Formation Mechanism of Microstructure in carbonized wood

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Carbon materials are classified by graphite-related and diamond related carbon materials. The former is composed of stacking hexagonal carbon layers based on sp^2-bonded carbon atoms; the latter consists of sp^3-bonded carbon atoms involved in tetrahedral bonds. Microstructure of graphite-related carbon materials such as a carbonized wood consists of mainly carbon crystallites, cross-linking between them, and oxygen-containing functional groups. The mechanical, electronic, and structural properties of the graphite-related carbon materials depend mainly on the three-dimensional arrangement of the carbon crystallites forming the carbon skeleton. The recent developments in wood-based carbon materials provide new application fields for the new functions of carbonized wood [1, 2], while at the same time demonstrating the necessity of finding a way to control its microstructure. The further development of various wood-based carbon materials requires that the carbonization process of wood and the formation mechanism of the microstructure of carbonized wood be sufficiently clarified, and that their microstructure on the nano scale be fully controlled. In the present study, the formation mechanism of the microstructure of carbonized wood was investigated systematically, focusing on the carbonization behavior and microstructural change in the carbonization process between 500 and 1800°C of Japanese cedar by spectroscopic and microscopic analysis. As a result, new interesting information was found with respect to the microstructure and its formation process in the wood carbonization. The details are summarized as follows.

Firstly, the carbonization behavior of wood at the early stage of the carbonization process between 500 and 1000°C is discussed in detail by comparison with that of cellulose and lignin [3]. A carbon crystallite composed of polyaromatic carbon planes in carbonized-wood, -cellulose, and -lignin was formed due to the decomposition and volatilization of non-aromatic functional groups up to 600°C. The degree of ordering of carbon crystallites at each heat treatment temperature is described in the ascending order of carbonized-lignin, -wood, and -cellulose. This could be due to differences among carbonized-wood, -cellulose, and -lignin in the degree of cross-linking, such as ether bridges and disordered aromatic structures, in the range of 500-600°C. It appears that the degree and process of carbon crystallites' development of carbonized wood are closer to those of carbonized cellulose than to those of carbonized lignin. This suggests that the degree of development of the carbon crystallites and the cross-linking for carbonized-wood, -cellulose, and -lignin during carbonization are closely related to the O/C atomic ratio before carbonization. Byrne and Nagle have proposed a cellulose microfibril dominance model for the formation mechanism of carbonized wood microstructures [4]. The present results prove that the microstructure in carbonized wood is strongly affected by the composition ratio of carbon to oxygen atoms in the raw wood.

Secondly, structural changes of sp^2-bonded carbons as the main carbon skeleton of carbonized wood between 500 and 1800°C was studied by XPS, Raman, XRD, and TEM [5]. The results of the spectroscopic analysis of carbonized wood showed that the microstructure of carbonized wood changes drastically at approximately 1400°C. The XPS and Raman results proved that the degree of disorder in carbon crystallites decreased significantly from 800 to 1400°C with decomposing of the cross-linkings such as oxygen-containing functional groups and amorphous phase sp^2-bonded carbon up to 1400°C. XRD results showed that the plane size of the hexagonal carbon layer in a carbon crystallite increased mainly up to 1400°C, and the number of the hexagonal carbon layers in a carbon crystallite increased significantly above 1400°C. TEM observation of wood carbonized at 700 and 1800°C visually showed that its predominant structure was turbostratic, and carbon crystallites approximately 1 nm in size at 700°C grew up to about a 3 to 10 nm size at 1800°C. The growth of the carbon crystallites was observed clearly above 1400°C.

Sp^3-bonded carbon of the sub-microstructural component in wood carbonized from 700 to 1800°C was qualified by Raman and TEM analysis [5]. The TEM results showed the existence of an onion-like and nano-diamond structure based on sp^3-bonded carbons in wood carbonized at 700°C, which suggested that the carbon structure of wood at the early stage of carbonization is a complex of various allotropic carbon structures [6, 7]. Nano-diamond based on sp^3-bonded carbon would be formed by the reaction between

sp^3-bonded carbon and volatilized oxygen atoms in carbonized wood at a low temperature of 700°C. The Raman spectra of carbonized wood proved that part of the microstructure in carbonized wood from 700 to 1800°C was made of the combination of sp^2- and sp^3-bonded carbon. Since sp^3-bonded carbon is the rigid cross-linking of carbon crystallites, the microstructure of carbonized wood could be highly disordered. It was found that the sp^3-bonded carbons were transformed from an amorphous to nanocrystalline structure with the growth of carbon crystallites in the temperature range above 1400°C. The structural development of rigid cross-linking of sp^3-bonded carbon would disturb the well-ordering of carbon crystallites in the high heat temperature range above 2000°C.

Finally, the microstructure in the cell walls of wood carbonized from 700 to 1800°C was clarified on the basis of the results of TEM observation and pinpoint Raman analysis [8]. The discrete layers in the cell walls of the raw wood were no longer observed at 700°C. SEM- and TEM-observations confirmed that the microstructure in a cell wall for carbonized wood was turbostratic in nature without any heterogeneity originating from the constitutional heterogeneity of wood. However, well-ordered carbon crystallites were observed on the inner surface of a cell wall for a sample carbonized at 1800°C. This surface layer could be formed by deposition of vaporized carbon gasses on the surface of cell walls during heat treatment, and may play an important role in the formation of the preferred orientation of carbon crystallites and multi-phase graphitization of carbonized wood at high temperatures [9].

On the base of the concerns mentioned above, the microstructural control in carbonized wood could be applied to the development of various wood-based carbon materials. As one possibility, the microstructure on the nano scale of carbonized wood would be controlled by the adjustment in quantity of sp^3-bonded carbon as cross-linkings of carbon crystallites. For the development of wood catalytic graphitization, carbonized wood, containing less amount of sp^3-bonded carbon, should be used as a carbon precursor because sp^3-bonded carbon disturb the well alignment of carbon crystallites as cross-linking during graphitization. On the other hand, for the addition of more stiffness to SiC and SiC/C composites, carbonized wood, including a large amount of sp^3-bonded carbon, should be utilized as a raw material in order to increase the number of the edge of carbon crystallites where silicon atoms react to carbon atoms. As another possibility, the microstructure between the inner surface and inside of the cell walls of carbonized wood would be controlled by the change of the permeability of volatized gases into cell lumen. By the development of well alignment carbon layers on the inner surface of cell walls of carbonized wood, it has heterogeneous microstructure between the inner surface and inside of cell wall. Such carbon materials are available to be as solid cathode batteries such as an electric double layer capacitor and lithium ion battery. Thus, the microstructural control in carbonized wood could be applied to the development of various wood-based materials, and be broadened the utilization of them as carbon materials.

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