

Thermoelectric Conversion Characteristics of SiC Ceramics Fabricated from 6H-SiC Powder

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6H-SiC 로 부터 제작한 SiC 세라믹스의 열전변환 특성

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요 약

다공질 SiC 세라믹스가 고온 열전변환 재료로써 유망한 것을 제안하였다. 다공질 α -SiC 및 α -와 β -SiC 의 혼합체의 열전 물성측정과 미세구조 관찰을 통해서 입성장에 따른 적층 결함, twin boundary 의 제거에 의해서 seebeck 계수가 증가하고, α -SiC 의 양이 증가함에 따라 도전율이 감소한다는 것을 실험적으로 해명하였으며, 6H-SiC 소결체의 열전물성에 미치는 첨가제의 영향에 대하여 고찰하였다. 아르곤 분위기 중 350-1050°C에서 도전율과 seebeck 계수를 측정하였으며, β -SiC 에 비해서 α -SiC 세라믹스의 열전변환 효율이 작았다. seebeck 계수의 절대값을 향상시키기 위해서 상의 균일성이 필요하며 α 상의 증가에 의해 도전율이 감소하였다. B 첨가의 경우 소결중에 상전이가 일어나지 않았지만 AlN 을 첨가하였을 경우 6H-SiC 에서 4H-SiC 로의 역상전이가 일어나서 결과적으로 도전성에 큰 영향을 미쳤다.

ABSTRACT

Porous SiC ceramics were proposed to be promising materials for high-temperature thermoelectric energy conversion. Through the thermoelectric property measurements and microstructure observations on the porous alpha SiC and the mixture of α - and β -SiC, it was experimentally clarified that elimination of stacking faults and twin boundaries by grain growth is effective to increase the seebeck coefficient and increasing content of α -SiC gives rise to lower electrical conductivity.

Furthermore, the effects of additives on the thermoelectric properties of 6H-SiC ceramics were also studied. The electrical conductivity and the seebeck coefficient were measured at 350°C to 1050°C in argon atmosphere. The thermoelectric conversion efficiency of α -SiC ceramics was lower than that of β -SiC ceramics. The phase homogeneity would be needed to improve the seebeck coefficient and electrical conductivity decreased with increasing the content of α -phase. In the case of B addition, XRD analysis showed that the phase transformation did not occur during sintering. On the other hand, AlN addition enhanced the reverse phase transformation from 6H-SiC to 4H-SiC, and this phenomenon had a great effect upon the electrical conductivity.

1. INTRODUCTION

Recently, energy conversion has been a very important subject for the utilization of energy. Particularly, thermoelectric energy conversion which converts thermal energy into the electric energy is suited for the utilization of dispersed energy and is attracting much attention.

Thermoelectric semiconductors composed of heavy elements, such as PbTe, Bi₂Te₃, etc., have already been commercially applied to both refrigeration and power generation¹⁾. However, the materials so far developed are easily oxidized, decomposed, or melt above 1000°C and are not satisfactorily suitable for high-temperature applications. On the other hand, since the ceramic semiconductors in general have high thermal stability and corrosion resistance, it would be highly effective to apply these materials to high-temperature thermoelectric energy conversion.

Porous ceramics of SiC have recently been found by the present authors²⁻⁴⁾ to show high thermoelectric conversion efficiency at 350°C to 1150°C. Electrical conductivity of porous n-type SiC ceramics 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.

The striking phenomenon observed then was that the absolute value of seebeck coefficient for both n-type and p-type SiC always increases with increasing temperature. 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 α -SiC sintered in nitrogen or argon atmosphere were investigated, specifically concentrating on how the ratio of content of α to β -phase affected their thermoelectric properties. Furthermore, B and AlN were used as additives for both controlling the carrier concentration and changing the microstructure, and

then 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

Commercial α (Showa Denko Co., Ltd., average particle size $\sim 0.4\mu\text{m}$), the powder is composed of almost all 6H-SiC and very small amount of 4H, 15R-SiC and beta (Central Glass CO., Ltd., average particle size $\sim 0.4\mu\text{m}$) SiC powders were isostatically pressed in a rubber mold and sintered at 2000°C to 2200°C (Fuji Denpa furnace, Model FVS-R-220) in nitrogen or argon atmosphere. Weight content ratio of α to β SiC was varied to examine how its ratio affects the thermoelectric properties. A rectangular bar was cut out from a sintered body, polished by an emery paper, and cleaned ultrasonically. Based on the assumption that nitrogen incorporated into the SiC lattice during sintering has negligible effects on the theoretical densities of 3.21 (β -SiC)⁵⁾ and 3.211g/cm³ (6H-SiC)⁶⁾, relative density of each specimen was calculated from its weight and size.

Scanning electron microscope (SEM) observations were conducted to examine the microstructure and average grain size was calculated on the micrographs. XRD measurements were carried out on the crushed powders using CuK α radiation with Ni filter and graphite monochromator.

2.2. THERMOELECTRIC PROPERTY MEASUREMENTS

Four ditches were put on a rectangular specimen with a diamond saw. Heads of the two Pt-Pt13%Rh thermocouples were embedded in the drilled holes at the two ends of a specimen and they were fixed by platinum wires wound along ditches. Electrical conductivity and thermoelectric power were measured simultaneously for the same specimen at 350°C to 1150°C in an argon atmosphere (Fig.1).

Electrical conductivity was measured using a d.c.

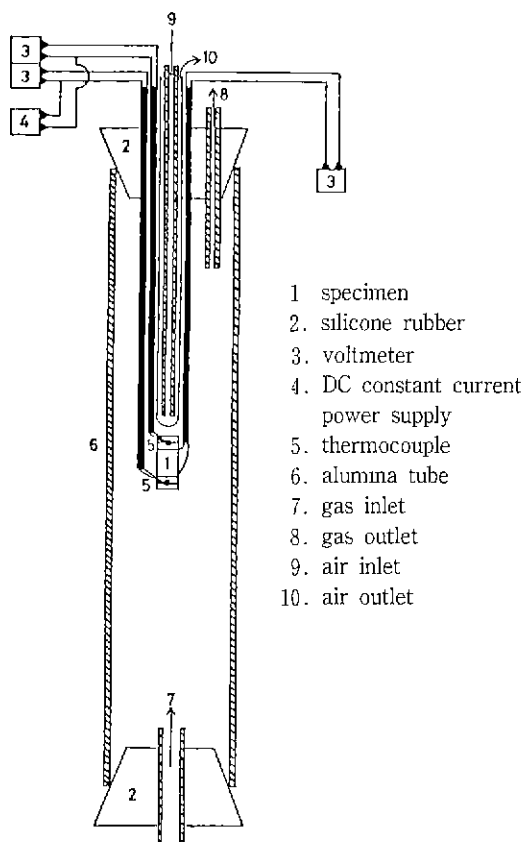


Fig.1. Schematic diagram of the apparatus for electrical conductivity & seebeck coefficient measurements.

four-probe technique. Ohm's law was always checked by changing the current value and the average voltage drop obtained from forward and reverse current directions was used to calculate the conductivity.

For thermoelectromotive force measurements, 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 2 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 seebeck coefficient was calculated from its slope.

3. RESULTS AND DISCUSSION

3.1. THERMOELECTRIC PROPERTIES OF α -SiC WITHOUT ADDITIVES

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 average grain size and relative density of sintered bodies were little changed with increasing sintering time (specimens S3 to S5) and slightly increased with increasing sintering temperature (specimens S3 and S6) without noticeable densification in nitrogen atmosphere. On the other hand, the grain growth occurred abruptly in argon atmosphere at above 2100°C. Though the reason for the difference in grain growth rate as shown in Fig.2 is not well known, it might be affected by nitrogen incorporated during the sintering process. That is, the grain growth in argon or vacuum atmosphere easily occurs by surface diffusion and/or evaporation condensation mechanism in SiC without additives^{6,7)}. However, if nitrogen is incorporated into the SiC lattice during sintering, the strain due to the difference in covalent

Table 1 Relative Densities and Average Sizes of SiC Grains for the Specimens Obtained under Various Processing Conditions.

Sample No.	Starting Material	Sintering Conditions			Sintered Body	
	$\alpha/(\alpha+\beta)$ Ratio	Temp (°C)	Time (h)	Atmosphere	R D (%)	Average Grain Size (μm)
S1	1	2000	3	Ar	58.9	1.48
S2	1	2100			59.5	large
S3	1	2000	0.5	N ₂	57.9	0.9
S4	1		1		58.1	1.0
S5	1		3		58.1	1.0
S6	1	2200	0.5	N ₂	59.1	1.75
S7	0.8				60.0	1.85
S8	0.6				60.2	2.25
S9	0.4				60.6	2.35
S10	0.2				61.5	2.75
S11	0				61.9	4.05

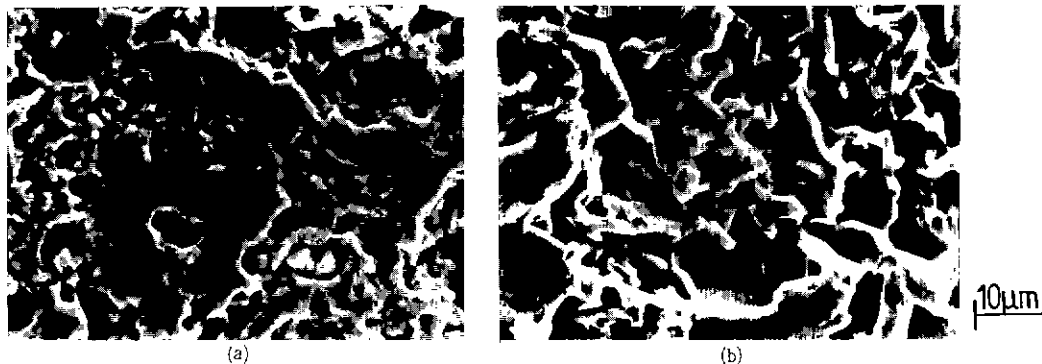


Fig.2. Scanning electron micrographs of the polished surfaces of the specimens sintered in (a) N₂ and (b) Ar for 3h at 2100°C.

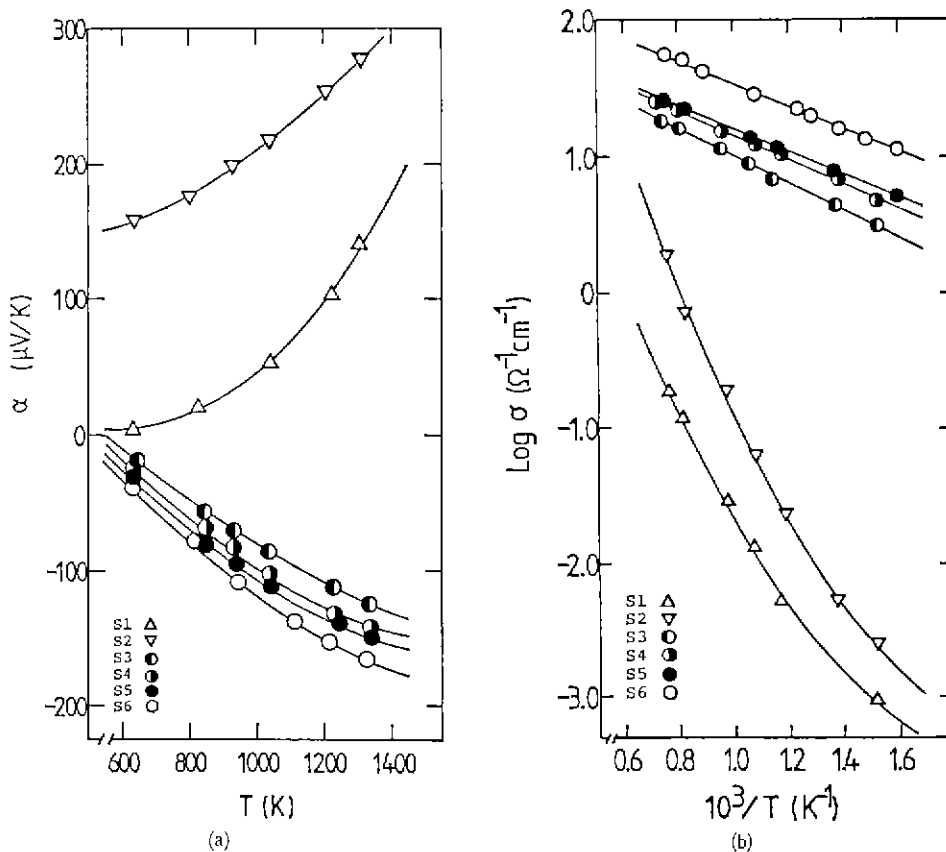


Fig.3. Temperature dependences of the seebeck coefficient (a) and electrical conductivity (b) for α -SiC obtained under various processing conditions.

radii among Si, C and N would be introduced into the lattice, and consequently, mass transfer for grain growth would become more suppressed as compared to

the case with no strain.

Fig.3(a) shows the temperature dependence of the seebeck coefficient for α -SiC obtained under various

processing conditions. Seebeck coefficients for the specimens prepared in nitrogen atmosphere (specimens S3 to S6) were always negative (n-type semiconduction) possibly due to nitrogen behaving as a donor and its absolute value increased with increasing temperature. On the other hand, seebeck coefficients for the specimens obtained in argon atmosphere (specimens S1 and S2) were positive (p-type semiconduction) indicating a dominant effect of the acceptor impurities (Al, Fe) contained in the starting powder and its value also increased with increasing temperature.

The temperature dependences of seebeck coefficient found in Fig.3(a) cannot be explained by a simple semiconductor theory taking account only of the electron diffusion generating the thermoelectromotive force under the temperature gradient. Phonon contribution to the seebeck effect, which is called a phonon-drag effect, has been found for metals and compound semiconductors at low temperatures⁶¹. Phonon-drag effect is associated with the interaction between current carriers and phonons leading to an apparent increase in the absolute seebeck coefficient. The model that the carrier electrons are predominantly dragged by the phonons scattered by the boundaries, such as grain surfaces, stacking fault planes, dislocations, etc. was the only one that could satisfactorily explain the observed temperature dependence²⁾. The present authors have also reported that the stacking fault density accompanied by grain growth in the sintered body of beta SiC decreased with increasing sintering temperature and also sintering time⁹⁾. It is considered from the present results that this is also the case for alpha SiC.

Electrical conductivity for the specimens sintered in nitrogen atmosphere was slightly dependent on temperature with an apparent activation energy ranging from 5.5 to 6.7J/mol, while that for the specimens prepared in argon atmosphere significantly dependent on temperature as shown in Fig.3(b). Larger activation energy for p-type conduction than

for n-type conduction in SiC has been reported by several workers¹⁰⁾ and this is supposed to be mainly due to the deep acceptor levels formed in the electronic band structure. It can be seen that electrical conductivity for the specimens sintered in nitrogen atmosphere increases with increasing both sintering temperature and sintering time (specimens S3 to S6) and this must be due to the difference in carrier concentration, since nitrogen incorporated into the SiC lattice during sintering behaves as an electron donor and its amount would increase as increasing sintering temperature. On the other hand, electrical conductivity for the specimens prepared in argon atmosphere was smaller than that in nitrogen atmosphere, possibly because of the low carrier (hole) concentration and low mobility.

3.2. THERMOELECTRIC PROPERTIES OF $(\alpha + \beta)$ -SiC MIXED PHASES

Fig.4 shows temperature dependences of electrical conductivity (a) and seebeck coefficient (b) for $(\alpha + \beta)$ -SiC sintered in nitrogen atmosphere. XRD analysis showed little change in $(\alpha + \beta)$ phase having occurred during sintering. Fig.4(a) shows that electrical conductivity decreases with increasing ratio of $\alpha/(\alpha + \beta)$ of the starting powder. This result is consistent with that of the previous report⁴⁾ that electrical conductivity is decreased by beta to alpha phase transformation, since carrier mobility and hence electrical conductivity of β -SiC is generally higher than that of α -SiC⁹⁾.

It can be seen in Fig.4(b) that seebeck coefficient for the specimen composed only of α - or β -phase is larger than that for the mixed phases. Theoretical expression of seebeck coefficient for a mixed phase has not been developed, so that the observed phase-composition dependence of seebeck coefficient cannot be well explained. However, it must be associated with the microstructural inhomogeneity, and homogeneity would be needed to improve the seebeck coefficient.

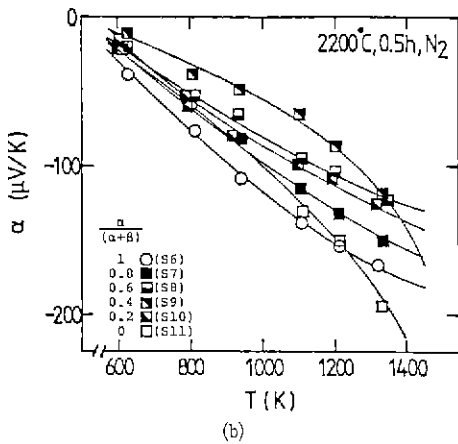
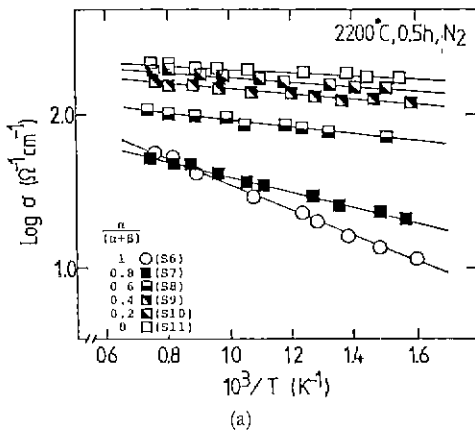


Fig.4. Temperature dependences of electrical conductivity (a) and the seebeck coefficient (b) for $(\alpha+\beta)$ -SiC sintered at 2200°C for 0.5h in N_2 atmosphere.

3.3. EFFECTS OF ADDITIVES ON THE THERMOELECTRIC PROPERTIES

3.3.1. Effect of B addition

Relative density and average grain size for the specimens sintered with B addition in N_2 and Ar atmosphere are shown in Table 2. It can be seen in the specimens sintered in nitrogen(specimens S12 to S14) that the grain growth during sintering was severely inhibited compared to the specimens sintered in argon(specimens S15 to S17).

XRD analysis(Fig.5) shows little change in SiC phase having occurred during sintering. However, a certain amount of added B is incorporated into SiC

Table 2. Relative Densities and Average Sizes of SiC Grains for the Specimens Sintered with B Addition at 2100°C for 3h.

Sample No.	Sintering Conditions		Sintered Body	
	Cont. (wt%)	Atmosphere	R.D (%)	Average Grain Size (μm)
S12	1	N_2	60.2	0.7
S13	3		61.6	0.4*
S14	10		61.2	0.4*
S15	1	Ar	61.2	large**
S16	3		58.8	large**
S17	10		56.7	large**

*Grain growth of alpha SiC little occurred. It seems that the average grain size decreased with increasing content of reaction-formed BN existing as very small grains(<0.2 μm).

**very large plate-like grains were observed.

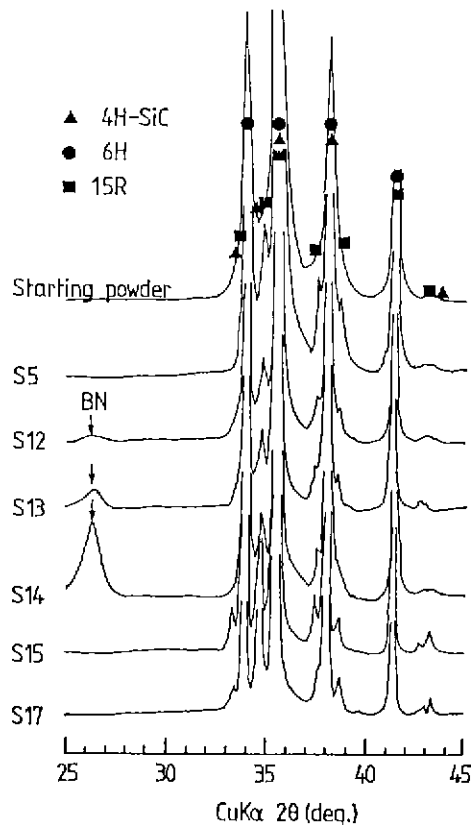


Fig 5 X-ray powder diffraction patterns of SiC sintered with B addition at 2100°C for 3h in N_2 or Ar atmosphere.

lattice and excess B forms BN through the reaction with nitrogen in the surrounding atmosphere¹³⁾, and the content of the formed BN increased with increasing content of added B.

It can be seen in Fig.6(a) that electrical conductivities of the specimens sintered in nitrogen atmosphere with B addition are lower than those without additives (specimens S3 to S6 in Fig.3(b)), which must be due to the compensation of acceptors (B) and donors (N) having taken place. As the B content increased, electrical conductivity decreased (open symbols in Fig.6(a)), which might be due to the formation of BN having low electrical conductivity and the change in microstructure, namely the reduced connectivity of SiC grains.

On the whole, electrical conductivity for the specimens sintered in argon atmosphere (closed symbols in Fig.6(a)) is smaller than for the N₂-sintered SiC, since the concentration and mobility of holes (the former) may be both smaller than those of

electrons (the latter). And electrical conductivity was little changed with the B content and was similar to that of the sample S2 (Fig.3(b)) sintered without B addition. These results would indicate that very little boron is incorporated into the SiC lattice and excess molten boron (the melting point of boron is 2030°C) disappears through evaporation.

Fig.6(b) shows the temperature dependence of seebeck coefficient for SiC with B addition. N-type semiconduction (negative sign) appears even in the sintered SiC with B addition, which indicates that content of nitrogen incorporated during sintering is much higher than that of B incorporated into SiC lattice.

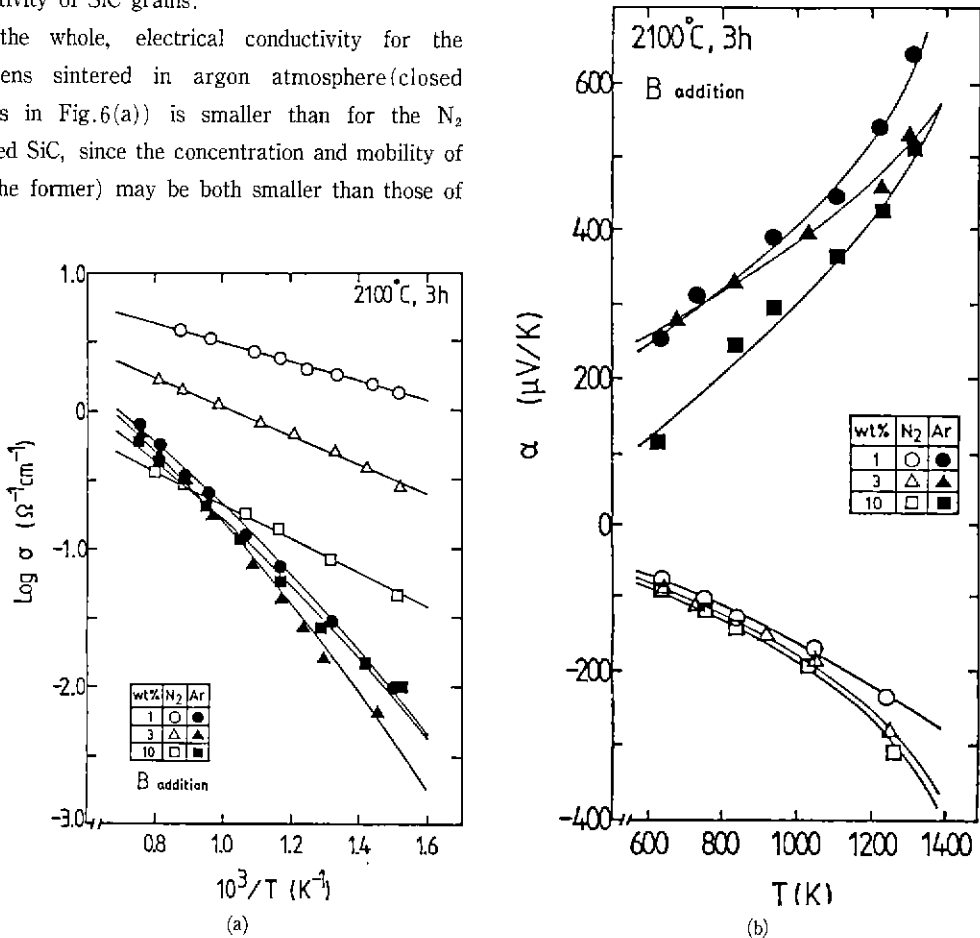


Fig.6. Temperature dependences of electrical conductivity (a) and the seebeck coefficient (b) for SiC sintered with B addition at 2100°C for 3h in N₂ or Ar atmosphere.

And it can be seen that the absolute value of seebeck coefficient practically remains unchanged with the change in the content of B addition, which would indicate that BN existing as the second phase would not largely affect the seebeck coefficient. Seebeck coefficient for the specimens sintered in argon atmosphere is always positive and shows slightly larger value than those for the N₂-sintered SiC and the sample sintered without addition(specimen S2 in Fig. 3(a)). Though the reason for the difference in them is not well known, this might be due to the change in microstructure and to the difference in carrier concentration and mobility.

3.2.2. Effect of AlN addition

Aluminum nitride is often used as a sintering aid for SiC and makes the compensated semiconductor, since it is composed of Al as an acceptor and N as a donor.

Relative density and average grain size for the specimens sintered with AlN addition in N₂ or Ar atmosphere are shown in Table 3. It can be seen in the specimens sintered in N₂ (specimens S18 to S20) that the grain growth little occurred just as the case for B addition. In Ar atmosphere, on the contrary, the average grain size increases with increasing content of AlN (specimens S21 to S23).

Though XRD analysis(Fig.7) of the specimens sintered in N₂ atmosphere show little phase change having occurred during sintering, in the specimens

sintered in Ar atmosphere reverse phase transformation from 6H-SiC to 4H-SiC has firmly occurred during sintering : the intensities of diffraction peaks of 4H-phase(2θ : 33.6, 34.8, 38.2, 43.3°) increase with increasing AlN addition, while those of 6H and 15R-phase(2θ : 34.2, 37.5, 41.5, 42.8°) decrease. The p-type impurities (Al and B) have been reported to stabilize hexagonal polytypes, while n-type impurity(N) tends to stabilize the cubic polytype¹²⁻¹⁴ Jepps et. al¹⁵ reported that the alpha to beta reverse transformation could be induced in reaction-bonded silicon carbide by high-temperature annealing(2500°C) under the high nitrogen pressure(3 MPa) : the greater the pressure of nitrogen, the faster the reaction rate In this work, however, reverse

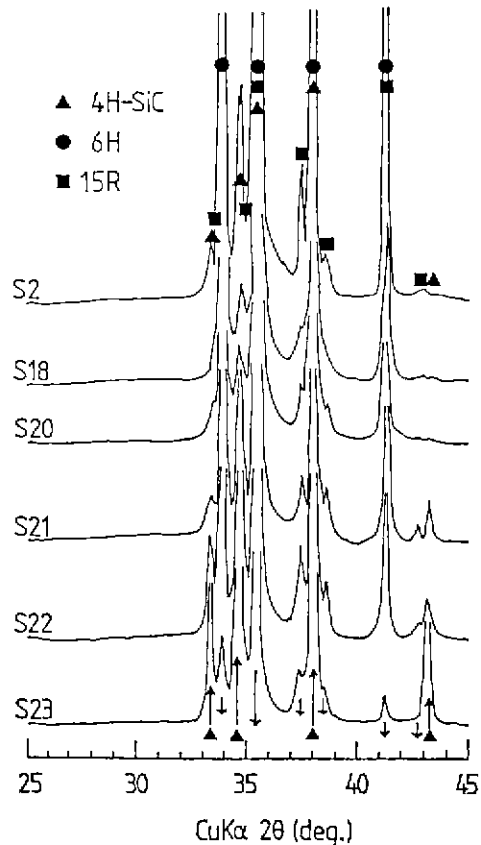


Fig.7. X-ray powder diffraction patterns of SiC sintered with AlN addition at 2100°C for 3h in N₂ or Ar atmosphere.

Table 3. Relative Densities and Average Sizes of SiC Grains for the Specimens Sintered with AlN Addition at 2100°C for 3h.

Sample No.	Sintering Conditions		Sintered Body	
	Cont. (wt%)	Atmosphere	R.D. (%)	Average Grain Size (μm)
S18	1	N ₂	58.0	1.6
S19	3		58.8	1.4
S20	10		57.8	1.1
S21	1	Ar	61.4	2.3
S22	3		62.9	large
S23	10		61.8	large

transformation has not occurred at all in nitrogen atmosphere but in argon. Table 3 and Fig.7 reveal that the grain growth and also reverse phase transformation become accelerated with increasing amount of AlN addition in argon atmosphere. And Cutler et al⁽⁶⁾. Have shown that AlN stabilizes the 2 H-SiC if solid solution formation occurs and it is surmised that aluminium oxycarbide, which also can enter the SiC lattice, may have a similar role in stabilizing or nucleating the 4H-SiC

Fig.8 shows temperature dependences of electrical conductivity and seebeck coefficient for SiC with AlN addition sintered at 2100°C for 3h in N₂ or Ar atmosphere. Electrical conductivity for the specimens sintered in Ar atmosphere is somewhat larger than that with B addition sintered under the same condition (Fig.6(a)), which might be due to the reverse phase transformation from 6H to 4H-phase, since carrier (hole) mobility in 4H is slightly higher than that in 6

H-SiC⁽⁵⁾. And it can be seen that electrical conductivity increases with increasing AlN addition and hence content of 4H-phase. Seebeck coefficient of AlN added SiC was somewhat smaller than that of B addition sintered under the same condition(Fig.6(b)), since the content of incorporation and microstructure are different. The reason for the difference in seebeck coefficient among AlN added specimens sintered in argon atmosphere would be seen that the content of 4 H-SiC transformed from 6H-SiC has been varied.

On the contrary, in the case of the specimens sintered in nitrogen atmosphere, electrical conductivity decreases with increasing content of AlN having low electrical conductivity, while the absolute value of seebeck coefficient increases

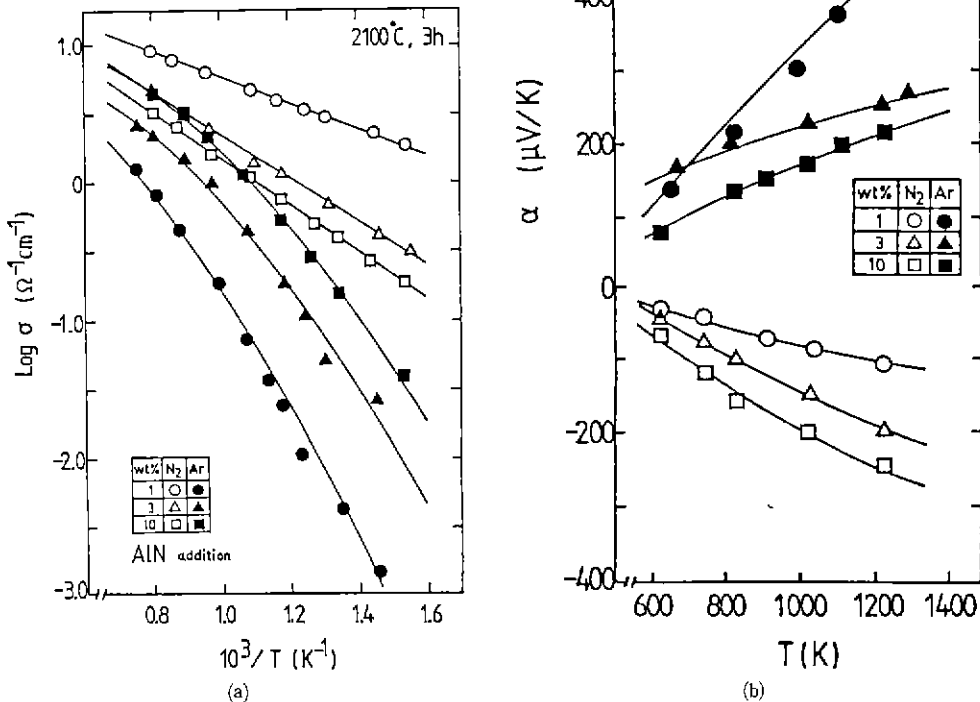


Fig.8. Temperature dependences of electrical conductivity (a) and the seebeck coefficient (b) for SiC sintered with AlN addition at 2100°C for 3h in N₂ or Ar atmosphere.

3.3. THERMOELECTRIC ENERGY CONVERSION BY POROUS 6H-SiC

The theoretical conversion efficiency of a thermocouple can be expressed as a function of material properties and junction temperatures. The maximum efficiency can be expressed as .

$$\eta = \frac{T_h - T_c}{T_h} \frac{M - 1}{M + (T_c/T_h)} \dots\dots\dots(1)$$

$$M = \sqrt{1 + ZT/2} \dots\dots\dots(2)$$

where, the figure of merit, Z, for a thermoelectric semiconductor is usually expressed by the following equation :

$$Z = \sigma \alpha^2 / K \dots\dots\dots(3)$$

where σ is electrical conductivity, α seebeck coefficient, and K thermal conductivity, respectively. For developing thermoelectric materials, a large number of works have been concentrated on increasing the figure of merit Z by increasing seebeck coefficient

and electrical conductivity and by reducing thermal conductivity.

Thermal conductivity of a sintered body is generally influenced by its density and purity¹⁷⁾. It was indicated in our previous reports^{2,4)} that thermal conductivity of porous SiC ceramics with ~60% relative density was lower than about 1/10 to 1/30 of the values for dense SiC ceramics. It is expected that thermal conductivities of the specimens prepared in this work have comparatively low thermal conductivity.

Fig.9 shows the temperature dependence of the power factor, $\sigma\alpha^2$. The power factors of the specimens sintered with additives are all smaller than those of non-additive specimens. So that to improve thermoelectric conversion efficiency of SiC ceramics, it would be necessary to select the optimum condition for the addition of other substances. And p-type specimens have lower power factors than n-type specimens, since the former have very low electrical conductivity in comparison with the latter. Consequently, it can be stated that control of microstructure and phase homogeneity would be very important for the thermoelectric conversion efficiency of SiC ceramics.

4. CONCLUSION

The following conclusions can be drawn from the present study.

- 1) The thermoelectric conversion efficiency of α -SiC ceramics is generally lower than that of β -SiC ceramics.
- 2) Phase homogeneity would be needed to keep large seebeck coefficient.
- 3) Larger content of nitrogen than added boron was dissolved into SiC during N₂-sintering.
- 4) The seebeck coefficient of alpha-SiC sintered in argon atmosphere was increased by the addition of B.
- 5) In argon atmosphere, AlN addition enhanced the reverse phase transformation from 6H-SiC to 4H-SiC.

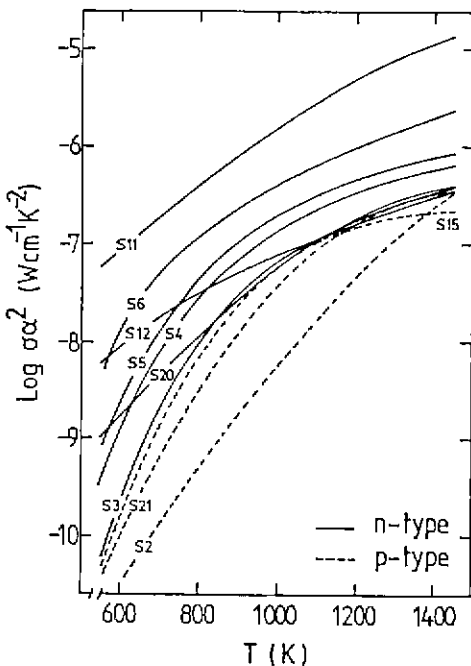


Fig.9. Temperature dependence of the power factor ($\sigma\alpha^2$) for porous SiC ceramics.

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