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Kinetic Studies of the Graphitization Process. III. Stages of Graphitization Process

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The dependence of the graphitization degree of carbon on residence time has been studied by many authors.[1–13] However, the rate equations of graphitization have not been clarified. In the present work, the dependence of c_0-spacing on residence time was measured on a coke in a limited range of heat treatment temperature, and the results were discussed in relation to the stages of graphitization process.

The sample used was a polyvinylchloride coke (PV-7) calcined to 680°C and pulverized to particle size 0.4—1.2 mm. The sample was heat-treated at temperatures 1950, 2000, 2100, 2200, 2300 and 2400°C for various residence times under a reduced pressure of about 0.01 Torr. The details on the procedure of heat treatment were reported.[11] When a graphite heater was used for the heat treatment above 2000°C under reduced pressure, the wall of the heater became thin due mostly to evaporation, and partly probably to the oxidation of graphite. This reduced the stability of heat treatment temperature (HTT). Therefore, the long time run of heat treatment was carried out by the repetition of short time runs (mostly 60 min), by replacing the used heater with a new one each time. It was confirmed previously[11] that the repeated heat treatment has the same effect on the c_0-spacing of the carbon sample as the continuous one if the total residence time is equal in each case.

For each heat-treated sample, mean value of c_0-spacing was measured from (004) diffraction line by referring to the inner standard of silicon. Diffraction profile of the line was obtained by using Ni-filtered CuKα radiation and a recording goniometer with a Geiger counter.

The changes of c_0-spacing with total residence time at different HTT are shown in Fig. 1, by means of the plot of c_0-spacing against logarithm of residence time, log t. The rate of change of the c_0-spacing with residence time is found to increase at about 6.84 Å and decrease again at about 6.76 Å for every HTT. Thus, the dependence of

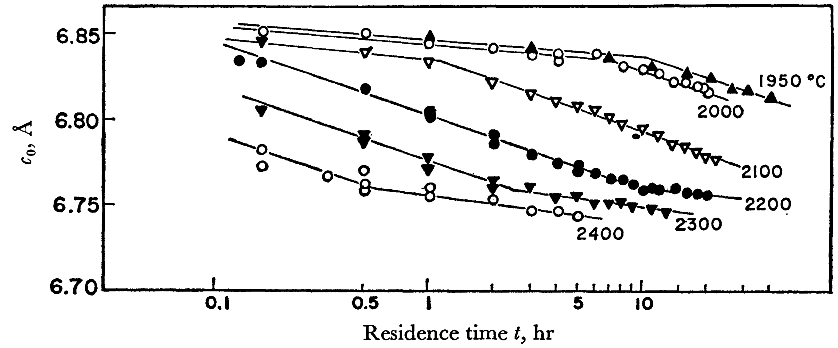

Fig. 1. The relation between c_0-spacing and logarithm of residence time.

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c_0 on log t can be divided into three stages, *i. e.*, $c_0 > 6.84$, $6.84 > c_0 > 6.76$, and 6.76 Å$> c_0$. In the stage $6.84 > c_0 > 6.76$ Å, the c_0-spacing seems to decrease linearly with logarithm of residence time, and the lines for every HTT are parallel to each other.

The superimposing method[4] can be applied to the present result, and the amount of shifting is determined more accurately. The effective activation energy obtained was 200 kcal/mol which was close to those obtained in previous works.[8,9,11] The dependence of c_0 on residence time t in the stage $6.84 > c_0 > 6.76$ Å is expressed by the equation

$$c_0 - c_0^0 = \beta \log (t/t_0),$$

where c_0^0 is a constant independent of HTT, β the slope of the line shown in Fig. 1 and t_0 is the value of t for $c_0 = c_0^0$. t_0 corresponds to the amount of shift in the superimposing method.

In the figures of c_0 *vs.* log t, the linear relation between c_0 and log t can be found only in a small range of c_0.[4,8,9,11] A pyrolytic carbon reported by Fischbach[4] showed a linear dependence of c_0 on log t in the range 6.82—6.73 Å.

The same data were analysed by the method proposed by Murty *et al.*[14] The relations obtained between log $\{(6.910-c_0)/t\}$ and log $(6.910-c_0)$ are shown in Fig. 2, where the value of 6.910 Å is the c_0-value of the original sample PV-7. In this case, the relation between log $\{(6.910-c_0)/t\}$ and log $(6.910-c_0)$ seems also to be linear. However, it appears to break at the c_0-values 6.84 and 6.77 Å. The lines are nearly parallel to each other in the range $6.84 > c_0 > 6.77$ Å. The dependence of c_0 on t can be expressed by

$$(6.910-c_0) = A \cdot t^n.$$

The value of n was obtained as 0.18 from the slope of these lines, and the activation energy of 200 kcal/mol was obtained from the linear dependence of intercept of the lines on HTT.

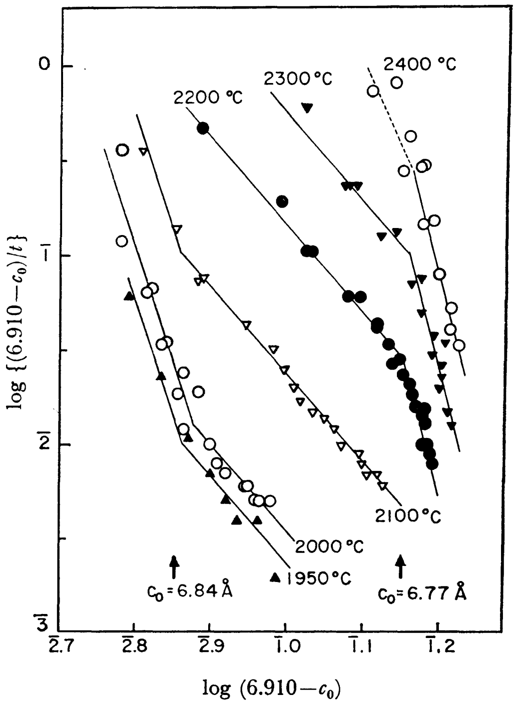

Fig. 2. The relation between log $\{(6.910-c_0)/t\}$ and log $(6.910-c_0)$.

For the stages, *i. e.*, $c_0 > 6.84$ and 6.76 Å$> c_0$, no details on the residence time dependence of c_0-spacing could be discussed, because of insufficient data.

From the results, the graphitization process of soft carbon can be concluded to consist of three successive stages, $c_0 > 6.84$, $6.84 > c_0 > 6.76$, and 6.76 Å$> c_0$. In the second stage, the change of c_0 from 6.84 to 6.76 Å is fairly large, though the corresponding range of HTT is narrow as 1950—2400°C.

The dividing of the graphitization process at c_0-spacing of about 6.85 Å is consistent with the results of other authors. Kuroda[15] has shown, by means of electron microscopy, that above 1850°C (below the c_0-spacing 6.85 Å in the petroleum coke) c-axes of crystallites align parallel to the normal of the grain. Mazza,[5] Mazza *et al.*,[6] and Forchioni *et al.*[7] have studied the development of the properties, including X-ray parameters, and shown that the graphitization process is divided into two stages, below HTT of 1900°C and above 1900°C (corresponding to the c_0-spacing 6.84 Å in the pitch coke). Inagaki *et al.*[16,17] have reached almost the same conclusion as that of Mazza *et al.*[6] on a petroleum coke and a polyvinylchloride coke from X-ray parameters. The main structural change in the first stage is the development of two-dimensional graphite-like layers. In relation to this stage, Inagaki[18] has proposed the idea of dewrinkling of carbon layers.

The dividing of the graphitization process around 6.76 Å has been reported only by Maire and Mering.[19] They have shown by Fourier analysis of (00l) diffraction lines that below the g-value of about 0.6 (above 6.77 Å in c_0-spacing), the crystallite size L_C increases and above 0.6 the strain decreases with graphitization.

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