DEPENDENCE OF DIAMOND SYNTHESIS ON THE NATURE OF THE INITIAL CARBON

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DEPENDENCE OF DIAMOND SYNTHESIS ON THE NATURE OF THE INITIAL CARBON

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At the present time there is a sufficiently well-argued conception of the polymorphic transformation of graphite into diamond under conditions of catalytic synthesis as a solid-phase rearrangement of the graphite crystal lattice (^{1}). Convincing confirmation of this is provided by the observed orientational correspondence of graphite and diamond crystallites during the synthesis of diamond from pyrographite (^{2}).

In considering the mechanism of the catalytic transformation, one must take into account the transition of carbon atoms from the state of trigonal hybridization (sp^2) to the state of tetrahedral hybridization (sp^3), as well as the probable formation of intermediate π-complexes of graphite monolayers with atoms of the metal catalyst. Hybridized tetrahedral (sp^3) atoms of the transition metal (with a filled d-shell) in a π-complex may serve as a seed for the epitaxial growth of the diamond lattice. It should be expected that the process of catalytic synthesis will be determined by the transport of the catalyst metal, and also by the formation of the intermediate complex, which depend on the nature of the initial carbon material.

A study of various organic polymers showed that the formation of diamond under conditions of catalytic synthesis depends on the chemical structure of the initial polymer (^{3}).

In the present communication, results are given for a study of diamond synthesis from carbon of chain structure–carbyne (—C $\equiv$ C—C $\equiv$ C—)–and from certain transition forms of carbon that differ in their ability to undergo homogeneous graphitization by a homogeneous mechanism. The criterion of such ability is the X-ray graphitization index γ_0, expressing the relative convergence of the layers of condensed aromatic carbon during heat treatment in a neutral medium up to 3000° (^{4})

$$\gamma_0 = (3.43 - d_{002})/(3.43 - 3.358),$$

where d_{002} is the interlayer spacing (in Å) in the sample treated at 3000°; 3.358 is the interlayer spacing in artificial graphite; 3.43 is the interlayer spacing in carbon of turbostratic structure, characteristic of the precrystallization stage of homogeneously graphitizing carbon (1900°) and of non-graphitizing carbon treated at 3000°.

As samples of graphitizing transition forms of carbon, coke from polyvinyl chloride (CH_2—CHCl—) and thermal carbon black ($\gamma_0 = 0.775$) were used; and as samples of non-graphitizing forms, coke from polyvinylidene chloride (—CH_2—CCl_2), channel black ($\gamma_0 = 0.187$), and acetylene black ($\gamma_0 = 0.264$).

All samples of transitional forms of carbon were preliminarily treated in argon at 1800°. Carbyne was heated in vacuum to 1000° with a slow temperature rise. The carbon materials in the form of powders, preliminarily pressed under a pressure of 0.1 kbar, together with the metal catalyst were placed in the reaction zone in a high-pressure chamber with direct, as well as independent, heating developed at the Institute of High Pressures of the USSR Academy of Sciences ([2]). The pressure was determined by calibrating the chamber with the aid of known phase transitions ([6],[7]) of bismuth (25.4; 26.9; 89.0 kbar), thallium (36.9 kbar), and barium (59 kbar). The temperature was measured with a chromel–alumel thermocouple. The diamond yields were determined by washing away the unreacted carbon with hydrochloric acid. For the kinetic characterization of the process, curves of the change in electrical resistance as a function of the holding time in the reactor were recorded. Also determined was the magnitude of the concentration of paramagnetic centers in the initial carbon and diamond samples on an RE-1301 instrument.

Table 1

Characteristics of the initial carbon materials, conditions, and results of diamond-synthesis experiments

Material	$u \cdot 10^{18}$, spins/g	Graphitizability of carbon, γ_0	Pressure, kbar	Temp., °C	Time, sec	Diamond yield, %
Graphite	0.0	1.0	90	1700	7	100
Carbyne	100	does not graphitize	70	1500	180	diamonds not obtained

Material	$u \cdot 10^{18}$, spins/g	Graphitizability of carbon, γ_0	Pressure, kbar	Temp., °C	Time, sec	Diamond yield, %
Carbyne	100	does not graphitize	70	1600	45	diamonds not obtained
Coke from polyvinyl chloride	<0.01	graphitizes	85	1500	10	82
Coke from polyvinylidene chloride	<0.01	does not graphitize	85	1700	80	25
Thermal carbon black	<0.01	0.775	85	1700	5	94
Channel carbon black	0.8	0.187	85	1700	50	57
Acetylene carbon black		0.264	90	1700	55	49

Table 1 gives the characteristics of the initial carbon material, the synthesis conditions, and the diamond yield. As the experimental results show, under the indicated synthesis conditions carbyne does not transform into diamond.

When cokes and carbon blacks are compared, a dependence is observed of the diamond yields on their ability to graphitize homogeneously. Thus, the nongraphitizing carbon of coke from polyvinylidene chloride, at a substantially longer holding time in the chamber and at a higher temperature, gives a lower diamond yield in comparison with the graphitizing carbon of coke from polyvinyl chloride. The diamond yield from the carbon of thermal carbon black, characterized by a higher graphitization index, substantially exceeds the diamond yield from the carbon of channel and acetylene carbon black with a lower graphitization index.

Differences in the course of diamond synthesis from different carbon samples are manifested especially clearly in the electrical-resistance curves, which to a certain extent reflect the kinetics of the process.

Fig. 1. Dependence of electrical resistance on time in the process of synthesis of diamonds from graphite (OSCh grade) (1), polyvinyl chloride coke (2), and polyvinylidene chloride coke (3)

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Fig. 2. Dependence of electrical resistance on time in the process of synthesis of diamonds from thermal (1), channel (2), and acetylene (3) carbon black

Figure 2: Fig. 2. Dependence of electrical resistance on time in the process of synthesis of diamonds from thermal (1), channel (2), and acetylene (3) carbon black

Figure 1 presents the curve of the dependence of electrical resistance on the holding time in the chamber for graphitizing coke from polyvinyl chloride and nongraphitizing coke from polyvinylidene chloride. The carbon of the coke is characterized by a low rate of the diamond-formation process.

When the electrical-resistance curves of carbon blacks that differ in their ability to graphitize homogeneously are compared, an induction period of the diamond-formation process is observed for channel and acetylene carbon blacks with a lower graphitization index, whereas for thermal carbon black ($\gamma_0 = 0.775$) the induction period is absent. The cause of the observed differences in the rate of the process and in diamond yields should be sought in the features of the chemical structure of the carbon of the samples studied.

The inability of carbyne to transform into diamond under synthesis conditions, which was also observed earlier ([2]), may be explained by the fact that carbyne consists only of atoms with *sp*-hybridization, and its chain micromolecules contain only triple conjugated bonds, as well as cumulated double bonds ([4]). The conditions for the formation of intermediate π-complexes with tetrahedral hybridization of atoms of the transition metal, as may be assumed, are not provided in this system owing to the absence of condensed aromatic carbon layers.

As was shown earlier ([5]), nongraphitizing carbon is characterized by the presence of thermally stable lateral bonds between packets of monolayers of condensed aromatic carbon of the type of conjugated triple ($-\mathrm{C} \equiv \mathrm{C}-$) and cumulated double ($= \mathrm{C} = \mathrm{C} =$) bonds,

Fig. 1. Dependence of electrical resistance on time in the process of synthesis of diamonds from graphite (OSCh grade) *(1)*, polyvinyl chloride coke *(2)*, and polyvinylidene chloride coke *(3)*

Fig. 2. Dependence of electrical resistance on time in the process of synthesis of diamonds from thermal *(1)*, channel *(2)*, and acetylene *(3)* carbon black

forming a polymeric carbon framework. The inability to graphitize homogeneously, as well as the magnitude of the graphitization index for incompletely graphitizing and graphitizing carbon materials, as was assumed, is connected with the density of the spatial network of such bonds, which inhibit the process of homogeneous graphitization. In other words, the ability of carbon to graphitize homogeneously is connected with the concentration of atoms in the state of *sp*-hybridization that enter into a polymeric combination with atoms of another type of hybridization.

In contrast to this, the spatial networks of lateral bonds in graphitizing carbon are formed by less stable double bonds of the polyene type (—CH = CH—), which are destroyed at high temperature and do not hinder the azimuthal orientation of aromatic carbon layers into the crystal lattice of graphite.

The data presented in the present study indicate a correlation between the rate of the diamond-formation process, as well as the yield of diamond, and the content in the carbon substance of triple bonds (the concentration of atoms with *sp*-hybridization) in the initial carbon material. It is known that nongraphitizing carbon material, in contrast to graphite, is characterized by rigidity of structure owing to the presence of thermally and chemically stable lateral bonds between packets of atomic layers and therefore does not swell in the liquid medium of a strong oxidizing agent, or in a neutron flux. The observed retardation of the diamond-formation process should presumably be connected with additional difficulties in the transport

of the atoms of the metal catalyst and the formation of π-complexes in the rigid polymeric structure of non-graphitizing carbon.

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