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Microstructural investigation of wood charcoal made by spark plasma sintering

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Introduction

Wood-based carbonized materials from unused or waste woods are sought as environmental cleaning products and raw materials for carbons,[1] thereby opening the door for new utilization. The graphitization of carbons is important in the production of artificial graphite in industry. An attempt was made to qualify the degree of graphitization in the process of carbonization using X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared spectroscopy (FT-IR), and X-ray diffractometry.[2,3] X-ray diffraction scans showed that atomic order in the carbonized wood was developed by increasing the heat treatment temperature to more than 1500°C. Layer height and order increased between 1500° and 2500°C, demonstrated by the significant increase of the {002} reflection.[3] However, up to now the graphite structure in wood charcoal has not been proved using high-resolution transmission electron microscopy.

The carbonization process of wood, where graphite is produced, is usually conducted in electric furnaces in a laboratory. When applied to industry this process is not economical because so much energy is required to heat materials to this high temperature, and much time is necessary to cool it from the desired temperature. The establishment of an economical, effective heat conversion system is necessary to promote the development of wood-composite products with new functions based on wood charcoal.

Spark plasma sintering (SPS) is a novel powder consolidation method to produce permanent magnets, ceramics, alloys, and so on.[4] Plasma generates among the powder when pulse voltage is applied to it. It densifies materials in a short time at high temperature and with high current discharge. SPS has three advantages: It segregates the minimum molecular chain, purifies the growth of crystallites, and prevents oxidization at boundaries among particles.

The SPS method was applied to wood charcoal, whose volume electric resistance and thermal conductivity are similar to those of graphite.[5] In this paper the similarity in the physical properties between sintered wood charcoal and graphite is shown by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

Materials and methods

Materials

About 20-year-old sugi (*Cryptomeria japonica* D.Don) logs were obtained from Hyogo Prefecture. Specimens in the shape of a disk cut from the logs with a diameter of 30 mm and height of 60 mm were heated in an electric oven, increasing the temperature at 4°C/min up to 700°C. After the target temperature was obtained, the temperature in the oven was kept constant for 30 min and then allowed to cool naturally. The carbonized samples were milled into powder (20 mesh pass).

Sintering method

The wood charcoal powder was placed in a mold made of carbon and then pressed. It was sintered by heating through activation by a plasma treatment. Plasma current was added to the raw materials through the carbon mold. The sintering condition was as follows: temperature 2490°C,

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pressure 500 kgf/cm^2, current 1400 A, voltage 4.2 V, and sintering time 5 min. After sintering, the specimen was obtained with a gravity of 0.101 g, thickness 1.02 mm, and bulk density 1.26 g/cm^3. The volume electric resistance was 10×10^{-5} m·Ω, the same order for 4×10^{-5} m·Ω of graphite,[6] and the thermal diffusivity was about 3.0 W/(m·K), similar to the 1.6 W/(m·K) of pyrolytic graphite vertical to the plane of the graphite layer.[7]

Observation by SEM and TEM

The composition and microstructure of the sintered wood charcoal were examined on sections from the specimens by SEM (JSM-5310). The specimen for TEM was then prepared with the precision ion polishing system (Gatan model 691). The obtained specimen was analyzed by TEM (Philips CM200).

Results and discussion

Figure 1 shows the SEM image of the wood charcoal sintered at 2490°C for 5 min. The cell walls tightly contacted during the sintering process so the lumens of all cells became flat. The length of the flat lumens shortened in some cells, which was assumed to be the result of the sintering at high temperature and pressure. It is estimated that the deformation of the cells in micro-scale influences the physical properties (bulk density, volume electric resistivity, and thermal conductivity) to some degree.

Figure 2 shows the features of wood charcoal sintered at 2490°C for 5 min. The merging and interlinking of different graphitic microfibrils can be seen by TEM. This change may be caused by heat diffusion between the charcoal elements and ion electric field diffusion. When compared to the conventional method, the growth of the crystallites during the SPS method proceeded at a lower temperature and in a shorter time, which was supported by the X-ray diffraction pattern. The TEM observations revealed that the microstructural characteristics appeared, in order of frequency, in the amorphous region, the randomly oriented region, and the oriented region.

Figure 3 is a high-resolution TEM micrograph of 002 lattice fringes (LF) imaging of wood charcoal. The high quality of the orientation and compactiveness is brought into evidence, as shown in Fig. 3, part 1. The fringes are long and almost perfect at this area, which is definite evidence that graphitization partly occurred. The plane of the graphite is observed where the plane distance is 3.5 Å, close to the 3.354 Å of graphite.[8] An amorphous layer is observed at the upper right portion of Fig. 3. The carbons are greatly distorted in this area in Fig. 3, part 2. All stacks are reduced to two or three basic structural units arranged edge to edge.[9]

It has been believed that wood charcoal is non-graphitized material. In this study the graphitization of wood charcoal was observed by TEM for the first time. The formation of a graphite structure in sintered wood charcoal proves that its volume electric resistivity and heat conductivity are similar to those of graphite. Further study of the microstructure of the graphitization process of wood char-

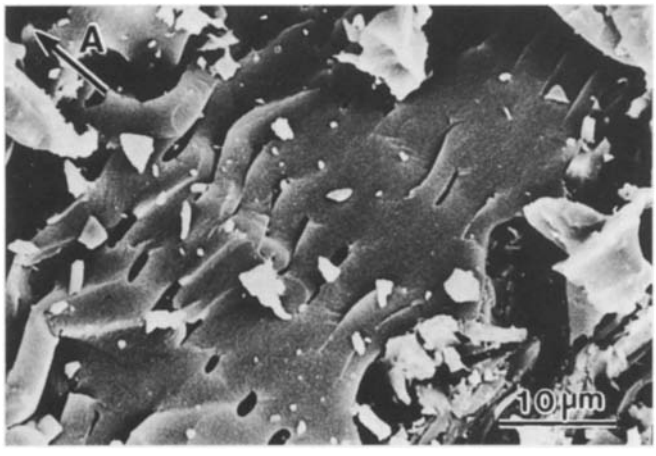

Fig. 1. Scanning electron micrograph of wood charcoal sintered at 2490°C for 5 min. *A*, direction of pressure during the sintering process

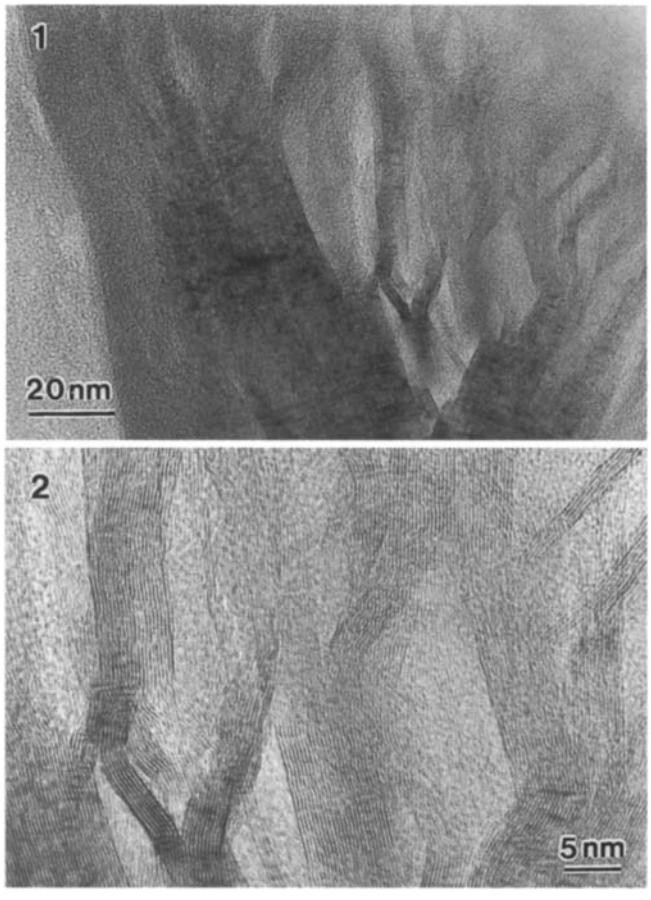

Fig. 2. Feature in wood charcoal sintered at 2490°C for 5 min, seen by transmission election microscopy (TEM). **1** At the atomic level note the merging and interlinking of different graphitic fibrils. **2** Enlarged image of **1**

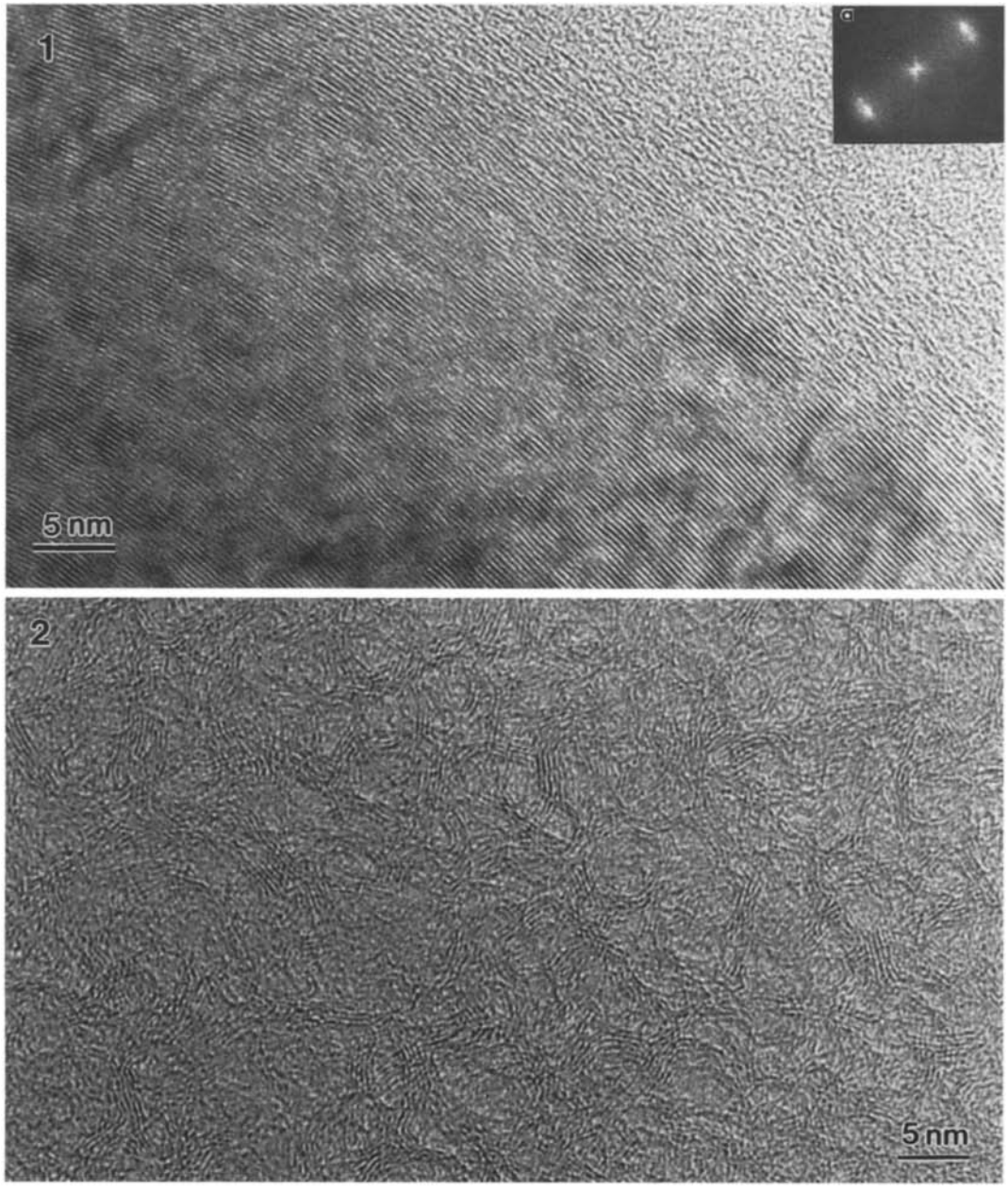

Fig. 3. High-resolution electron micrograph of 002 lattice fringes (LF) imaging of wood charcoal sintered at 2490°C for 5 min, TEM. **1** The fringes are long and almost perfect at lower left. **2** Two or three imperfect parallel groups are randomly oriented. **a** Fourier-transform imaging of lower left in **1**

coal is necessary, changing the sintering conditions, such as heat treatment temperature, pressure, catalysts, and so on.

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