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Figure 1

Figure 1: Figure 1

Abstract

Full Text

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KINETICS AND MECHANISM OF HOMOGENEOUS GRAPHITIZATION OF CARBON

(Presented by Academician A. A. Skochinskii, 13 VII 1957)

The process of homogeneous graphitization of carbon (2000—2800°) is characterized by the continuous improvement of three-dimensional order in the graphite crystal lattice through azimuthal orientation of parallel basal nets in packets, prepared already in the "pre-crystallization" stage ([1,2]). According to X-ray diffraction data, in the process of homogeneous graphitization no coexistence of amorphous and crystalline phases is observed, and therefore it should be assigned to orientational processes, similar to the processes of formation of oriented polymers, not associated with phase transformations ([3]). In the present work we give the results of an X-ray diffraction study of the kinetics and mechanism of graphitization of cracking and pyrolysis petroleum cokes under isothermal conditions at temperatures of 2000, 2150, 2300, 2420, and 2800°. Graphitization was carried out in a furnace with a graphite heater in an atmosphere of nitrogen and argon. The maximum deviations of the temperature from the set value were ±25°. Depending on the duration of the isothermal holding in the furnace, bands (hkl) appear on the X-ray diffraction patterns (Fig. 1), whose intensity and sharpness increase monotonically. The half-width of the (hkl) and ($00l$) bands also decreases. These changes in the X-ray diffraction patterns reflect the process of azimuthal orientation in packets of parallel basal nets of carbon, with the emergence and further improvement of three-dimensional order of carbon.

Fig. 1. Microphotograms of cracking coke calcined at different temperatures and holding times.
1—2000°, 13 hr; 2—6—isotherm 2300° with holding times: 2—1/2 hr, 3—1 hr, 4—$1^{1/2}$ hr, 5—3 hr, 6—4 hr, 7—2800°, 1/2 hr.

In addition, a regular decrease in the interplanar spacing d_{002} is observed (Fig. 2), which is also associated with the azimuthal orientation of the carbon layers into a denser packing. The character of the changes in the X-ray diffraction

Figure 2

Figure 2: Figure 2

Figure 3

Figure 3: Figure 3

patterns indicates a direct relation between d_{002} and the three-dimensional ordering of carbon, which provides a basis for introducing a measure of ordering according to

Fig. 2. Decrease in the interplanar spacing d_{002} as a function of holding time at different temperatures. Accuracy of determination of d_{002} is ± 0.002 Å. 1–2000°, 2–2150°, 3–2300°, 4–2420°, 5–2800°. *a*–cracking coke, –pyrolytic coke, –points corresponding to holding for 13 h at 2000°.

the decrease in interplanar spacing Δd, which can be determined by the relation

$$\gamma = \frac{\Delta d}{\Delta_0} = \frac{3.425 - d_{002}}{0.069}, \tag{1}$$

where Δ_0 is the total interval of changes in d_{002} during the transition from nongraphitized carbon with $d_{\text{nongraph}} = 3.425$ Å to the smallest value $d_{\min} = 3.356$ Å of completely graphitized carbon.

Fig. 3. Dependence of the X-ray density and of the ratio of integrated intensities I_{112}/I_{110} on the degree of ordering.

The quantity γ introduced by us has a statistical meaning, determining the probability of simultaneous stacking of neighboring carbon monolayers on both sides of the given one with formation of a layer of elementary cells, and is connected with the previously introduced (4, 1) probability u of the oriented arrangement of two neighboring carbon monolayers.

From the volume ω and mass M of an elementary cell, the X-ray density was determined as a function of d_{002}:

$$\rho = \frac{M}{\omega} = \frac{7.627}{d_{002}}, \tag{2}$$

where d_{002} is in Å and ρ is in g/cm^3. Eliminating d_{002} from (1) and (2), one obtains the dependence of the X-ray density on the degree of ordering γ (Fig. 3). The plot of the dependence of the ratio of integrated intensities

I_{112}/I_{110} on γ (Fig. 3) for specimens obtained at different temperatures and holding times is convenient for practical determination of the degree of graphitization (2). The change in the degree of three-dimensional ordering of carbon

Fig. 4

Figure 4: Fig. 4

as a function of the isothermal holding time, with allowance for the correction for non-isothermality in the initial moments of heating, is well described by the monomolecular kinetic equation

Fig. 4. Dependence of the rate constant K of isothermal graphitization on temperature. 1—2000°, 2—2150°, 3—2300°, 4—2420°. a—cracking coke, b—pyrolysis coke.

$$\gamma = 1 - e^{-K\tau}, \tag{3}$$

which finds direct confirmation in the graph of the dependence of $\lg(1-\gamma)$ on τ (Fig. 4). Table 1 gives the rate constants K of isothermal graphitization at different temperatures.

Table 1

T, °K	$K \cdot 10^4$ ($\sec^{-1}$) cracking coke	$K \cdot 10^4$ ($\sec^{-1}$) pyrolysis coke
2273	0.083	0.080
2423	0.441	0.417
2573	1.042	1.031
2693	2.246	2.460

The average experimental value of the activation energy proved to be close for both cokes and has the value $A = 92 \pm 5$ kcal/g-atom.

The comparatively high value of the activation energy indicates that the kinetics of graphitization is determined by a chemical process. The experimental activation energy is considerably lower than the energy of rupture of bonds between atoms in the basal network of carbon ($\sim$ 170 kcal/g-atom). This serves as independent confirmation of the orientational mechanism of homogeneous graphitization. A recrystallization mechanism associated with rearrangement of the carbon networks may be assumed at higher graphitization temperatures, for the so-called non-graphitizing carbon materials. The high energy barrier of the orientational process should be attributed to the rupture of multiple bonds between the carbon atoms of the side radicals that form the connection between the basal carbon networks of neighboring "crystallites." The carbon atoms constituting the side radicals probably differ from the carbon of the basal networks in their valence state. It may be assumed that they are in one

of the three possible states of s-p hybridization of the electron orbitals, with two σ-bonds at an angle of 180° and two π-bonds perpendicular to the carbon

chain. It should be noted that the presence of strong lateral bonds between the carbon layers of neighboring "crystallites" determines the high-polymeric nature of graphitized carbon materials and the associated features of their properties.

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Note: Figure translations are in progress. See original paper for figures.