Preliminary

Surface Characterization of Wood Charcoal under Different Carbonization Conditions[*1]

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Introduction

The characteristic functions of wood charcoal of electrical conductivity and adsorptive property are considered to be affected by its microstructure which changes according to carbonization conditions such as carbonized temperature, heating rate and atmosphere. The microstructure of wood carbon is considered to be drastically changed at 500 to 800°C and electron microscopic studies have shown that various nano-carbon structures such as C60 fullerene, onion-like and diamond structure were formed in wood charcoal around these temperature ranges[1–3]. These findings showed a close relation between the function and microstructure of wood charcoal.

The chemical structure such as type of functional group and chemical bond of wood charcoal during carbonization is also thought to be related to its characteristic properties and functions. X-ray photoelectron spectroscopy (XPS) is a powerful tool for analyzing the surface characteristics of wood charcoal due to its good surface sensitivity and ability to provide structural analysis for chemical bonding[4].

In this paper, the effects of carbonization conditions such as the carbonized temperature, heating rate and reaction time on the surface chemical structure of wood charcoal were studied by XPS.

Materials and Methods

Oven-dried chips of sugi sapwood *(Cryptomeria japonica)* were carbonized in a laboratory-scale furnace. Raw samples were heated at the heating rate of 2, 4, 8°C/min. up to the target temperatures of 500, 600, 700 and 800°C in a nitrogen gas atmosphere, maintained at these temperatures for 1 or 3 hr, and then cooled down to room temperature.

All carbonized samples were powdered and dried at 105°C for 24 hr for analysis by XPS. XPS spectra were obtained by AXIS-HS [Shimadzu/KRATOS] using an $MgK\alpha$ (1253.6 eV) X-ray source operated at 150 W in a vacuum of $3–5 \times 10^{-9}$ Torr. High-resolution scans of C1s were performed with the pass energy adjusted to 20 eV.

Results and Discussion

The FWHM (full width at half maximum) values of the C1s spectrum, which indicate the degree of carbonization and the order of laminated hexagonal carbon layers of carbon materials[5], are shown in Fig. 1. It is said that the FWHM of C1s spectra narrows with the development of carbonization and the lattice structure of hexagonal carbon layers. The FWHM values of the wood charcoal prepared in this experiment decreased up to 700°C of carbonized temperature. However, FWHM was not significantly different among the various heating rates and reaction times. The development of the carbonization stage and the formation of laminated hexagonal carbon layers was assumed to progress up to 700°C in all samples.

A curve fitting of the C1s spectrum was carried out by non-linear least squares curve fitting with Gaussian distribution and Shirley background subtraction. The spectra were fitted to six peaks[4,6]. The binding energy of C-C was assigned at 284.6 eV and of C-H was shifted to +0.5–0.8 eV from the C-C peak. In addition to the C-C and C-H, the spectra were fitted to three peaks of oxygen-containing groups, with chemical shifts of +1.4–1.8 eV

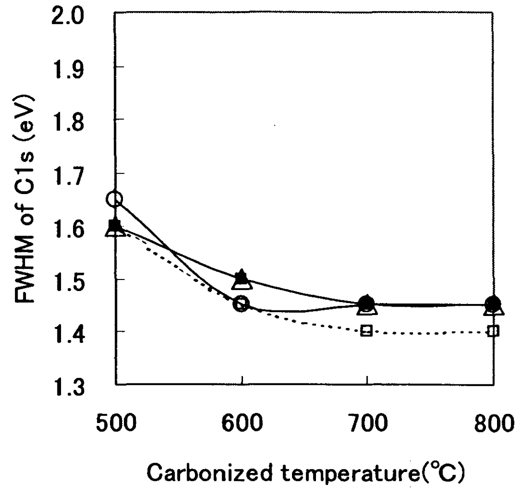

Fig. 1. Effects of carbonized temperature on the FWHM of C1s spectrum of wood charcoal at different heating rates and reaction times. Legend: ○; heating rate of 2°C/min, ■; heating rate of 4°C/min, △; heating rate of 8°C/min, □; heating rate of 4°C/min and reaction time of 3 hr.

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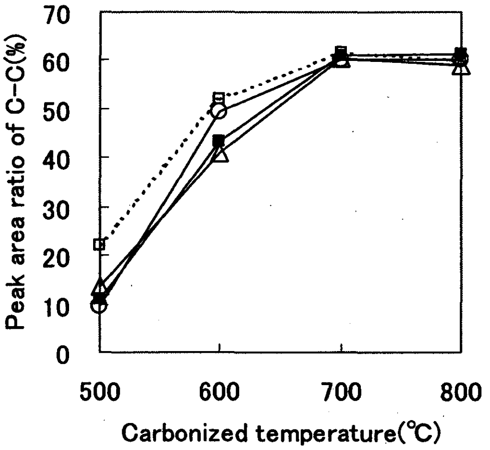

Fig. 2. Changes of the peak area ratio of aromatics carbon (C-C) obtained from the curve fitting of C1s spectrum with Gaussian distribution at different carbonized temperatures, heating rates and reaction times. Legend: see Fig. 1.

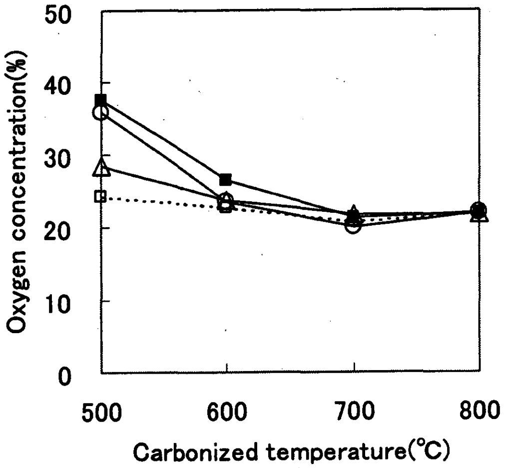

Fig. 3. Effects of carbonized temperature on the oxygen concentration, obtained by curve fitting of C1s spectrum of wood charcoal at different heating rates and reaction times. Legend: see Fig. 1.

(O1), +2.8–3.2 eV (O2) and +4.3–4.7 eV (O3), and +6.4–6.8 eV for Plasmon. These assignments of the functional groups are normally used to O1 for C-OH, O2 for C=O and O3 for COOH, for which proof the assignment of the chemical shifts to each functional group is underway.

The effects of the carbonized temperature and the heating rate on the peak area ratio of C-C are evaluated in Fig. 2. With increases in the carbonized temperature from 500 to 700°C, the peak area ratios of C-C increased in all the carbonization conditions. While the peak area ratio of C-C increased with the increase of the reaction time from 500 to 600°C, little difference was observed in the peak area of C-C by changing the heating rates.

The oxygen concentration of wood charcoal decreased with the increase of the carbonized temperature (Fig. 3). The heating rate and reaction time affected the oxygen concentration below the carbonized temperatures of 700°C, however, no significant difference was observed above 700°C among the various heating rates and reaction times.

It is expected that the chemical structure of wood charcoal with aliphatic and oxygen-containing components mainly changes to the framework of hexagonal carbon layers at temperatures up to 700°C, and the development of the order of the laminated hexagonal carbon layers occurs mainly at temperatures above 700°C. The carbonization conditions of the heating rate and reaction time influence the changes of the chemical structure in the range of 500–600°C, but do not significantly affect the chemical structures at 700–800°C.

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