Thermoelectric properties of SiC/C composites from wood charcoal by pulse current sintering

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Abstract

Traditional energy production based on fossil fuels, such as oil, coal, and natural gas, is on the verge of exhaustion. Attention has gathered for thermoelectric energy conversion technology, as clean power generation, which does not depend on a fossil fuel. Many efforts are directed towards the development of materials to be used in thermoelectric conversion at high temperature. SiC is such a candidate material with a high thermal, chemical and mechanical stability. With this in mind SiC/C composites were investigated by sintering a mix of wood charcoal and SiO_2 powder (32-45 μm) at 1400, 1600 and 1800°C under N_2 atmosphere. Pulse current heating was applied, a method known for its fast sintering rate. Thermoelectric properties of SiC/C composites were investigated by measuring Seebeck coefficient, electrical conductivity and thermal conductivity as a function of heat treatment temperature and reaction time. The Seebeck coefficient showed a p-type to n-type transition at a heat treatment temperature around 1600°C. The electrical conductivity showed a steady increase with temperature for all three heat treatment temperature with as only irregularity that the values for 1600°C were the lowest of them all. In thermal conductivity, the samples heated at 1800°C showed high values at room temperature which strongly decreased with increase in measurement temperature. Therefore, thermoelectric properties were improved with an increase in measurement temperature. A maximum in the figure of merit of 3.38×10^{-7} K^{-1} was reached at 200°C in the sample heated at 1400°C for 30 min. Results suggested that SiC/C composite made from a powder of wood charcoal and SiO_2 can be used as a thermoelectric material for applications subjected to elevated temperatures.

1. Introduction

Research on the development of new energy sources has recently received a lot of attention due to concern about environmental problems. Traditional energy production based on fossil fuels, such as oil, coal, and natural gas, is on the verge of exhaustion because of the limited nature of raw material of fossil fuels. Moreover, the air pollution substances are discharged by the use of fossil fuels to the environment. Attention has gathered for thermoelectric energy conversion technology, as clean power generation, which does not depend on a fossil fuel.

Many efforts have been devoted to the development of thermoelectric materials; however, most of them are to be used only at low temperature. Therefore, these efforts are directed towards the development of materials to be used in thermoelectric conversion at high temperature. SiC-based material is such a candidate material with a high thermal, chemical and mechanical stability. It has been reported that SiC composites have a high figure of merit at high temperature.[1, 2] For n-type conduction, an effective doping element is N performed by sintering under a nitrogen atmosphere.[3]

On the other hand, research on SiC composites based on biomass has recently gathered a lot of attention.[4-6] Due to abundance of waste wood and high strength properties of SiC ceramics, SiC composites has widely been used for industrial

applications. Some attempts have already been reported to develop SiC composites based on wood charcoal.[7, 8]

In our research, we have manufactured SiC/C composites from wood charcoal by a pulse current sintering method. The pulse current sintering method is a novel process where metals, ceramics, and composites can be sintered in a short time. [9, 10] As the current passes through the graphite dies as well as the sample, the sample is heated from both the inside and outside at the same time. In this technique the phenomenon of microscopic electric discharge between particles is generated under pressure. Compared with the hot pressing methods, the pulse current sintering method can be an alternative to fast sintering of fully dense materials.[11] Using this method, heat treatment can be controlled and process time can be shortened considerably.

We produced SiC/C composites by mixing powder of wood charcoal and SiO_2 and sintering them together under N_2 atmosphere in a pulse current sintering device. In this paper, the microstructure and thermoelectric properties of the specimen were studied.

2. Experimental procedure

Japanese cedar (*Cryptomeria japonica*) was chopped into 30 mm large pieces. These pieces were heated in a laboratory-scale electric furnace with a heating rate of 4°C/min

up to a temperature of 700°C and kept there for 1 hr. As protective gas, Ar was used with a flow rate of 100 ml/min. Afterwards the furnace was cooled down naturally to room temperature. The wood charcoal powder and SiO_2 powder (Nacalai Tesque Co. Ltd) sized 32-45μm were prepared using a sieve and vibration mill. Samples with 50 wt SiO_2 powder were prepared based on the dry weight of wood charcoal. The powder mix was put into a 10 mm diameter graphite die, which was heated up to 1400°C , 1600°C and 1800°C at a rate of 500°C/min and with a holding time of 10 or 30 min under an N_2 gas flow of 1 l/min using a pulse current sintering apparatus (VCSP-II). After the reaction, it was naturally cooled to room temperature. A pressure of 40 MPa was applied right from the start of the heating and was released immediately after the reaction. The temperature was measured at the front surface of the graphite die by an optical pyrometer monitoring the reaction temperature. After the SiC/C was cut into discs of 10 mm in diameter and approximately 1 mm in thickness, it was used for X-ray diffraction, scanning electron microscopy (SEM), electrical conductivity and thermal conductivity. For Seebeck measurements, the SiC/C was cut into rectangular shaped samples of $1 \times 1 \times 5$ mm^3.

An X-ray diffraction device (RINT-ultra X18) was used to analyze the crystal structure. The microstructure of the fracture surface of the specimen was observed by SEM (JEOL JSM-5310). Seebeck coefficients were measured under a vacuum in a temperature range from room temperature to 450°C. The electrical conductivity was measured under vacuum in a temperature range from room temperature to 800°C by Van der Pauw's method using DC & AC Hall effect measurements (ResiTest 8300). The specific thermal capacity and the thermal diffusivity of the specimens were measured under vacuum in a temperature range from room temperature to 800°C by the

laser-flash method, using a thermal-constant analyzer (TC-7000H). The thermal conductivity was calculated using the following equation:

$$K_T = \rho\, Cp\, \kappa \qquad\qquad\qquad (1)$$

where K_T: thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$), ρ: bulk density ($g \cdot cm^{-3}$), Cp: specific thermal capacity ($J \cdot g^{-1} \cdot K^{-1}$), κ: thermal diffusivity ($cm^2 \cdot s^{-1}$).

The figure of merit of the specimen was calculated using the following equation:

$$(2)$$

$$Z = \frac{S^2 \sigma}{K_T}$$

where Z: figure of merit (K^{-1}), S: Seebeck coefficient (V/K), σ: electrical conductivity ($\Omega^{-1} m^{-1}$)

3. Results and discussion

Microstructure

X-ray powder scans were recorded for samples kept at 1400, 1600 and 1800°C for 10 and 30 min (Fig. 1). Clear peaks of β-SiC were observed, corresponding to the β-SiC phase: (111), (220) and (311) at 2θ of 36°, 60° and 72°, respectively. The sharpest β-SiC peaks appeared at 1600°C, on the other hand, the SiO_2 peaks clearly appeared only at 1400°C. It is reported that Si_3N_4 has a high n-type thermoelectric property.[12] However, peaks of Si_3N_4 did not appear in the result.

Figure 2 shows SEM images of cross sections of samples heated for 30 min at 1400°C, 1600°C and 1800°C. In Fig. 2(a) the particles seem to be closely packed among each other. As the SiO_2 peaks were clearly observed only at 1400°C in Fig. 1, it is suggested that SiO_2 was melted and covered the whole fractured surface of the specimen. As the arrows indicate, large-sized open pores were observed among the particles in Fig. 2(b). As the sharpest β-SiC peaks appeared in the specimen of 1600°C in Fig. 1, the formation of β-SiC was actively promoted on the surfaces of wood charcoal at 1600°C and as a result large-sized pores appeared. In Fig. 2(c) the particles were more closely packed than in the previous two cases. The wood charcoal has become denser following the increase in heat treatment temperature.

The bulk density of specimens heated at 1600°C showed drastically decreased values compared with the other specimens as shown in Fig. 3. Thicker β-SiC coating on the surfaces and large-sized pores of wood charcoal at 1600°C were consistent with the results of X-ray diffraction analysis and SEM observation.

Thermoelectric properties

Figure 4 shows the temperature dependence of the Seebeck coefficient (S) of samples heated for 30 min. As the sample heated at 1400°C showed a positive sign, only this sample is expected to be a p-type semiconductor. The value of S was insensitive to a change in temperature up to 500°C. The Seebeck coefficient of samples heated at 1600 and 1800°C showed a negative sign, corresponding to a n-type semiconductor. The absolute value of S of samples heated at 1800°C did increase considerably with

temperature. It seems that the p-type to n-type transition takes place at a heat treatment of 1600°C.

Figure 5 shows the temperature dependence of the electrical conductivity of samples heated at 1400, 1600 and 1800°C for 10 and 30 min. The electrical conductivity of all samples increased with an increase in measurement temperature. The electrical conductivity of samples heated at 1400°C was larger than that of samples heated at 1600°C, which may be caused by the open pores observed by SEM. In general, one can say that the electrical conductivity of SiC/C samples is close to that of graphite due to the high conductivity of the extra SiC coating on the wood charcoal.

The thermal conductivity of the samples was calculated by using equation (1). The results are plotted in Fig. 6. The thermal conductivity of the sample heated at 1800°C was relatively high at room temperature, but decreased drastically with an increase in measuring temperature. In contrast to metals, in which electrons carry heat, SiC ceramics transport heat primarily by phonons. Phonon-phonon interaction plays an important role in thermal conduction of SiC.[13] The SiC being formed inside the open pores and on the free surfaces of wood charcoal in the SiC/C composite relates directly to the increase in thermal conductivity. Thermal conductivity decreases with phonons being scattered by pores.[14] Therefore, the micro structural change, as shown in Fig. 3, influences not only the electrical conductivity but also the thermal conductivity.

The figure of merit of the samples was calculated by using equation (2). The results are plotted in Fig. 7. The sample heated at 1400°C showed a high value over the whole temperature range from room temperature to 400°C. The samples heated at 1600°C and

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1800°C showed a figure of merit which greatly increased with an increase in measurement temperature. It can be considered that this happened as a result of an increase in the Seebeck coefficient and electrical conductivity with increasing measurement temperature. In the sample heated at 1800°C, the figure of merit was extra affected by a considerable drop in thermal conductivity with increasing measurement temperature up to 800°C. A maximum in the figure of merit of 3.38×10^{-7} K^{-1} was obtained at 200°C in the sample heated at 1400°C for 30 min. These results suggest good prospects of using SiC/C composites made from a mix of wood charcoal and SiO_2 powder as a thermoelectric material for high temperature applications.

4. Conclusion

We developed a SiC/C composite from a mixed powder of wood charcoal and SiO_2 using a pulse current sintering device. The Seebeck coefficient showed a p-type to n-type transition during a heat treatment temperature at 1600°C. The thermoelectric properties improved at higher measurement temperatures. A maximum in the figure of merit of 3.38×10^{-7} K^{-1} was obtained at 200°C in the sample heated at 1400°C for 30 min.

Acknowledgments

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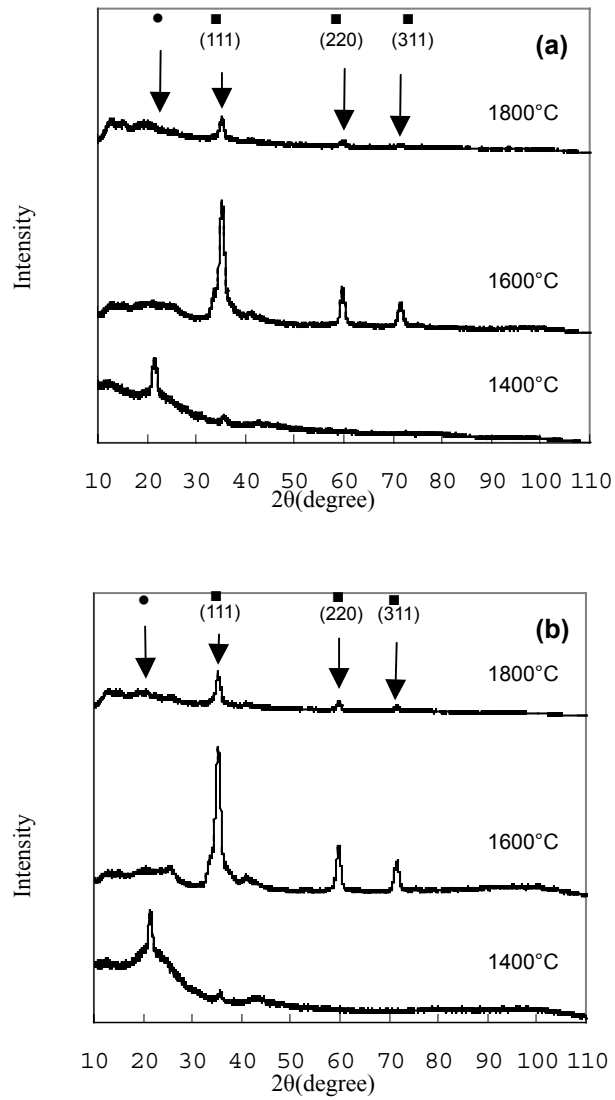
Fig. 1. X-ray powder-scans of specimen heated at 1400, 1600 and 1800°C, (a) holding time 10 min, (b) holding time 30 min.
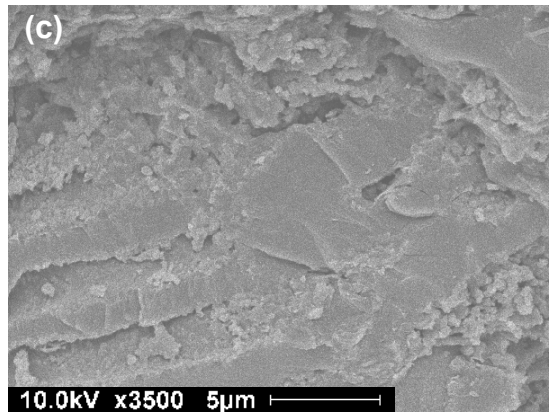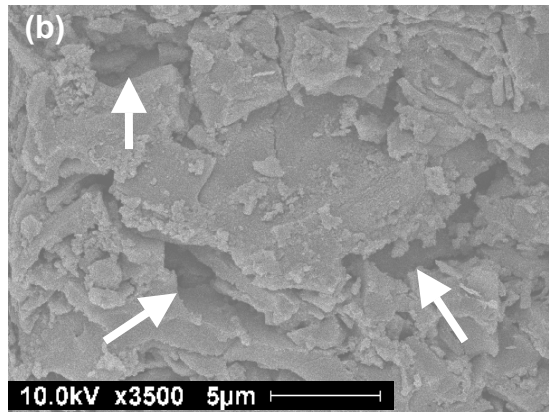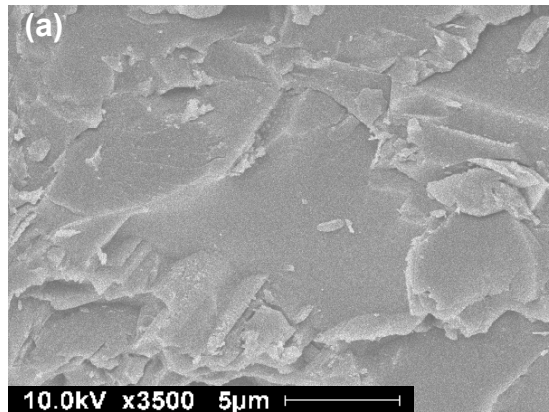Legends: ■ β-SiC ● SiO$_2$

Fig. 2. SEM image of cross section of specimen heated for 30 min (a) at 1400°C,
(b) at 1600°C and (c) at 1800°C.
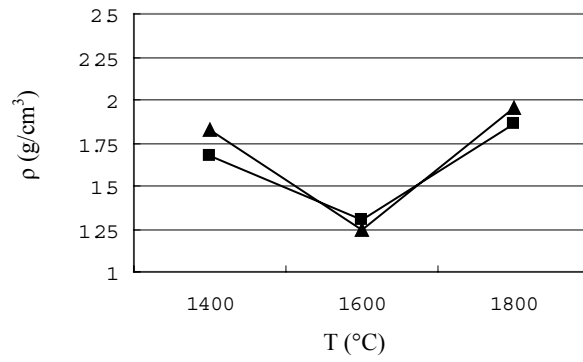Legends: arrows indicate the open pore

Fig. 3. Relationship between bulk density (ρ) and heat treatment temperature (T).
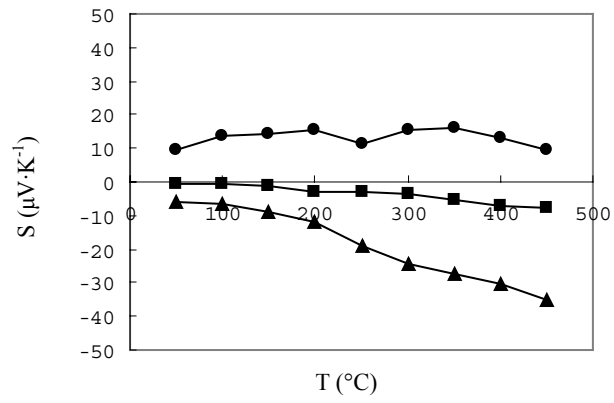Legends: ▲: holding time 10 min, ■: holding time 30 min

Fig. 4. Temperature dependence of Seebeck coefficient (S) of specimen heated for 30 min.
Legends: ●: heat treatment temperature 1400°C, ■: heat treatment temperature 1600°C, ▲: heat treatment temperature 1800°C
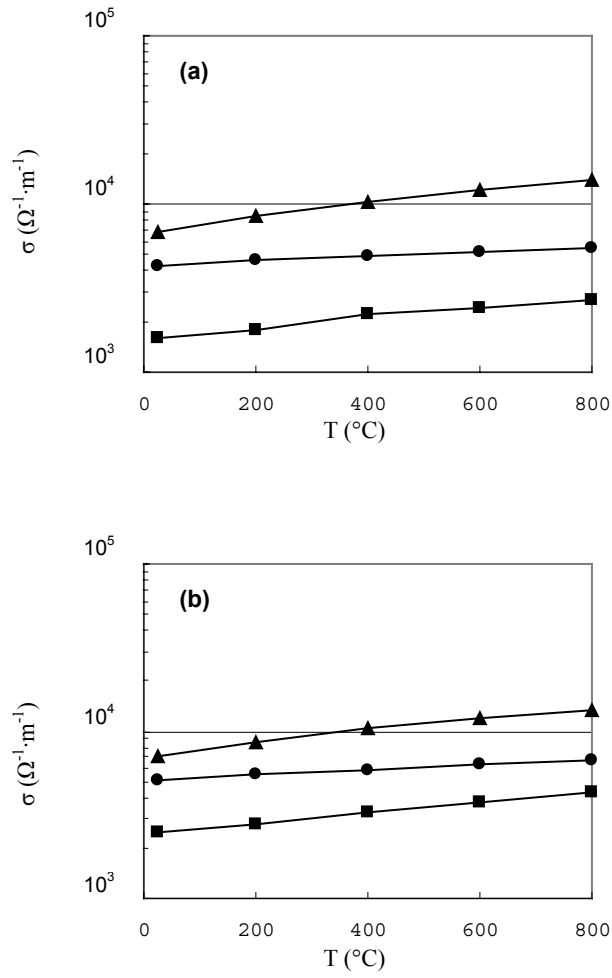
Fig. 5. Temperature dependence of electrical conductivity (σ) of specimen heated
(a) for 10 min and (b) for 30 min.
Legends: ●: heat treatment temperature 1400°C, ■: heat treatment temperature
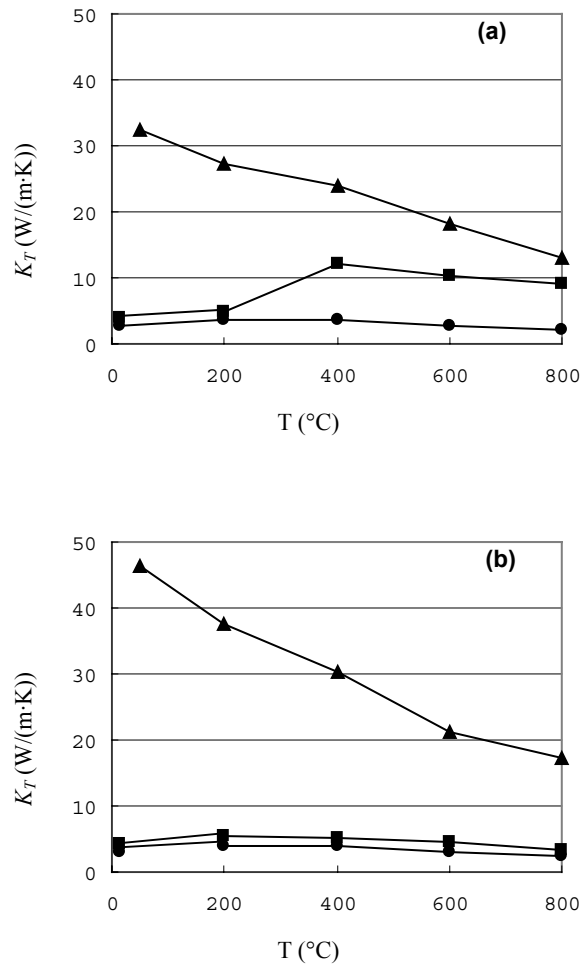1600°C, ▲: heat treatment temperature 1800°C

Fig. 6. Temperature dependence of thermal conductivity (K_T) of specimen heated (a) for 10 min and (b) for 30 min.
Legends: ●: heat treatment temperature 1400°C, ■: heat treatment temperature 1600°C, ▲: heat treatment temperature 1800°C
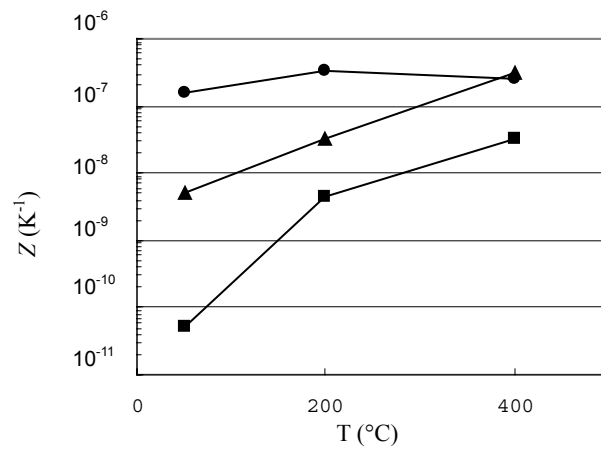
Fig. 7. Temperature dependence of the figure of merit (Z) of specimen heated for 30 min.
Legends: ●: heat treatment temperature 1400°C, ■: heat treatment temperature 1600°C, ▲: heat treatment temperature 1800°C

Illustration legends

Fig. 1. X-ray powder-scans of specimen heated at 1400, 1600 and 1800°C, (a) holding time 10 min, (b) holding time 30 min.

Legends :   ■   β-SiC ● SiO_2

Fig. 2. SEM image of cross section of specimen heated for 30 min (a) at 1400°C, (b) at 1600°C and (c) at 1800°C.

Legends: arrows indicate the pore

Fig. 3. Relationship between bulk density (ρ) and heat treatment temperature (T).

Legends: ▲: holding time 10 min, ■: holding time 30 min

Fig. 4. Temperature dependence of Seebeck coefficient (α) of specimen heated for 30 min.

Legends:●: heat treatment temperature 1400°C, ■: heat treatment temperature 1600°C, ▲: heat treatment temperature 1800°C

Fig. 5. Temperature dependence of electrical conductivity (σ) of specimen heated (a) for 10 min and (b) for 30 min.

Legends:●: heat treatment temperature 1400°C, ■: heat treatment temperature 1600°C, ▲: heat treatment temperature 1800°C

Fig. 6. Temperature dependence of thermal conductivity (κ) of specimen heated (a) for 10 min and (b) for 30 min.

Legends:●: heat treatment temperature 1400°C, ■: heat treatment temperature 1600°C,

▲: heat treatment temperature 1800°C

Fig. 7. Temperature dependence of the figure of merit (Z) of specimen heated for 30 min.

Legends:●: heat treatment temperature 1400°C, ■: heat treatment temperature 1600°C,

▲: heat treatment temperature 1800°C