

XRD AND TEM ANALYSIS OF DISORDERED STRUCTURE OF CARBON MATERIALS WITH LOW CRYSTALLINITY

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Introduction

Carbon materials with low crystallinity, such as cokes and activated carbons, include disordered stacking structure with aromatic layers, together with single layers and disorganized carbon atoms[1]. X-ray diffraction (XRD) measurement is one of the most conventional methods to evaluate the stacking structure, although quantitative analysis with the profile is often difficult due to broadness of peaks. One way to overcome this difficulty is a statistical analysis as suggested by Hirsch[2], and another is a comparison of calculated result with experimental data.

We aim to examine the applicability of these analyzing methods to experimental XRD patterns of typical carbon materials heat-treated below 1000°C. Results are also compared with those by observation with transmission electron microscope (TEM).

Experimental

Phenol-formaldehyde resin (novolac type) and carbonaceous mesophase spherule (MCMB, Osaka Gas Co.Ltd) were heat-treated at 600, 700, 800, 900 and 1000 °C in N₂ flow. Hereinafter, samples are indicated with "PF" or "MC" followed by the heat-treatment temperature.

XRD patterns of the ground samples were measured with CuKα radiation at 40kV-80mA, by step-scanning method (Δθ=0.2°, 25 sec/step). After correcting the systematic error and absorption and polarization factor, the Compton scattering was removed to obtain coherent scattering intensity. TEM observation was performed at an accelerating voltage of 200 kV.

Results and Discussion

Figure 1 shows the XRD coherent intensities of the samples for $s=2\sin\theta/\lambda$ (θ: diffraction angle, λ: wave length of X-ray). There are three broad peaks in each profile. In these peaks, 002 band is attributed to stacking structure of aromatic layers. It was slightly shifted to large s and became clear between 600 and 800 °C, indicating gradual development of stacking structure. MC series are known to be graphitizable carbon, and every

peak appeared more clearly than that in PF profile heat-treated at the same temperature.

In TEM 002 lattice image of the samples (Fig.2), aromatic layers were observed as short fringes.. Table 1 summarizes the approximate length of fringes in 002 lattice image (L)[1] for each sample determined by image analysis technique. Basal spacing of aromatic layers (d_{002}) determined with XRD profile, and average stacking number of layers in a stack (N_{av}) estimated by Hirsch's method, are also shown in the table.

According to Warren and Bodenstern[3], scattering intensity ($j(s)$) is generally described by Debye equation as $j(s) = \sum_m \sum_n \frac{\sin 2\pi s r_{mn}}{2\pi s r_{mn}}$, where r_{mn} is a distance between atom m and n . For aromatic hexagonal layers of radius R , stacked by the number M with interlayer distance z , the diffraction intensity of them ($j(M)$) is calculated by converting the Debye's equation to

$$j(M) = i(0) + (1 - \frac{1}{M})2i(1) + (1 - \frac{2}{M})2i(2) + \dots + (1 - \frac{M-1}{M})2i(M-1), \quad (1)$$

where

$$i(q) = \frac{0.2427}{s} \int_{r=qz}^{r=r_m} [\arccos u - u(1-u^2)^{\frac{1}{2}}] \sin 2\pi s r dr,$$

$$u = \frac{[r^2 - (qz)^2]^{\frac{1}{2}}}{2R} \quad \text{and} \quad r_m = [(2R)^2 + (qz)^2]^{\frac{1}{2}},$$

assumed q is a distance of any pair of stacking group of aromatic layers. Equation (1) then describes the diffraction profile by aromatic layers of defined situation. In this study, z and $2R$ correspond to d_{002} and L in Table 1.

Figure 3 summarizes the basic concept to obtain fraction of carbon atoms in aromatic layers. Intensity per atom in disorganized texture is given by f^2 , according to the diffraction theory. On the experimental intensity, let α be the ratio of the peak area above the line connecting minimum, to the area below the connecting line, and fraction of carbon atoms in aromatic layer (x) is given by

$$x = \frac{\alpha}{\frac{A_1}{A_3} + \alpha(1 - \frac{A_2}{A_3})}. \quad (2)$$

Definition of A_1 , A_2 and A_3 for theoretical profile are shown in Fig.3. Considering the presence of single layers which is not counted in evaluation of N_{av} ³⁾, the real average number of aromatic layers including single layers is at most 2. Therefore, it is appropriate to use the calculated profile for $M=2$ in order to evaluate α and x values.

Table 2 shows α and x for 002 band for PF series. Carbon atoms indicated by a fraction $1-x$ includes those in single aromatic layers and in disorganized parts. fraction of disorganized carbons and those in single layers were decreased between 600 and 800 °C. For PF types of resins, cross-linkage structure between aromatic layers are considered to develop during heat-treatment up to about 1000°C. Disorganized carbon presumably corresponds to carbon atom in this cross-linkage structure, and single layer is fixed with the linkage to the position not parallel to the neighboring layers. The result for MC series will be also discussed.

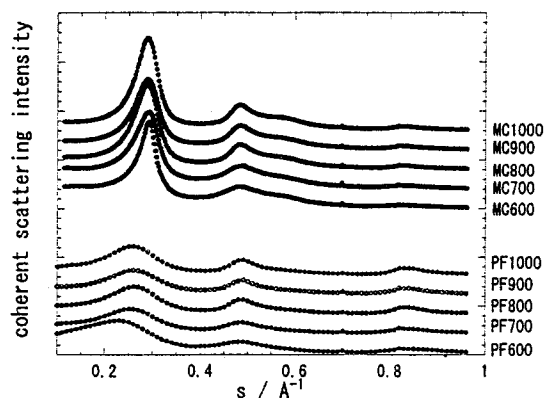


Fig. 1 XRD coherent intensities of the samples.

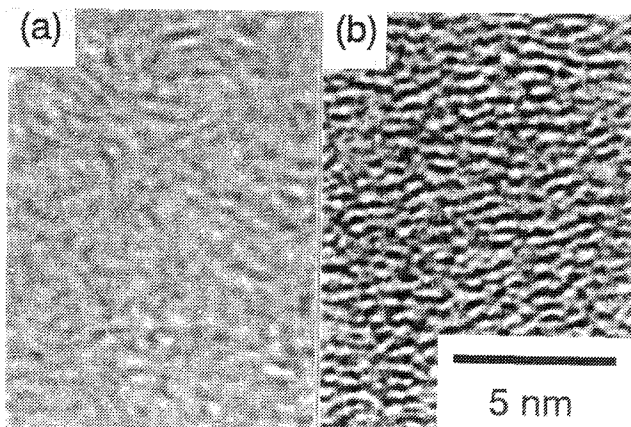


Fig.2 TEM 002 lattice image of (a) PF800 and (b) MC800.

Conclusion

Experimental XRD profiles of heat-treated phenol-formaldehyde resin (PF) and carbonaceous mesophase spherule (MC) were compared with profiles calculated by Warren-Bodenstein method, by using experimental crystallographic parameters obtained with XRD and TEM. Fraction of carbon atoms in stacked layers were evaluated from experimental and calculated profiles. It was quantitatively shown that fraction of disorganized carbons and those in single layers were decreased between 600 and 800 °C for PF series.

References

- [1] Yoshizawa N, Yamada Y, Shiraishi M. *J Mat Sci* 1998; 33: 199-206.
- [2] Hirsch PB. *Proc Roy Soc* 1954; A226: 143-169.
- [3] Warren BE, Bodenstien P. *Acta Cryst* 1965; 18: 282-286.

Table 1 Crystallographic data of the samples.

sample	d_{002} / nm	L / nm	N_{av}
PF600	0.42	0.80	2.13
PF700	0.39	0.81	2.26
PF800	0.38	0.90	2.31
PF900	0.38	1.00	2.32
PF1000	0.38	1.02	2.34
MC600	0.38	0.89	2.71
MC700	0.38	1.17	2.66
MC800	0.38	1.25	2.78
MC900	0.37	1.47	2.82
PC1000	0.37	1.74	2.92

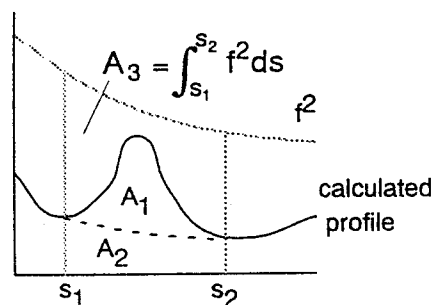


Fig. 3 Basic concept to evaluate carbon fraction in aromatic layers.

Table 2 Fraction of carbon atoms estimated by Warren-Bodenstein's method.

sample	α	x	$1-x$
PF600	0.44	0.23	0.77
PF700	0.75	0.34	0.66
PF800	0.94	0.56	0.44
PF900	0.88	0.53	0.47
PF1000	0.98	0.57	0.43