論　　文

CHARACTERISTICS OF BAKED CARBON MATERIAL PREPARED BY SPARK PLASMA SINTERING

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Carbon materials were prepared by the spark plasma sintering (SPS) method with a short period, and without adding binders and additives. The purpose of this study is to examine the effects on several properties of carbon materials by SPS. The bulk density, shore hardness, shear strength and compressive strength of carbon materials treated by SPS method were measured. In case of treatment temperature of 1800 °C, and pressure of 60MPa, these values were the highest observed in this study. Microstructure of carbon materials were examined by scanning electron microscope (SEM). Results of cross section observation by SEM, number and size of pore of carbon materials treated by SPS method were decreased with increasing treatment temperature and pressure. Crystal structure of carbon materials were analyzed by X-ray diffractometry.

Key Words : *Carbon materials, Spark plasma sintering, Rapid baking*

1. INTRODUCTION

We showed that dense graphitic material can be obtained in a fairly short time by spark plasma sintering (SPS), which uses natural graphite powder as a starting material[1]. SPS is a material coordinating method in which a powder sample filled in a mold for graphite is sintered by the sparks generated among particles with the application of direct-pulsed current[2),3)]. The characteristics of this method are that a high-density product can be obtained in a short time, and the material can be sintered at a temperature lower than that required in hot pressing and hot isostatic pressing (HIP). To date, SPS has been used to develop materials such as ceramics and functionally graded materials[4)-6)], and overall investigations of the SPS have been reported[7),8)]. SPS has recently paid attention as a new fabrication method for carbon materials; however, few studies on the application of SPS have been reported[9),10)].

In present study, we fabricated binderless baked carbon material by SPS using high-purity coke powder as the starting material and examined the effects of SPS treatment conditions on the mechanical properties and structures of the baked carbon material. In addition, we expanded our basic knowledge of baked carbon material fabricated by SPS by measuring the electrical and thermal characteristics, analyzing the crystal structure and observing the microstructure of the baked carbon material.

2. EXPERIMENTAL METHODS

We used high-purity coke powder manufactured by Tokai Carbon Co.,Ltd as the starting material. Table 1 shows the characteristics of the raw coke powder. The SPS system used in the experiment was DR.SINTER, SPS-1050, manufactured by Izumi Technology company,Ltd. Baked carbon material was fabricated in the following way. A mold for graphite was filled with 3 g of raw coke powder and placed in the SPS system. Under vacuum, the coke powder was heated up to the prescribed temperature at a rate of 120 °C /min and with the application of

Table 1 Characteristics of the raw coke powder.

Average diameter	10~15μm
Absolute specific gravity	2.00
Purity	99.8% or higher
Impurities contained (ppm)	
Na	600
Si	550
Al	350
Fe	330
Zn	250
Mg	34
K	26
P	10

pressure, and then kept at the prescribed temperature for 3 min. After cooling for approximately 2 h, a disk-shaped baked carbon material sample 20 mm in diameter and 5 mm thick was removed. SPS treatment was conducted at heat treatment temperatures (HTT) of 1600 °C and 1800 °C, at pressures of 20, 30, 40, 50 and 60 MPa, and the baked carbon material was fabricated.

We measured the bulk density, hardness (shore hardness), shearing strength and compressive strength of the baked carbon material obtained. For the baked carbon material fabricated under the conditions of HTT 1800 °C-60 MPa, we measured specific resistance using the four-terminal method and measured the coefficient of thermal expansion and thermal conductivity. For the baked carbon material fabricated under the conditions of HTT 1600 °C-60 MPa and HTT 1800 °C-60 MPa, the samples were ground and subjected to X-ray diffraction analysis, and we observed the cross section using scanning electron microscopy (SEM).

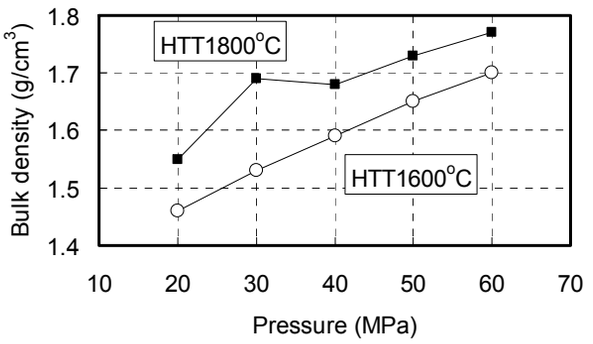

Fig.1 Bulk density of the baked carbon materials.

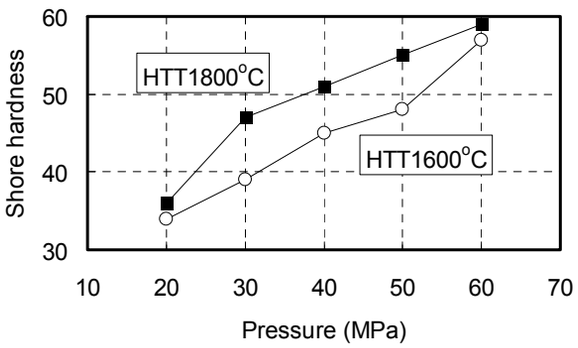

Fig.2 Shore hardness of the baked carbon materials.

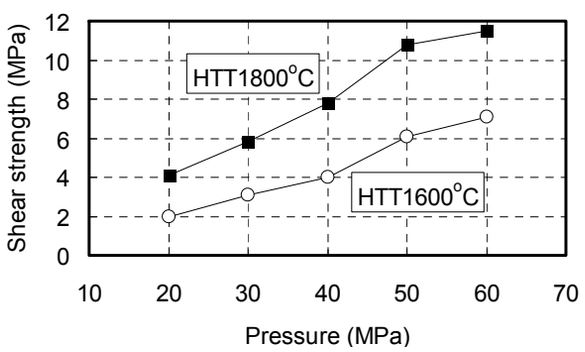

Fig.3 Shear strength of the baked carbon materials.

3. RESULTS AND DISCUSSION

By SPS, baked carbon material made of coke powder was obtained at a sintering time of less than 18 min in an entire fabrication time including cooling of less than 2 h, without adding binders or additives. Using SPS, the simplification of the fabrication of baked carbon material with a short sintering time was made possible. The baked carbon material thus obtained was solid and did not degrade or collapse.

The bulk density and shore hardness of the baked carbon material increased as HTT and pressure were increased, and showed the highest values when the baked carbon material was fabricated under conditions of HTT 1800 °C-60 MPa. Fig. 1 shows the change in the bulk density of the baked carbon material fabricated under different HTTs and pressures, and Fig. 2 shows the change in shore hardness. The bulk density and shore hardness of the baked carbon material fabricated under the conditions of HTT 1800 °C-60 MPa were 1.77 g/cm^3 and 59, respectively. These values are higher than the bulk density and shore hardness of extruded artificial

graphite used in general processing, which are 1.72 g/cm^3 and 44, respectively. Similarly to bulk density and shore hardness, mechanical properties of the obtained baked carbon material were improved as HTT and pressure increased. Fig. 3 shows the change in the shear strength of the baked carbon material fabricated at various HTTs and pressures. The best mechanical properties were obtained when the baked carbon material was fabricated under the conditions of HTT 1800 °C-60 MPa, at which the shearing strength and compressive strength of the material were 11.5 MPa and 11.3 MPa, respectively. The bending strength of extruded artificial graphite used in general processing was 24.5 MPa[11], although the mechanical properties of the baked carbon material could not be directly compared with those of artificial graphite because the test piece of the baked carbon material used to measure mechanical properties was not in the size prescribed by Japanese Industrial Standards (JIS)[12]. The mechanical properties of the baked carbon material were improved as the bulk density, accordingly the structural density, of the baked carbon material increased with HTT and pressure. This tendency is also indicated in the observations by SEM. Due to the capabilities of the SPS system used, HTT cannot be increased beyond 1800 °C; however, pressure can be increased. By applying higher pressure during SPS treatment, further improvement in the mechanical properties of baked carbon material is expected.

Table 2 shows the characteristics of the baked carbon material fabricated under the conditions of HTT 1800 °C-60 MPa, under which bulk density, shore hardness and mechanical properties were the highest. For the baked carbon material fabricated under the conditions of HTT 1800 °C-60 MPa, specific resistance was 56.1 μΩm, the coefficient of thermal expansion was 3.8×10^{-6}/K, and thermal conductivity was 20 W/m•K. For an extruded artificial graphite used in general processing, the specific resistance was 7.5 μΩm, the coefficient of thermal expansion in the extrusion direction was 3.6×10^{-6}/K, that vertical to the extrusion direction was 4.1×10^{-6}/K, and the thermal conductivity was 162 W/m•K. Compared with artificial graphite, the specific resistance of the baked carbon material was high and its thermal conductivity was small. In general, it is known that the crystallinity of carbon materials affects these characteristics; therefore, we examined the graphitic crystallinity of baked carbon material.

We carried out X-ray diffraction analysis on raw coke powder and baked carbon materials fabricated under the SPS conditions of HTT 1600 °C-60 MPa and HTT 1800 °C-60 MPa (Fig. 4). In the raw coke powder, a broad diffraction pattern of carbon in the vicinity of $2\theta=26^\circ$ was observed. After SPS treatment, the diffraction pattern intensity in the vicinity of 26° increased, and the diffraction pattern intensity increased with HTT. When natural graphite powder was used as a starting material, SiC was generated by SPS treatment due to the presence of ash in natural graphite[1]; however, in this study, diffraction patterns other than those due to carbon were not identified.

Table 2 Characteristics of the baked carbon material. (HTT1800 °C -60MPa)

Bulk density (g/cm^3)	1.77
Shore hardness	59
Shear strength (MPa)	11.5
Compressive strength (MPa)	11.3
Specific resistance (μ Ω m)	56.1
Coefficient of thermal expansion (10^{-6}/K, 200～400°C)	3.8
Thermal conductivity (W/m・K)	20

We calculated the lattice constant (d(002)) and crystallite size (Lc(002)) of baked carbon material fabricated under the conditions of HTT 1800 °C-60 MPa, and examined graphitic crystallinity. When the baked carbon material was fabricated under the conditions of HTT 1800 °C-60 MPa, d(002) and Lc(002) were 0.3427 nm and 27 nm, respectively. When the raw coke powder was heat-treated at a

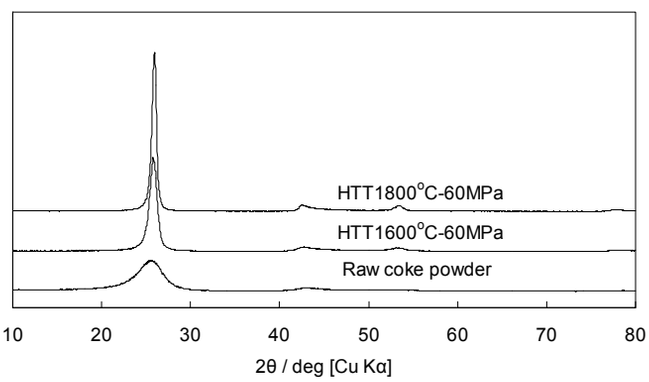

Fig.4 XRD patterns of the raw coke powder and the baked carbon materials.

temperature of 2800 °C, d(002) and Lc(002) were 0.3363 nm and 60 nm, respectively. The theoretical Lc(002) value calculated based on the basic structure of graphite was 0.3354 nm. Compared with these values, the graphitic crystallinity of the baked carbon material was low. On the basis of these results, we determined that the specific resistance of the baked carbon material was large and the thermal conductivity was small because the graphitic crystallinity of the baked carbon material was low compared with that of artificial graphite.

We observed the cross section of the baked carbon materials fabricated under conditions of HTT 1600 °C-60 MPa and HTT 1800 °C-60 MPa, and Fig. 5 shows the results. In the case of HTT 1600 °C-60 MPa (Fig. 5-1), many holes with a diameter of approximately 60-70 μm were observed; however, in the case of HTT 1800 °C-60 MPa (Fig. 5-2), only a few small holes with diameters of approximately 30 μm were observed and the structure of the baked carbon material was determined to be dense. For the baked carbon material fabricated under the SPS conditions of HTT 1800 °C-60 MPa, bulk density, shore hardness and mechanical properties were improved because the number of voids decreased and the structure became dense. We observed the baked carbon material fabricated under conditions of HTT 1800 °C-60 MPa with a higher magnification. No molten part was observed on the powder surface; interparticle voids were observed; interparticle binding was not observed.

In the SPS treatment of natural graphite powder, the existence of ash seems to contribute to the binding of the powder[1]. Treatment temperatures higher than 2500 °C and the existence of pores in the graphite are necessary for binding the graphite using SPS[10]. We studied the binding mechanism of raw powder on the basis of the characteristics of SPS[3),9)] and the results of this study. A rapid increase in the temperature of the raw powder occurred due to the thermal diffusion effects and electrical field diffusion effects of SPS, and the crystal structure of graphite was formed. In addition, with the generation of Joule heat due to SPS treatment, the plastic deformation of powder samples was promoted, and the binding and densification of baked carbon material occurred under the effect of applied pressure. We will study the effects of SPS treatment on baked carbon material in detail in the future.

4. CONCLUSION

Using SPS, we fabricated solid baked carbon made of coke powder in short times without adding binder or other additives. The bulk density, shore hardness and mechanical properties of the baked carbon fabricated depended on HTT and pressure during the SPS treatment. As HTT and pressure increased, the structure of the baked carbon became dense with fewer voids, and mechanical properties were improved. For the baked carbon fabricated under the conditions of HTT1800 °C-60MPa, for which it shows the highest quality, the bulk density, shore hardness and thermal expansion coefficient were similar to or higher than those of typical artificial graphite. The graphite crystallinity of the baked carbon was low compared with, for example, coke powder which was heat-treated at a temperature of 2800 °C, and this was determined to have an effect on the specific resistance and heat conductivity of the baked carbon.

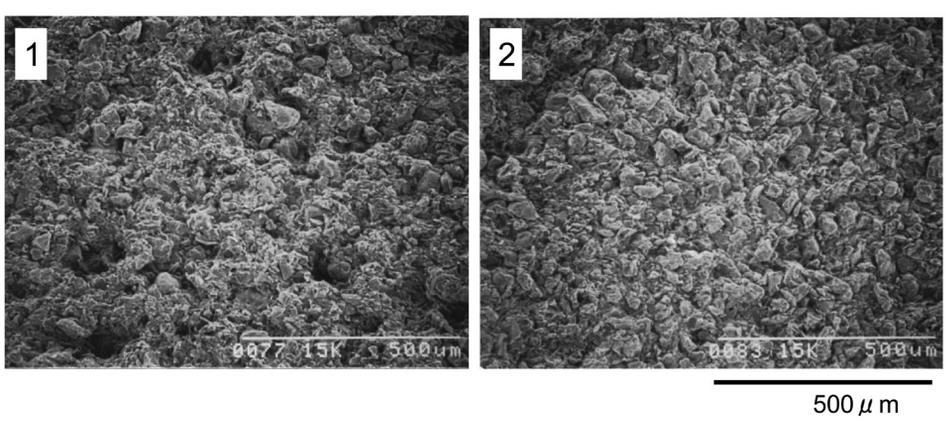

Fig.5 SEM micrographs of the baked carbon materials.
1: HTT1600°C -60MPa, 2: HTT1800°C -60MPa

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