Thermoelectric Properties of B_4C - SiB_n ($n=4, 6, 14$) *In-situ* Composites

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B_4C - SiB_n ($n=4, 6, 14$) *in-situ* composites were prepared by arc-melting and by a heat-treatment in an argon atmosphere. As-prepared specimens consisted of B_4C , SiB_{14} and free-silicon. The SiB_4 phase formed by the heat-treatment for 5.4 ks at 1663 K, and SiB_6 phase was observed by the heat-treatment for 19.8 ks. The solid solution of Si into B_4C and SiB_{14} was observed after the heat-treatment. The heat-treatment caused almost no change in thermal conductivity, but the decrease in electrical conductivity. The Seebeck coefficient (α) increased significantly by the heat-treatment. The stacking faults associated with metastable SiB_4 phase formation could contribute to the increase in α . The greatest dimensionless figure-of-merit (ZT) value obtained in this study was 0.29 at $T=1100$ K.

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I. Introduction

Boron-rich borides, particularly boron carbide (B_4C), are candidate high-temperature thermoelectric materials due to their high Seebeck coefficient (α), electrical conductivity (σ) and low thermal conductivity (κ)⁽¹⁾⁽²⁾. It is known that the thermoelectric properties of B_4C depend strongly on preparation procedures. For example, the polycrystalline hot-pressed B_4C with large grains (several-hundred microns) showed low α values⁽³⁾, but the specimens prepared by arc-melting had high α values⁽¹⁾. Boron carbide films prepared by chemical vapor deposition had various α and σ values depending on the deposition conditions⁽⁴⁾. The electrical conduction in B_4C could be mainly dominated by phonon-assisted hopping of small bipolaron, and the great α values are caused by the hopping between deep trap levels which were formed at twin boundaries or stacking faults⁽⁵⁾. The dispersion of second phases might introduce many boundaries and stacking faults in the B_4C , which will contribute to the improvement of the thermoelectric properties of B_4C ⁽⁶⁾⁻⁽⁸⁾.

In this study, we selected silicon borides as the second phase in the B_4C -based composites, because silicon borides such as SiB_{14} , SiB_6 and SiB_4 have desirable thermoelectric properties and good compatibility with B_4C ⁽⁹⁾. Moreover, free-silicon is often formed by arc-melting in the B-C-Si system⁽⁸⁾⁽¹⁰⁾⁽¹¹⁾. The appropriate heat-treatment of the arc-melted specimens will enable one to produce several kinds of B_4C -based composites in which SiB_4 , SiB_6 and/or SiB_{14} is contained. In this paper, we describe the microstructures and thermoelectric properties of the B_4C - SiB_n ($n=4, 6, 14$) *in-situ* composites.

II. Experimental

B_4C , silicon and boron powders were weighed and mixed in an agate mortar with a small amount of methanol. The compositions on the B_4C - SiB_4 , B_4C - SiB_6 and B_4C - SiB_{14} tie-lines (a1 to a4, b1 to b4, c1 to c4, respectively) were prepared as indicated in Fig. 1. The powder mixtures were pressed to pellets (ϕ 15 mm $\times$ 10 mm) and arc-melted in argon gas. The arc-melted button-like specimens (about ϕ 20 mm $\times$ 5 mm) were heat-treated in an argon flow. After several preexperiments, we chose the appropriate heat-treatment temperature as 1663 K where SiB_4 and SiB_6 appeared.

The phases and their lattice parameters of the as-prepared (no heat-treatment) and heat-treated specimens were studied by powder X-ray diffraction (CuK_{α}) (XRD). The microstructures were examined by scanning electron microscopy (SEM), transmission electron microscopy

Fig. 1 Compositions of the arc-melted specimens.

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(TEM) and electron probe microanalysis (EPMA). The electrical conductivity (σ) measurement was conducted in argon using a four-probe method. The Seebeck coefficient (α) were measured by an ac method⁽¹²⁾ in a vacuum. The thermal conductivity (κ) measurement was conducted in a vacuum using a laser-flash technique. The density was measured with an Archimedeian method in toluene. All the measurements were carried out from room temperature to 1100 K. The values of figure-of-merit (Z) were calculated from the formula, $Z = \alpha^2 \sigma / \kappa$.

III. Results and Discussions

1. Microstructure changes

All the as-prepared specimens consisted of three phases, *i.e.*, B_4C , SiB_{14} and free-silicon, and no SiB_4 and SiB_6 phases were identified. The phases of B_4C (melting point is 2723 K) and/or SiB_{14} (melting point is 2293 K) might have solidified firstly, then the remaining liquid phase could solidify to boron-containing free-Si.

Figures 2 and 3 show the changes in the XRD patterns and SEM micrographs of b4 specimen with the heat-treatment time. Strong peaks of free-Si with those of B_4C and SiB_{14} were observed in the as-prepared b4 specimen. In Fig. 3(A) (as-prepared), black (a), grey (b) and white (c) parts were B_4C , SiB_{14} and free-Si, respectively. By the heat-treatment for 5.4 ks, SiB_4 phase ((d) in Fig. 3(B)) formed due to the reaction between SiB_{14} and free-Si.

Fig. 2 Changes of X-ray diffraction patterns of b4 specimen with the heat-treatment at 1663 K.

The further heat-treatment for 19.8 ks caused the formation of the SiB_6 phase ((e) in Fig. 3(C)) with the disappearance of the SiB_4 phase.

Figure 4 represents the changes in hexagonal lattice parameters (a_H and c_H) of B_4C in the a2 specimen and those of SiB_{14} in the c3 specimen with the heat-treatment time. The a_H values of B_4C were almost unchanged, but the c_H values of B_4C increased significantly with increasing heat-treatment time. It has been reported that there is a solid solution range of Si in B_4C (usually described as $B_{4+\delta}(C, Si)$), and the c_H values of $B_{4+\delta}(C, Si)$ are greater than those of B_4C without solid solution of Si⁽¹⁾⁽¹³⁾. This trend was observed in the present study as shown in Fig. 4. Both the a_H and c_H values of SiB_{14} increased with the

Fig. 3 SEM micrographs of (A) as-prepared b4 specimen, and after the heat-treatment for (B) 5.4 ks and (C) 19.8 ks at 1663 K (a: B_4C , b: SiB_{14} , c: free-Si, d: SiB_4 and e: SiB_6).

Fig. 4 Changes of hexagonal lattice parameters (a_H and c_H) of B_4C for a2 specimen and SiB_{14} for c3 specimen with the heat-treatment time.

heat-treatment time. This is also in agreement with the reported trend that the lattice parameters of SiB_{14} (usually described as $SiB_{14+\delta}$, $\delta=0\sim35$) increase with increasing Si content⁽⁹⁾⁽¹⁴⁾⁽¹⁵⁾. Therefore, it can be concluded that the Si to B ratios in $SiB_{14+\delta}$ phases obtained in the present study increased with the heat-treatment.

Table 1 summarizes the phase changes with the heat-treatment. By the heat-treatment for 19.8 ks, a1, b1 and c1 specimens changed to a single phase of B_4C . The c2, c3 and c4 specimens with higher B contents changed to two-phase mixtures of B_4C and SiB_{14} . The specimens with higher Si contents (a2 to a4 specimens for the B_4C - SiB_4 tie-line, and b2 to b4 specimens for B_4C - SiB_6 tie-line) became two-phase mixtures of B_4C and SiB_6 . We confirmed that no phase change happened by further heat-treatment for more than 19.8 ks.

Figure 5 represents a possible phase diagram of the B-C-Si system at 1663 K. Kieffer *et al.* reported the phase diagram of the B-C-Si system at 1973 K⁽¹⁶⁾. They prepared samples by a solid state reaction at 1973 K for 54

Fig. 5 Phase diagram of B-C-Si system at 1663 K (broken line: Kieffer's work⁽¹⁶⁾ at 1973 K).

ks using B, C and Si powders, and examined the phase relationship using XRD, chemical analysis and microscopy. Their phase diagram is almost the same as Fig. 5 except the two-phase region of B_4C - SiB_{14} , as indicated by a broken line. The SiB_4 phase is not indicated in Fig. 5, because SiB_4 is unstable at more than 1543 K⁽¹⁴⁾ and decomposes to Si and SiB_6 phases as shown in Fig. 2.

2. Thermoelectric properties

The thermoelectric properties of all the specimens indicated in Fig. 1 were measured before and after the heat-treatment, and were classified into three groups. In the following, the a1, c2 and b4 specimens were selected as typical examples for the three groups.

Figure 6 shows the temperature dependence of electrical conductivity (σ). The σ values of all the as-prepared specimens decreased by the heat-treatment. The σ values of the a1 specimen increased with increasing temperature (*i.e.*, semiconductor-like conduction). The as-prepared a1 specimen consisted of B_4C mainly with small amounts of free-Si and SiB_{14} phases. This specimen changed to a single phase of $B_{4+\delta}$ (C,Si) with the disappearance of the free-Si and SiB_{14} by the heat-treatment. The decrease in σ for the a1 specimen could be associated with the change from a B_4C -based mixture into a homogeneous $B_{4+\delta}$ (C,Si). The c2 specimen showed almost the same trend as the a1 specimen, but its σ values were smaller than those of the a1 specimen. This trend is understood by the fact that the σ values of SiB_{14} are much smaller than those of B_4C ⁽⁸⁾, and the c2 specimen contains much SiB_{14} phase. Since almost no free-Si remained in the a1 and c2 specimens after the heat-treatment for 5.4 ks, the σ values showed no change by further heat-treatment. On the other hand, since the b4 specimen contained a large amount of free-Si forming a net-work structure, the σ values indicating the metallic conduction decreased significantly by the heat-treatment due to the decrease of the amount of free-Si.

Figure 7 shows temperature dependence of Seebeck coefficient (α). In all cases, the α values increased significantly after the heat-treatment for 5.4 ks. The α

Table 1 Phase changes with the heat-treatment.

Specimens	Product phases		
	As-prepared	1663 K/5.4 ks	1663 K/19.8 ks
a1 b1 c1	$B_4C > Si, SiB_{14}$	$B_4C > SiB_4, SiB_{14} \gg Si$	B_4C
c2 c3 c4	$SiB_{14}, B_4C > Si$	$B_4C, SiB_{14} \gg SiB_4, Si$	B_4C, SiB_{14}
a2 a3 a4	B_4C, SiB_{14}, Si	$B_4C, SiB_4 > Si, SiB_{14}$	$B_4C, SiB_6 \gg SiC$
b2 b3 b4			SiB_6, B_4C

values of the c2 and b4 specimens further increased after the heat-treatment for 19.8 ks; however, the values of the a1 specimen decreased to the values before the heat-treatment. The α values of the c2 specimen increased, being almost three times greater than those before

the heat-treatment. The collected literature values of the thermoelectric properties for B_4C and silicon borides^{(1)(4)(8)(9)(17)–(22)} are shown in **Table 2**. The α values of B_4C prepared by arc-melting or sintering are in the range from 100 to 300 $\mu V K^{-1}$ at 300 to 1100 K. The reported

Fig. 6 Temperature dependence of electrical conductivity (σ) for a1, c2 and b4 specimens.

Fig. 7 Temperature dependence of Seebeck coefficient (α) for a1, c2 and b4 specimens.

Table 2 Thermoelectric properties of boron carbides and silicon borides in the temperature range from 300 to 1100 K (#: 300 to 440 K).

Products	Preparation	$\sigma / S m^{-1}$	$\alpha / \mu V K^{-1}$	$\kappa / W m^{-1} K^{-1}$	Ref.
B_4C	Arc-melting	$6.5 \times 10^2 \sim 1.8 \times 10^4$	180 ~ 280	9.8 ~ 12.2	(1)
B_5C		$1.0 \times 10^0 \sim 6.3 \times 10^3$	180 ~ 85	6.4 ~ 9.2	
B_9C		$1.3 \times 10^3 \sim 1.0 \times 10^4$	120 ~ 165	5.0 ~ 5.3	
B_4C	Hot-pressing	$1.3 \times 10^2 \sim 3.2 \times 10^3$	100 ~ 220	18 ~ 28	(17)
$B_{7.8}C$		$5.0 \times 10^2 \sim 1.0 \times 10^4$	100 ~ 250	5 ~ 6	
B_4C	CVD	$5.0 \times 10^1 \sim 2.0 \times 10^3$	100 ~ 170		(4)
$B_{9.62}C$		$1.0 \times 10^3 \sim 1.0 \times 10^4$	150 ~ 240		
SiB_{14}	CVD	$1.0 \times 10^{-3} \sim 2.5 \times 10^3$	300 ~ 400		(18)
SiB_{14}		$1.0 \times 10^0 \sim 4.0 \times 10^3$	30 ~ 190		
SiB_{14}	Arc-melting	$4.0 \times 10^0 \sim 6.3 \times 10^2$	100 ~ 380	5.4 ~ 10.0	(8)
SiB_{14}	CVD			4 ~ 5	(19)
$SiB_{14} + SiB_6$	Plasma Sintering	$3.2 \times 10^1 \sim 7.9 \times 10^1$	450 ~ 900	5.2 ~ 8.5	(9)
SiB_6	CVD	$2.0 \times 10^1 \sim 7.9 \times 10^2$	220 ~ 320	13 ~ 17	(20)
SiB_6	Hot-pressing	$1.0 \times 10^2 \sim 2.0 \times 10^3$	200 ~ 360		(21)
SiB_6	Hot-pressing	$6.3 \times 10^2 \sim 2.0 \times 10^4$		7.7 ~ 9.6#	(22)
SiB_4	CVD	$6.3 \times 10^3 \sim 1.0 \times 10^4$	90 ~ 120	14 ~ 17	(20)
SiB_4	Hot-pressing	$1.6 \times 10^1 \sim 3.2 \times 10^3$		7.7 ~ 9.6#	(22)

Fig. 8 Temperature dependence of thermal conductivity (κ) for a1, c2 and b4 specimens.

Fig. 9 Temperature dependence of dimensionless figure-of-merit (ZT) for a1, c2 and b4 specimens.

greatest α value of SiB_n ($n=4, 6, 14$) is about $400 \mu\text{VK}^{-1}$. The greatest value in this study was about $1000 \mu\text{VK}^{-1}$ at 1000 K for the c2 specimen after the heat-treatment for 19.8 ks. This value is much greater than those of B_4C and SiB_n . It has been reported that the α values of boron-rich borides, particularly B_4C , increase by the formation of stacking faults such as twin boundaries⁽⁵⁾. It is assumed that the complicated phase changes in the c2 specimen during the heat-treatment might have yielded substantial increases of stacking faults and other defects in the B_4C matrix accompanying a significant increase in α ⁽²³⁾.

Figure 8 shows temperature dependence of thermal conductivity (κ). The heat-treatment caused almost no change in κ . In the present study, the specimens contain free-Si which decreases with increasing heat-treatment time. However, the κ values of free-Si could strongly depend on the purity, *e.g.*, $142 \text{ Wm}^{-1} \text{ K}^{-1}$ for high purity Si⁽²⁴⁾, and $33 \text{ Wm}^{-1} \text{ K}^{-1}$ for impure Si containing 4mol%B. The contents of impurities, particularly B in the free-Si in the present specimens may have caused a decrease in κ of the free-Si phase. The phase changes from $\text{SiB}_{14} + \text{Si}$ to SiB_4 , and to SiB_6 proceeded by the heat-treatment. These phase changes hardly affected the κ values. As indicated in Table 2, the κ values of SiB_{14} , SiB_4 and SiB_6 are almost the same. The CVD specimens have slightly greater κ values than the sintered specimens. Since the arc-melted specimens are fine-grained polycrystalline, the microstructures of the specimens in the present study are similar to those of the sintered specimens rather than to those of the CVD ones. The κ values of the b4 specimen whose main phase is SiB_6 , are in good agreement with the reported values of sintered SiB_6 .

Figure 9 shows temperature dependence of dimensionless figure-of-merit (ZT). The ZT values increased exponentially with increasing temperature. The effect of

Fig. 10 Effect of the heat-treatment on dimensionless figure-of-merit (ZT) for a1, c2 and b4 specimens.

heat-treatment on the ZT values were represented in **Fig. 10**. At less than 1000 K, the ZT values decreased with increasing heat-treatment time; however, the a1 and c2 specimens after the heat-treatment for 5.4 ks had greater ZT values at 1100 K. By the heat-treatment for 19.8ks, the ZT values of the c2 and b4 specimens slightly increased at 1100 K. The greatest ZT value obtained in this study was 0.29 at $T=1100 \text{ K}$ for the a1 specimen after the heat-treatment for 5.4 ks. **Figure 11** compares the ZT values obtained in this study with those of several boron-rich borides⁽¹⁾⁽²⁾⁽⁶⁾⁻⁽⁸⁾⁽¹⁰⁾. The greatest ZT value obtained in this study was a little smaller than that of

Fig. 11 Temperature dependence of dimensionless figure-of-merit (ZT) for several boron rich borides and composites.

B_4C -6mol% TiB_2 composites⁽⁷⁾, but mostly greater than those of many other boron-rich borides. Since the specimens prepared in this study contain silicon as a major element, they are higher in oxidation resistance than usual boron-rich compounds⁽²²⁾⁽²⁵⁾, being advantageous for the use in an oxidizing atmosphere.

IV. Conclusions

B_4C - SiB_n ($n=4, 6, 14$) *in-situ* composites were prepared by arc-melting and by a heat-treatment in an argon atmosphere. The changes of their microstructures and thermoelectric properties with the heat-treatment time at 1663 K were studied.

As-prepared specimens consisted of B_4C , SiB_{14} and free-Si. SiB_4 phase formed by the heat-treatment for 5.4 ks. Then the SiB_4 phase disappeared with the formation of SiB_6 or SiB_{14} phase by the heat-treatment for 19.8 ks depending on Si content. The heat-treatment also caused the solid solution of Si into the B_4C and SiB_{14} phases.

The heat-treatment caused the increase in the Seebeck coefficient (α), the decrease in electrical conductivity (σ) and almost no change in thermal conductivity (κ). The significant increase of α could be associated with the formation of stacking faults with the phase changes. The greatest ZT value obtained in this study was 0.29 at $T=1100$ K for the a1 specimen after the heat-treatment for 5.4 ks, whose main phase was B_4C with small amounts of SiB_4 and free-Si.

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