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Introduction

Wood charcoal has been classified as nongraphitizable carbon, and the nongraphitizability is related to its porous structure. It is believed that this fine structure is a result of the randomly oriented crystallization of carbon. This is a consequence of the rigid cross-linking of the crystallites, which impedes parallel orientation of crystallites or graphitization.[1]

There are various allotropic nanophases of carbon, such as graphite, onion-like structures, nanotubes, and fullerenes. Most of them are formed from amorphous carbon under hydrothermal conditions.[2] Onion-like structures have aroused interest owing to their ability to transform to diamond under beam radiation.[3] For device applications, the hydrogenation of diamond-like carbon films is frequently analyzed by electron energy loss spectroscopy (EELS).[4] It is clear that various nano-structured carbons, such as diamond and nano-cells, can rather easily be formed from nongraphitizable carbon under hydrothermal conditions.

Oberlin reported an electron microscopic study of the microstructure of nongraphitizable carbon,[5] but few papers have discussed the microstructure in wood charcoal. As a result of electron microscopic observations of wood charcoal at temperatures up to 2500°C, we found the same parallel structure in wood charcoal as in natural graphite.[6] Furthermore, onion-like particles were observed in wood charcoal carbonized at as low a temperature as 700°C.[7] These findings showed that wood charcoal is a potential source of carbon materials. The present paper reports on the microstructure in wood charcoal carbonized at 700°C as studied in detail by electron microscopy.

Materials and methods

Materials

About 50-year-old Japanese cedar (*Cryptomeria japonica* D. Don) was carbonized at 700°C using a laboratory-scale electric furnace. Carbonized samples were heated at about 10°C/min to the heat-treatment temperature and held there for 1 h to ensure uniform heating throughout, and then cooled in a nitrogen gas atmosphere.

Transmission electron microscopy

The samples were prepared for electron microscopy using two methods. Pure charcoal was powderized, dispersed by ultrasonic means in an isopropyl alcohol solution, and spread over a holey carbon grid (powderized method). An ultramicrotome was used to obtain slices at a thickness of about 50 nm so that some slices could pinpoint the individual details (sliced method). Observations were made on specimens cut along the fiber direction.

The samples were analyzed in a JEOL 2010F analytical transmission electron microscope (TEM) operated at 200 kV and fitted with a Gatan post column energy filter, a JEOL 4000EX high-resolution TEM operated at 400 kV, and a Philips XL30S high-resolution scanning electron microscope (SEM).

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Results and discussion

The yielding, merging, and interlinking of graphitic layers could best be seen in wood charcoal by high-resolution TEM. Onion-like particles were occasionally observed in various areas of the samples prepared by the powderized method.[7] Spherical structures were observed consisting of graphitic layers in the form of concentric rings, sometimes with a small crystalline nucleus in the center, as was reported by the Stuttgart group.[8] From a determination of the lattice fringes, the inner core was found to have a diamond structure. A similar crystalline nucleus, but now outside the onion-like structure, is shown in Fig. 1. Figure 1a was obtained with the analytical microscope. Figure 1b is the area corresponding to the square in Fig. 1a. The diffraction pattern depicted in Fig. 1c was obtained after fast Fourier transformation (FFT) of this area. This characteristic picture contains three pairs of diffraction spots in addition to the central beam, two sets of 111 spots, and one set of 200 spots. The angle between the 200 and 111 diffraction spots is in good agreement with the 54.74° in the [110] pole of the face centered cubic (fcc) structure. They are indexed as in Fig. 1c. The ratio of the magnitude of the diffraction vector of the 200 and that of the 111 is in good agreement with the calculated value of $2/\sqrt{3}$ for the [110] pole of diamond. Verification of the absolute lattice spacing of the crystalline patch was checked as follows: Figure 1a was calibrated using the supposition that the crystalline patch corresponds to diamond. The spacing of diamond for 111 planes is 0.206 nm,[8] and that of graphite for 002 planes is 0.337 nm. As a result of the calibration, graphite fringes measure 0.323 nm. This value is slightly smaller than that for graphite but sufficiently close to state that the small crystallite in Fig. 1 corresponds to diamond.

There are specific features recognized in the EELS patterns of amorphous, graphitic, and diamond-like carbon. Figure 2 shows the difference in the EELS spectra for carbonized Japanese cedar and the amorphous carbon foil. The additional peak in the curve for cedar indicates the presence of pyrolitic graphite.[9] However, the diamond structure turned out to be unstable under the influence of the electron beam, and its EELS spectrum could not be recorded.

A typical micrograph of the porous structure in wood charcoal carbonized at 700°C is shown in Fig. 3. The micropores were not distributed uniformly. Figure 3a is a high-resolution SEM image of the surface of the carbonized sample material just before preparation of a TEM sample. The dark dots represent pores. A typical TEM micrograph of a sample prepared according to the sliced method is shown in Fig. 3b. It was difficult to observe the porous

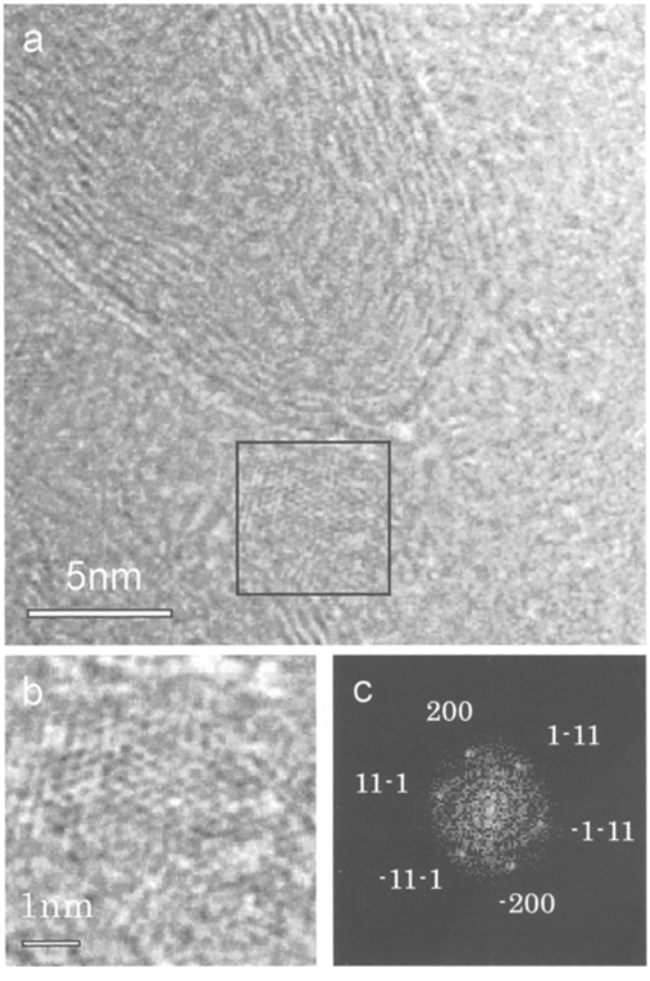

Fig. 1. **a** Diamond structure outside an onion-like structure in wood charcoal carbonized at 700°C for 1 h. **b** Selected image of a meta-stable patch of diamond. **c** Numerical diffractogram of the selected area showing the [110] pole of diamond

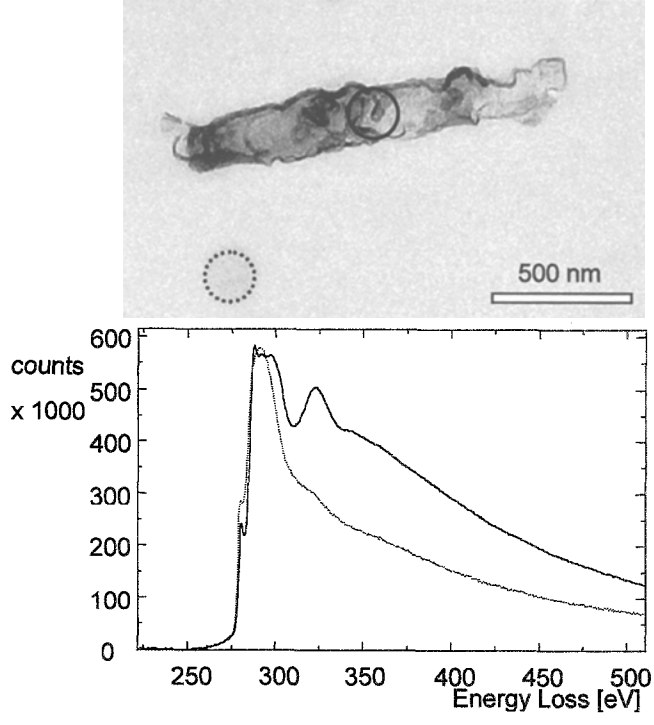

Fig. 2. Difference in energy loss spectra between Japanese cedar heated for 1 h at 700°C (*unbroken curve*) and the underlying carbon foil (*dotted curve*)

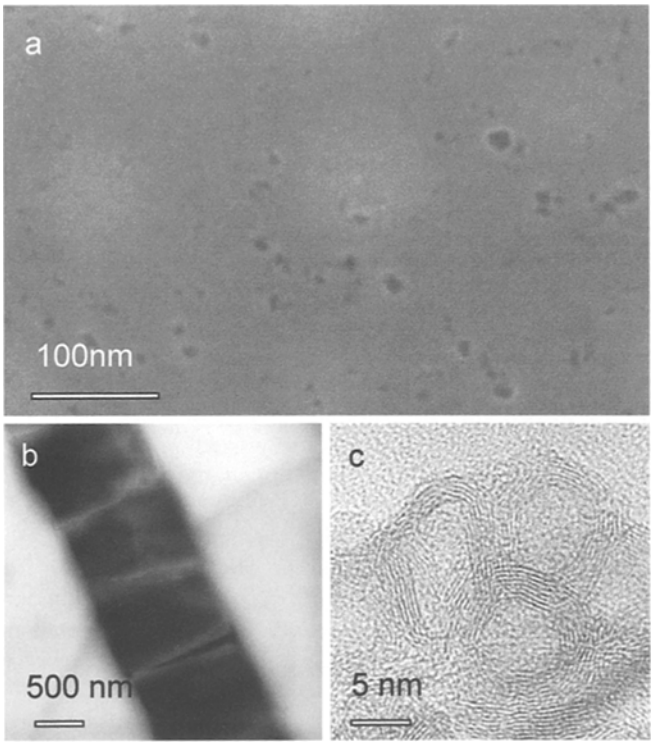

Fig. 3. **a** High-resolution scanning electron micrography (SEM) image of pore structure of the surface of wood charcoal carbonized at 700°C for 1 h. **b** Transmission electron micrography (TEM) image of wood charcoal prepared by the sliced method. **c** High-resolution TEM image of the pore structure in wood charcoal

structure, as the slice turned out to be rather thick. A typical high-resolution TEM image of the pores in wood charcoal prepared by the powderized method is shown in Fig. 3c. The diameters of the pores were roughly estimated to be 1 to 10 nm. The area around the pores in Fig. 3c is structured as oriented graphitic layers.

Conclusions

Various carbon structures were observed in the wood charcoal sample: the well known pyrolytic graphite layers, onion-like particles, and diamond structure. It is suggested that wood charcoal carbonized at 700°C is a complex of various carbon structures. The pore structure was observed by electron microscopy, and it is supposed that the microstructure and pores are closely related. Further study of the microstructure during the carbonization process of charcoal is necessary to better understand the characteristic functions of wood charcoal for utilizing it as a source of carbon material.

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