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Growth of cone-shaped carbon material inside the cell lumen by heat treatment of wood charcoal

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Key words Wood charcoal · Vapor-grown carbon · X-ray diffraction · SEM

Introduction

Wood charcoal is a potential source of carbon material with various allotropic structures. Recently, onion-like particles¹ and diamonds² have been found in wood charcoal. It is commonly regarded as a nongraphitic carbon³ because graphite crystallites of wood charcoal have essentially random orientation, which occurs in turbostratic carbon even with high temperature treatment. In such a case, the layer plane spacing is generally 0.344 nm,⁴ somewhat larger than that of graphite (0.335 nm) because of the repulsion force between the carbon atoms of adjacent-layer planes.

There have been several studies of graphitization of wood charcoal.^{5,6} Recently Hata et al. observed graphitic microfibrils in the wood cell wall treated by spark plasma sintering using transmission electron microscopy.⁷ Graphitization of wood cell wall advances through solid-state carbonization, under which multiphase graphitization yields a mixture of authentic graphite, turbostratic carbon, and other less-ordered carbon. The result is a mosaic of graphite crystallite without orientation.

In this study we found a carbon material in wood charcoal that seemed to be made from vaporized carbon or pyrolysis gases from the wood cell wall treated at high temperature (2500°C). The carbon material has a cone or spindle shape and a helical surface, which is not coincident

with any microanatomical tissue from the wood plant. This carbon material is a newly produced structure that is not transmuted by the solid state from parent wood cells.

Materials and methods

Materials

Preliminary charcoaled sapwood of Japanese cedar (*Cryptomeria japonica* D. Don) and bamboo madake (*Phyllostachys bambusoides* Sieb. et Zucc) prepared at 300°–400°C for 3 h in an outdoor furnace were used as starting samples. The samples were cut into 2 × 2 × 5 (L direction) cm for Japanese cedar and 1 × 2 × 5 (L direction) cm for madake and then were treated using an electric furnace SDS46–4 (Shinsei Denro Seisakusho) or SCC-30/220 (Kurata Giken Seisakusho). Samples were heated at a rate of 10°C/min at a pressure of 10–20 Pa and held for 1 h at 1000°, 1500°, 2000°, or 2500°C, respectively, under Ar gas, the pressure inside the furnace being kept at 0.005–0.01 MPa, then cooled to room temperature at a rate of 30°C/min.

X-ray diffraction

For X-ray diffraction, the heat-treated samples were powdered and packed into glass capillaries. The specimen was irradiated by X-rays from a Rigaku X-ray generator with a 50 kV/100 mA CuK α beam filtered by Ni inside the evacuated Laue camera, and a powder pattern was recorded with an imaging plate (Fujifilm). Calibration was achieved by a diffractogram from a mixture of NaF and the sample powder.

Scanning electron microscopy and energy dispersive X-ray analysis

The specimens were observed directly without any metallic coating using a JEOL 4000 scanning electron microscope

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(SEM) operated with an accelerating voltage of 10–20 kV. Energy dispersive X-ray (EDX) analysis was performed simultaneously with an accelerating voltage of 20 kV on the observed area using an EMAX-5770X (Horiba, Japan) equipped with an Si semiconductor sensing device, with which boron to uranium ($5 \leq$ atomic numbers ≤ 92) is detectable.

Results and discussion

X-ray diffraction

The X-ray diffraction profile of Japanese cedar treated at 1000°–2500°C is shown in Fig. 1. Two major peaks appear at $2\theta = 25^\circ$ and 43° approximately, close to (002) and (101) of graphite. The intensity of these peaks increases with an increase in the treatment temperature. There is no change in peak position between 1000°C and 1500°C, although there is a shift to a wider angle for the samples treated above 2000°C, indicating that the layer plane spacing decreases. Furthermore, a sharp peak appeared for the sample treated at 2500°C. This peak corresponds to a d -spacing of 0.343 nm, which corresponds to the layer plane of turbostratic carbon.⁴ For the sample treated at 2500°C, another broad peak at a lower angle is seen in the vicinity of the sharp peak. The sample treated at 2500°C has at least two elements: less-ordered carbon with a widely spaced layer plane and a more crystallized fraction with a layer plane spacing of 0.343 nm. This result is similar to that reported by Yamane et al.⁶ and indicates that multiphase graphitization occurred at 2500°C, but turbostratic carbon is dominant.

SEM and EDX analysis

The SEM observations revealed that the preliminary or secondary charcoaled samples differed from the non-heat-treated sample in the following ways: (1) No borderline was observed between adjacent cell walls or between bordered

pit frame and margo due to adhesion by the heat treatment. (2) Granules approximately 10 nm in diameter were attached to the cell wall. In all of the heat-treated samples the other anatomical features remained unchanged. No difference could be seen between the preliminary charcoaled samples and samples treated at 1000°–2000°C. This fact indicates that the anatomical change seen by SEM has already been achieved with preliminary charcoaling at 300°–400°C. It also indicates that anatomical features remain unchanged, although the fine structure (e.g., the crystalline order) changes drastically, as shown in Fig. 1.

Strange cone-shaped structures were observed in the sample treated at 2500°C (Fig. 2B, arrowhead), although the other features of original wood structures are similar to those treated at temperatures below 2000°C (Fig. 2A). Many cone-shaped materials of a few micrometers diameter and 10–20 μm in length were attached to the cell wall (Fig. 2B,C). The features of the newly found material are completely different from those seen in the initial wood cells. These cone-shaped materials were observed regardless of the kind of cell (whether tracheid or parenchyma) or the part of the annual ring (whether earlywood or latewood).

We focused on a cone-shaped material in Japanese cedar, and EDX analysis was performed on the area indicated in Fig. 3. An electron accelerated at 20 kV is considered to enter specimens with a thickness of approximately 4.5 μm ,⁸ which is shorter than the length of the flamed cone-shaped material (Fig. 3). Thus, the elemental analysis was regarded as being on the cone-shaped material. Only the characteristic carbon spectrum was detected. No elements other than carbon could be observed with this analysis, which indicates that the cone-shaped material is composed of carbon. The cone-shaped material was also found inside the cells of bamboo charcoaled at 2500°C (Fig. 4), which gave similar X-ray spectra.

The cone-shaped carbon material was not found on the surface, only inside the specimen block treated at 2500°C. Thus, the cone-shaped carbon is thought to be the structure resulting from vaporized carbon or pyrolysis gases inside the cell lumen. There is a well-known example of vapor-grown carbon fiber: whisker-like graphite.⁹ Our cone-shaped carbon resembles the whisker-like graphite because both are vapor-grown carbon materials, but they seem to have a different structure. Cone-shaped carbon is easily broken in cross section, as seen in Fig. 2C (arrows). On the other hand, this kind of cross-breaking does not easily occur with whisker-like graphite, which has a plane layer stacked parallel to the length of the whisker. The cone-shaped carbon closely resembles the “columnar grown carbon” of Haanstra et al., which has a broken surface of conical shape.¹⁰

In general, vapor-grown carbon, whether whisker-like graphite or columnar-grown carbon, needs organic gas as a source of carbon and the matrix on which the carbon structure grows. In this case both are provided by the wood charcoal itself, and the cone-shaped carbon grows by heating to 2500°C, whereas turbostratic carbon appears in the cell wall simultaneously. Further study may clarify the structural change of the cell wall and generation of the gas

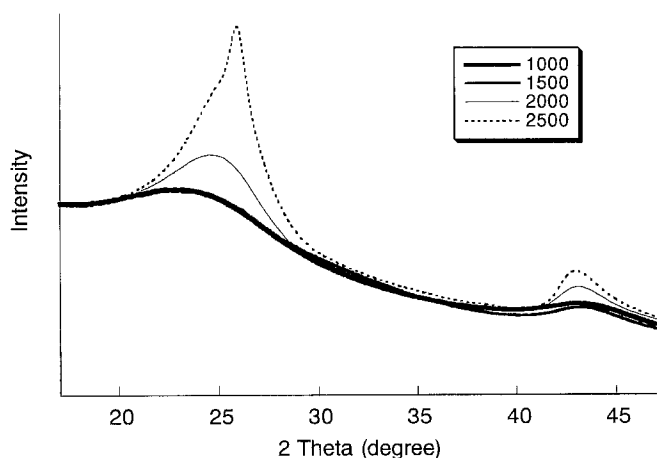
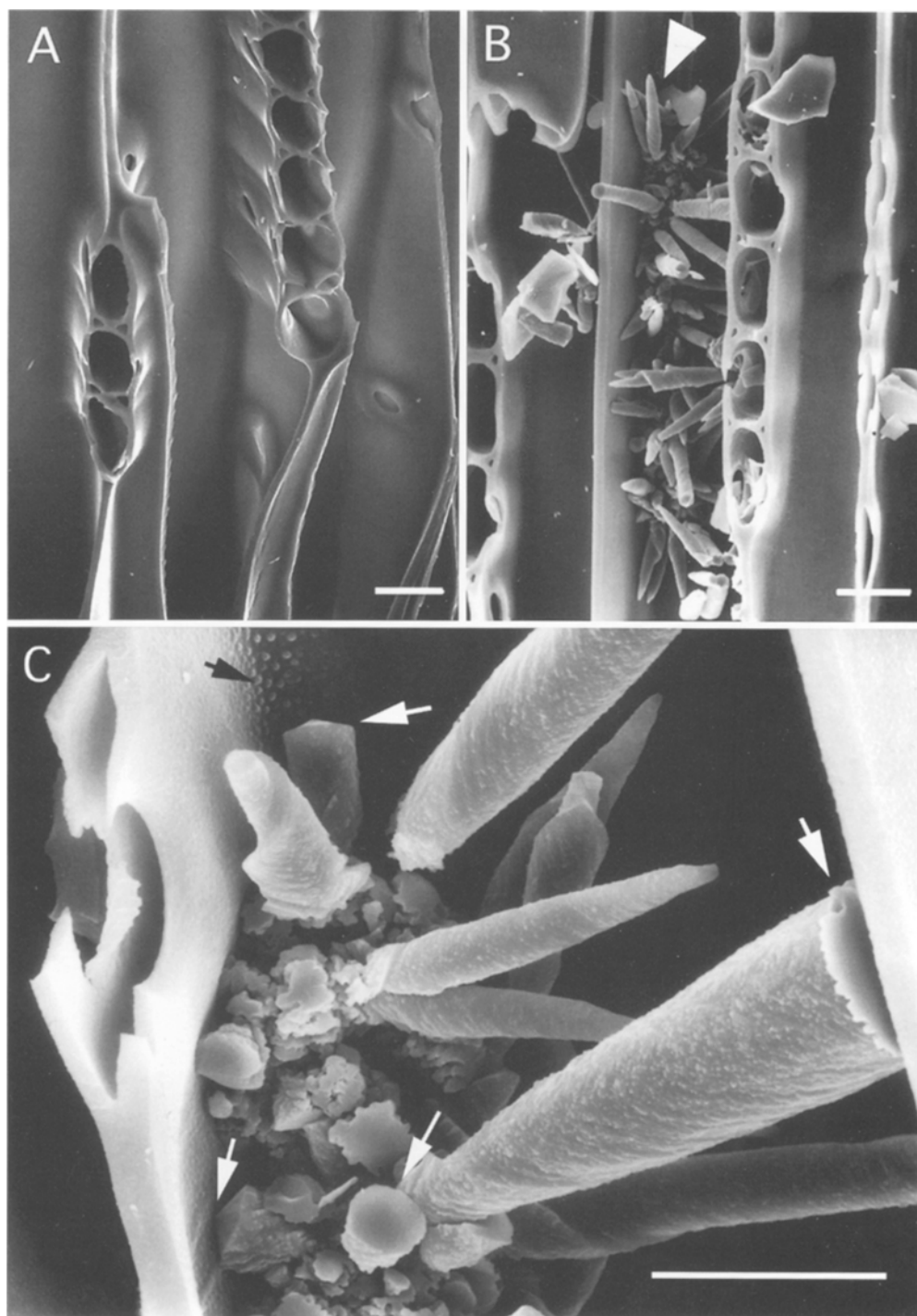


Fig. 1. X-ray diffractogram of Japanese cedar charcoal treated at 1000°, 1500°, 2000°, and 2500°C

Fig. 2A–C. Scanning electron microscopy (SEM) images of Japanese cedar charcoal. **A** Tracheid and ray parenchymal cell of the tangential plane treated at 2000°C. **B** As in **A** but treated at 2500°C. Cone-shaped carbon materials appear in the middle cell of the micrograph (*arrowhead*). **C** Cone-shaped carbon grown by treatment at 2500°C. The fracture plane of the cone is vertical to the direction of the cone length and is conical (*white arrows*). Note the granules on the cell wall surface (*black arrow*). Bars **A**, 10 μm ; **B**, 10 μm ; **C**, 5 μm



inside the cell lumen. It is also necessary to elucidate the kind of gas that contributed to the growth of the cone-shaped carbon material and whether the small amount of ash included in wood acts as the nuclei of the growth of the cone-shaped carbon.

In this study we found vapor-grown carbon from wood charcoal. It is difficult to derive a large aggregation of defect-free graphite from solid-state carbonization of wood. Thus, crystallites of diamond or graphitic structures are small if they form at all; however, the vapor-growth system

does not have such a limitation. The vapor-grown, cone-shaped carbon might give a clue for increasing the possibility of making new materials from wood charcoal.

Conclusions

With treatment at 2500°C, wood cell walls partially transform into a turbostratic carbon structure, which has an X-

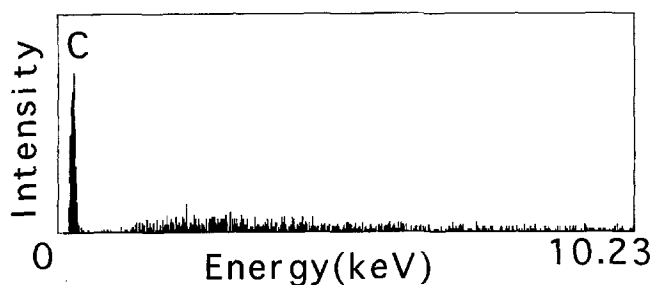
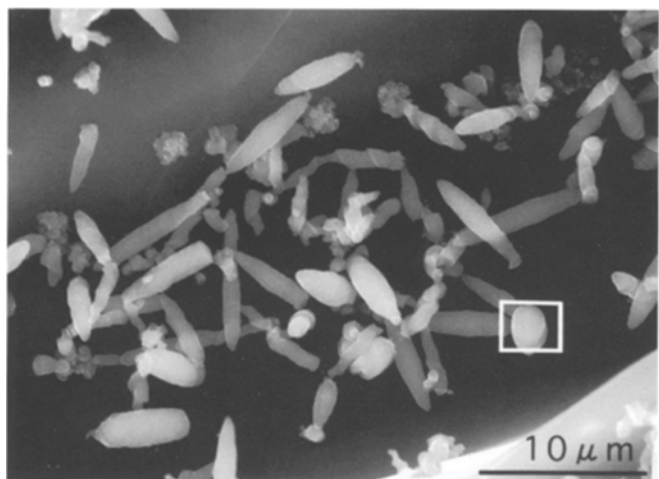


Fig. 3. X-ray microanalysis (*lower*) of cone-shaped carbon material from the boxed area of the SEM image (*upper*)

ray diffraction peak corresponding to a layer plane spacing of 0.343 nm. Despite this change, there was no apparent change within the cell wall seen by SEM.

Cone-shaped carbon material was formed inside the cell lumen after treatment at 2500°C. This is not a feature originating from any wood cell organism and seems to result from vaporized carbon or pyrolysis gases that originate within the cell wall.

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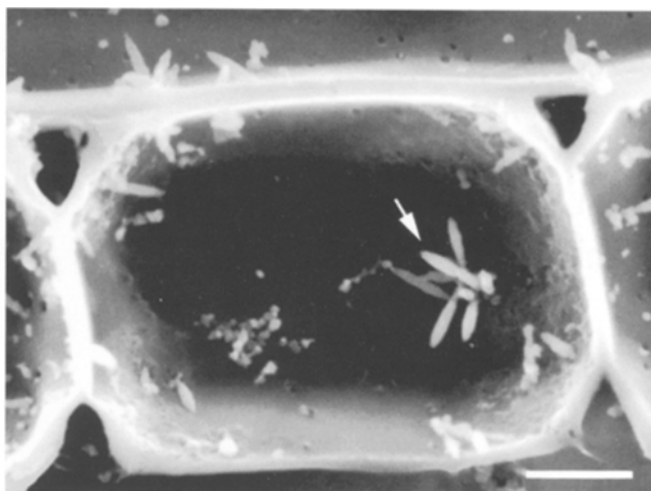


Fig. 4. SEM image of cone-shaped carbon grown inside a bamboo parenchymal cell (*arrow*). Bar 20 μm

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