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Intensity Ratio between (00*l*) Diffraction Lines of a Coke and a Simple Model of Carbon Layer Plane

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It is known that the (004) diffraction line of non-graphitizing carbon is hardly detectable and that it develops gradually to become so with the increase in heat treatment temperature.

In the present work, the X-ray diffraction intensities of (00*l*) lines were measured on polyvinylchloride cokes heat-treated at different temperatures and the change of the intensity ratio between the (00*l*) lines was discussed from the standpoint that it was caused by the change of displacement of carbon atoms in the *c*-direction from the carbon layer plane.

Experimental and Results

The original sample was PV-7, a polyvinylchloride coke carbonized at 680°C. This sample was heat-treated at different temperatures between 1000 and 2600°C for 60 min in the flow of nitrogen by using a graphite resistance tube furnace. The heat treatment temperature (HTT) was measured by an optical pyrometer, which was calibrated by a standard lamp for optical pyrometry. For the heat-treated samples, intensities of (002) and (004) diffraction lines were measured by a fixed counting technique, using a goniometrer with Geiger counter. The measured intensity at each diffraction angle θ was corrected, being divided by Lorentz-polarization, the square of atomic scattering and absorption factors. The corrected intensities were plotted as a function of $\sin\theta$. The area under the profile of (00*l*) line, measured by a planimeter, is the integrated intensity of diffracted beames $I(00l)$ and is proportional to the square of the geometrical structure factor of the line. This proportionality for (002) and (004) lines must be equal to each other since both profiles of the lines were measured on the same specimen. Therefore, the ratio of intensities of (004) to (002) lines, $I(004)/I(002)$, is equal to the ratio of the square of geometrical structure factors of (004) to (002) lines, $|A(004)|^2/|A(002)|^2$.

The observed ratio $I(004)/I(002)$ is shown in

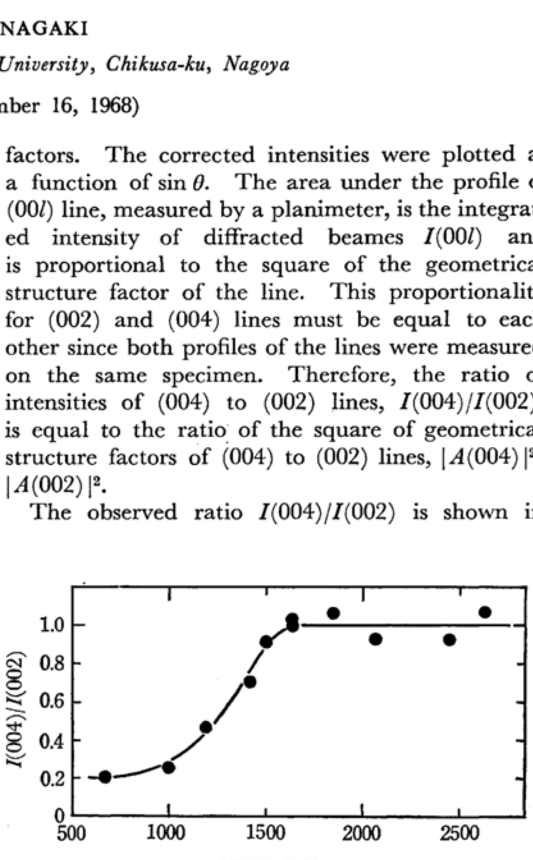

Fig. 1. Change of the observed intensity ratio, $I(004)/I(002)$ with HTT.

Fig. 1, as a function of HTT. The ratios for the carbon subjected to heat treatment at low temperature are practically smaller than 1.00. They appear to equal 1.00 above 1600°C.

For the heat-treated samples, the c_0-spacing was measured by using the inner standard of silicon and a recording goniometrer. In Fig. 2, the intensity ratio $I(004)/I(002)$ is plotted against the c_0-spacing of the sample. The sample having c_0-spacing larger than 6.86 Å has an intensity ratio smaller than 1.00.

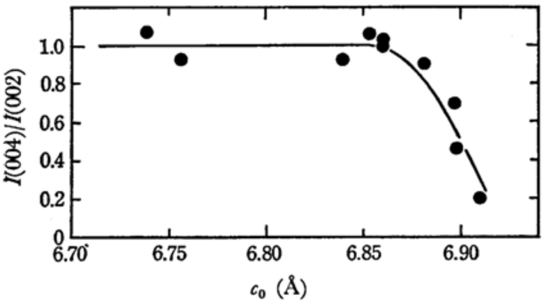

Fig. 2. Change of the observed intensity ratio $I(004)/I(002)$ with c_0-spacing.

Discussion

The measured intensity ratio can have a relatively large error, about ±0.05 for the sample heat-treated at 2600°C and even greater for the samples subjected to heat treatment at low temperature such as 1400°C. Though no corrections for the instrumental factors were performed, the omission of such corrections was not the cause of the error in the ratio. A large part of the error resulted from the ambiguity of the determination of the background of X-ray diffraction. Even if the ratio $I(004)/I(002)$ has a relatively large ambiguity, the ratios of the carbons heat-treated at low temperatures were found to be actually smaller than the value of graphite 1.00.

The geometrical structure factor of $(00l)$ diffraction lines is given by

$$|A(00l)|^2 = \{\sum \cos 2\pi l z\}^2 + \{\sum \sin 2\pi l z\}^2$$

It depends only on relative position z along c-axis of carbon atoms in a unit cell. In graphite, all carbon atoms are coplanar, having the z-value of 0 and 1/2. The geometrical structure factors of $(00l)$ lines, of which l-index is even, equal one another and the ratio of the two of them equals unity. If some carbon atoms displace from the normal position of graphite by Δz along c-axis, the value of the geometrical structure factor becomes smaller than that of ideal graphite. The effect of reduction is greater for larger l-index lines. Therefore, the observed small ratio of $I(004)/I(002)$ can be interpreted as the result of out-of-plane displacements of carbon atoms. This means that the carbon layers are uneven or wrinkled.

According to the idea mentioned above, the present result shows that the displacement of carbon atoms disappears, in other words, all carbon atoms in carbon layer become coplanar, at about 1600°C or when the c_0-spacing becomes 6.85—6.86 Å. With the idea that the graphitization process is divided into two stages at the c_0-spacing of about 6.85 Å,1-3) the present result suggests that the structural change in the first stage of the graphitization process ($c_0 > 6.85$ Å) is the decrease in the displacement of carbon atoms, in other words, "dewrinkling" of carbon layer planes, and that the three-dimensional ordering proceeds only after the carbon layer planes are straightened.

The idea of the displacement of carbon atoms is similar to that of Ruland.4) However, he considered the displacement of carbon atom not only on the first stage but also on the second stage of graphitization process. This wrinkling model presented herewith is also consistent qualitatively with the electron microscopic observation by Kuroda.5) He observed mosaic structure in a flake of carbon. In the present model, however, wrinkling of carbon is in the atomic scale.

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