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Abstract

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HOMOGENEOUS AND HETEROGENEOUS CRYSTALLIZATION OF CARBON

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During the thermal treatment of a number of carbonaceous substances (petroleum and pitch cokes, caking bituminous coals, cokes from many organic polymers, etc.) at temperatures above 2000° K, a peculiar and highly characteristic process is observed: the homogeneous transformation of carbon into graphite without the coexistence of amorphous and crystalline phases. In this process of homogeneous crystallization of carbon, the graphite crystal lattice arises and is perfected by the azimuthal rotation and convergence of atomic carbon layers in stacks of parallel layers of amorphous carbon and by the elimination of rotational defects in the crystallites that have formed (^1). An X-ray study of the kinetics of the process under isothermal conditions (^2) showed that homogeneous crystallization is described as a monomolecular reaction and is characterized by a high apparent activation energy, ~92 kcal/g-atom, which indicates the coupling of the rotation of carbon layers with the thermal destruction of lateral carbon chains linking layers in neighboring stacks. These data, as well as the continuous change in the properties of carbon (density, heat capacity, electrophysical properties, etc.) observed in the course of homogeneous crystallization, substantially confirm the concept of the polymeric structure of transitional forms of carbon ($^{3-}$7). The presence of oxygen or halogens in the initial substance promotes the formation of very strong lateral bonds of the polyacetylene-chain type of carbon, =C=C=C=, owing to dehydrogenation transformations of lateral radicals with the elimination of H_2O and HX during thermal treatment. When the network of strong lateral bonds thus formed is sufficiently dense, homogeneous crystallization is inhibited, and transitional forms of crystalline carbon arise with different limiting degrees of graphitization γ at 3000° K, or even a nongraphitizing form ($\gamma = 0$) (^{6,}7).

On the other hand, all carbonaceous substances undergo a heterogeneous transition into graphite, which is characterized by the coexistence of amorphous carbon and the crystallites that form with a relatively perfect crystal lattice. Heterogeneous crystallization is associated with evaporation and condensation of supersaturated carbon vapors on crystallization centers and proceeds at an appreciable rate only at temperatures above 3200° K. However, by the X-ray method the presence of heterogeneous carbon is detected only in nongraphitiz-

Fig. 1. Intensity curves of sugar-coke specimens: a –small volume, b –large volume, v –2870° K –120 min. (a and b). 1–2370° K –30 min.; 2–2370° K –120 min.; 3–2800° K –30 min.; 4–2870° K –120 min.; 5–3070° K –30 min.

Figure 1: Fig. 1. Intensity curves of sugar-coke specimens: a –small volume, b –large volume, v –2870° K –120 min. (a and b). 1–2370° K –30 min.; 2–2370° K –120 min.; 3–2800° K –30 min.; 4–2870° K –120 min.; 5–3070° K –30 min.

ing substances (sugar coke, oxidized bituminous coals, activated carbons, cokes from oxygen-containing organic polymers, etc.).

For sugar coke, heterogeneous crystallization is observed at the comparatively low temperature of ~700° K. The lowering of the temperature of heterogeneous crystallization in this case, as may be supposed, is associated with the catalytic decomposition of carbon monoxide at crystallization centers, which are formed at the expense of the oxygen bound in the substance of the sugar coke. Thus oxygen serves as a carrier of carbon to the crystallization centers through the gas phase. A similar process of carbon transfer also occurs in the presence of silicon or other

elements in the carbonaceous substance that form volatile compounds with carbon.

In confirmation of the mechanism considered here for heterogeneous crystallization through the gas phase, the present work gives the results of a study of the crystallization of sugar coke. Under the condition that crystalline carbon is formed by deposition from the gas phase, one could expect, in sufficiently small volumes of sugar coke, termination of the crystallization process because of leakage of the gas phase. In this connection we studied the completeness of the transition of carbon into graphite as a function of the mass of the initial sugar coke. In addition, in order to characterize the crystalline phase, the interlayer spacings d_{002} were determined in the products of heterogeneous crystallization of sugar coke and of homogeneous crystallization of coke from coal-tar pitch as a function of the calcination temperature.

Fig. 1. Intensity curves of sugar-coke specimens: *a* –small volume, *b* –large volume, *v* –2870° K –120 min. (*a* and *b*). 1–2370° K –30 min.; 2–2370° K –120 min.; 3–2800° K –30 min.; 4–2870° K –120 min.; 5–3070° K –30 min.

Figure 1 gives the intensity curves for two series of products of isothermal calcination of sugar coke (coked at 800° K), with masses of the specimens of the initial coke of 0.8 g in one series and 22 g in the other, po-

obtained under identical annealing conditions in the temperature range 1000-3300° K in an argon medium.

With increasing temperature and treatment time, the asymmetry of the crystalline maximum (002) increases, which indicates the two-phase nature of the specimen and an increase in the degree of order of the crystalline phase. With

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

an increase in the amount of material being treated, the amount of heterogeneous crystalline phase also increases, manifested in an increase in the intensity of the |002| maximum (Fig. 1b). The dependence of the amount of crystalline phase on the volume of the annealed sugar coke is clearly manifested in the modulation of the two-dimensional maximum (10) (8) and in the appearance of the three-dimensional crystalline maximum |112| (Fig. 1c).

Figure 2 gives the data of an x-ray determination of the interlayer spacing d_{002} in specimens of sugar coke, coal-tar-pitch coke, and natural (Taiginka) graphite treated at various temperatures; data are also given on the determination of d_{002} for sublimed and fused graphites. The smallest value of the interlayer spacing d_{002} was found for fused and natural graphites, which corresponds to the highest degree of three-dimensional ordering of carbon atoms in the crystallites.

Fig. 2. Dependence of d_{002} on treatment temperature: 1 —natural Ceylon and artificial fused graphite, 2 —Taiginka graphite, 3 —crystalline part of the product of thermal treatment of sugar coke, 4 —coal-tar-pitch coke, 5 —carbon from carbon monoxide on an iron contact, 6 —nongraphitizing part of sugar coke, 7 —sublimed carbon

In crystallites of sublimed graphite the atomic ordering is relatively small, despite the high temperature to which the specimen was subjected in the crystallization process. This should be explained by the small dimensions of the carbon layers in the crystallites formed during condensation of supersaturated carbon vapor with a large number of crystalline nuclei.

Fig. 3. Dependence of d_{002} on treatment temperature: 1 —anthracite, 2 —lean coal, 3 —coal-tar-pitch coke

The observed dependence of d_{002} on the annealing temperature for the crystalline part of the products of thermal treatment of sugar coke indicates a complex mechanism of heterogeneous crystallization of carbon with superposition of two processes: the growth of carbon layers and their azimuthal orientation in the crystallites being formed. With increasing annealing temperature, the crystallites of the deposited carbon have a relatively high three-dimensional atomic ordering, which corresponds to a decrease in rotational defects of the crystal lattice. Comparison with the interplanar spacing in crystallites of carbon deposited from carbon monoxide on an iron contact at 973° K confirms the gas-phase nature of the heterogeneous crystallization of sugar coke and also shows that the process of eliminating rotational defects proceeds intensively only at temperatures above 2200° K.

The data considered lead to the conclusion that heterogeneous crystallization proceeds by the deposition of crystalline carbon from the gas phase and is accompanied by a process of homogeneous crystallization. The degree of perfection of the crystal lattice in the products of heterogeneous crystallization at all annealing temperatures is greater than in the products of homogeneous crystallization, as indicated by the position of the corresponding d_{002} curves. It follows from this that the rate of the process of elimination of rotational defects in crystallites deposited from the gas phase is correspondingly greater than in crystallites formed during homogeneous crystallization. This may be connected with the deposition of carbon from the gas phase on the inner surface of pores in the form of oriented layers of the glossy-carbon type. A similar increase in the rate of homogeneous crystallization, associated with the orientation of crystallites, is observed for highly metamorphosed coals distinguished by a high degree of anisotropy, namely lean coals and anthracite.

Figure 3 gives a comparison of interlayer spacings for lean coal, anthracite, and coke from coal-tar pitch at different annealing temperatures.

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