

Paper

Structure and Oxidation Behavior of Carbon/Ceramic Composite Material Synthesized by Spark Plasma Sintering

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Using coke, together with SiC or B₄C powders as raw materials, carbon/ceramic composites were prepared by a spark plasma sintering process of a short duration. The oxidation resistance of the composite containing B₄C powder was higher than that of the composite containing SiC powder. The temperature at which the weight decrease of the composite containing 10 wt% B₄C powder began shifted to the high-temperature side compared with that of the carbon material composed only of coke. Approximately 44% of the initial weight of the specimen remained even after thermogravimetric analysis in air up to 1000 °C. By X-ray diffraction analysis, diffraction peaks corresponding to B₂O₃ were observed. This finding indicates that B₄C in the composite is oxidized to B₂O₃, which then forms an oxidation-resistant film, leading to an increase in the oxidation resistance of the composite.

Key Words: composite, ceramic, rapid baking, spark plasma sintering, oxidation behavior

1. Introduction

Spark plasma sintering (SPS) enables high-speed sintering at low temperature and suppresses crystal growth in sintered bodies. Therefore, SPS has been used for the preparation and study of various materials¹⁾⁻³⁾. The authors have been carrying out research on the preparation and property evaluation of carbon materials by SPS. On the basis of the results obtained thus far, it was confirmed that carbon materials can be synthesized without the addition of any binders in an extremely short sintering time by SPS and that the synthesized carbon materials have good properties equivalent or superior to those of commercially available artificial graphite materials^{4),5)}. In this study, carbon/ceramic composite materials using few processes in a short time by SPS were synthesized. Furthermore, a

thermogravimetric analysis of the synthesized composite material was carried out to examine its oxidation behavior in air. In addition, the crystal structure of the material was analyzed using an X-ray diffraction apparatus, and the oxidation resistance mechanism of carbon/ceramic composite materials synthesized by SPS was clarified.

2. Experimental Method

As materials of the carbon/ceramic composite, coke powder (purity of 99.8% or more, average particle size of 10-15 μm), SiC powder (purity of 98% or more, average particle size <125 μm) and B₄C powder (purity of 99% or more, average particle size <105 μm) were used. The powder mixture obtained by adding a predetermined amount of SiC

powder or B₄C powder to the coke powder was used as a raw material. The proportion of SiC powder or B₄C powder added was 2, 6 or 10 wt% with respect to the weight of the coke powder. The raw powder containing a predetermined amount of SiC powder or B₄C powder was placed in the SPS apparatus (DR. SINTER SPS-1050, Izumi Technology Company Ltd.) and sintered at 1800°C while applying a pressure of 60 MPa in vacuum to the prepared carbon/ceramic composite with a diameter of 20 mm and a thickness of 5 mm. The bulk density and Shore hardness of the obtained composite material were measured. To examine the oxidation behavior of the composite material, a thermogravimetric analysis of a specimen of the composite material with dimensions of 5×5×5 mm³ was carried out in air using a thermogravimetric apparatus (TG/DTA-6300, Seiko Instruments Inc.) up to 1000°C. The conditions of the thermogravimetric analysis were an airflow rate of 50 ml/min and a temperature increase at a rate of 10°C/min. Furthermore, the crystalline structure of the composite material was analyzed using an X-ray diffraction apparatus (RINT-22VK/PC, Rigaku Corporation).

3. Results

SPS was completed in 18 min, and carbon/ceramic composites were synthesized in 2 hours including the cooling time. All the carbon/ceramic composite specimens were black. They were highly firmly structured without powdering or breakage. **Table 1** summarizes the densities and Shore hardnesses of the specimens. The hardness of the composite material increases as the amount of SiC or B₄C powder added increases. The bulk density of the composite material containing 10 wt% SiC powder is 1.94 g/cm³ and that containing 10 wt% B₄C powder is 1.99 g/cm³. The Shore hardness of the composite material is almost constant regardless of the amount of SiC or B₄C powder added. It was 62 with 10 wt% SiC powder and 64 with 10 wt% B₄C powder. The bulk density and Shore hardness of the carbon material composed only of coke are 1.77 g/cm³ and 59,

Table 1 Bulk density and shore hardness of carbon/ceramic composites and carbon material.

Amount of ceramic powder added / wt%	Bulk density / g cm ⁻³	Shore hardness
SiC	2	62
	6	63
	10	62
B ₄ C	2	64
	6	64
	10	64
Carbon material	1.77	59

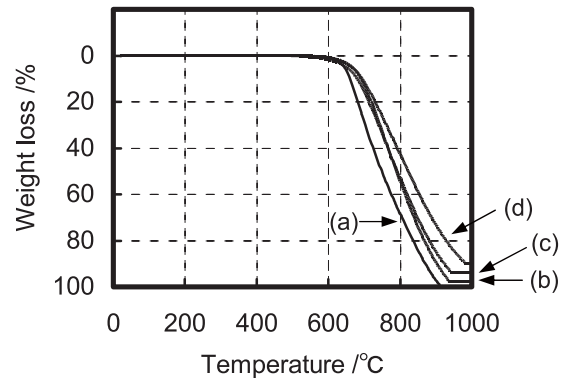


Fig.1 Weight loss curves of carbon material and carbon/SiC composites : (a)carbon material, (b)composite (SiC 2 wt%), (c)composite (SiC 6 wt%), and (d) composite (SiC 10 wt%).

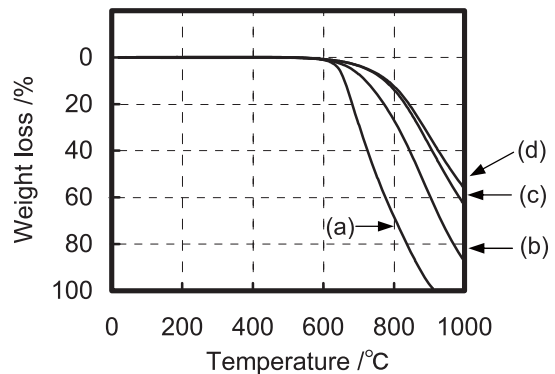


Fig.2 Weight loss curves of carbon material and carbon/B₄C composites : (a)carbon material, (b)composite (B₄C 2 wt%), (c)composite (B₄C 6 wt%), and (d) composite (B₄C 10 wt%).

respectively. The bulk density and Shore hardness of the composite material are higher than those of the carbon material.

Thermogravimetric analysis was carried out to examine the oxidation behavior of the composite

material. **Fig. 1** shows the results of the thermogravimetric analysis of the composite material containing SiC powder. For the carbon material composed only of coke, its weight decreases at approximately 600°C, and the entire specimen is oxidized and combusted at approximately 900°C. The percentage of weight decrease of the composite material containing SiC powder at 1000°C in air is 98% (2 wt% SiC), 94% (6 wt% SiC) and 90% (10 wt% SiC). Therefore, when SiC powder was added, no increase in the oxidation resistance of the composite material was observed.

Fig. 2 shows the results of the thermogravimetric analysis of the composite material containing B₄C powder. The temperature at which the weight decrease of the composite material containing B₄C powder began increases; in addition, the composite material still remains after the thermogravimetric analysis, indicating an increase in the oxidation resistance of the material. The percentage of weight decrease of the composite material containing B₄C powder at 1000°C in air is 88% (2 wt% B₄C), 64% (6 wt% B₄C) and 56% (10 wt% B₄C). The oxidation resistance increases, with increasing amount of B₄C. In the composite material containing 10 wt% B₄C powder, the temperature at which the weight decrease began significantly increases, and approximately 44% of the specimen remains even after the thermogravimetric analysis up to 1000°C.

Curves (a) and (b) appearing in **Fig. 3** show the results of the X-ray diffraction analysis of the composite materials containing 10 wt% SiC and B₄C powders, respectively. Diffraction peaks corresponding to Carbon and SiC are seen in curve (a). Diffraction peaks corresponding to Carbon and B₄C are seen in curve (b). No diffraction peaks corresponding to reaction products are observed. The specimen of the composite material containing 10 wt% B₄C remained after the thermogravimetric analysis was ground and subjected to X-ray diffraction analysis. A diffraction peak corresponding to B₂O₃ was observed in curve (c). On the basis of this result, the increase in the oxidation resistance of the composite material containing B₄C powder is considered to be a result of the formation of an oxidation-resistant B₂O₃ film through the oxidation of B₄C. In addition, the lattice constant

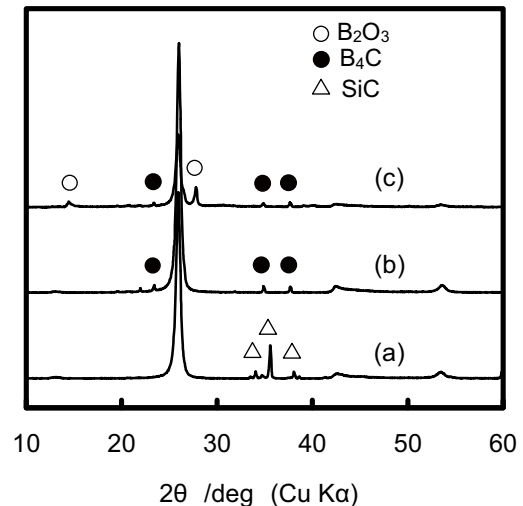


Fig.3 XRD patterns of carbon/ceramic composites : (a)SiC 10 wt%, original, (b)B₄C 10 wt%, original, and (c) B₄C 10wt % after TGA up to 1000°C.

(d(002)) and crystallite diameter (Lc(002)) of the composite material containing 10 wt% B₄C powder were measured. The results indicate that d(002) was 0.3414 nm and Lc(002) was 26 nm. The growth of the graphite structure was less significant in the composite material containing B₄C powder than in the carbon material composed only of coke.

4. Discussion

There are several reports on the structure and oxidation behavior of the carbon composite material with added SiC or B₄C powder⁽⁶⁻⁸⁾. To prepare such materials, processes such as impregnation or coating are required, necessitating many preparation processes and much time for heat treatment. In this study, we succeeded in synthesizing a carbon/ceramic composite material using few processes and a short sintering time by SPS.

From the results of the thermogravimetric analysis, the oxidation resistance of the composite material with added B₄C powder was found to be increased, and no oxidation suppression effect was observed in the composite material with added SiC powder. In general, the oxidation of B₄C starts at approximately 500°C, and B₂O₃ is formed at approximately 700°C. This B₂O₃ serves as an oxidation-resistant film, leading to an increase in the oxidation resistance of the composite material. The

oxidation of SiC is considered to start gradually at approximately 800°C and SiO₂ is formed at 1100-1200°C. It is considered that SiO₂, which shows the oxidation suppression effect, was not formed in the composite material containing SiC powder, at temperatures of up to 1000°C adopted in the thermogravimetric analysis in this study; therefore, oxidation resistance was not exhibited. It is considered that the oxidation suppression effect of the composite material containing SiC powder may arise in the high-temperature region of approximately 1200°C.

In general, a graphite structure accompanying catalytic graphitization develops in carbon materials upon adding B₄C⁹⁾. However, in this study, the results of lattice constant and crystallite size measurements did not indicate any development of the graphite structure in the composite material containing B₄C powder. Miyazaki et al. reported that the addition of a small amount of B₄C of 10 wt% or less promotes the development of the graphite structure^{10),11)}. The low graphite crystallinity in this study was considered to be due to the use of SPS, which suppresses crystal growth. It is considered that graphite crystallinity influences the oxidation resistance of carbon materials. A detailed examination of the relationship between the effects of SPS on the crystalline structure and oxidation resistance should be carried out in the future.

5. Conclusions

Using coke, SiC and B₄C powders as raw materials, carbon/ceramic composite materials were synthesized by SPS for a short duration. The oxidation resistance of the composite material containing B₄C powder was higher than that of the composite containing SiC powder. The temperature at which the weight decrease of the composite material containing 10 wt% B₄C powder began shifted to the high-temperature region compared with that of the carbon material composed only of coke. Approximately 44% of the specimen remained

even after thermogravimetric analysis in air up to 1000°C. By X-ray diffraction analysis, a diffraction peak corresponding to B₂O₃ was observed. This finding indicates that B₄C in the composite material is oxidized to B₂O₃, which then forms an oxidation-resistant film, leading to an increase in the oxidation resistance of the composite material.

References

- 1) Imai, T., Naito, Y., Yamamoto, T. and Ohyanagi, M. : Translucent nano mullite based ceramic fabricated by spark plasma sintering, *J. Ceram. Soc. Japan*, 114, pp.138-140, 2006.
- 2) Kawagoe, D., Ioku, K., Fujimori, H. and Goto, S. : Transparent β-tricalcium phosphate ceramics prepared by spark plasma sintering, *J. Ceram. Soc. Japan*, 112, pp.462-463, 2004.
- 3) Kun, W., Zhengyi, F., Weimin, W., Yucheng, W., Jinyong, Z. and Qingjie, Z. : Study on fabrication and mechanism in of porous metals by spark plasma sintering, *J. Mater. Sci.*, 42, pp.302-306, 2007.
- 4) Hoshii, S., Kojima, A. and Goto, M. : Preparation of graphitic materials by spark plasma sintering method, *J. Mater. Sci. Lett.*, 20, pp.441-443, 2001.
- 5) Hoshii, S., Kojima, A. and Goto, M. : Preparation and Several Properties of Carbon Materials by Spark Plasma Sintering Method, *J. Mater. Sci. Jpn.*, 40, pp.47-51, 2003.
- 6) Kawaguchi, M. : Preparation, nanostructures and properties of carbonaceous materials containing boron and nitrogen, *TANSO*, No.227, pp.107-114, 2007.
- 7) Itoh, M., Suzuki, D., Sasaki, Y., Uchida, S. and Narisawa, M. : Highly oxidation-resistant carbon-silicon-metal oxide hybrids derived from a silicon-containing polymer precursor, *TANSO*, No.226, pp.32-37, 2007.
- 8) Shibano, K., Kamiya, K., Yoshizawa, S. and Sugawa, O. : Fire retardation mechanism of carbon composite board by covering boron oxide, *TANSO*, No.216, pp.8-12, 2005.
- 9) Ohya, A. : Catalytic Graphitization, *TANSO*, No.102, pp.118-131, 1980.
- 10) Miyazaki, K., Yoshida, H. and Kobayashi, K. : Graphitization of Glass-like Carbon by Boron Carbide Additives, *TANSO*, No.119, pp.215-221, 1984.
- 11) Miyazaki, K., Yoshida, H. and Kobayashi, K. : Structural Change in Natural Graphite heat-treated with Boron Carbide, *TANSO*, No.128, pp.2-6, 1987.

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