Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of the European Ceramic Society 25 (2005) 2735–2738
www.elsevier.com/locate/jeurceramsoc

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

Masashi Fujisawa [a,*], Toshimitsu Hata [a], Paul Bronsveld [b], Vinicius Castro [a], Fumio Tanaka [a], Hikari Kikuchi [c], Yuji Imamura [a]

[a] *Research Institute for Sustainable Humanosphere, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan*
[b] *Materials Science Centre, University of Groningen, The Netherlands*
[c] *S S Alloy Co. Ltd., Techno Plaza, Room 308, Kagamiyama 3-13-26, Higashihiroshima, Hiroshima 739-0046, Japan*

Available online 5 April 2005

Abstract

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 with a pulse current sintering method. Thermoelectric properties of SiC/C composites were investigated by measuring the Seebeck coefficient and the electrical and thermal conductivities 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 temperatures. For the thermal conductivity, the samples heated at 1800 °C showed high values at room temperature which strongly decreased with increase in measurement temperature. In total, thermoelectric properties were improved with an increase in measurement temperature. A maximum in the figure of merit of $3.38 \times 10^{-7}\,K^{-1}$ was reached at 200 °C in the sample heated at 1400 °C for 30 min.
© 2005 Elsevier Ltd. All rights reserved.

Keywords: Thermoelectric properties; Carbon; SiC; Electron microscopy; Electrical conductivity

1. Introduction

Research on the development of new energy sources has recently received a lot of attention due to concern about environmental problems. 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 and 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]

On the other hand, research on SiC composites based on biomass has recently drawn a lot of attention.[2] Due to both abundance of waste wood and high strength properties of SiC ceramics, SiC composites has widely been used for industrial applications.

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.[3] As the current passes through the graphite dies as well as through the sample, the sample is heated from both the inside and outside at the same time. Compared with the hot pressing methods, the pulse current sintering method can be an alternative to fast sintering of fully dense materials.[4]

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 pa-

* Corresponding author. Tel.: +81 774 38 3664; fax: +81 774 38 3664.
E-mail address: fujisawa@rish.kyoto-u.ac.jp (M. Fujisawa).

0955-2219/$ – see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2005.03.131

per, 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 under an Ar gas flow (100 ml/min) and kept there for 1 h. The wood charcoal powder and SiO_2 powder (Nacalai Tesque Co. Ltd.) sized 32–45 μm 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, 1600 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 mm × 1 mm × 5 mm.

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 by Van der Pauw's method using DC and AC Hall effect measurements (ResiTest 8300) and the thermal conductivity by the laser-flash method using a Thermal-constant Analyzer (TC-7000H) were measured under vacuum in a temperature range from room temperature to 800 °C.

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

$$Z = \frac{S^2\sigma}{K_T} \quad (1)$$

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

3. Results and discussion

3.1. Microstructure

X-ray powder scans were recorded for samples kept at 1400, 1600 and 1800 °C for 10 and 30 min (Fig. 1). Clear

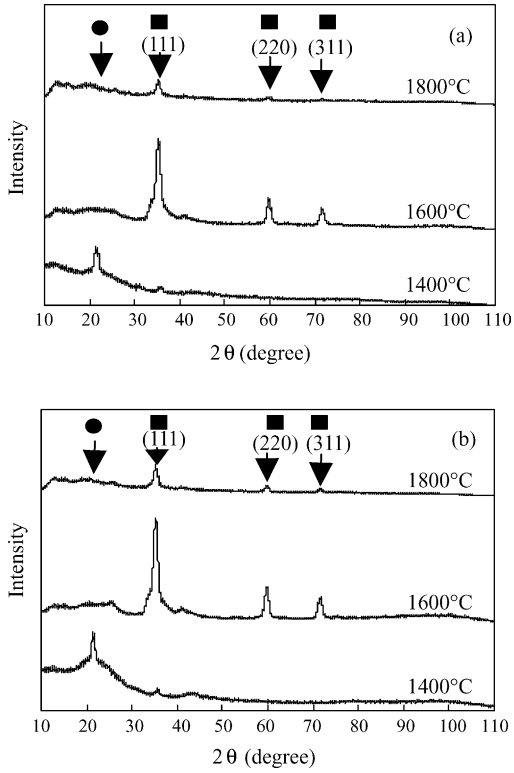

Fig. 1. X-ray powder-scans of specimen heated at 1400, 1600 and 1800 °C: (a) holding time 10 min and (b) holding time 30 min. (■) β-SiC and (●) SiO_2.

peaks of β-SiC were observed, corresponding to the β-SiC phase: (1 1 1), (2 2 0) and (3 1 1) at 2θ of 36°, 60° and 72°, respectively. The sharpest β-SiC peaks appeared at 1600 °C, while the SiO_2 peaks clearly appeared only at 1400 °C. It is reported that Si_3N_4 has a high n-type thermoelectric property.[5] However, peaks of Si_3N_4 did not appear in the result.

Fig. 2 shows SEM images of cross sections of samples heated for 30 min at 1400, 1600 and 1800 °C. In Fig. 2a 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. 2b. As the sharpest β-SiC peaks appeared in the specimen of 1600 °C in Fig. 1, the formation of β-SiC was most pronounced on the surfaces of wood charcoal at 1600 °C and as a result large-sized pores appeared. In Fig. 2c 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.

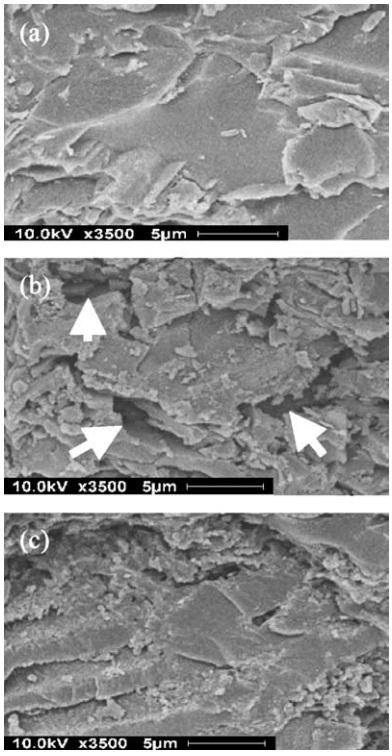

Fig. 2. SEM image of cross section of specimen heated for 30 min: (a) at 1400 °C; (b) at 1600 °C and (c) at 1800 °C. Arrows indicate the pore.

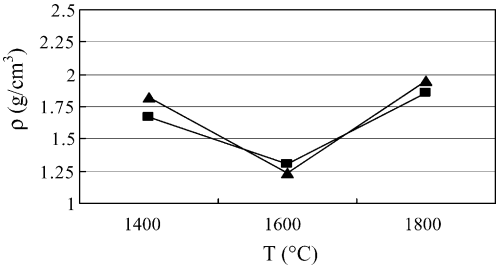

Fig. 3. Relationship between bulk density (ρ) and heat treatment temperature (T): (▲) holding time 10 min and (■) holding time 30 min.

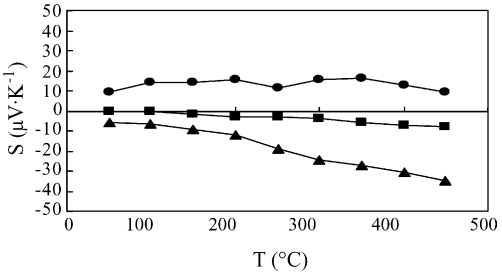

Fig. 4. Temperature dependence of Seebeck coefficient (S) of specimen heated for 30 min: (●) heat treatment temperature 1400 °C; (■) heat treatment temperature 1600 °C and (▲) heat treatment temperature 1800 °C.

3.2. Thermoelectric properties

Fig. 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 450 °C. The Seebeck coefficient of samples heated at 1600 and 1800 °C showed a negative sign, corresponding to an 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 temperature of 1600 °C.

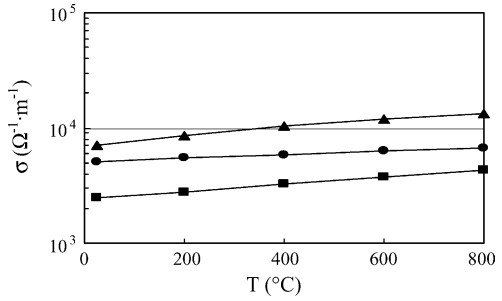

Fig. 5. Temperature dependence of electrical conductivity (σ) of specimen heated for 30 min: (●) heat treatment temperature 1400 °C; (■) heat treatment temperature 1600 °C and (▲) heat treatment temperature 1800 °C.

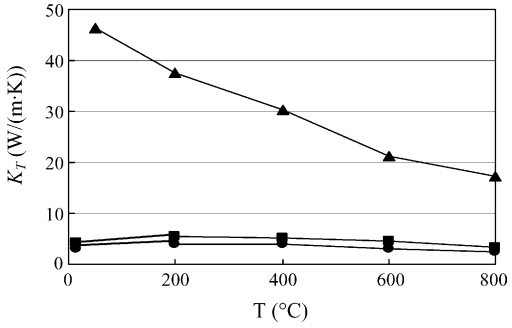

Fig. 6. Temperature dependence of thermal conductivity (K_T) of specimen heated for 30 min: (●) heat treatment temperature 1400 °C; (■) heat treatment temperature 1600 °C and (▲) heat treatment temperature 1800 °C.

Fig. 5 shows the temperature dependence of the electrical conductivity of samples heated at 1400, 1600 and 1800 °C for 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 the SiC/C samples is close to that of SiC due to the high conductivity of the extra SiC coating on the wood charcoal.

The results of the thermal conductivity 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 the thermal conduction of SiC.[6] 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

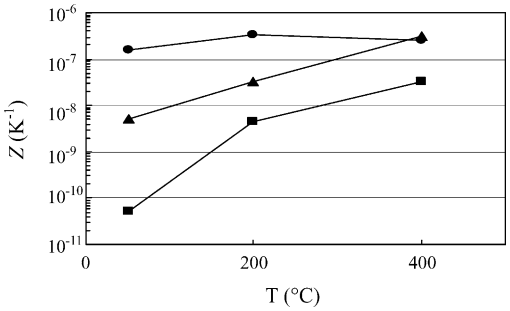

Fig. 7. Temperature dependence of the figure of merit (Z) of specimen heated for 30 min: (●) heat treatment temperature 1400 °C; (■) heat treatment temperature 1600 °C and (▲) heat treatment temperature 1800 °C.

increase in thermal conductivity. Thermal conductivity decreases with phonons being scattered by pores.[7] Therefore, the micro structural change, as shown in Fig. 2, influences not only the electrical conductivity but also the thermal conductivity.

The figure of merit of the samples was calculated by using Eq. (1). 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 and 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. 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 $3.38 \times 10^{-7}\,K^{-1}$ 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 $3.38 \times 10^{-7}\,K^{-1}$ was obtained at 200 °C in the sample heated at 1400 °C for 30 min.

Acknowledgments

The authors would like to thank Dr. S. Nami Kartal, Research Institute for Sustainable Humanosphere, for his critical comments on the paper, Mr. A. Urata, International Servo Data Corporation, for his support in mesurement of Seebeck coefficient and Mr. S. Mizuta and Mr. Y. Uchida, Toyo Corporation, for their support in mesurement of electrical conductivity.

References

1. Koumoto, K., Shimohigoshi, M., Takeda, S. and Yanagida, H., Thermoelectric energy conversion by porous SiC ceramics. *J. Mater. Sci. Lett.*, 1987, **6**, 1453–1455.
2. Greil, P., Lifka, T. and Kaindl, A., Biomorphic cellular silicon carbide ceramics from wood. I. Processing and microstructure. *J. Eur. Ceram. Soc.*, 1998, **18**, 1961–1973.
3. Gao, L., Wang, H. Z., Hong, J. S., Miyamoto, H., Miyamoto, K., Nishikawa, Y. *et al.*, Mechanical properties and microstructure of nano-SiC-Al_2O_3 composites densified by spark plasma sintering. *J. Eur. Ceram. Soc.*, 1999, **19**, 609–613.
4. Tamari, N., Tanaka, T., Tanaka, K., Kondoh, I., Kawahara, M. and Tokita, M., Effect of spark plasma sintering on densification and mechanical properties of silicon carbide. *J. Ceram. Soc. Jpn.*, 1995, **103**, 740–742.
5. Kitagawa, H., Kado, N. and Noda, Y., Preparation of n-type silicon carbide-based thermoelectric materials by spark plasma sintering. *Mater. Trans.*, 2002, **43**, 3239–3241.
6. Takeda, Y., Development of high-thermal-conductive SiC ceramics. *Am. Ceram. Soc. Bull.*, 1988, **67**, 1961–1963.
7. Suhlz, B., Thermal conductivity of porous and highly porous materials. *High Temp. High Press.*, 1981, **13**, 649–660.