Thermoelectric Properties of Boron Compound-Doped α-SiC Ceramics

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The effects of boron compound additive on the thermoelectric properties of α-SiC ceramics were studied. Porous SiC ceramics with 57–62% relative density were fabricated by sintering the pressed α-SiC powder compacts with B, B₄C, and BN at 2000–2100°C for 3 h in Ar and/or N₂ atmosphere. The sintered bodies were analyzed by means of X-ray diffraction (XRD) and scanning electron microscopy (SEM). Lattice parameter measurements revealed incorporation of a certain amount of added B into the SiC lattice and negligible phase transformation during sintering. The Seebeck coefficient, electrical conductivity and thermal conductivity were measured at 600–900°C in Ar and/or vacuum atmosphere. The kind of additives, the amount of addition and sintering atmosphere had significant effects on the thermoelectric properties. On the whole, the excess addition had a harmful influence upon electrical conductivity. The thermoelectric figure of merit of B-doped SiC was lower than that of n-type SiC.

Key-words: α-SiC, p-type, B, B₄C, BN, Electrical conductivity, Seebeck coefficient, Thermal conductivity, Figure of merit

1. Introduction

Thermoelectric energy conversion utilizing nuclear heat sources has been employed for several decades to generate power for deep space probes. The development of thermoelectric materials has recently been resurrected once again for applications such as high-temperature thermoelectric power generation. For effective utilization of solar heat, nuclear energy and waste heat from industries, materials possessing high thermoelectric energy conversion efficiency and usable at high temperatures are intensely required.

Generally, the thermoelectric materials can be classified into three classes by the temperature which indicates the maximum value of figure of merit; the low (T ≈ 100°C), middle (200–600°C) and high (above 700°C) temperature materials. Compound semiconductors, such as Bi₂Te₃, PbTe, and their solid solutions, have already been commercially applied to both refrigeration and power generation. However, the materials so far developed are easily oxidized, decomposed, or melt above 1000°C and are not suitable for high-temperature applications.

Silicon carbide is now being considered for high-temperature structural applications because of its extreme hardness, excellent thermal and mechanical properties, and high thermal shock resistance. Furthermore, silicon carbide is considered to be a potentially useful material for high-temperature electronic devices as its band gap is large compared to silicon and the p-type and/or n-type conduction can be controlled by impurity doping.

Porous n-type SiC ceramics fabricated from β-SiC powder have been found to show high thermoelectric conversion efficiency at 800°C to 1000°C. Electrical conductivity of porous n-type SiC was comparable to or even higher than the reported values of single crystals, while thermal conductivity was kept as low as 1/10 to 1/30 of that for a dense ceramic. It was pointed out that microstructural inhomogeneities would have significant effects on thermoelectric properties and microstructure control would become an unavoidable problem in materials development for thermoelectric energy conversion.

In this work, thermoelectric properties of p-type SiC ceramics fabricated from α-SiC powder were investigated. B, B₄C, and BN were used as additives for controlling carrier concentration, and their effects on the thermoelectric conversion efficiency of SiC ceramics were studied.

2. Experimental procedure

2.1 Fabrication of porous SiC ceramics and their characterization

Porous SiC ceramics with ~60% relative density were fabricated by sintering the pressed α-SiC powder (Cerac Inc., purity; 99% up, average particle size; ~0.4μm) compacts (compaction pressure; 200kg/cm²) with additives at 2000–2100°C for 3 h in Ar and/or N₂ atmosphere. B (Cerac Inc., purity; 99% up, ~325mesh), B₄C (Cerac Inc., purity: 99.5%, ~325mesh), and BN (Cerac Inc., purity: 99.5%, average particle size: ~1μm) were employed as additives. X-ray diffraction (XRD) analysis was performed to examine the phases present and precise lattice parameters of the sintered body were measured using CuKα radiation with Ni filter and high-purity silicon as an internal standard. Scanning electron microscope (SEM) observations were carried out to examine the microstructure of sintered bodies.

2.2 Measurements of thermoelectric property

Four grooves were put on a rectangular specimen. Heads of the two Pt–Pt13%Rh thermocouples were embedded in the drilled holes at the two ends of a specimen and they were held in place with Pt wires placed along the grooves. The electrical conductivity and thermoelectric power were measured simultaneously for the same specimen at 600–900°C in Ar atmosphere. Electrical conductivity was measured using a d.c. four-probe technique. Ohm’s law was always checked by changing the current value. The average voltage drop obtained from forward/reverse current directions was used to calculate the conductivity. For thermoelectromotive force measurements, a temperature gradient in the specimen was generated by flowing cool air in an alumina protection tube placed near the one end of the specimen. The temperature difference between the two ends was controlled to be 5 to 10K by varying the flow rate of air. Plots of thermoelectromotive force vs. temperature difference gave rise to a straight line in all cases, and the Seebeck coefficient was calculated from its slope.

Thermal diffusivity and specific heat capacity were measured...
by a usual laser flash method. One side of a disc specimen cut out from a sintered body was pasted with glassy carbon for effective absorption of the laser energy. A thermocouple was fixed on the rear side to measure the temperature rise after the flash of laser pulse. Thermal diffusivity and specific heat capacity were measured separately at 600–900°C in vacuum. Calibration of the apparatus was carried out using a sapphire single crystal before each measurement. The thermal conductivity was calculated from thermal diffusivity, specific heat capacity, and density.

3. Results and discussion

3.1 Thermoelectric properties of the undoped α-SiC

Microstructure variation with varying processing conditions is expressed in terms of the relative density and average grain size as shown in Table 1. It can be seen that the grain growth occurred slightly with increasing sintering temperature in Ar atmosphere. On the other hand, the grain growth was little occurred in N2 atmosphere, it can be seen also in Fig. 1. It might be affected by nitrogen incorporated during the sintering process. That is, the grain growth in Ar atmosphere easily occurs by surface diffusion and/or evaporation condensation mechanism in SiC.51,53 However, if nitrogen is incorporated into the SiC lattice, mass transfer for grain growth would become suppressed by the strain due to the difference in covalent radii.

Figure 2 shows the temperature dependence of the Seebeck coefficient for the undoped α-SiC. The Seebeck coefficients for specimens sintered in Ar were positive (p-type semiconducting) possibly due to a dominant effect of the acceptor impurities (Al, Fe) contained in the starting powder and their values increased with increasing temperature. The present author has already analyzed the observed abnormal temperature dependence of the Seebeck coefficient in terms of the phonon-drag effect.61 That is, a decrease in the stacking fault density accompanied by grain growth and crystallite growth must have increased the phonon mean free path, enhancing the phonon-drag effect leading to an apparently larger Seebeck coefficient. On the other hand, the Seebeck coefficients for specimen sintered in N2 atmosphere were negative (n-type conduction) possibly due to nitrogen behaving as a donor and their absolute values also increased with increasing temperature.

Figure 3 shows the temperature dependence of electrical conductivity. It can be seen that the electrical conductivity increased as increasing sintering temperature, which must be due to the change in carrier concentration. That is, a certain amount of the acceptor and/or donor impurities is incorporated into the SiC lattice and its amount increases with increasing sintering temperature.

3.2 Thermoelectric properties of additive doped α-SiC

Silicon Carbide is produced commercially with >95% theoretical density when B and C are added. B4C is also well used as a sintering aid of SiC. Prochazka53 has suggested that B promotes solid-state sintering by segregating selectively in grain boundaries and excess B produces a B-rich phase at the grain boundaries.

In this work, XRD analysis showed little change in SiC phase

<table>
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<tr>
<th>Sample No.</th>
<th>Additive</th>
<th>Content (mass%)</th>
<th>Temp (°C)</th>
<th>Time (h)</th>
<th>Atmosphere</th>
<th>R.D. (%)</th>
<th>Average Grain Size (μm)</th>
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having occurred during sintering in Ar atmosphere and the peak of excess B was not detected (Fig. 4(b)–(d)). It can be seen in Table 1 that the average grain size of SiC grains increased with amount of B addition without noticeable densification (specimen A3–A5). B$_2$C (A6–A8) and/or BN (A9–A11) doped specimens were similar to the case of B addition, but the amount of additives appeared to have little effect on average grain size.

The results of lattice parameter measurements for undoped and/or B-doped specimens showed in Table 2 that $a$ and $c$ of main phase (6H-SiC) are all larger than the standard value ($a$: 0.30806 nm, $c$: 1.51173 nm),11 it possibly due to incorporation of the impurities (Al, Fe) contained in the starting powder into the SiC lattice. Furthermore, it can be also seen in Table 2 that $a$ and $c$ of B-doped specimens are generally smaller than those of undoped specimen, which was expected since the covalent radius of B (0.082 nm) is smaller than that of Si (0.111 nm). Whereas, the lattice parameters was little changed with amount of B addition. Vodakov et al.13 reported that a solubility limit of B in SiC at 2500°C is about 0.1 mass%. Therefore, the range of B content in this work might be above a solubility limit of B.

The SEM observations (Fig. 5) revealed that the grain size increases slightly with increasing B addition ((a)–(c)) and 1 mass% B doped specimen has high grain-to-grain connectivity. On the other hand, B$_2$C (d) and/or BN (e) doped specimens have low grain-to-grain connectivity.

Figure 6 shows temperature dependences of electrical conductivity and the Seebeck coefficient for SiC with B addition sintered at 2100°C for 3 h in Ar atmosphere. It can be seen in Fig. 6(a) that electrical conductivity of B-doped specimens are higher than that of undoped specimens sintered in Ar atmosphere and this must be due to the difference in carrier concentration, since B incorporated into the SiC lattice. And it appeared that electrical conductivity decreased with increasing the amount of B addition, except for the result of 1 mass% addition of B. This might be due to the effect of B segregated in grain boundaries and the difference in microstructure.

A polycrystalline material is composed of small crystallites joined together by grain boundaries. The grain boundary is a complex structure, usually consisting of a few atomic layers of disordered atoms. Seto9 reported that the electrical transport properties of polycrystalline silicon films are governed by carrier trapping at the grain boundary. That is, the trapping states are capable of trapping carries and thereby immobilizing them. This reduces the number of free carriers available for electrical conduction. Consequently, the electrical conductivity of B-doped specimens decreased with increasing the amount of excess B segregated in grain boundaries. The electrical conductivity of 1 mass% B-doped specimen was higher, it might be explained from the view point of the microstructure. That is, 1 mass% added specimen has the best grain-to-grain connectivity among three kinds of specimens. This result is consistent with the previous report9 that the electrical conductivity of n-type β-SiC increases with increasing compaction pressure, that is, the grain-to-grain connectivity of β-SiC became larger as increasing compaction pressure without noticeable change of relative density and average grain size. Better grain-to-grain connectivity must have played a role partly in increasing conductivity.

The Seebeck coefficients were positive possibly due to a dominant effect of the acceptor impurity, B and were about the same value in all specimens (Fig. 6(b)).

Figure 7 shows temperature dependences of electrical conductivity and the Seebeck coefficient for SiC with B$_2$C addition sintered at 2100°C for 3 h in Ar atmosphere. It can be seen in Fig. 7(a) that electrical conductivity of B$_2$C-doped specimens are slightly lower than that of B-doped specimens. Shaffer10 reported that a solubility limit of B$_2$C in SiC at 2200°C is 0.5 mass%, a little higher than that of B. Although B$_2$C has higher solubility limit, B$_2$C-doped specimens have somewhat lower electrical conductivity, this might be due to the difference in microstructure, mainly connectivity of SiC grains (Fig. 5(d)). The Seebeck coefficients (Fig. 7(b)) were similar to the case of B addition, except for the result of 3 mass% addition of B$_2$C caused by microstructure ho-

**Table 2. Lattice Parameters of B-Doped SiC Sintered at 2100°C for 3h in Ar Atmosphere**

<table>
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<tr>
<th>Sample No</th>
<th>B Content (mass%)</th>
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Fig. 5. Scanning electron micrographs of SiC sintered at 2100°C for 3 h in Ar atmosphere; (a) 0.5 mass% B, (b) 1 mass% B, (c) 3 mass% B, (d) 1 mass% B₄C, and (e) 1 mass% BN addition.

Fig. 6. Temperature dependences of electrical conductivity (a) and the Seebeck coefficient (b) for B-doped SiC sintered at 2100°C for 3 h in Ar atmosphere.
Figure 7. Temperature dependences of electrical conductivity (a) and the Seebeck coefficient, (b) for B$_4$C-doped SiC sintered at 2100°C for 3 h in Ar atmosphere.

Figure 8. Temperature dependences of electrical conductivity (a) and the Seebeck coefficient (b) for BN-doped SiC sintered at 2100°C for 3 h in Ar atmosphere.

mogeneity. Figure 8 shows temperature dependences of electrical conductivity and the Seebeck coefficient for SiC with BN addition sintered at 2100°C for 3 h in Ar atmosphere. It can be seen in Fig. 8(a) that electrical conductivity of BN-doped specimens is lower than that of B and B$_4$C-doped specimens. And it appeared that electrical conductivity decreased with increasing the amount of BN addition. This must be due to the compensation of acceptor (B) and donor (N), the effect of excess BN having low electrical conductivity, and the low grain-to-grain connectivity (Fig. 5(e)). On the contrary, the Seebeck coefficient increased with increasing the amount of BN addition (Fig. 8(b)), possibly due to the increase of a insulating phase caused by excess BN.

There are two shapes, Π-type and V-type in the thermoelectric module. In the case of V-type, p- and n-type materials were simultaneously sintered in the same condition. An early study of n-type SiC$_2^{13,6}$ indicated that incorporation of nitrogen is very effective, so thermoelectric properties of B$_4$C-doped specimens sintered in N$_2$ atmosphere were also studied. X-ray powder diffraction pattern of SiC sintered with 1 mass% B addition in N$_2$ atmosphere is shown in Fig. 4(e). XRD analysis is similar to the case of Ar atmosphere except the formation of BN. That is, excess B forms BN through the reaction with N$_2$.

Figure 9 shows the temperature dependence of the Seebeck coefficient for SiC with B addition sintered at 2100°C for 3 h in N$_2$ atmosphere. The Seebeck coefficient was always negative. n-type semiconduction appeared even in the sintered SiC with B addition, which indicates that quantity of nitrogen incorporated during sintering is much higher than that of B incorporated into SiC lattice. And it can be also seen that the absolute value of the Seebeck coefficient increased as increasing the amount of B addition. Figure 10 shows the temperature dependence of electrical conductivity. It can be seen that electrical conductivity decreased as increasing the amount of B addition. As previously stated, it might be due to the carrier compensation and the increase of an insulating phase.

3.3 Thermoelectric energy conversion by porous SiC with B addition

For the purpose of materials design for thermoelectric energy conversion, it is convenient to define a figure of merit (Z) for an individual material as

\[ Z = \frac{\sigma \alpha^2}{\kappa} \]

where \( \sigma \), \( \alpha \), and \( \kappa \) are electrical conductivity, the Seebeck coeffi-
cient and thermal conductivity, respectively. That is, to increase thermoelectric energy conversion efficiency, a material having high electrical conductivity, large Seebeck coefficient, and low thermal conductivity is need. Thermal conductivity of a sintered body is generally influenced by its density and purity. It can be seen in Fig. 11 that thermal conductivity of porous SiC ceramics with B addition is lower than about 1/10 of the values for dense SiC ceramics.

Figure 12 shows the temperature dependence of a figure of merit calculated using the data shown in Figs. 2, 3, 6, and 11. The figure of merit increased with increasing temperature. However, B-doped p-type SiC has lower figure of merit than N-doped n-type SiC, since the former has very low electrical conductivity in comparison with the latter. Hence it can be stated that the thermoelectric properties of p-type SiC ceramics could be further improved by appropriate doping and a precise control of microstructure.

4. Conclusions

The results of this study are summarized as follows:

1. A certain amounts of added B, B$_4$C and BN were incorporated into the SiC lattice and the excess addition had harmful influence upon electrical conductivity.

2. Electrical conductivities of B-doped specimens were higher than those of non-doped specimens, and had the maximum value by 1 mass% addition. The Seebeck coefficients of B-doped specimens were positive and about the same value in all specimens.

3. In the case of B$_4$C addition, electrical conductivity was slightly lower than that of B-doped specimens. The Seebeck coefficients were similar to the case of B addition.

4. Electrical conductivities of BN-doped specimens were lower than those of B and B$_4$C-doped specimens. And it appeared that electrical conductivity decreased with increasing the amount of BN addition, which might be caused by the carrier compensation and the effect of excess BN having low electrical conductivity. The Seebeck coefficients increased with increasing the amount of BN addition.
(5) The Seebeck coefficient of B-doped specimens sintered in N₂ atmosphere was always negative, since the quantity of nitrogen incorporated during sintering is much higher than that of B incorporated into SiC lattice. The absolute value of the Seebeck coefficient increased as increasing the amount of B addition. On the contrary, electrical conductivity decreased as increasing the amount of B addition.

(6) Thermal conductivity of B-doped SiC was lower than about 1/10 of the values for dense SiC ceramics.

(7) The figure of merit of B-doped SiC increased with increasing temperature. On the whole, p-type SiC with B addition had lower figure of merit than n-type SiC.

References