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SiC/C composites prepared from wood-based carbons by pulse current sintering with SiO_2: Electrical and thermal properties

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Abstract

A powder mix of wood charcoal and SiO_2 was sintered into a SiC/C composite. The heat treatment temperatures were 1400–1800 °C, the SiO_2 concentration 0, 10, 30 and 50 wt.% with respect to the dry weight of wood charcoal. The microstructure, electrical resistance and thermal conductivity were studied. SEM and EDX confirmed that a 1 μm thick layer of β-SiC was formed on the surface of the wood charcoal pieces. The bulk density did increase only slightly with temperature and SiC contents. The electrical resistance decreased slightly with temperature but increased with SiO_2 contents. The thermal conductivity did increase both with temperature and SiC contents. By coating the wood charcoal in this rather natural way by such a ceramic layer we can use the SiC/C composite at least up to 1800 °C, far beyond the carbon oxidation limit of 500 °C.

Keywords: Carbon; SiC; Electron microscopy; Electrical properties; Thermal properties; Composites

1. Introduction

Wood charcoal has been focused upon as an important material with functions such as gas absorber[1] or electrical conductor,[2] functions which are greatly influenced by the carbonization process.

We have applied a new method in which a pulsed electric current is directed straight through graphite dies and sample.[3,4] The pulse current sintering method is a novel process where metals, ceramics, and composites can be sintered in short time.[5–7] As the current passes through the graphite dies as well as the sample, the sample is heated from both the inside and the 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.[8] In this way one can control and shorten the heat treatment considerably.

In recent years, research on SiC composites based on biomass has gathered a lot of attention.[9–15] First of all there is a lot of waste wood and secondly SiC ceramics exhibit a high strength, a good thermal conductivity, heat-resistance and wear ability. Therefore, it has been widely used for industrial applications. It does not come as a surprise that already some attempts has been reported to develop SiC composites based on wood charcoal.[16,17]

In this research, we tried to make SiC/C composites by mixing powder of char and SiO_2 and sinter them together in a pulse current sintering device. The microstructure, electrical

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resistance and thermal conductivity 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 for 1 h. 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 was mixed with SiO_2 powder (Nacalai Tesque, Kyoto, Japan) using a vibration mill and a sieve so that the size became 32–45 μm. Samples with 0 wt.% SiO_2 (C-0), 10 wt.% SiO_2 (C-10), 30 wt.% SiO_2 (C-30) and 50 wt.% SiO_2 (C-50) 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 temperatures between 1400 and 1800 °C at a rate of 500 °C/min and with a holding time of 5 or 30 min under an Ar gas flow of 0.1 ml/min using a pulse current sintering apparatus (VCSP-II) as sketched in Fig. 1. After the reaction, it was naturally cooled to room temperature. Pressure at 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. Finally, the SiC/C was cut into discs of 10 mm in diameter and approximately 1 mm in thickness.

An X-ray diffraction device (RINT-ultra X18) was used to analyze the crystal structure. The composition in the specimen was analyzed by scanning electron microscopy (SEM; FEI XL30S, JSM-5310) with an energy dispersive X-ray spectrometer (EDX). The electrical resistance was measured at room temperature by a four-probe-method (Loresta HP MCP-T410). The specific thermal capacity and the thermal diffusivity of the specimens were measured at room temperature by the laser-flash method, using a thermal-constant analyzer (TC-7000H). The thermal conductivity was calculated using the following equation:

$$K = \rho C_p \alpha \quad (1)$$

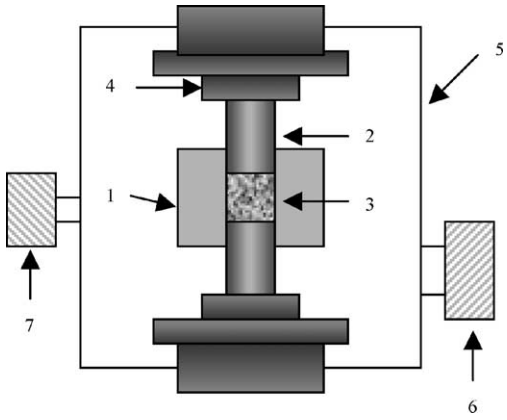

Fig. 1. Schematic diagram of a pulse current sintering apparatus. (1) Graphite die, (2) graphite punch, (3) sample, (4) copper plate, (5) chamber, (6) vacuum pump, and (7) optical pyrometer.

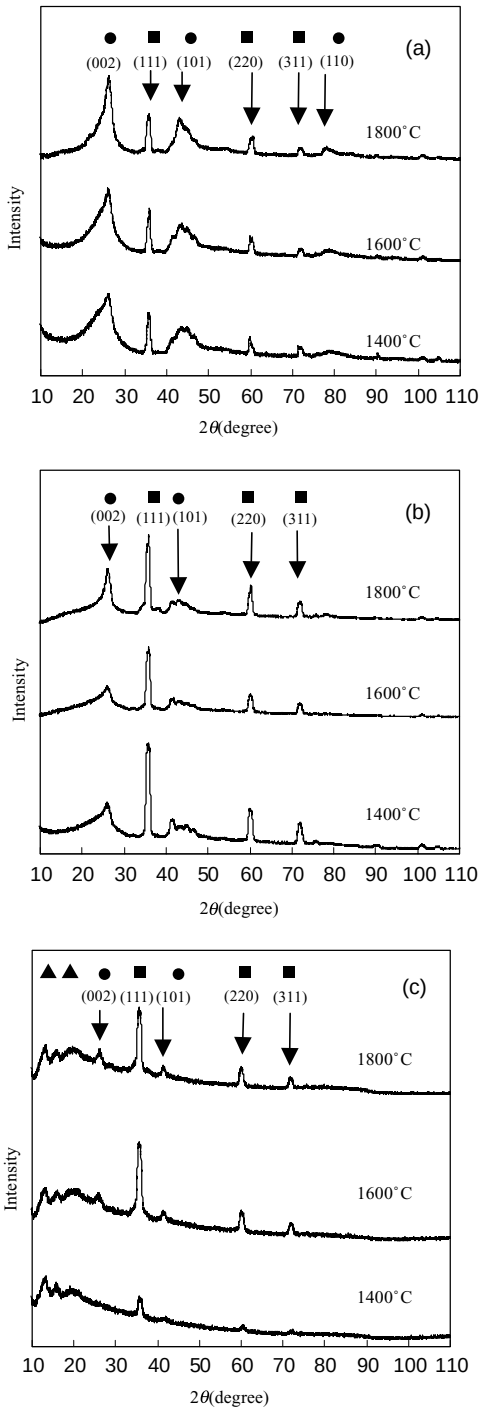

Fig. 2. X-ray powder-scans of specimen heated at 1400, 1600 and 1800 °C for (a) C-10 wt.% SiO_2, (b) C-30 wt.% SiO_2, (c) C-50 wt.% SiO_2. (●) C, (■) β-SiC, (▲) SiO_2.

where K is the thermal conductivity (W/m/K), ρ is the bulk density (g/cm^3), C_p is the specific thermal capacity (J/g/K), and α is the thermal diffusivity (cm^2/s).

3. Results and discussion

3.1. Microstructure

In Fig. 2 X-ray powder scans are reproduced for the C-10, C-30 and C-50 samples which were kept at 1400, 1600 and 1800 °C for 30 min. The C and SiC peaks could be observed in all samples. The carbon peaks correspond to the graphitic phase: (0 0 2), (1 0 1) and (1 1 0). The detection of such C peaks can be considered as proof that unreacted carbons are present which do not form SiC. The SiO_2 peaks could barely be indexed only in the C-50 sample. The SiC peaks correspond to the β-SiC phase: (1 1 1), (2 2 0) and (3 1 1). They became bigger than those for carbon as the SiO_2 contents increased. This is due to the fact that the amount of active carbon decreases in the formation of β-SiC. It is considered that there is an optimum ratio of SiO_2 to carbon so as to form β-SiC.

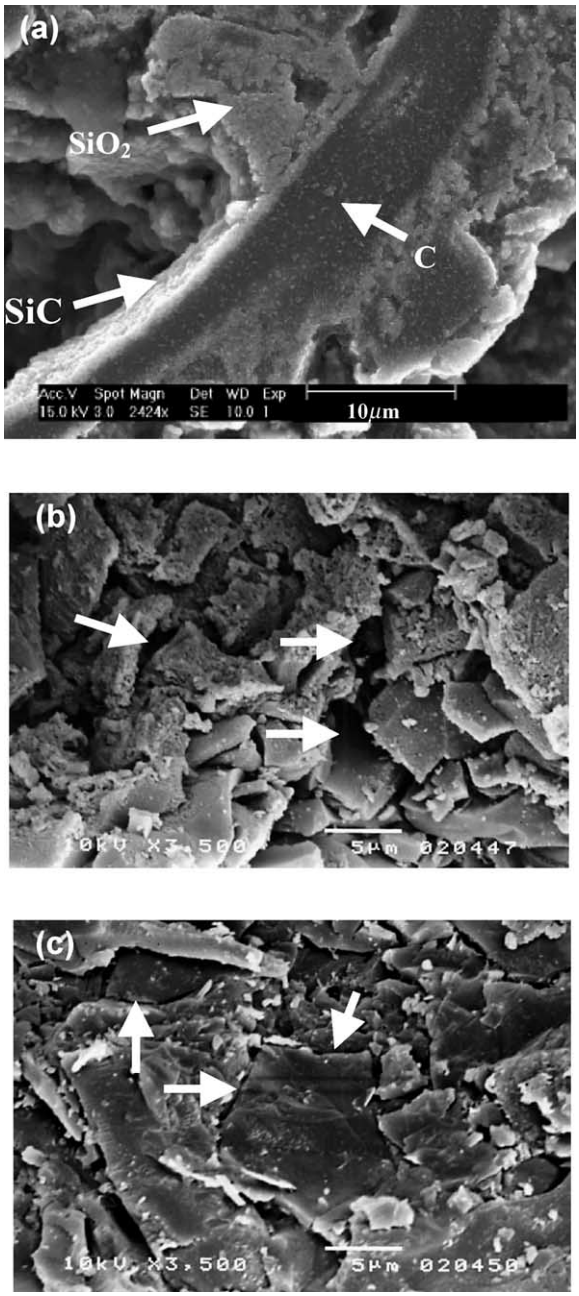

Fig. 3. SEM/EDX image of the C-50 wt.% SiO_2 specimen heated at 1600 °C for 30 min (a). SEM image of broken surface of C-30 wt.% SiO_2 specimen heated (b) at 1400 °C for 30 min and (c) at 1800 °C for 30 min.

Fig. 3a shows a SEM image of the C-50 sample heated at 1600 °C for 30 min. It was confirmed by EDX analysis that a SiC layer was formed on the surface of the wood charcoal pieces. Fig. 3b and c shows SEM images of broken surfaces of the C-30 sample heated for 30 min at 1400 and 1800 °C, respectively. As the arrows show, the particles were more closely packed with an increase of heat treatment temperature. The samples' structure sintered by pulse current sintering changed in a similar way as samples produced by spark plasma sintering (SPS) which were previously reported.[5,7,8] In the pulse current sintering method, densification has taken place much faster than in the hot pressing methods. In Fig. 3b the shape of the wood charcoal pieces of which the surface has reacted with the SiO_2 are still recognizable. This is less so in Fig. 3c. Similar changes were observed in the other sample. The change in structure depends on reaction time, temperature and pressure, all influencing the properties of the end product severely.

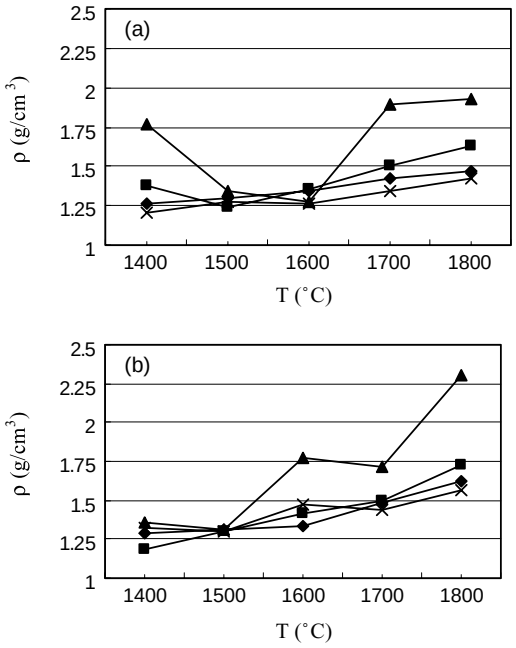

Fig. 4. Relationship between bulk density and heat treatment temperature (a) holding time 5 min, (b) holding time 30 min. (◆) C-10 wt.% SiO_2, (■) C-30 wt.% SiO_2, (▲) C-50 wt.% SiO_2, (×) C-0 wt.% SiO_2.

The bulk density of the composite is shown in Fig. 4. It shows only a slight tendency to increase with SiO_2 contents and heat treatment temperature for both 5 and 30 min reaction time. A maximum in the bulk density of 2.25 g/cm^3 was reached in the C-50 sample after 30 min at 1800 °C.

3.2. Electrical properties

The electrical resistance at room temperature of samples heated at temperatures between 1400 and 1800 °C, for 5 or 30 min, are shown in Fig. 5. The electrical resistance decreased with an increase in heat treatment temperature but showed almost no dependence on concentration or reaction time. The C-50 sample showed a slightly different behavior.

As shown in Fig. 3a, a thin film of SiC is formed as coating on to the charcoal surface. In previous papers, it was reported that charcoal that forms a more graphitic layered structure shows a higher electrical conductivity.[2,3,18] In this research, high electrical conductivity was indeed observed in samples with a graphitic organization of the carbon structure of the charcoal, as seen in the results of XRD. As the SiC layer is very thin, the influence on the electrical resistivity is relatively small.

It seems that the micro structural difference between 5 and 30 min of heating time and the subsequently thicker SiC layer prevent these curves to overlap. The amount of SiC increases with an increase in SiO_2 addition. As the heat treatment temperature increases and the reaction time gets longer, a higher formation of SiC is also promoted. So, it is expected that the electrical resistivity of the SiC/C composite can be controlled by heat treatment temperature, reaction time and the addition of SiO_2.

As the electrical resistance in this experiment shows 10^{-4} to $10^{-5}\,\Omega$ m, it is considered that the SiC/C composite is well conducting. It can be applied as thermoelectric material which makes it very attractive for the electric power generation industry.[19–21]

3.3. Thermal properties

Similar to the electrical measurements also thermal data were collected. The bulk density, specific heat capacity and thermal diffusivity were measured on samples at room temperature after being treated from 1400 to 1800 °C for 5 or 30 min. These data can be found in Table 1. The thermal

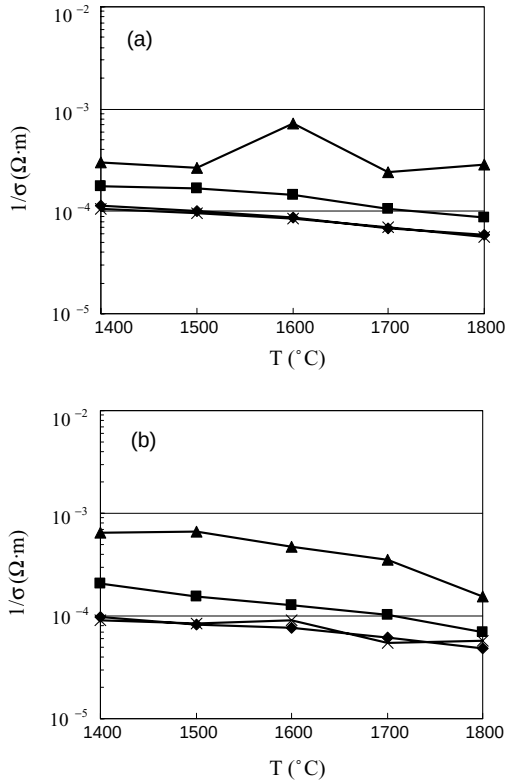

Fig. 5. Relationship between electrical resistivity and heat treatment temperature (a) holding time 5 min, (b) holding time 30 min. (◆) C-10 wt.% SiO_2, (■) C-30 wt.% SiO_2, (▲) C-50 wt.% SiO_2, (×) C-0 wt.% SiO_2.

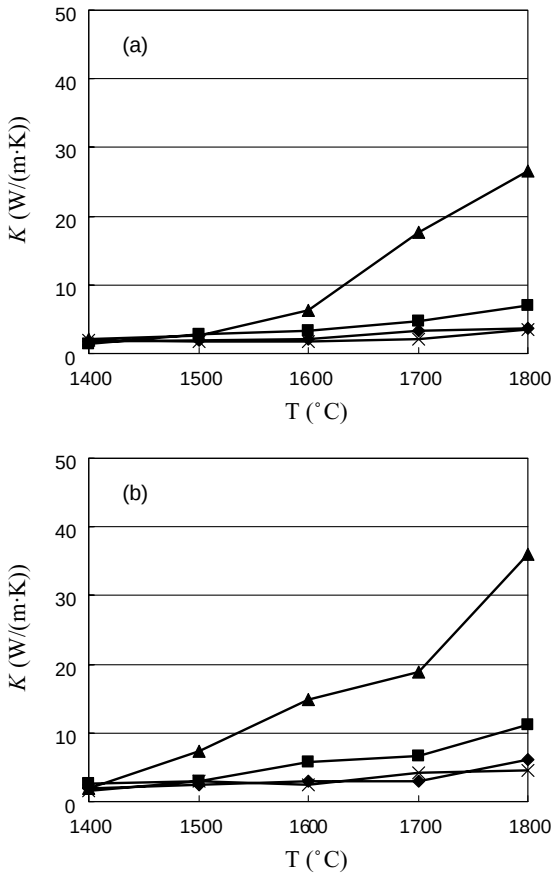

Fig. 6. Relationship between thermal conductivity and heat treatment temperature (a) holding time 5 min, (b) holding time 30 min. (◆) C-10 wt.% SiO_2, (■) C-30 wt.% SiO_2, (▲) C-50 wt.% SiO_2, (×) C-0 wt.% SiO_2.

Table 1
Thermal constants of the sample

Sample	Reaction time (min)	Heat treatment temperature (°C)	Bulk density (g/cm^3)	Specific heat capacity($\times 10^{-1}$ J/g/K)	Thermal diffusivity ($\times 10^{-2}$ cm^2/s)
C-10 wt.% SiO_2	5	1400	1.26	8.66	1.55
	5	1500	1.33	6.65	2.23
	5	1600	1.36	7.02	2.24
	5	1700	1.43	7.36	3.08
	5	1800	1.49	6.82	3.58
	30	1400	1.33	7.35	2.00
	30	1500	1.35	7.40	2.37
	30	1600	1.37	8.76	2.51
	30	1700	1.49	5.89	3.45
	30	1800	1.61	8.64	4.42
C-30 wt.% SiO_2	5	1400	1.44	6.93	1.46
	5	1500	1.30	7.01	3.13
	5	1600	1.34	7.75	3.18
	5	1700	1.49	6.35	5.03
	5	1800	1.64	7.28	5.81
	30	1400	1.20	9.73	2.29
	30	1500	1.33	6.04	3.65
	30	1600	1.40	8.56	4.80
	30	1700	1.50	7.65	5.73
	30	1800	1.70	7.73	8.47
C-50 wt.% SiO_2	5	1400	1.75	6.59	1.75
	5	1500	1.39	8.79	2.13
	5	1600	1.32	7.95	6.04
	5	1700	1.93	7.31	12.50
	5	1800	2.16	6.54	18.84
	30	1400	1.53	7.34	1.74
	30	1500	1.44	7.17	7.19
	30	1600	1.74	8.22	10.45
	30	1700	1.59	6.47	18.32
	30	1800	2.28	6.64	23.79
C-0 wt.% SiO_2	5	1400	1.26	8.73	1.72
	5	1500	1.30	6.90	1.92
	5	1600	1.22	6.70	2.22
	5	1700	1.38	6.03	2.54
	5	1800	1.40	6.50	3.77
	30	1400	1.31	6.97	1.69
	30	1500	1.32	8.98	2.54
	30	1600	1.38	7.17	2.46
	30	1700	1.43	6.73	4.32
	30	1800	1.57	7.30	4.04

diffusivity increased with SiO_2 contents as well as with heat treatment temperature. The bulk density and the specific heat capacity hardly changed. Consequently, it can be said that the thermal diffusivity has a major influence on the thermal conductivity.

The thermal conductivity of the samples was calculated by using Eq. (1). The results are plotted in Fig. 6. The thermal conductivity increased with an increase in heat treatment temperature for all samples and for both 5 and 30 min reaction time except for the C-0 sample. The thermal conductivity of the C-0 sample made of only wood charcoal hardly changed. It is in the C-50 sample that the thermal conductivity increased most, due to the influence of the SiC layer formed on the surface of the charcoal. The maximum of 36 W/m/K was recorded in the C-50 sample at 1800 °C for 30 min.

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.[22] The interface layer of SiC being formed in the SiC/C composite relates directly to the increase in thermal conductivity.

Pores greatly influence thermal conductivity. The thermal conductivity decreases with phonons being scattered due to pores. It seems that the micro structural change, as shown in Fig. 3b and c, changes not only the electrical resistance but also the thermal conductivity.[23] Therefore, it is to be expected that the thermal conductivity of the SiC/C composite

can be controlled by heat treatment temperature, reaction time and the addition of SiO_2.

In this experiment we fabricated a SiC/C composite from a mixed powder of wood charcoal and SiO_2, and succeeded in developing a material with a low electrical resistivity and a high thermal conductivity.

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 microstructure, electrical resistance and thermal conductivity were measured. SEM observations showed that the wood charcoal was covered with a 1 μm thin coating. X-ray diffraction revealed the coating to be β-SiC. Due to this coating it is possible to use this composite at least up to temperatures of 1800 °C.

References

1. Pulido, L. L., Hata, T., Imamura, Y., Ishihara, S. and Kajimoto, T., Removal of mercury and other metals by carbonized wood powder from aqueous solutions of their salts. *J. Wood Sci.* 1998, **44**, 237–243.
2. Imamura, Y., Development of new functional carbon materials from wood charcoal (in Japanese). *Shokubai* 1999, **41**(4), 254–258.
3. Yamane, T., Ishihara, S. and Okuda, H., Electric and thermal properties of wood charcoal made by spark plasma sintering (in Japanese). *Tanso* 1998, **182**, 95–100.
4. Hata, T., Yamane, K., Kobayashi, E., Imamura, Y. and Ishihara, S., Microstructural investigation of wood charcoal made by spark plasma sintering. *J. Wood Sci.* 1998, **44**, 332–334.
5. 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.
6. Gao, L., Wang, H., Kawaoka, H., Sekino, T. and Niihara, K., Fabrication of YAG-SiC nanocomposites spark plasma sintering. *J. Eur. Ceram. Soc.* 2002, **22**, 785–789.
7. Gao, L., Wang, H. Z., Hong, J. S., Miyamoto, H., Miyamoto, K., Nishikawa, Y. *et al.*, SiC-ZrO_2(3Y)-Al_2O_3 nanocomposites superfast densified by spark plasma sintering. *Nanostruct. Mater.* 1999, **11**, 43–49.
8. 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.
9. Ota, T., Ichiyama, H., Hikichi, Y. and Akahane, H., Production of ceramic wood by mimicking fossil wood. *Annu. Rep. Ceram. Res. Lab.* 1997, **7**, 21–24.
10. Ota, T., Hikichi, Y., Kawakami, H. and Akahane, H., Preparation of SiC ceramic woods by mimicking fossil woods—No. 3 (in Japanese). *Annu. Rep. Ceram. Res. Lab.* 1998, **8**, 39–47.
11. 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.
12. Greil, P., Near net shape manufacturing of ceramics. *Mater. Chem. Phys.* 1999, **61**, 64–68.
13. Sieber, H., Hoffmann, C., Kaindl, A. and Greil, P., Biomorphic cellular ceramics. *Adv. Eng. Mater.* 2000, **2**(3), 105–109.
14. Martinez-Fernandez, J., Varela-Feria, F. M. and Singh, M., High temperature compressive mechanical behavior of biomorphic silicon carbide ceramics. *Scr. Mater.* 2000, **43**, 813–818.
15. Singh, M., Environment conscious ceramics (ecoceramics). *Ceram. Sci. Eng. Proc.* 2000, **21**(4), 39–44.
16. Greil, P., Lifka, T. and Kaindl, A., Biomorphic cellular silicon carbide ceramics from wood. II. Mechanical properties. *J. Eur. Ceram. Soc.* 1998, **8**, 1975–1983.
17. Varela-Feria, F. M., Martinez-Fernandez, J., de Arellano-Lopez, A. R. and Singh, M., Low density biomorphic silicon carbide: microstructure and mechanical properties. *J. Eur. Ceram. Soc.* 2002, **22**, 2719–2725.
18. Mochidzuki, K., Soutric, F., Tadokoro, K., Antal, Jr. M.J., Toth, M., Zelei, B. *et al.*, Electrical and physical properties of carbonized charcoals. *Ind. Eng. Chem. Res.* 2003, **42**, 5140–5151.
19. Pai, C.-H., Koumoto, K. and Yanagida, H., Effect of sintering additives on the thermoelectric properties of SiC ceramics. *J. Ceram. Soc. Jpn.* 1989, **97**, 1170–1175.
20. Kato, K., Asai, K., Okamoto, Y., Morimoto, J. and Miyakawa, T., Temperature and porosity dependence of the thermoelectric properties of SiC/Ag sintered materials. *J. Mater. Res.* 1999, **14**, 1752–1759.
21. 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.
22. Takeda, Y., Development of high-thermal-conductive SiC ceramics. *Am. Ceram. Soc. Bull.* 1988, **67**, 1961–1963.
23. Suhlz, B., Thermal conductivity of porous and highly porous materials. *High Temp. High Press.* 1981, **13**, 649–660.