THE ESTIMATION OF THE ROTATIONAL MISORIENTATION BY THE PROJECTED PROBABILITY FUNCTION OF A DISPLACEMENT OF CARBON LAYER PLANES

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INTRODUCTION

It is well-known that the *hk* reflection of the carbon with low graphitizability is asymmetric which is sharp at the lower angle side and broad at the higher. Houska & Warren[1,2] reported that such a profile is observed when the carbon layer planes in stacks rotate randomly along c-axis, which is often called 'turbostratic stacking', and that the higher angle side profile can be expressed by

$$P'_{2\theta}(hk) = \frac{KmF^2(1+\cos^2 2\theta)}{4\sin\theta(\sin\theta - \sin\theta_0)^{1/2}} \sum_{n=-\infty}^{\infty} A_n(hk)\cos 2\pi n h_3 ,$$

$$h_3 = (\sin^2\theta - \sin^2\theta_0)^{1/2} \cdot 2d_{002}/\lambda , \qquad (1)$$

where K, m, F, d_{002}, λ and θ_0 are the scale factor, multiplicity, structure factor, average interlayer spacing, wave length of X-ray and diffraction angle of *hk*0 line, respectively. They showed that the probability for the adjacent hexagonal layers to have the graphitic relation, p_1 (degree of graphitization), is obtained from the Fourier coefficients, $A_n(hk)$, in Eq.(1) based on the following equation

$$p_1 = -2A_1(10) = A_1(11) . \qquad (2)$$

Houska & Warren also showed that the projected probability function (PPF), $P'(X_n, Y_n)$, can be synthesized from $A_n(hk)$ by

$$P'(X_n, Y_n) = \sum_h \sum_k A_n(hk)\exp[-2\pi i(hX_n + kY_n)] , \qquad (3)$$

where X_n and Y_n denote the displacements along *a*- and *b*-axes of carbon layer plane of *n* th plane. They calculated the PPF of the 1st nearest layer plane of carbon black heat-treated at 2300°C and obtained a pattern with two broad peaks at the coordinates of (1/3,2/3) and (2/3,1/3)[2]. They interpreted the pattern to mean that when ordering takes place between the nearest layer planes, the pairs have the graphitic relation of

$$(X_1, Y_1) = (2/3, 1/3) or (1/3, 2/3) . \qquad (4)$$

In the present study, the degree of misorientation of mesocarbon microbeads (MCMB) heat-treated at different temperatures was investigated by the theory of Houska & Warren.

EXPERIMENTAL

MCMBs heat-treated at the temperature range of 2200-2800 °C were used for the present analysis. The profiles of 10 and 11 of MCMBs heat-treated were measured with Cukα using RINT2500 diffractometer (Rigaku Denki Co., Ltd.). Since the 21 reflection can not be measured with Cukα because of its diffraction angle higher than 140° in 2θ, Mokα is used. The measurement was carried out by a step-scanning technique with an interval of 0.02°. The accumulation time was adjusted so that the maximum intensity obtained was ten to thirty thousands counts. The tube-voltage and current were 40 kV and 200 mA, respectively.

The Fourier coefficients were determined according to the method developed by Noda et al.[3]. The two-dimensional 10 and 11 reflections are generally superimposed by 004 and 006 reflections, respectively. Therefore, the effect of 00*l* reflections on these reflections should be removed in order to analyze with high accuracy. In this study, asymmetric pseudo-Voigt function was applied for the peak separation. The 10 reflection was separated in five peaks of 100, 101, 102, 103 and 004, and 11 reflection, four peaks of 110, 112, 105 and 006. Since 20 reflection was too weak for accurate determination, the equation for the Fourier coefficients of

$$A_n(20) = A_n(10) \qquad (5)$$

was applied, which was derived by Houska & Warren. The determination of the Fourier coefficients were made for these separated *hk* line profiles. The PPF of the 1st nearest layer plane was synthesized from the coefficients obtained according to Eq.(3).

RESULTS AND DISCUSSION

Figure 1 shows the PPF of the 1st nearest layer planes of MCMBs heat-treated at several temperatures. There is a ghost around the origin because of the small number of the term in Fourier series and the positions of the two peaks with the coordinates of (2/3,1/3) and (1/3,2/3) rotate slightly from the diagonal line of the unit cell. The rotation is considered to be due to the misorientation. The angle of misorientation estimated from the PPFs decreased from 7.9° to 0.6° with increasing the heat treatment temperature (HTT). Figure 2 is the simulation of the turbostratic nature of layer stacking for MCMBs based on the rotation angle estimated from the results of Fig.1. In any case, there observed a moiré pattern formed by a pair of the adjacent layer planes exhibiting the coexistence of AB and AA stackings. p_1 value has been generally interpreted as the probability for the adjacent hexagonal layers to have the graphitic relation. Considering the simulation results, p_1 value can be interpreted as a fraction of the area occupied by the AB stacking.

Such an analysis will be available in order to elucidate the in-plane structure of intercalation compounds derived from the turbostratic carbons. For example, the 1st stage lithium-intercalated graphite (LiC_6) has an in-plane structure of p($\sqrt{3} \times \sqrt{3}$)R30° which requires AA-stacking sequence. However, if the degree of graphitization of pristine carbon is low, the island structure of p($\sqrt{3} \times \sqrt{3}$)R30° ordering would be formed according to the moiré pattern. As a result, the C/Li atomic ratio will be larger than the theoretical value of 6[6].

References

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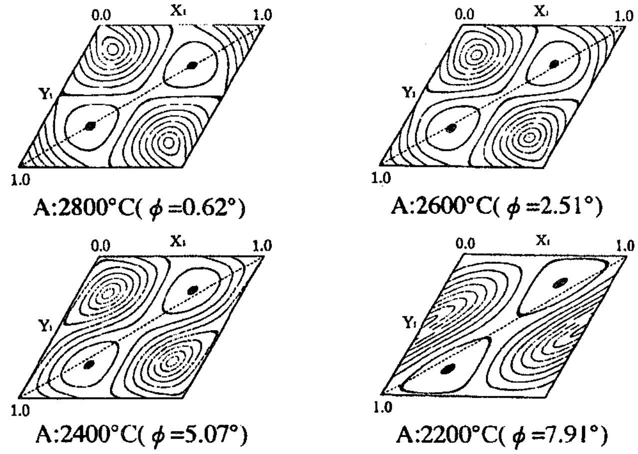

Fig.1 The projected probability functions of the 1st nearest neighbor layer planes of MCMBs heat-treated at different temperatures *f* denotes the angle of misorientation.

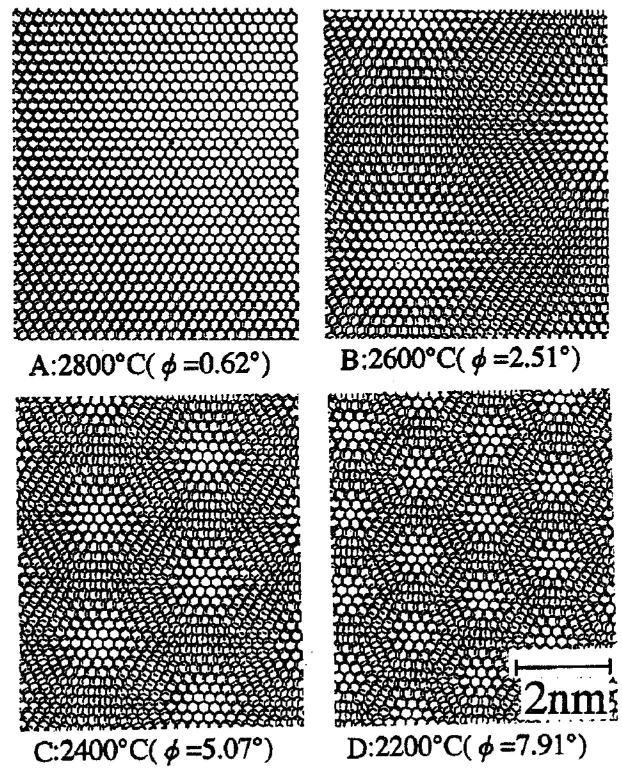

Fig.2 Simulation of the rotational misorientation between the adjacent layer planes for MCMBs heat-treated at different temperatures