## Development of novel silicon carbide thermoelectric materials from carbonized wood

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Research on the development of new energy sources has been quite vigorous due to concerns about environmental problems. Nonrenewable resources, such as fossil fuels, coal, fuel oil, and natural gas, will become increasingly scarce in the future. Moreover, air pollutants, such as nitrogen oxides, sulfur dioxide, VOCs and heavy metals, are discharged into the environment. Thermoelectric energy conversion technology has also attracted a great deal of attention. Thermoelectric energy conversion, which does not depend on hydrocarbons, is a type of clean power generation that directly converts thermal energy into electric energy. In particular, waste energy, which is discharged form factories and cars in great quantities, can be collected and recycled [1]. Considerable efforts have been devoted to the development of thermoelectric materials that can be used at high temperatures. Ceramic semiconductors have been investigated as thermoelectric materials for use at high temperatures. When the temperature difference is given between the two ends of a solid sample, a thermoelectromotive force is generated as free electrons and holes are moved from the hot side to the cold side.

SiC-based materials with high thermal, chemical and mechanical stabilities are candidate materials that may enable a thermoelectromotive forces to be generated at a high temperature range [2-6]. It has been reported that SiC composites have high figures of merit at high temperatures [7]. The objective of this study was to improve the thermoelectric properties of SiC composites obtained from carbonized wood. I focused on novel SiC thermoelectric materials that could be used at high temperatures.

Firstly, the development of SiC/C composites from wood-based carbon using the pulse current sintering method, as well as their electrical and thermal properties were investigated. SiC/C composites were investigated by sintering a mix of wood charcoal and $SiO_2$ powder (32-45 μm) at 1400-1800°C in a $N_2$ atmosphere with the pulse current sintering method. X-ray diffraction revealed the coating to be β-SiC. 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 increased only slightly with sintering temperature and SiC content. The electrical resistance decreased slightly with sintering temperature but increased with $SiO_2$ content. The thermal conductivity increased with both sintering temperature and SiC content. 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. It is to be expected that the electrical and thermal conductivity of the SiC/C composite can be controlled by sintering temperature and the addition of $SiO_2$ [8, 9].

The thermoelectric properties of SiC/C composites were investigated. The thermoelectric properties of SiC/C composites sintered at 1400, 1600 and 1800°C in a $N_2$ atmosphere were investigated by measuring the Seebeck coefficient and the electrical and thermal conductivities. The Seebeck coefficient exhibited a p-type to n-type transition at a sintering temperature around 1600°C. The electrical conductivity showed a steady increase with temperature for all three sintering temperatures. For the thermal conductivity, the samples sintered 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 sintered 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 [10].

Secondly, the porosity of porous SiC composites from wood-based carbon was investigated. Porous SiC ceramics have been investigated because of their even better thermoelectric properties [7]. Porous SiC composites by oxidizing a SiC/C composite sintered at 1400, 1600 and 1800°C under $N_2$ using a pulse current sintering device were developed. Raman spectroscopy revealed the presence of β-SiC and the successful removal of excess carbon. The pore size of the porous SiC sample sintered at 1600 °C was larger than that of the sample sintered at 1800 °C. The porous SiC ceramic had a much lower thermal conductivity than the non-oxidized SiC/C composite and is, therefore, a more promising material for thermoelectric applications.

The improvement of the thermoelectric properties of porous SiC composites was investigated. The thermoelectric properties of porous SiC composites sintered at 1600 and 1800°C in a $N_2$ atmosphere were investigated by measuring the Seebeck coefficient, the electrical conductivities and the thermal conductivity in the temperature range from 323 K to 973 K. The Seebeck coefficient of all samples showed n-type conduction and the absolute value of the Seebeck coefficient of the porous SiC samples with oxidation was much larger than those of the SiC/C samples without oxidation. The electrical conductivity of the SiC/C samples without oxidation was larger than that of the porous SiC samples with oxidation. The thermal conductivity of porous SiC samples with oxidation was much lower than that of SiC/C samples without oxidation, at least for the one at 1800°C. The thermoelectric properties improved at higher measurement temperatures (Fig. 1). A maximum figure of merit of $2.01 \times 10^{-5}$ $K^{-1}$ was obtained at 973 K in porous SiC samples sintered at 1800°C with oxidation. This meant a two orders of magnitude improvement in the value for the figure of merit over our previous results [10].

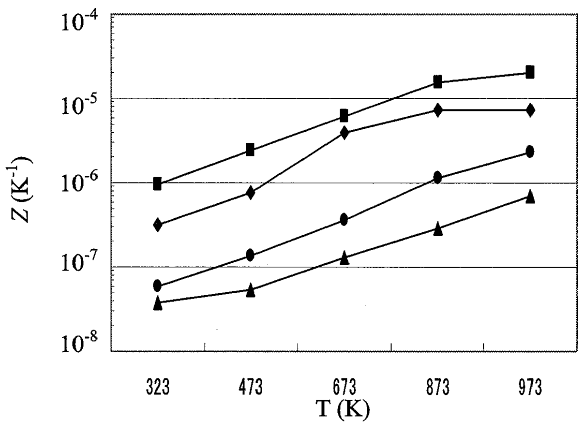


Fig. 1. Temperature dependence of the figure of merit of specimens sintered with and without oxidation. ▲ SiC/C composites sintered at 1600°C without oxidation; ● SiC/C composites sintered at 1800°C without oxidation; ◆ porous SiC composites sintered at 1600°C with oxidation; ■ porous SiC composites sintered at 1800°C with oxidation.

These results obtained in a series of current investigations add a valuable contribution to the development of thermoelectric materials used at high temperature. Porous SiC materials from carbonized wood can be used as thermoelectric materials for high temperature applications. Highly efficient thermoelectric generation can be realized by the application of novel SiC materials.

REFERENCES

[1] Funahashi, R., Mihara, T., Mikami, M. and Urata, S., 2005, 886, 493-498

[2] Banerjee, P.K., Pereira, J.M.T., Mitra, S.S. and Dutta, R., Journal of Non-Crystalline Solids, 1986, 87, 1-29.

[3] Pereira, J. M. T., Banerjee, P. K. and Mitra, S. S., Thin Solid Films, 1985, 127, 337-350.

[4] Nagels, P. and Gevers, M. R. R., Journal of Non-Crystalline Solids, 1983, 59/60, 65-68.

[5] Castro, V., Fujisawa, M., Hata, T., Bronsveld, P., Vystavel, T., Hosson, J. D., Kikuchi, H., and Imamura, Y., Key Engineering Materials, 2004, 264-268, 2267-2270

[6] Furuno, T., and Fujisawa, M., Wood and Fiber Science, 2004, 36(2), 269-277

[7] Koumoto, K., Shimohigoshi, M., Takeda, S., and Yanagida, H., J. Mater. Sci. Lett., 1987, 6, 1453-1455.

[8] Fujisawa, M., Hata, T., Bronsveld, P., Castro, V., Tanaka, F., Kikuchi, H., Furuno, T. and Imamura, Y., J. Eur. Ceram. Soc., 2004, 24, 3575-3580

[9] Fujisawa, M., Hata, T., Bronsveld, P., Castro, V., Tanaka, F., Kikuchi, H., Furuno, T. and Imamura, Y., Wood Research., 2003, 90, 15-16

[10] Fujisawa, M., Hata, T., Bronsveld, P., Castro, V., Tanaka, F., Kikuchi, H. and Imamura, Y., J. Eur. Ceram. Soc., 2005, 25, 2735-2738