Effects of Sintering Additives on the Thermoelectric Properties of SiC Ceramics

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SiCセラミックスの熱電変換特性に及ぼす添加物の効果

The effects of sintering additives on the thermoelectric properties of SiC ceramics were studied. Porous SiC ceramics with ~60% relative density were fabricated by sintering the pressed β-SiC powder compacts with additives (B, AlN) at 1900°-2100°C for 0.5-5h in nitrogen atmosphere. The sintered bodies were analyzed by means of XRD and SEM. In the case of B addition, XRD analysis showed that little phase transformation occurred during sintering and that BN was formed by the reaction with N,

Lattice parameter measurements revealed incorporation of a certain amount of added B into the β-SiC lattice. On the other hand, in the case of 10wt% AlN addition, XRD and SEM analyses showed a phase transformation of β-SiC to mainly 4H-SiC during sintering. The electrical conductivity and the Seebeck coefficient were measured at 350°-1050°C in argon atmosphere. The average grain size and the quantity of additives had significant effects on the thermoelectric properties of SiC.

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1. Introduction

For effective utilization of solar heat, nuclear energy and waste heat from industries, materials possessing high thermoelectric energy conversion efficiency specifically applicable at high temperature above 1000°C are required. For this purpose, it was attempted in this study to develop SiC ceramics for thermoelectric energy conversion material. 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. Recently, porous SiC ceramics have been found to show high figures of merit for thermoelectric energy conversion. 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, B and AlN were used as additives for controlling carrier concentration and then effects on the thermoelectric conversion efficiency of SiC ceramics were studied.

2. Experimental

2.1 Fabrication of porous SiC ceramics and their characterization

Porous SiC ceramics with ~60% relative density were fabricated by sintering the pressed β-SiC powder (Central Glass Co. Ltd., average particle size ~0.4 μm) compacts (compaction pressure : 200 kg/cm²) with additives at 1900°-2100°C for 0.5-5h in nitrogen atmosphere. B (99% up pure) and AlN (99% up pure) 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 Cu Ka 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 Electrical measurements for porous SiC ceramics

Electrical conductivity was measured at 350°-1050°C in argon atmosphere using a d.c.
four-probe technique with platinum lead wires. Thermoelectromotive force was measured simultaneously using the two Pt-Pt 13% Rh thermocouples embedded in the holes drilled at the two ends of the specimen. The temperature difference between the two ends was controlled by flowing cold air in the alumina protection tube placed near one end of the specimen.

3. Results and discussions

3.1. Effect of B addition

SiC is now produced commercially with >95% theoretical density when B and C are added. Whilst the sintering characteristics of SiC with B addition in vacuum or argon atmosphere are generally well reported, the study in nitrogen atmosphere is very few. Prochazka et al. has suggested that B promotes solid-state sintering by increasing grain boundary diffusivities and excess B appears a B-rich phase at the grain boundaries. On the other hand, Carter et al. indicated that B does not segregate to SiC grain boundaries, which is consistent with Sherman’s observation.

X-ray powder diffraction patterns of SiC sintered with B addition in nitrogen atmosphere are shown in Fig. 1. XRD analysis shows little phase transformation having occurred during sintering. As the content of added B increases, the content of the formed BN increases. This phenomenon could be seen in the specimen sintered at 1900°C. Furthermore, lattice parameters for the B added specimens (4.3547–4.3569 Å) are all smaller than the standard value, 4.3596 Å, whereas that of β-SiC with no additive (4.3588 Å) is slightly smaller than the standard value. This result revealed that a certain amount of added B is incorporated into the SiC lattice and contraction of the lattice upon incorporation of B suggests that B substitutes for Si. Whereas, little contraction of the lattice upon incorporation of N suggests that N substitutes for C. Excess B forms BN through the reaction with in the surrounding atmosphere. It can also be judged from the broadness of the XRD peak corresponding to BN that the crystallinity of the formed BN is poor. The SEM observations revealed that grain growth little occurred. In the case of 10 wt% B added β-SiC, microstructure differs significantly from those with smaller amount of B addition.

![Fig. 1. X-ray powder diffraction patterns of SiC with B addition sintered at 2100°C for 3 h in N₂ atmosphere.](image1)

![Fig. 2. Temperature dependence of electrical conductivity for SiC with B addition sintered at 2100°C for 3 h in N₂ atmosphere. Dotted line expresses that of sintered SiC with no additive.](image2)

![Fig. 3. Temperature dependence of the Seebeck coefficient for SiC with B addition sintered at 2100°C for 3 h in N₂ atmosphere. Dotted line expresses that of sintered SiC with no additive.](image3)
Electrical conductivity was almost independent of temperature as shown in Fig. 2. It appeared that electrical conductivity decreased with increasing both the amount of B addition and the content of the formed BN, except for the result of 3 wt% addition of B. It can be seen in Fig. 2 that electrical conductivities of B added β-SiC are lower than that of β-SiC with no additive (the dotted line), which must be due to the compensation of acceptors (B) and donors (N) having taken place. The difference between 3 wt% addition and 10 wt% addition must have been caused by the change in microstructure, namely the connectivity of SiC grains in 3 wt% added specimen is higher than that in 10 wt% added specimen, partly due to the BN formation.

Figure 3 shows the temperature dependence of the Seebeck coefficient for SiC with B addition. The relationship between temperature difference and thermoelectromotive force was always linear and the Seebeck coefficient was calculated from its slope. The Seebeck coefficient was always negative and its absolute value increases with increasing temperature. The temperature dependences of the Seebeck coefficient found in the present study for porous SiC ceramics can not be explained by means of a simple semiconductor theory taking account only of the electron diffusion generating the thermoelectromotive force under the temperature gradient. The present author have already analysed the observed abnormal temperature dependence of Seebeck coefficient in terms of the phonon-drag effect, where the carrier electrons are predominantly dragged by the phonons scattered by the boundaries, such as grain surfaces, stacking fault planes, dislocations, etc. In this case, the phonon-drag Seebeck coefficient, $a_\text{d}$, can be expressed by the following equation according to Parrott:  

$$|a| = |a_\text{n}| + \frac{L^* s}{\mu T} \alpha$$

where $a_\text{n}$ is the normal Seebeck coefficient stemmed only from electron diffusion, s the mean velocity of phonons, $L^*$ the mean free path of phonons, $\mu$ the carrier mobility, and $T$ the absolute temperature, respectively. It can be judged from this equation that decrease in the stacking fault density accompanied by grain growth would have increased the phonon mean free path, $L^*$, enhancing the phonon-drag effect leading to apparently larger Seebeck coefficient. N-type semiconduction (negative Seebeck coefficient) appeared even in the sintered SiC with B addition, which indicates that quantity of nitrogen incorporated during sintering (nitrogen behaves as an electron donor) is much higher than that of B incorporated into SiC lattice. And it can be seen that as the amounts of B addition and BN formation increases, absolute value of Seebeck coefficient increases. Though the reason for the difference in Seebeck coefficient among B added specimens is not well known, an early study on thermoelectric properties for SiC by the present authors indicated that thermoelectromotive force of sintered SiC...
was increased by the addition of B or BN, the effect of BN being larger than that of B.

In the next place, the effect of sintering time was investigated. Figures 4 and 5 show the temperature dependences of the electrical conductivity and Seebeck coefficient for β-SiC with 1 wt% B addition sintered at 2000°C and 2100°C, respectively. It can be seen that the change in sintering time at 2000°C had little effect upon the thermoelectric properties. On the contrary, the Seebeck coefficient increased with increasing sintering time at 2100°C. It was pointed out by the present authors that the Seebeck coefficient increases with increasing grain size, and that the grain growth has a great effect upon stacking fault density. Such a tendency was also found in this study. It is observed in Fig. 6 that the grain size little changes with sintering time at 2000°C ((a)-(c)), but on the other hand, the grain size
increases with increasing sintering time at 2100°C (Fig. 7). Furthermore, Fig. 7 shows that the intensity of the unsymmetric reflection (the so-called prism reflection) near (111) peak \((2\theta (\text{CuK}_{\alpha})=33.5^\circ)\), which corresponding to the stacking fault density\(^{11}\) decreases with increasing sintering time.

3.2 Effect of AlN addition

AlN is also generally well used as a sintering aid of SiC. In the present case, the compensated semiconductor can be made by AlN addition for the reason that AlN is composed of Al as an acceptor and N as a donor.

X-ray powder diffraction patterns of SiC sintered with AlN addition are shown in Fig. 8. XRD analysis shows that phase transformation from \(\beta\)-SiC to mainly 4H-SiC has occurred during sintering and it is found that phase transformation is enhanced by increasing AlN addition. Though the formation of 4H-SiC polytype in the presence of Al is well known, the mechanism for this effect still remains unknown. Cutler et al.\(^{12}\) have shown that AlN stabilizes the 2H-SiC if solid solution formation occurs and it is surmised that aluminum oxycarbide, which also can enter the SiC lattice, may have a similar role in stabilizing or nucleating the 4H-SiC. Tajima et al.\(^{13}\) have shown that at 2200°C the solubility limit of aluminum in silicon carbide is 1.0 wt%. The change in the lattice parameter indicates that Al substitutes for Si. However, in the present study, the change in the lattice parameter (4.3593Å) is little occurred. It should be due to the simultaneous incorporation of N from the surrounding atmosphere. The SEM observations revealed that the grain size increases with increasing sintering temperature and as the addition of AlN increases, grain growth and also phase transformation become accelerated.

Electrical conductivity was almost independent of temperature as shown in Fig. 9. It can be seen that electrical conductivities of AlN added SiC \((\alpha+\beta)\) sintered at 2100°C are all lower than that of 1 wt% AlN added SiC (mostly \(\beta\)) sintered at 2000°C (the dotted line). This result must have been caused by the fact that \(\beta\)-SiC having high carrier mobility has transformed to \(\alpha\)-SiC (4H, 6H) having lower carrier mobility.\(^{14}\) Therefore,
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the specimen which transformed nearly to $\alpha$-phase (10 wt% AlN added SiC) had the lowest electrical conductivity.

Figure 10 shows the temperature dependence of the Seebeck coefficient for SiC added with AlN. It can be seen that the change in both microstructure and phase composition has great effects upon the Seebeck coefficient.

3.3 Thermoelectric energy conversion by porous SiC with additives

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

$$Z = \sigma a^2 / \kappa$$

where $\sigma$, $a$, and $\kappa$ are the electrical conductivity, Seebeck coefficient and thermal conductivity, respectively. Namely, to increase thermoelectric energy conversion efficiency, a material having high electrical conductivity, large Seebeck coefficient, and low thermal conductivity is needed. Thermal conductivity of a sintered body is generally influenced by its density and purity. The present authors indicated that thermal conductivity of porous SiC ceramics with $\sim 60\%$ relative density was lower than about 1/10-1/30 of the values for dense SiC ceramics. It is expected that thermal conductivity be lowered by impurity addition and the specimens investigated still have low thermal conductivity.

Figure 11 shows the temperature dependence of the power factor, $\sigma a^2$. The power factors of the specimens sintered with 3 wt% B and 1 wt% AlN additions are somewhat larger than that of $\beta$-SiC with no addition (the dotted line) in the high-temperature region. Hence it can be stated that thermoelectric conversion efficiency of SiC ceramics could be further improved by selecting the optimum condition for the addition of other substances and high-temperature processing.

4. Conclusion

The following conclusions can be drawn from the present study.

1. A certain amount of added B was incorporated into the SiC lattice and the excess B formed BN by the reaction with N$_2$.

2. The quantity of nitrogen incorporated into $\beta$-SiC during sintering is higher than that of B.

3. AlN enhanced $\beta$ $\rightarrow$ 4H phase transformation.

4. By the addition of B or AlN, electrical conductivity decreased, because of the compensation of acceptors and donors (in the case of B addition) and the phase transformation (in the case of AlN addition).

5. Seebeck coefficient of sintered SiC was increased by the addition of B or AlN.

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