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Preparation of Si infiltrated SiB_6-TiB_2 composites

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SiB_6 and TiB_2 ceramics show good thermal properties, electrical conductivity, and excellent hardness. Unfortunately, these materials have poor sinterability. In this study, the preparation of SiB_6-TiB_2 composites using SiB_6 and TiB_2 powders was investigated to determine the sinterabilities and properties. We have performed two reaction stages for the preparation of Si-Ti-B-C depending on the sintering conditions. The Vickers hardness at room temperature of an STC sample and 7S3TC sample shows the highest value of about 23 GPa at 40 mass% carbon of STC-4, respectively. The X-ray diffraction patterns of sintered bodies of SiB_6-TiB_2 by Si infiltration show SiB_6 and C including carbonized phenolic resin has changed to B_4C and SiC. No pores were observed in any of specimens by scanning electron microscopy (SEM). Maximum point of electrical conductivity of 7S3TC and STC was 7.3×10^4 S/m and 5×10^4 S/m at 973 K, respectively.

Key words: Silicon boride, Titanium boride, Infiltration, Vickers hardness.

Introduction

Silicon hexaboride (SiB_6) [1] ceramic have been studied at high temperature, showing high thermal electrical conductive, and high hardness [2-4] and previously we have reported on the Si-B-C system [5-6]. Silicon hexaboride (SiB_6) has been shown to be potentially a useful material because of its excellent chemical resistance properties and it has attracted a great deal of attention as a material for thermoelectric applications at high temperatures. Ceramic materials such as borides, nitrides and carbides are a natural choice for several advanced structural applications due to their extraordinary hardness coupled with stability at high temperature. Titanium diboride (TiB_2) is a compound with both ionic and covalent bonds [7], which has necessitated high sintering temperatures. Titanium diboride (TiB_2) is primarily known for its extreme hardness and its chemical stability even at high temperatures. Furthermore titanium diboride (TiB_2) is an excellent conductor of electricity and heat, a property very rare among ceramic materials. The melting point of titanium diboride (TiB_2) is very high (3498 K) and it has a good oxidation resistance up to 1273 K. Unfortunately, there have been few reports regarding the properties of SiB_6-TiB_2 ceramics.

In this study, the preparation of SiB_6-TiB_2 composites with Si infiltration was investigated to determine the sinterabilities using pressureless sintering at 1973 K and Si infiltration at 1703 K in an Ar atmosphere to give good thermal property and electrical conductivity.

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Experimental Procedure

A flow chart for the preparation of SiB_6-TiB_2 composite is shown Fig. 1. Silicon hexaboride-titanium diboride (SiB_6-TiB_2) composites were fabricated using SiB_6 (particle size: 60 μm, Cerac, Inc. USA) and TiB_2 (particle size: 4.25 μm, Japan New Metals co., Ltd.) at ratios of 50 to 50 and 70 to 30 as starting materials. They was mixed with additives of 10 mass%, 20 mass%, 30 mass%, 40 mass% and 50 mass% C powder(particle size: 5 μm, Kojundo Chemical Lab. Co., Ltd. Japan) and 30 mass% phenolic resin (KEU-98, Kolon Chemical Co., Ltd., Korea). The comparative composition of each specimen was summarized in Table 1. These powders were fabricated using a cold isostatic press (CIP) at 100 MPa after uniaxially pressing at 20 MPa, and then sintering was performed in two reaction stages for the preparation of SiB_6-TiB_2 composites depending on the sintering conditions. The first composite was prepared

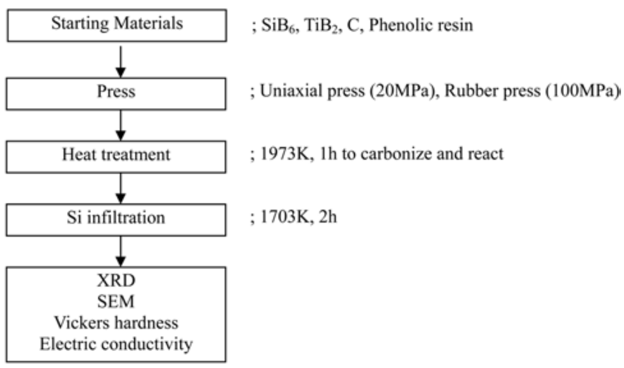

Fig. 1. Flow chart for the preparation and characterization of SiB_6-TiB_2 composites.

Table 1. Synthesis processes and products of all samples

Sample	Composition (mass%)				Vickers hardness (GPa)	Bulk densiy (g/cm^3)
	SiB_6	TiB_2	C	Phenolic resin		
STC-1	50	50	10	-	15.8	2.78
STC-2	50	50	20	-	14.9	2.79
STC-3	50	50	30	-	16.8	2.82
STC-4	50	50	40	-	23.3	2.80
STC-5	50	50	50	-	20.3	2.83
STCP-1	50	50	10	30	13.4	2.81
STCP-2	50	50	20	30	14.1	2.83
STCP-3	50	50	30	30	15.7	2.83
STCP-4	50	50	40	30	20.4	2.96
STCP-5	50	50	50	30	16.3	2.97
7S3TC-1	70	30	10	-	13.6	2.61
7S3TC-2	70	30	20	-	14.9	2.63
7S3TC-3	70	30	30	-	15.7	2.61
7S3TC-4	70	30	40	-	22.9	2.71
7S3TC-5	70	30	50	-	17.9	2.65

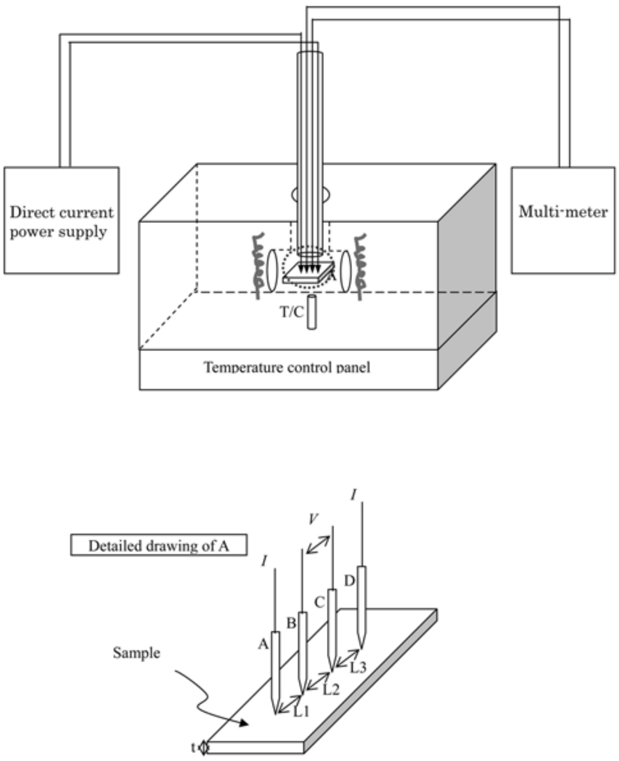

Fig. 2. Schematic diagram of DC four-point method.

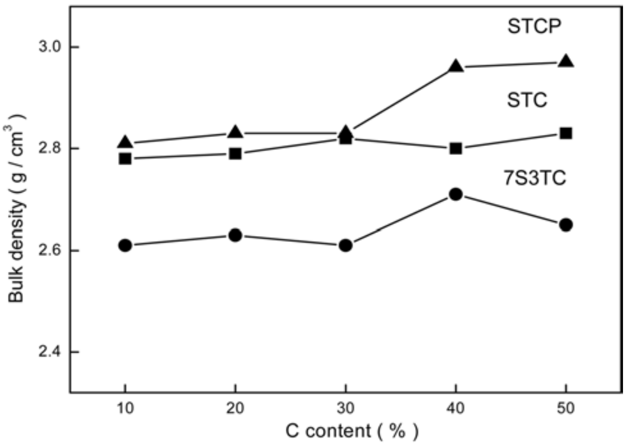

Fig. 3. The results of bulk density of the Si infiltrated SiB_6-TiB_2 composites containing carbon and carbonized phenolic resin.

by pressureless sintering at 1973 K in an Ar atmosphere for 1 hour in order to react with SiB_6-C and carbonize the phenolic resin. The second composite was prepared by the Si infiltrated method. The infiltration temperature was 1703 K and the holding time was 2 hours in an Ar atmosphere. The infiltrated bodies were cut into 5 × 5 × 10 mm blocks and polished with a diamond disk for Vickers hardness measurements at room temperature. The bulk density of each specimen was calculated by the Archimedes method from its weight and size after polishing. The crystalline phases of the infiltrated samples were determined by X-ray diffraction (XRD). Fracture surfaces of the specimens were observed using a scanning electron microscope (SEM). The electrical conductivity of the infiltrated bodies was measured by a DC four-point method from room temperature to 1273 K for a series of holding times (Fig. 2). The maximum holding time was 180 minutes.

Results and Discussion

Fig. 3 shows the bulk density of the SiB_6-TiB_2 composite Si infiltrated at 1703 K in an Ar atmosphere for 1 hour. The bulk density shows a tendency to increase with increasing carbon and phenolic resin contents. The STCP-5 sample which contains phenolic resin has highest bulk density (2.97 g/cm^3). The Vickers hardness also shows a tendency to increase with increasing carbon and phenolic resin contains as shown in Fig. 4. The Vickers hardness at room temperature shows the highest value of about 23 GPa for the STC-4 sample containing 40 mass% C and there was an immediate sharp increase. The Vickers hardness of 7S3TC and STCP which contain 40 mass% C also shows good values of about 23 GPa and 20 GPa,

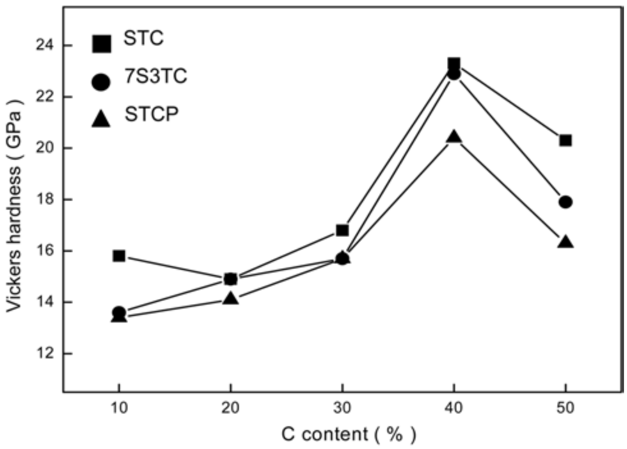

Fig. 4. The Vickers hardness of the Si infiltrated SiB_6-TiB_2 composites containing carbon and carbonized phenolic resin.

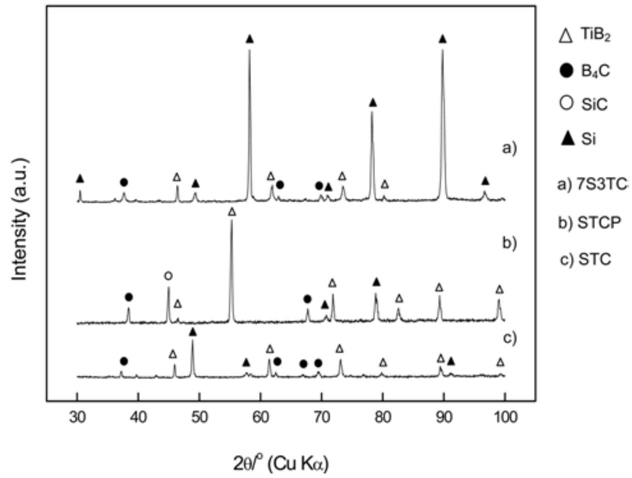

Fig. 5. X-ray diffraction patterns of the sintered bodies.

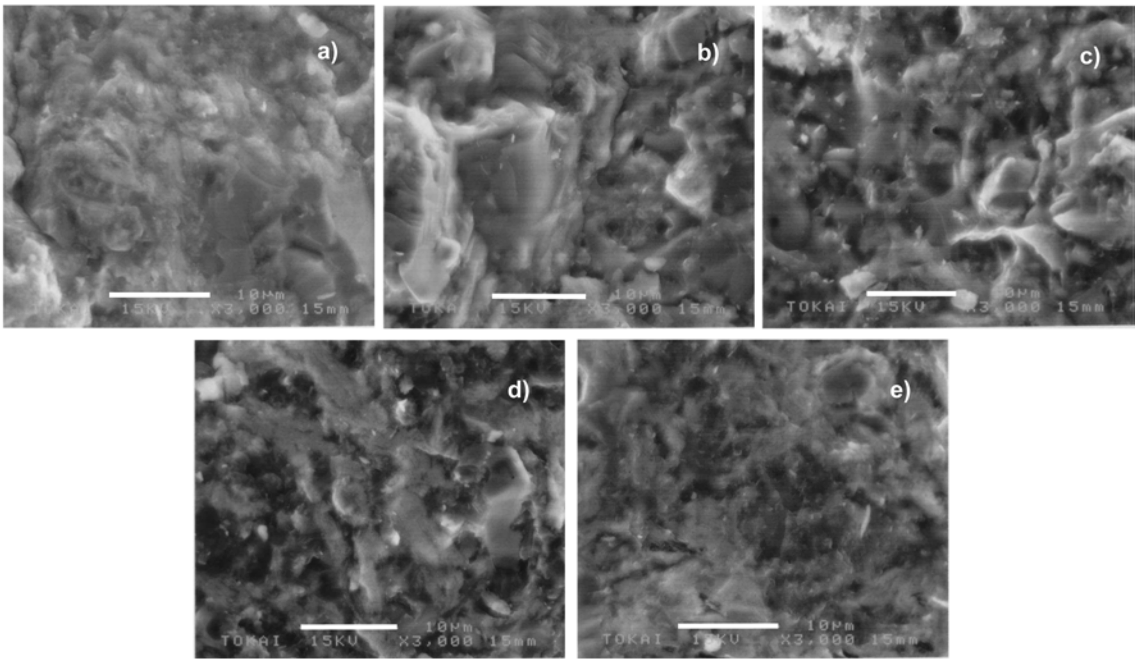

Fig. 6. SEM image of STC samples: (a) 10 mass%, (b) 20 mass%, (c) 30 mass%, (d) 40 mass%, and (e) 50 mass% carbon.

respectively. The Vickers hardness of all specimens gradually decreases to 20.3 GPa, 17.9 GPa, and 16.3 GPa, respectively. The data of bulk density and Vickers hardness shows reverse values in the case of the STCP series.

Fig. 5 shows the results of the X-ray diffraction analysis of samples sintered at 1703 K for 2 hours in an Ar atmosphere. It was observed that move silicon carbide and boron carbide were made in the carbon and carbonized phenolic resin containing samples. The silicon boride (SiB_6) and carbon (C) also reacted with the phenolic resin as a carbon source according to the following equation:

$$2SiB_6 + 5C = 2SiC + 3B_4C \quad (1)$$

On the other hand, since titanium diboride (TiB_2) is a compound with both ionic and covalent characters [6], and needs a high sintering temperature, the titanium diboride (TiB_2) did not react with the carbonized phenolic resin, the carbon and silicon at 1703 K in an Ar atmosphere. Peaks from TiB_2 were only detected.

Figs. 6, 7 and 8 show scanning electron microscope (SEM) images of the fracture surfaces of SiB_6-TiB_2 composites containing C with phenolic resin by Si infiltration at 1703 K for 2 hours in an Ar atmosphere. No pores were observed in any of the specimens. A similar aspect of each fracture surface is shown in all the specimens. The amount of reacted SiC and B_4C from the SiB_6 increased with an increase in the amount of carbon and carbonized phenolic resin. In particular it can be seen that the amount of reacted SiC and B_4C are increasing substantially in Fig. 7. The reason is because the amount of carbon and carbonized phenolic resin affected the as-received SiB_6.

Fig. 9 shows the temperature and time dependence of

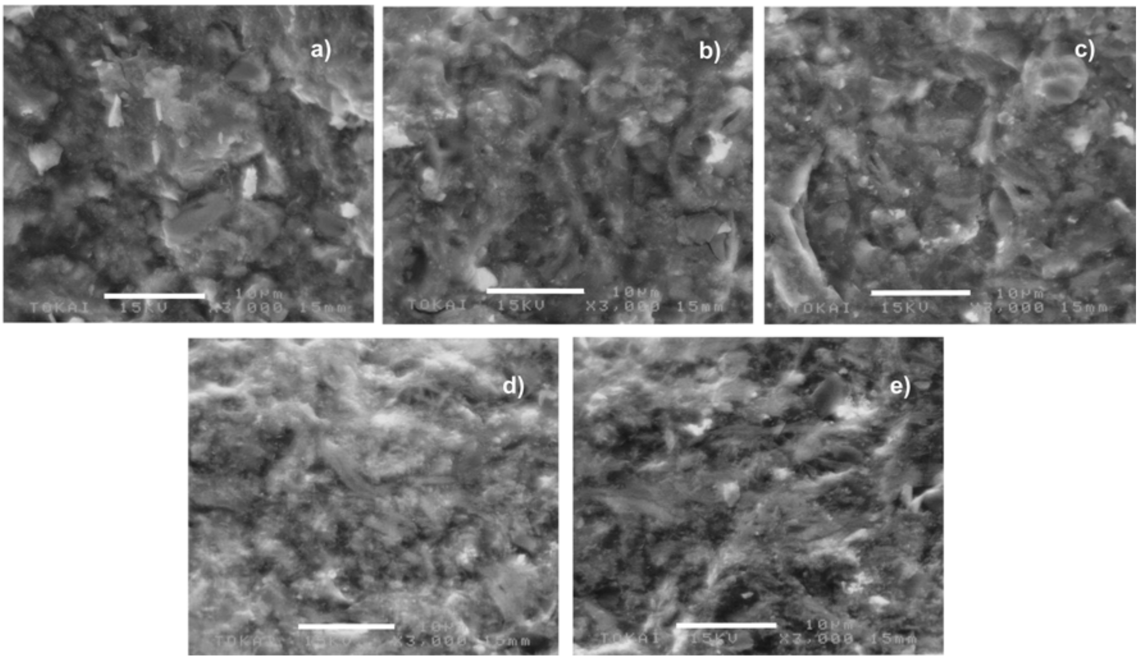

Fig. 7. SEM images of STCP samples: (a) 10 mass%, (b) 20 mass%, (c) 30 mass%, (d) 40 mass%, and (e) 50 mass% carbon with 30 mass% phenolic resin.

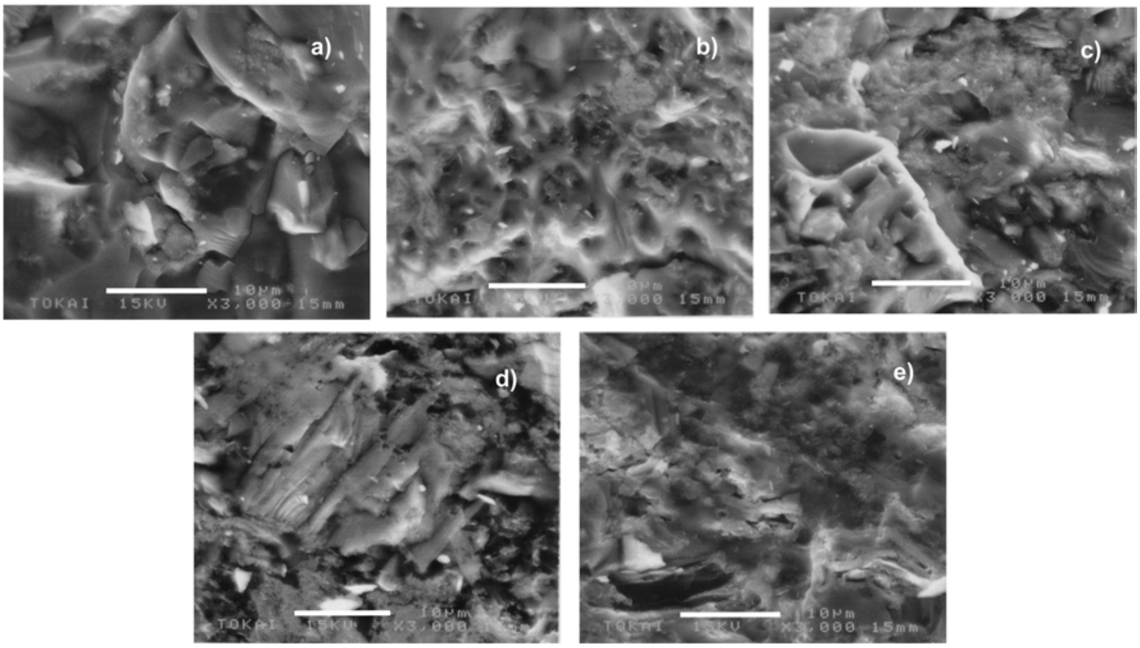

Fig. 8. SEM images of 7S3TC samples: (a) 10 mass%, (b) 20 mass%, (c) 30 mass%, (d) 40 mass%, and (e) 50 mass% carbon.

the electrical conductivity of the sintered bodies. The value of the electrical conductivity of the as-received SiB_6 sintered body increased with an increase in the temperature. However, the electrical conductivity of the as-received TiB_2 sintered body rapidly decreased from room temperature to 323 K. The rise brings the electrical conductivity to 4×10^4 S/m at 973 K and then the rate change of the electrical conductivity gradually decreases. The electrical conductivity of the 7S3TC sintered bodies was higher than the STC sintered bodies at 973 K. The highest point of electrical conductivity of 7S3TC and STC was 7.3×10^4 S/m and 5×10^4 S/m at 973 K, respectively. The electrical conductivity of STC describes a parabola from 423 K to 723 K. It was seen that the electrical conductivity of STC was very high 35.4×10^4 S/m and 22.7×10^4 S/m at 20 minutes and 150 minutes holding time. The electrical conductivities of STCP and 7S3TC were about 4.3×10^3 S/m and 1.8×10^4 S/m for a holding time at 1273 K. It is

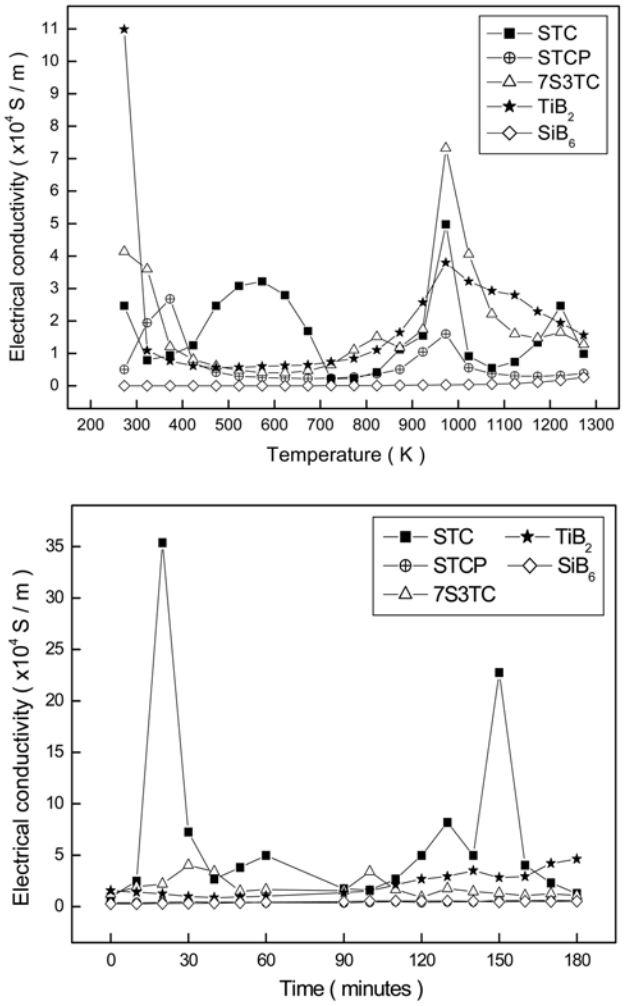

Fig. 9. Temperature and time dependence of the electrical conductivity of the sintered bodies.

developed that the sample showed the tendency of the electrical conductivity of the semiconductor.

Conclusions

In this study, it was found that good sintered bodies of SiB_6-TiB_2 could be made at 1703 K for 2 hours by Si infiltration. The STCP-5 including phenolic resin sample had the highest bulk density (2.97 g/cm^3). The Vickers hardness at room temperature of the STC sample and 7S3TC sample shows the highest value of about 23 GPa with 40 mass% carbon of STC-4, respectively. The X-ray diffraction patterns of sintered bodies of SiB_6-TiB_2 by Si infiltration showed that SiB_6 and C including carbonized phenolic resin changed to B_4C and SiC. No pores were observed in nay of specimens by scanning electron microscopy (SEM). The electrical conductivity of the 7S3TC sintered body was higher than the STC sintered body. The maximum electrical conductivity of 7S3TC and STC were 7.3×10^4 S/m and 5×10^4 S/m at 973 K, respectively. The electrical conductivity of 7S3TC was maintained at about 1.8×10^4 S/m for all holding times at 1273 K. It is developed that the sample showed the tendency of the electrical conductivity of the semiconductor.

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