC and $B_4C$. The Seebeck coefficient was lower in 70 wt.%$B_4C$ than in 30 wt.%$B_4C$, and decreased by $Al_2O_3$ addition.

The 30 wt.%$B_4C$ composite exhibited the extremely high Seebeck coefficient, which is comparable to that of 70 wt.%$B_4C$ eutectic composite reported by Goto et al.

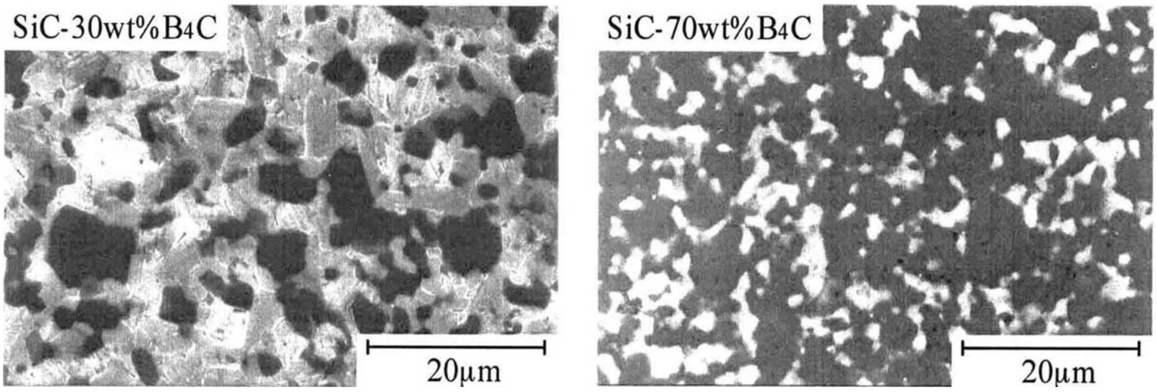

Fig. 2. SEM photographs of etched surface of SiC–$B_4C$ composites (hot pressing: 2000 °C without additive).

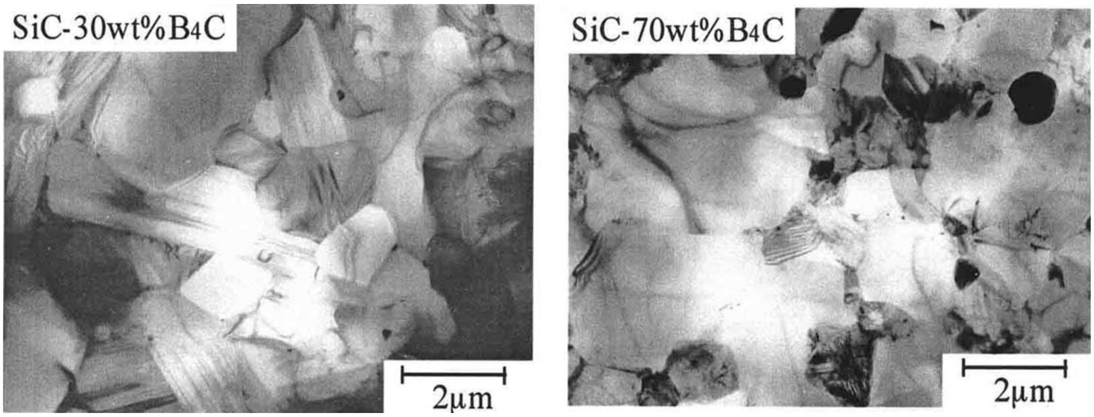

Fig. 3. TEM photograph of SiC–$B_4C$ composite (hot pressing: 2000 °C without additive).

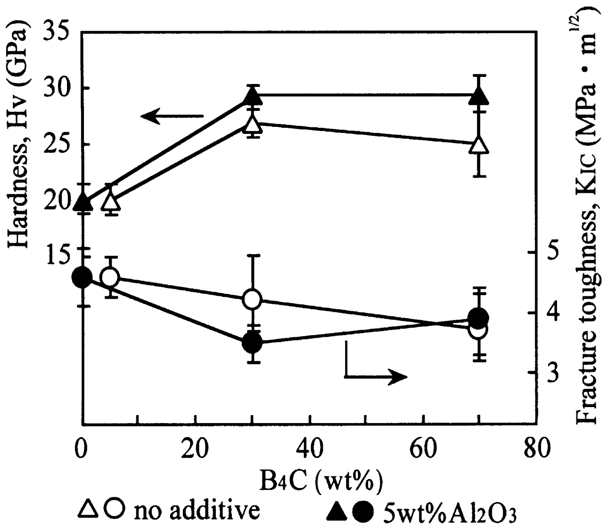

Fig. 4. Hardness and fracture toughness of SiC–$B_4C$ composites (hot pressing: 2000 °C).

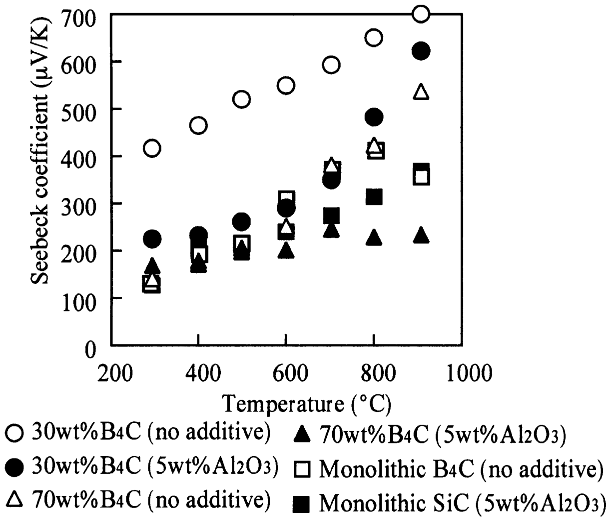

Fig. 5. Seebeck coefficient of SiC–$B_4C$ composites (hot pressing: 2000 °C).

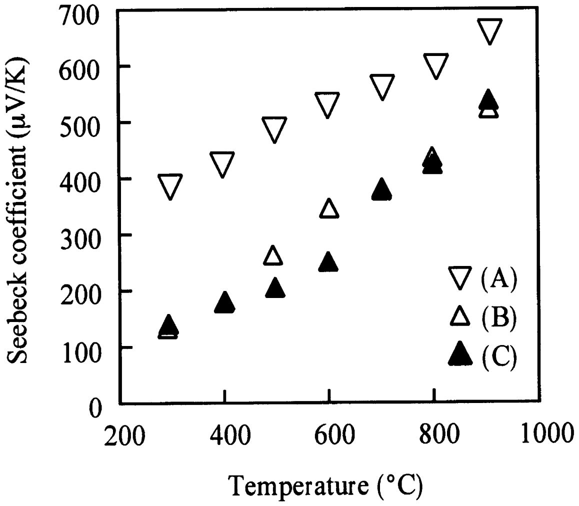

Fig. 6. Seebeck coefficient of SiC–70wt.%$B_4C$ composites (hot pressing: 2000 °C without additive).

although the composition was different. The Seebeck coefficient of SiC–$B_4C$ composite increased with a rise of temperature. Especially, the temperature dependencies in 30 wt.%$B_4C$ with $Al_2O_3$ additive and 70 wt.%$B_4C$ without additive were very large. It was reported that the temperature dependencies of SiC was explained by the phonon drag effect relating to plane defects such as stacking fault in crystalline grains and grain boundaries.[5] In 70 wt.%$B_4C$ eutectic composite fabricated by arc melting method, the high Seebeck coefficient and the large temperature dependency were presumed to be related to the plane defects such as fine lamellar structure of eutectic composite and many stacking faults.[2] In the present work, the stacking faults in SiC and $B_4C$ phases were also observed as shown in Fig. 3. The presence of stacking faults may be one reason for the high Seebeck coefficient of 30 wt.%$B_4C$.

The finer microstructure of 30 wt.%$B_4C$ than 70 wt.%$B_4C$ was caused by the starting powders and may affect the higher Seebeck coefficient. Therefore, 70 wt.%$B_4C$ composites were fabricated by the other powders. Sample (A) was an in-site composite, which was fabricated by 30 nm β-SiC, 0.1 μm boron and 20 nm carbon powders. $B_4C$ phase was formed by boron and carbon powder during hot pressing. (B) was prepared by 30 nm β-SiC and 1.3 μm $B_4C$ powders. (C) was the earlier-mentioned sample in Fig. 5. The grain size of (A) was below 1 μm and the composite structure was finer than those of (B) and (C). The fine structure of (A) was caused by in-site reaction between fine powders during hot pressing, whereas $B_4C$ powder used in (B) and (C) was not so fine. As shown in Fig. 6, the Seebeck coefficient of (A) was very high and comparable to 30 wt.%$B_4C$ composite in Fig. 5. (B) was the same level to (C). The finer microstructure of (A) may affect its higher Seebeck coefficient as same as Fig. 5.

## 4. Conclusion

SiC–$B_4C$ composites were fabricated by hot pressing of β-SiC and $B_4C$ powder mixture. The relative density of sintered body reached above 99% at temperatures around 2000 °C without additive. The densification was promoted by $Al_2O_3$ addition and the sintered body was densified at 1800 °C. Compared with monolithic SiC, the hardness increased in SiC–$B_4C$ composite but the fracture toughness decreased. $Al_2O_3$ addition increased the hardness but had no effect to improve the fracture toughness. SiC–30wt.%$B_4C$ composite exhibited the Seebeck coefficient of about 700 μV/K at 900 °C. Such a high Seebeck coefficient is very attractive. In SiC–$B_4C$ system, the high Seebeck coefficient may be associated with the fine defect structure, like as grain boundary and stacking fault.

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