Synthesis and Thermoelectric Properties of Boron-rich Silicon Borides

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Boron-rich silicon borides in a boron content range 90.0 to 97.0 at% were prepared by arc-melting and spark plasma sintering. The plasma-sintered specimens consisted of SiB_n when boron content over 93.7 at%, and the mixture of $\text{SiB}_n + \text{SiB}_6$ when boron content below 93.7 at%, while all the arc-melted specimens consisted of SiB_n and free silicon. The thermoelectric properties, involving electrical conductivity, thermal conductivity as well as Seebeck coefficient were studied and the effects of the phase composition and microstructure on the thermoelectric properties were discussed. The dimensionless thermoelectric figure of merit values ($Z = \alpha^2 \sigma / \kappa$) of all the obtained silicon borides increased with increasing temperature. The plasma-sintered specimen containing 90 at% B showed the largest ZT value, which reached 0.2 at 1100 K.

Keywords: high temperature thermoelectric material, boron-rich silicon boride, arc melting, plasma sintering, electrical conductivity, thermal conductivity, Seebeck coefficient, figure of merit.

I. Introduction

In thermoelectric conversion technology, development of high temperature thermoelectric materials with a large figure of merit ($Z = \alpha^2 \sigma / \kappa$) value is demanded for improving conversion efficiency, since the conversion efficiency is in proportion to the hot junction temperature and Z value⁽¹⁾. Boron-rich silicon borides are a candidate material for high temperature thermoelectric conversion because their Seebeck coefficient (α) and electrical conductivity (σ) are moderately large, and generally increase with temperature⁽¹⁻⁴⁾. On the other hand, the thermoelectric properties of the boron-rich silicon borides vary sensitively with their composition and structure, while there are many types of silicon borides particularly at the boron-rich region⁽⁵⁻⁷⁾. The authors have studied the phase relations of Si-B system in boron-rich region by solid state reaction⁽⁸⁾. In the present work, boron-rich silicon borides with various compositions were prepared by arc-melting (AM) and spark plasma sintering (SPS). Seebeck coefficients (α), electrical conductivity (σ) and thermal conductivity (κ) were measured in a temperature range of 400 – 1100 K, and the dimensionless thermoelectric figure of merit Z ($Z = \alpha^2 \sigma / \kappa$) values were evaluated. In this report, the emphasis will be placed on the effects of phase composition and microstructure to the thermoelectric properties.

II. Experimental

Silicon borides were prepared by arc-melting and spark plasma sintering in a boron content range of 90.0 to 97.0 at%. The silicon boride powders prepared by solid state reaction were used as the starting materials. In arc-melting experiments, the pressed disk-shaped pellets (10 mm thick and 20 mm in diameter) were placed on a water-cooled copper hearth and melted by arc spark in an argon atmosphere. In plasma sintering, the spark plasma sintering equipment (Sumitomo Coal Mining: SPS-1050) was used. The sintering test was carried out in a vacuum using a graphite die (20 mm in diameter) at 1873 K for 5 minutes under a pressure of 80 MPa.

The phases were identified by X-ray diffraction (XRD). Rod-like pieces (3×3×15 mm) were cut out for the electrical conductivity and Seebeck coefficient measurements, and disk-shaped pieces (2 mm thick and 10 mm in diameter) were cut out for the thermal conductivity measurements. Microstructure and phase distribution were observed by a superprobe (JEOL: JXA-8621MX). Electrical conductivity was measured using a D.C. four-probe method. Thermoelectromotive force (e.m.f.) was measured under small temperature gradients (ΔT : 2 – 10 K) and Seebeck coefficient was determined from the slope of e.m.f. against ΔT . Thermal conductivity was measured using laser-flash technique. All measurements were performed in the temperature range of 300 to 1100 K.

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Fig. 1. X-ray diffraction patterns of arc-melted (a) and plasma-sintered (b) silicon boride specimens containing 90 at% B.

III. Results and discussion

1. Composition and microstructure

Our previous results by solid reaction indicated that the stable phases should be non-stoichiometric SiB_n ($n=15-49$, rhombohedral) in a single phase when the boron content between 93.7 and 98 at%, and the mixture of SiB_6 + SiB_n between 86 and 93.7 at% B⁽⁸⁾. Figure 1 shows the typical X-ray diffraction patterns of the arc-melted (Fig.1a) and plasma sintered (Fig.1b) specimens. In the present boron content region (90 to 97 at%), all the arc-melted specimens consisted of free silicon and SiB_n phases, and the content of free silicon decreased with increasing boron contents. The free silicon in the arc-melted specimens is a non-equilibrium phase which must be formed during the rapid quenching process. On the other hand, the plasma-sintered specimens consisted of SiB_n with boron content over 93.7 at%, and the mixture of SiB_n + SiB_6 with boron content below 93.7at%, that is, the same as the starting powder.

Figure 2 shows the typical morphologies of the arc-melted (Fig.2a) and plasma-sintered (Fig.2b) specimens containing 90 at% B. The EPMA study showed that, the bright parts corresponds to the higher silicon content phase, that is, the free silicon phase in Fig.2a and SiB_6 phase in Fig.2b, respectively. For the arc-melted specimen, the free silicon phase is interconnected to form a network structure and the SiB_n dispersed in silicon when boron content is

Fig. 2. Microstructures of arc-melted (a) and plasma-sintered (b) silicon boride specimens containing 90 at% B.

Fig. 3. Temperature dependence of electrical conductivity.
(●) SPS-90at%B; (○) SPS-94at%B; (▲) AM-90at%B;
(△) AM-94at%B.

Fig. 4. Temperature dependence of thermal conductivity. (●) SPS-90at%B; (○) SPS-94at%B; (▲) AM-90at%B; (△) AM-94at%B.

Fig. 5. Temperature dependence of Seebeck coefficient. (●) SPS-90at%B; (○) SPS-94at%B; (▲) AM-90at%B; (△) AM-94at%B.

below about 91 at%. SiB_n becomes matrix phase and silicon disperses reversely in the SiB_n matrix when boron content is over about 91 at%. In the plasma-sintered specimens, both SiB_n and SiB_6 were detected when $B < 93.7$ at%, and no SiB_6 phase but SiB_n single phase was detected when $B > 93.7$ at%.

2. Thermoelectric properties

Figure 3 shows the temperature dependence of electrical conductivity. The arc-melted specimen containing 90 at% B had the largest conductivity which is almost independent of

Fig. 6. Temperature dependence of ZT value. (●) SPS-90at%B; (○) SPS-94at%B; (▲) AM-90at%B; (△) AM-94at%B.

temperature. This tendency is similar to that of silicon and is considered to be caused by the Si network structure. The other specimens had near conductivity values, which were smaller than the former and increased with increasing temperature. This behavior is almost the same as that of SiB_n reported previously⁽³⁾.

Figure 4 shows the temperature dependence of thermal conductivity. They decreased with increasing temperature for all the specimens. This tendency was in agreement with that reported by Darolles et al⁽⁴⁾. The arc-melted specimen containing 90 at% B had the greatest values, which must be caused by the existence of large amount of free silicon phase.

Figure 5 shows the temperature dependence of Seebeck coefficient. It showed a slight decrease with increasing temperature for the sintered specimen containing 94 at% B, while the others increased with increasing temperature. The arc-melted specimens containing 90 at% B and 94 at% B had almost the same values which changed from 100 to 300 $\mu\text{V K}^{-1}$ with temperature. The Seebeck coefficients of the plasma sintered specimen containing 90 at% B showed a significant increase with increasing temperature. A large Seebeck coefficient (about 900 $\mu\text{V K}^{-1}$ at 1100 K) was achieved for this specimen. The large value and large temperature increment of the Seebeck coefficient for the sintered silicon boride may be caused by the hopping conducting, which is sensitively affected by the microstructure^{(1), (9-11)}. The details on the relations of microstructure and hopping conducting for silicon borides are on being studied.

Figure 6 depicts the temperature dependence of ZT value ($ZT = \alpha^2 \sigma T / \kappa$). They increased with increasing temperature over the considered temperature range for all the specimens. Especially, the plasma-sintered specimen containing 90 at% B exhibited the greatest ZT value with a

significant increase with temperature, and it reached about 0.2 at 1100 K.

IV. Conclusion

Boron-rich silicon borides were prepared by arc-melting and spark plasma sintering. The specimens prepared by arc-melting consisted of silicon and SiB_n phases. The ones prepared by plasma sintering consisted of SiB_n ($n=15-49$) single phase or the mixture of $\text{SiB}_n + \text{SiB}_6$, depending on the boron content range. The dimensionless figure of merit increased with increasing temperature. Among all the specimens, the plasma-sintered silicon boride containing 90 at% B showed the greatest Seebeck coefficients (α) and ZT values. The values of α and ZT at 1100 K were about $900 \mu\text{V K}^{-1}$ and 0.2, respectively.

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