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Abstract

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THERMOPHYSICAL PROPERTIES OF TRANSITIONAL FORMS OF CARBON

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The peculiar behavior of carbon, with the characteristic homogeneous transition of amorphous carbon into the crystalline lattice of graphite without the coexistence of amorphous and crystalline phases and with a wide range of continuous change in properties, is undoubtedly connected with its tendency toward polymerization, noted already by D. I. Mendeleev ([1]). In the initial stages of carbonization of organic substances, polymeric structures arise which are preserved even during high-temperature treatment and are characteristic of carbonized substances in the form of an aggregate of planar atomic layers of aromatic carbon, linked to one another by lateral radicals ([2,3]). Homogeneous crystallization is due to the polymeric nature of carbon ([4]) and proceeds as an orientational process, similarly to the crystallization of many chain organic polymers ([5]); transitional forms correspond to the multitude of states of carbon in the course of its homogeneous crystallization, including states in the precrystallization stage ([6]).

The present work gives the results of an investigation of the specific heat (c_p), as well as the coefficients of thermal diffusivity (a) and thermal conductivity (λ), of transitional forms obtained by high-temperature treatment of petroleum coke, channel black, and thermal black. The initial petroleum coke had a density of 1.405 g/cm^3, ash content 0.08%, and volatile yield 5.13%. The channel black (C 94.59%; H 0.68%; O 4.79%) had an ash content of 0.09%, and the thermal black (C 99.65%; H 0.27%; O 0.08%) an ash content of 0.01%. The particle sizes were: coke ~ 0.5 mm, blacks $< 1\,\mu$.

Calcination of the samples was carried out under isothermal conditions at temperatures from 1000 to 3000° in a furnace with a graphite heater in an atmosphere of nitrogen and argon. c_p and a of the samples were determined at room temperature by the method of regular thermal regime proposed by G. M. Kondrat' ev ([7]), modified for small quantities of substance ([8]). λ was determined by calculation from the data for c_p and a, as well as the bulk weight β ($\lambda = c_p a \beta$).

Figures 1, 2, and 3 present the results of measurements of c_p and a, as well as calculations of λ, for the objects studied as a function of treatment temperature with isothermal holding for 10 and 30 min. Figure 4 gives kinetic curves for the

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

dependence of c_p on the time of isothermal holding in the furnace at treatment temperatures of 1600 and 2500°.

The observed different course of change in c_p for all the objects studied indicates different paths, for each of them, of structural transformations of carbon under the same calcination conditions. The value of a for powders depends to a large extent on the packing density of the particles (bulk weight β). Observations show that for channel and thermal blacks, in contrast to petroleum coke, the packing density of the particles under identical experimental conditions for determining a depends little on the treatment temperature. The changes in β are 0.55–0.65 for coke and 0.23–0.25 for blacks.

The large difference in the absolute values of a and λ for the products of thermal treatment of carbon blacks and petroleum coke should be attributed, to a considerable extent, to the packing density of the particles and to the porous structure. However, the nature of the change in these quantities for each object as a function of the treatment temperature is substantially determined by structural transformations of carbon.

Fig. 1. Dependence of the specific heat capacity on the treatment temperature: a—thermal black, b—channel black, v—petroleum coke (c_p—kcal/kg $\cdot$ deg)

Fig. 2. Dependence of the temperature-conductivity coefficient on the treatment temperature. Designations are the same as in Fig. 1 (ordinate axis—$a \cdot 10^4$ m^2/h)

A carbonized substance' s polymeric carbon framework, as should be assumed, includes only part of the side radicals forming the spatial network of valence bonds. Another part of the peripheral radicals does not enter this network and remains in the form of a "fringe" connected with each aromatic carbon layer. By substantially supplementing the vibrational-rotational spectrum, this part of the structure makes a significant contribution to the magnitude of the internal energy and, consequently, to the heat capacity of the carbonized substance.

Fig. 3. Dependence of the thermal-conductivity coefficient on the treatment temperature. Designations are the same as in Fig. 1 (ordinate axis λ—10^3

Fig. 3

Figure 3: Fig. 3

kcal/m · h · deg)

In interpreting the thermophysical properties of the products of thermal treatment of carbonized substances, it is necessary to take into account the changing ratio of all three main parts of the structure, namely: the flat atomic layers of aromatic carbon; the side radicals binding them and forming a spatial network; and also the part of the side radicals constituting the "fringe."

For petroleum coke, different courses of decrease in c_p are observed in three intervals of treatment temperature (Fig. 1), which should be attributed to three stages of structural transformations of carbon. Up to 1800°, the relatively gentle course of the decrease in heat capacity, in our assumption, corresponds to the growth of carbon layers due to destruction of side radicals.

At this stage the total number of side radicals is considerably reduced. However, owing to recombination of the bonds liberated in the side radicals, continuous restoration of the spatial network occurs and the polymeric character of the structure is preserved. In the interval 1800-2000°, corresponding to the actual precrystallization stage,

there is a sharp decrease in c_p, associated with the inclusion of another mechanism of growth of the carbon layers by the coalescence of neighboring layers. The possibility of coalescence of the carbon layers was prepared in the first stage by their liberation from the "fringe."

In the two described stages of the process, the decrease in c_p was determined by an increase in the fraction of carbon organized into planar atomic layers, and by a decrease in the number of lateral radicals in the "fringe."

Above 2000° in the stage of homogeneous crystallization, the decrease in c_p depends on the convergence of the carbon layers in the process of their azimuthal orientation from $d_{\max} = 3.42$ Å in the precrystallization stage to $d_{\min} = 3.35$ Å in fully graphitized carbon. The decrease in c_p, as was shown earlier ([9]), is linearly related to the increase in the degree of homogeneous graphitization, which is determined by the convergence of the carbon layers

$$\gamma = 3.42 - d_{002}/(3.42 - 3.35),$$

where d_{002} is the interlayer spacing varying in the process of crystallization. The dependence of a and λ on the heat-treatment temperature of petroleum coke is described by an S-shaped curve with an inflection point near 1800°.

Fig. 4. Dependence of specific heat on the time of isothermal treatment. a—coke carbon, $t = 500°$; b—PS-grade carbon, $t = 700°$; v—channel black, $t = 1600°$; g—channel black, $t = 2500°$; d—thermal black, $t = 2500°$ (c_p—kcal/kg · deg).

The main factors determining the continuous change of λ of petroleum coke as a function of the treatment temperature in the first two stages of transformation

Fig. 4. Dependence of specific heat on the time of isothermal treatment. a—coke carbon, $t = 500°$; b—PS-grade carbon, $t = 700°$; v—channel black, $t = 1600°$; g—channel black, $t = 2500°$; d—thermal black, $t = 2500°$ (c_p—kcal/kg · deg).

Figure 4: Fig. 4. Dependence of specific heat on the time of isothermal treatment. a—coke carbon, $t = 500°$; b—PS-grade carbon, $t = 700°$; v—channel black, $t = 1600°$; g—channel black, $t = 2500°$; d—thermal black, $t = 2500°$ (c_p—kcal/kg · deg).

of the carbon structure, in addition to the decrease in c_p, should be considered to be the scattering of elastic waves of atomic vibrations in the substance at structural inhomogeneities and the increase in the electronic component of λ of the carbon layers, associated with their growth. The electronic component in the direction normal to the layers also determines the increase in λ in the stage of homogeneous crystallization, as is evidenced by the previously established linear dependence on γ of the thermal-conductivity coefficient λ ([9]) and of the specific resistance ρ ([6]).

Table 1

Treatment temp., °C	Duration of isothermal hold, min.	Degree of graphitization, γ: petroleum coke	Degree of graphitization, γ: thermal black	Degree of graphitization, γ: channel black
1700	10	0	0	0
2000	10	0.10	0.04	0
2300	30	0.38	0.55	0
2420	30	0.87	—	—
2500	30	1.0	0.77	0
3000	10	1.0	0.77	0.09

Thermal black, having approximately the same temperature for the onset of crystallization (2000°) as petroleum coke, differs by incomplete crystallization at a high temperature corresponding to a limiting degree of graphitization $\gamma = 0.77$ (Table 1). A significantly smaller decrease in c_p of thermal black in the stage of homogeneous crystallization is evidently associated with this. The uniform course of the decrease in c_p before the onset of crystallization, by which thermal black differs from petroleum coke, and the inability to undergo complete crystallization have a common physical cause. As was shown earlier ([10]), the cause preventing homogeneous crystallization of carbon is

formation of a spatial network with more heat-resistant bonds between carbon layers of the type = C = C = C =, which do not undergo thermal destruction

up to 3000°. For the same reason, the process of coalescence of the carbon layers is delayed, as a result of which there is no sharp decrease in c_p in the precrystallization stage in the treatment-temperature interval 1800–2000°, and there is also no inflection point on the curves of the change in λ and a.

The course of the change in c_p, λ, and a for channel black as a function of treatment temperature is distinguished by very low values of c_p up to $\sim$ 1300°, a maximum near 1700°, and a decrease in c_p, λ, and a in the interval 2700–3000°. Channel black, unlike other forms of carbon, does not crystallize homogeneously and, in the initial state, is characterized by a high oxygen content (4.79%). The reason for the peculiar course of the change in its thermophysical properties at high treatment temperatures, as well as its practically complete inability to crystallize, is the presence of a spatial network of heat-resistant bonds, relatively denser than in thermal black. The formation of such a network should be attributed to the process of dehydrogenation during the destruction of oxygen-containing side radicals, with splitting off and the formation of carbon chains of the allene type, which bind the carbon layers [10].

In the carbon substance of channel black (in the initial state and at a treatment temperature $<$ 1300°), the oxygen contained in the side radicals creates an additional spatial network of oxygen bridge bonds of the type C—O—C, which determines the relatively low values of c_p. The sharp maximum on the curve of the change in c_p of channel black as a function of t_{treat} should be explained by the destruction of the spatial network with oxygen bonds and the transition of the side radicals from the network into the "fringe."

The maxima on the kinetic curves of c_p for fossil coals (Fig. 4) at t_{treat} corresponding to the temporal transition of coal into a liquid state [12] can be explained by the destruction ("melting") of a spatial network of valence bonds with still lower heat resistance. Similar effects of "melting" of a spatial network of bonds were also observed for organic polymers, for example for polyvinyl acetate [11], with a maximum of c_p at lower temperatures corresponding to weaker intermolecular bonds.

The results of the present investigation show that the properties of carbonaceous materials are substantially determined by the polymeric character of the carbon structure and by the nature of the spatial network of atomic bonds. Only the limiting graphitized form of carbon ($\gamma = 1$) is characterized by the absence of a spatial network of bonds.

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