Formation of Graphite Structure in Carbon Crystallites

E. A. Belenkov

Chelyabinsk State University, ul. Br. Kashirinykh 129, Chelyabinsk, 454136 Russia e-mail: belenkov@cgu.chel.su Received March 29, 2000; in final form, February 14, 2001

Abstract—The formation of graphite structure in carbon crystallites 0.2 to 100 nm in size is examined. It is shown that the energetically favorable structure of such crystallites differs from that of graphite. The interatomic distances and interplanar spacing d_{002} in the crystallites depend on their in-plane dimension L_a . A model is proposed according to which the only mechanism of graphitization in microcrystalline carbon materials is crystallite growth.

INTRODUCTION

The structural changes produced in carbon materials by high-temperature heat treatment, grinding, or neutron irradiation are always accompanied by changes in crystallite size [1–6]. These processes are usually considered separately. According to Veselovskii [1], graphitization of carbon materials at 2500–3000°C reduces to crystallite growth. By contrast, in a number of works, the consideration of the processes taking place in carbon materials is confined to crystallization induced by high-temperature heat treatment or amorphization induced by grinding or neutron irradiation [1–7]. Such approaches are incapable, however, of adequately describing the observed variations in the lattice parameters of carbon materials with crystallite size [1, 2, 5, 6, 8–11].

In carbon materials consisting of crystallites less than 100 nm in size, the lattice parameters a and c are, respectively, smaller and larger than those in graphite. In terms of the theory of phase transformations, this behavior can be interpreted as due to a corrugation of graphite layers as a result of the attachment of carbon atoms [4-7]. By analogy with intercalation compounds, various configurations and, accordingly, several metastable phases may be expected to result [4–7], without changes in interatomic distances. In this approach, the changes in interplanar spacings must be larger in more defect-rich crystallites. However, according to Fujimoto et al. [9], the intercalation capacity of large crystallites is higher, whereas experimental data indicate that the largest changes in lattice parameters occur in fineparticle carbon materials. Moreover, no metastable phases were detected in the detailed x-ray diffraction studies by Mateos et al. [12].

RELATIONSHIP BETWEEN INTERATOMIC DISTANCES AND CRYSTALLITE SIZE

Consider the origin of the correlation between the crystallite size and interatomic distances in carbon materials. The carbon–carbon bond distance in carbon polymorphs and organic molecules is known to vary widely [2, 13]: $R_{C-C} = 0.154$ nm in diamond, 0.1422 nm in graphite, 0.139 nm in benzene molecules, and 0.133 nm in ethylene. The changes in R_{C-C} are due to the effect of the bond order χ [2, 13], defined as the ratio of the maximum possible number of single bonds to the actual bond number. The variation of R_{C-C} with χ is well described by the relation

$$R_{\rm C-C} = A + B/\chi, \tag{1}$$

where the coefficients A = 0.1068 nm and B = 0.0472 nm are determined from the known interatomic distances in various carbon materials. These coefficients differ somewhat from the A = 0.1034 nm and B = 0.051 nm reported in [2], because, in this work, interatomic distances were taken with different weights, depending on the estimated error of determination.

One important question to be answered is whether or not the bond order depends on the crystallite size. It is reasonable to assume that the difference in R_{C-C} between carbon materials and graphite is due to the effect of bond order. Changes in bond order may be due to the fact that each terminal carbon atom in graphite layers forms two covalent bonds, while each atom within the layers forms three bonds.

In subsequent calculations, a crystallite of a carbon material is thought of as a stack of parallel layers (Fig. 1a) in which the carbon atoms are linked by covalent bonds and form a graphite-like structure (Fig. 1b).

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Fig. 1. Model for a crystallite of a carbon material: (a) stack of layers, (b) structure of an individual layer.

Following Fujimoto *et al.* [9], we describe the layer dimension by parameter p = 1, 2, 3, ... (Fig. 2). Then, the number of atoms per layer, N, and the *a*-axis layer dimension, L_a , are given by

$$N = 6p^{2},$$

$$L_{a} = 2R_{C-C}\cos 30^{\circ}(2p-1).$$
(2)

In calculating the bond order in an individual crystallite, we assume that all the layers are identical and, hence, the χ in the crystallite is equal to that in an individual layer. The maximum possible number of single bonds in a layer is 4*N*. Actually, there are two bonds per terminal atom and three bonds per interior atom. Therefore,

$$\chi = 4N/(3N-m), \qquad (3)$$

where *m* is the number of terminal atoms. Since m = 6p, we have

$$\chi = 4/\left(3 - \frac{1}{p}\right),\tag{4}$$

$$R_{\rm C-C} = A + 0.25 B \left(3 - \frac{1}{p} \right), \tag{5}$$

$$L_a = 2\cos 30^{\circ} \left(A + 0.25B \left(3 - \frac{1}{p} \right) \right) (2p - 1).$$
 (6)

The crystallite sizes and interatomic distances calculated by formulas (5) and (6) are listed in Table 1. The plot of R_{C-C} vs. L_a is shown in Fig. 3. With increasing crystallite size, R_{C-C} approaches that in graphite.

On the whole, the calculated curve in Fig. 3 agrees with experimental data [2, 10, 11] but lies somewhat higher, presumably because of the significant experimental error in the mean size of coherently scattering domains (CSDs) and the noncylindrical shape of real crystallites. In conventional procedures for determining the CSD size from x-ray diffraction profile analysis, the interplanar spacings are assumed to be identical in all crystallites, and only alternating microstrains are allowed for [14]. Since, as shown above, the interplanar spacings in carbon materials depend on the crystallite size, the results obtained by standard procedures should be regarded as a first approximation. An accurate determination of the mean crystallite size must rely on x-ray diffraction profile analysis by the regularization



Fig. 2. Carbon layers with p = (a) 1, (b) 2, and (c) 3.



Fig. 3. (1) Calculated and (2) experimental [10] R_{C-C} vs. L_a data.

method, in which the mean size is determined from the crystallite size distribution [15].

RELATIONSHIP BETWEEN THE LAYER SPACING AND CRYSTALLITE SIZE

According to experimental data, the lattice parameter c of microcrystalline carbon materials is larger than that of graphite [2–8]. In terms of phase transforma-

Table 1. Interatomic distance R_{C-C} and bond order χ as functions of L_a , N, and p

р	Ν	т	χ	$R_{\rm C-C}$, nm	L_a , nm
1	6	6	2	0.13040	0.23
2	24	12	1.6	0.13630	0.71
3	54	18	1.5	0.13827	1.20
4	96	24	1.4545	0.13925	1.69
5	150	30	1.42857	0.13984	2.18
6	216	36	1.41176	0.14023	2.67
8	384	48	1.39130	0.14073	3.66
10	600	60	1.37931	0.14102	4.64
15	1350	90	1.36364	0.14141	7.10
20	2400	120	1.35593	0.14161	9.57
30	5400	180	1.34831	0.14181	14.49
40	9600	240	1.34454	0.14190	19.42
50	15000	300	1.34228	0.14196	24.34
100	60000	600	1.33779	0.14208	48.97
200	240000	1200	1.33556	0.14214	98.23
300	540000	1800	1.33482	0.14216	147.49
400	960000	2400	1.33445	0.14217	196.75
500	1500000	3000	1.33422	0.14217	246.01
1000	6000000	6000	1.33378	0.14219	492.31

tions, this difference is due to various interlayer defects. However, just like in the case of interatomic distances, this approach is incapable of explaining the observed effect of crystallite size on c and the fact that some carbon materials (carbon black, carbon fibers, and others) cannot be graphitized even by heat treatment at 3000°C, whereas petroleum cokes are graphitized at 2500–2700°C. To elucidate the origin of this difference, we carried out computer simulation by the interatomic-potential method [16], whose applicability to carbon materials was substantiated in earlier studies [17–19].

CALCULATIONAL APPROACH

In the interatomic-potential method [16], the energy of van der Waals forces between adjacent carbon layers is calculated as the sum of pair interaction potentials,

$$E = \sum_{i=1}^{N} \sum_{j=1}^{N} [-Ar_{ij}^{-6} + B\exp(-\alpha r_{ij})], \qquad (7)$$

where r_{ij} is the distance between atom *i* in one layer and atom *j* in an adjacent layer; *N* is the total number of atoms in a layer; and *A*, *B*, and α are empirical coefficients [16]. For convenience, we calculated the interaction energy per graphite unit cell (two carbon atoms):

$$E_{\rm u} = 2E/N. \tag{8}$$

We considered circular, perfect graphite-like layers in which each atom forms at least two covalent bonds (Fig. 4). The center of the layer is situated midway between two carbon atoms in model 1 (Fig. 4b) and coincides with the center of a hexagon in model 2 (Fig. 4a). The possible dimensions of perfect layers are $L_a = 0.6, 0.79, 1.2$ nm, etc., in model 1 and 0.3, 0.9, 1.2 nm, etc., in model 2 (Table 2).

First, d_{002} was varied at zero in-plane translation vector between adjacent layers (each atom of the upper layer is located over the corresponding atom of the lower layer). Next, d_{002} was fixed at the value minimizing E_u , and the energy was computed as a function of the in-plane translation vector (Fig. 5),

$$\mathbf{S} = x\mathbf{i} + y\mathbf{j},\tag{9}$$

where **i** and **j** are the unit vectors along the *X* and *Y* axes, respectively. The value of *x* was varied from -0.1846 to 0.1846 nm in 0.0205-nm steps; *y* was varied from -0.1066 to 0.1066 nm in 0.0213-nm steps. In this way, E_u was computed for 209 translation vectors **S**. The results were used to construct E_u contours (Fig. 6).

In this way, we found the translation vectors minimizing E_u and then refined the energetically favorable value of d_{002} . Analogous computations were also carried out for infinite layers made up of unit cells each containing two atoms. Since the energy of the interaction between a unit cell and an adjacent infinite layer is the same for all unit cells, the total interlayer interaction



Z'

Fig. 4. Models (a) 2 (L_a = 0.9 nm, N = 24, m = 12) and (b) 1 (L_a = 0.75 nm, N = 16, m = 10) of carbon layers.

Fig. 5. Schematic showing the in-plane translation vector between adjacent layers.



Fig. 6. E_u contours (J/mol) in the **S** plane for $L_a = (a) 0.9$ nm, (b) 1.4 nm, (c) 3.1 nm, and (d) ∞ .



energy is equal to the product of the interaction energy per unit cell with the number of unit cells. The total interaction energy reaches a minimum concurrently

Table 2. d_{002} and E_u as functions of L_a and N

L_a , nm	N	<i>d</i> ₀₀₂ , nm	E _u , J/mol	Model
0.2	2	0.37092	-1078.26	1
0.3	6	0.35683	-2652.67	2
0.6	10	0.35249	-3454.26	1
0.79	16	0.34879	-4322.65	1
0.9	24	0.34643	-5049.75	2
1.2	42	0.34432	-5758.12	2
1.2	42	0.34411	-5841.51	1
1.4	62	0.34295	-6313.08	1
1.4	54	0.34325	-6181.82	2
1.6	84	0.34222	-6653.96	2
1.6	72	0.34243	-6483.89	1
1.8	96	0.34187	-6806.16	2
1.82	100	0.34187	-6830.91	1
2.05	122	0.34145	-7021.49	1
2.1	138	0.34110	-7134.96	2
2.26	150	0.34110	-7197.65	2
2.47	184	0.34067	-7357.18	1
2.6	204	0.34067	-7431.65	2
2.9	258	0.34007	-7580.83	2
3.1	282	0.34007	-7647.49	2
3.32	324	0.34007	-7721.84	1
3.36	348	0.34016	-7761.62	2
∞	~	0.33796	-8840.47	1

with the interaction energy per unit cell. Therefore, calculations can be confined to only one unit cell (two atoms). Given that the interatomic interaction decreases rapidly with increasing distance, calculations can be simplified further. According to our estimates, the infinite layer can be replaced by a layer 3.0 nm in diameter, since a further increase in diameter changes the interaction energy by less than 0.1%.

CALCULATION RESULTS

The calculation results for zero translation vector are presented in Table 2. The value of d_{002} was found to vary with L_a (Fig. 7). The data points obtained in models 1 and 2 fall on the same curve. As L_a increases from 0.6 to 3.1 nm, d_{002} decreases from 0.35249 to 0.34007 nm. As L_a tends to infinity, d_{002} gradually decreases to 0.33796 nm. The curve obtained for the energetically favorable translation vector is similar to that shown in Fig. 7, but the d_{002} values are lower by about 0.0023 nm than those computed with zero translation vector: for infinite layers, we obtain $d_{002} =$ 0.3357 nm, in perfect agreement with the $d_{002} =$ 0.3354 nm in ideal graphite. In addition, E_u decreases from -2652.67 J/mol at $L_a = 0.6$ nm to -8840.47 J/mol at infinite L_a (Table 2).

The calculated E_u data are shown in Fig. 6. At small L_a , the translation vector **S** minimizing the interaction energy differs from that in graphite: $|\mathbf{S}| = 0.0387$ nm at $L_a = 0.9$ nm (Fig. 6a). Increasing L_a to 1.4 and 3.1 nm increases the magnitude of the energetically favorable translation vector to 0.0775 and 0.11618 nm, respectively (Figs. 6b, 6c). As L_a tends to infinity, the magnitude of the translation vector approaches 0.142 nm: half of the atoms in each layer are situated over atoms of the lower layer, and the rest of the atoms are situated over the centers of hexagons (Fig. 6d). This configuration is characteristic of graphite. Moreover, at small L_a , there is a multitude of translation vectors minimizing $E_{\rm u}$, separated by very low, if any, potential barriers (Fig. 6a), which permits unactivated translations. Increasing L_a leads to the localization of energetically favorable translations and increases the potential barriers (Figs. 6b, 6c). Thus, the lack of order in the arrangement of carbon layers is also a consequence of the small dimensions of carbon crystallites.

GRAPHITIZATION MECHANISM

Thus, the present results suggest that carbon crystallites differ in structure from graphite on account of their small L_a (<100 nm), and there is no need to assume the presence of interlayer defects. Nanometer-sized carbon crystallites have an equilibrium, energetically favorable structure in which the lattice parameter *a* (covalent bonding) is shorter and *c* (van der Waals forces) is longer than those in graphite. The graphitization

induced by heat treatment and graphite amorphization induced by grinding or neutron irradiation are consequences of the associated changes in crystallite size. Therefore, the formation of graphite structure is due to crystallite growth, accompanied by transformations of the crystal structure.

Crystallite growth involves mass transport processes and may be due to either motion and mergence of layers coming in contact or atomic diffusion. The latter mechanism, involving the detachment of carbon atoms from layers, is more likely at high temperatures. In this case, the average crystallite size increases only if the diffusion flow from a unit surface area is larger for smaller crystallites. This is possible if the bond energy of terminal atoms decreases with increasing L_a .

The bond energy comprises covalent and van der Waals contributions. Given that the latter constitutes \approx 5% of the total bond energy [2], our consideration can be confined to covalent bonding, whose energy is known to depend on the bond order. Since, as shown above, the bond order is higher in smaller crystallites, the atoms in small crystallites are bonded more strongly. For example, the covalent bond energy is \approx 460 kJ/mol at $L_a = 0.708$ nm and \approx 400 kJ/mol at $L_a =$ 7.103 nm. Therefore, the equilibrium concentration of unbonded carbon is higher at larger L_a . Since atomic diffusion from larger to smaller crystallites does not increase average L_a , the layer size increases via layer translations.

Indeed, our calculations demonstrate that layers can be translated relative to one another by $2|\mathbf{S}| \approx$ 0.15–0.28 nm. For $L_a \leq 3$ nm, the activation energy of such translations is below kT_a ($T_a = 100$ K). However, with increasing layer size, the potential barriers to be surmounted for layer translations grow, and, hence, higher activation temperatures are needed ($T_a \approx 1557$ K at $L_a = 8$ nm). Therefore, at a given temperature, crystallite growth is only possible to a certain limit; further growth requires an increase in temperature. These speculations are supported by the observed dependence of the activation energy for graphitization on L_a [2].

The existence of poorly graphitizing materials can then be understood in terms of crystallite size. For example, in carbon fibers, the longitudinal crystallite size and, accordingly, carbon layers are very large, so that layer translations do not occur even at 3000°C. At the same time, the transverse crystallite size in carbon fibers is only a few nanometers, which leads to marked differences from the graphite structure [19].

Carbon black consists of rigid spherical particles in which layer translations are also impossible because they require bond breaking, which is only possible above 3500°C, i.e., at temperatures of rapid graphite sublimation. Moreover, there is another possible obstacle to layer growth in carbon materials—random orientation of the layers about the normal to their plane. In such materials, thermally activated layer translations

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are unlikely to bring layers of neighboring crystallites into intimate contact, and crystallite growth is hindered, preventing the transformation to the graphite structure.

CONCLUSION

The interatomic distances and interplanar spacing d_{002} in carbon crystallites depend on the layer size L_a : in crystallites with $L_a < 100$ nm, the lattice parameter a is smaller and d_{002} is larger than those in graphite. As L_a tends to infinity, *a* and d_{002} approach those in graphite.

The in-plane translation vector between adjacent layers in crystallites with $L_a < 100$ nm depends on the layer dimension, which leads to various arrangements of layers and, accordingly, the lack of periodicity in [hkl] directions with $h \neq 0, k \neq 0$, and $l \neq 0$.

For $L_a < 3$ nm, there is a region of energetically favored translation vectors within which low-activation translations are possible.

As L_a increases from 0.3 nm to infinity, the contribution of van der Waals forces to the total bond energy increases by a factor of 3.3.

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