Modeling of Formation of a Crystal Structure in a Carbon Fiber

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Abstract—The method of an atom–atom potential has been used to simulate the process of three-dimensional ordering in a carbon fiber. It has been established that the deviation of the interlayer spacing d_{002} in a carbon fiber from the analogous value in graphite and the absence of three-dimensional structural ordering are explained by small dimensions of crystalline regions. Weak ability to graphitization observed for a carbon fiber is associated with a limited increase of dimensions of the crystalline regions.

The process of transformation of carbon materials with a disordered structure into graphite-the so-called graphitization—can occur during the high-temperature treatment of these materials [1, 2]. According to the turbostrate model of graphitization suggested by Warren and Franklin, crystalline regions in a starting carbon material consist of layers analogous to carbon layers in graphite but slightly misoriented with respect to one another. During heating, the degree of the mutual layer orientation increases, thus also increasing the dimensions of the crystalline regions. As a result, polycrystal line graphite is formed. Bragg and his coauthors believed that the major shortcoming of this model is its failure of predicting the value of the interlayer spacings d_{002} , which differs from the analogous distance in graphite [3, 4]. Later, Maire and Mering [5] suggested another model, in which the space between the layers is filled with carbon atoms bonded to these layers and distorting them. Thus, the graphitization process can be regarded as a number of successive phase transitions of the states with the fixed values of the above spacings. This approach explains the difference between the d_{002} values observed in various carbon materials from the corresponding spacing in graphite, but fails to explain some other experimental facts: first, the experimentally established relationship between the interlayer spacings and the crystallite dimensions in carbon materials [1, 6]; second, the existence of poorly graphitizable materials, e.g., carbon fibers, which cannot be graphitized even by the temperature treatment at temperatures above 3000°C, despite the well-known fact that the graphitization process in the petroleum cokes occurs at considerably lower temperature, ~2500°C [7–9].

The ambiguous interpretation of the graphitization process is explained by the fact that one usually deals with the experimentally determined averaged structural parameters of the material, whereas the corresponding models describe the structures of individual crystals. The direct experimental measurements of the structural parameters of individual crystals are rather difficult, and, therefore, one has to use computer simulation for determining the energetically advantageous structures of the crystalline regions. The use of a carbon fiber as an object of computer simulation is dictated by the fact that the graphitization process in a carbon fiber cannot be satisfactorily interpreted within the Maire–Mering model. Thus, we had the aim to simulate the process of structural ordering in carbon fibers.

STRUCTURAL MODEL AND COMPUTATIONAL PROCEDURE

The simulation is based on the Rowland model [9] according to which a carbon fiber consists of fibrils forming piles of layers-bands oriented mainly along the fiber axis. The structure of a layer of carbon atoms bound by covalent bonds was assumed to be similar to the graphite structure having two subtypes differing by the bond orientations within the layer. The first subtype is an analogue of carbon fibers obtained from poly-acrylenitrile (PAN-structure, Fig. 1a), whereas the second subtype, from hydrated cellulose (HC-structure, Fig. 1b). The layers-band length was taken to be infinite, whereas its width was measured as a number of atoms in the transverse section and ranged from 2 to 24 atoms.

Simulation of the graphitization processes reduces to the search for such mutual arrangement of the layers that would provide the minimum energy of their interaction. The computations were performed by the method of atom-atom potential [10], whose applicability to simulation of structural ordering in carbon materials has already been proven in a number of studies [11, 12]. According to this method, the energy of van der Waals interactions of each atom in the layer with any another atom of another layer can be calculated by the formula

$$E = -Ar^{-6} + B\exp(-\alpha r), \qquad (1)$$

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Fig. 1. Schematic of a graphite-like layer-band with a width of three atoms: (a) PAN structure $(L_{a\perp} = 0.426 \text{ nm})$; (b) HC structure $(L_{a\perp} = 0.492 \text{ nm})$. Elementary cells of the layer are hatched.



Fig. 2. Schematic of the mutual arrangement of two layers with widths of three atoms, with the displacement by a vector $\mathbf{S} = x\mathbf{i} + y\mathbf{j}$ for the PAN structure.

where *r* is the interatomic distance and *A*, *B*, and α are the empirical coefficients. For carbon–carbon interactions, the absolute values of these coefficients are [6]:

$$A = 1.49887 \text{ J nm}^{6}/\text{mol},$$

$$B = 1.75846 \times 10^{8} \text{ J/mol},$$
 (2)

$$\alpha = 35.8 \text{ nm}^{-1}.$$

Since the total binding energy for two infinite layers is infinite and equals the sum of the energies of interactions of all the atoms of one layer with all the atoms of the other layer, we calculated the specific binding energy E_y of the layers per two atoms forming an independent elementary layer cell in graphite. With this aim, it was necessary to determine an elementary layer cell in a carbon fiber (Fig. 1). Translating this elementary cell along the band, one can obtain the whole layer. Then the total energy of layer interactions is equal to the sum of the interaction energies of all the cells of one layer with all the cells of the other layer:

$$E_{\rm tot} = \sum_{i=-\infty}^{\infty} E_{\rm c} = N E_{\rm c}, \qquad (3)$$

where $N = \infty$ is the number of cells in the layer. The specific binding energy is equal to the double ratio of the binding energy of the elementary cell of the layer in a

carbon fiber to the number *n* of atoms in the cell:

$$E_{\rm s} = 2E_{\rm c}/n. \tag{4}$$

Moreover, calculating the energy E_c , one can replace an infinite layer by a layer of a finite length. The calculations show that it is sufficient to use a layer built by seven (Fig. 2) or eleven elementary cells (for the HC and PAN structures, respectively). A further increase of the layer length would change the energy E_c by less than 0.1%.

The computations were performed by varying the interlayer spacing d_{002} at the zeroth relative displacement of the layers, i.e., for such layer arrangement that each atom of the upper layer would be exactly above an atom of the lower layer. Then, the value of d_{002} at which the energy of the layer interactions is minimal was fixed, and the binding energies were calculated at various magnitudes of the vector **S** (Fig. 2) setting the relative displacement of the layers:

$$\mathbf{S} = x\mathbf{i} + y\mathbf{j},\tag{5}$$

where **i** and **j** are the translation unit vectors along the axes *x* and *y*, respectively (($|\mathbf{i}| = |\mathbf{j}| = 1$). The *x*-value for the HT structure varied from 0 to 3*a* (*a* = 0.142 nm is the shortest distance between the carbon atoms in the layer) at a variation step $\Delta x = 0.15a$. The value of *y* varied from $-2.5a\cos 30^\circ$ up to $2.5a\cos 30^\circ$ at a variation step $\Delta y = 0.5a\cos 30^\circ$. For the PAN structure, the corresponding variation ranges for $x \in [-2.5a\cos 30^\circ, 2.5a\cos 30^\circ]$ and $y \in [0, 3a]$ are $\Delta x = 0.5a\cos 30^\circ$ and

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Layer dimension, in numbers of atoms	Structure									
		HC		PAN						
	$L_{a\perp}$, nm	<i>d</i> ₀₀₂ , nm	E _s , J/mol	$L_{a\perp}$, nm	<i>d</i> ₀₀₂ , nm	E _s , J/mol				
2	0.246	0.3457	-5295.9	0.213	0.3469	-4950.1				
3	0.492	0.3428	-6366.0	0.426	0.3436	-6083.8				
4	0.738	0.3413	-6960.1	0.639	0.3420	-6734.1				
5	0.984	0.3407	-7330.2	0.852	0.3411	-7145.1				
6	1.230	0.3402	-7581.1	1.065	0.3405	-7425.9				
7	1.476	0.3398	-7761.8	1.278	0.3401	-7628.9				
8	1.722	0.3395	-7897.9	1.491	0.3399	-7782.4				
10	2.214	0.3393	-8089.1	1.917	0.3395	-7997.2				
12	2.705	0.3390	-8217.3	2.343	0.3392	-8143.2				
14	3.197	0.3389	-8308.6	2.769	0.3391	-8245.4				
16	3.689	0.3387	-8377.6	3.195	0.3389	-8323.2				
20	4.673	0.3386	-8473.4	4.047	0.3387	-8432.0				
24	5.657	0.3385	-8538.2	4.899	0.3386	-8504.5				
∞	~	0.3380	-8840.5	∞	0.3380	-8840.5				

Table 1. Interlayer spacing d_{002} and specific energies E_c of van der Waals interactions for various widths of graphite-like layers in a carbon fiber for the model in which the layers are located one above the other without any displacement

Table 2. Interlayer spacings d_{002} , the displacements of the layers with respect to one another set by the vector *S*, and the specific energy E_s of van der Waals interactions for layers of different lengths $L_{a\perp}$

Layer dimension, in numbers of atoms	Structure										
	НС				PAN						
	$L_{a\perp}$, nm	S , nm	<i>d</i> ₀₀₂ , nm	E _s , J/mol	$L_{a\perp}$, nm	S , nm	<i>d</i> ₀₀₂ , nm	E _s , J/mol			
2	0.246	0.1840	0.3422	-5446.0	0.213	0.1231	0.3452	-5021.9			
3	0.492	0.1644	0.3398	-6517.7	0.426	0.1231	0.3418	-6173.9			
4	0.738	0.1576	0.3386	-7112.0	0.639	0.1231	0.3401	-6824.3			
5	0.984	0.1540	0.3380	-7481.9	0.852	0.1232	0.3392	-7251.6			
6	1.230	0.1509	0.3376	-7732.5	1.065	0.1232	0.3386	-7536.6			
7	1.476	0.1499	0.3373	-7913.0	1.278	0.1233	0.3382	-7742.5			
8	1.722	0.1465	0.3370	-8048.9	1.491	0.1235	0.3379	-7898.3			
10	2.214	0.1461	0.3369	-8239.9	1.917	0.1269	0.3374	-8118.9			
12	2.705	0.1449	0.3366	-8367.6	2.343	0.1294	0.3371	-8267.3			
∞	~	0.1420	0.3357	-9006.5	8	0.1420	0.3357	-9006.5			

 $\Delta y = 0.15a$. We calculated the energy of layers interactions for 231 magnitudes of the vector **S**.

We also determined the magnitudes of the vectors setting the mutual arrangement of the layers such that the energy of their interaction was minimal. Then, using the thus found magnitudes of S, we refined the most energetically advantageous value of the interlayer spacing d_{002} .

RESULTS OF COMPUTATIONS AND DISCUSSION

The results of model computations are listed in Tables 1 and 2. It has been established that the interlayer spacings at which the energy of the layer interactions is minimal depend on the layer widths. For the layer arrangement such that each atom of one layer is



Fig. 3. (a) The variation of the interlayer spacing d_{002} (1) PAN and HC structures at $\mathbf{S} = 0$, (2) PAN structure at $\mathbf{S} \neq 0$, (3) HC structure at $\mathbf{S} \neq 0$) and (b) the relative arrangement of the layers in the (1) HC structure, (2) PAN structure as functions of the layer width.

located above the atom of another layer (i.e., S = 0), the experimental points of the HC and the PAN structures fit the same curve (Fig. 3a). Thus, at the layer width ~0.45 nm, the interlayer d_{002} spacing is ≈ 0.3434 nm. An increase of the layer width $L_{a\perp}$ up to 5 nm results in a decrease of d_{002} down to 0.3386 nm. A further increase of the layer width to infinity is accompanied by a gradual decrease of the interlayer spacing to 0.3380 nm. The estimation of the energetically advantageous spacings of the layer arrangement corresponding to the minimum spacing along all the three dimensions, i.e., at $S \neq$ 0, demonstrates the differences in the process of d_{002} reduction provided by an increase of $L_{a\perp}$ for the HC and PAN structures. For the HC structure built by the layers of the same dimensions, the interlayer spacings are less than for the PAN structure (Fig. 3a). Thus, at $L_{a\perp} \approx 1.5$ nm, we have d_{002} (PAN) = 0.3378 nm and $d_{002}(\text{HC}) = 0.3372$ nm. However, if the transverse dimension tends to infinity, the interlayers spacings for both structures tend to a value of 0.3357, which is close

to the analogous value characteristic of graphite. Simultaneously with a decrease of the interlayer spacings, an increase of the layer width provides a reduction of the specific interaction energy. At the zeroth **S** vector, the absolute value of E_s decreases from -4950.1 J/mol at the transverse layer dimensions 0.213 nm to -8840.5 J/mol at infinite layer dimensions. If the energy of the layer interaction is also minimized because of the most advantageous mutual layer displacement ($\mathbf{S} \neq 0$), then $E_s = -5021.9$ J/mol at $L_{a\perp} = 0.213$ nm and $E_s = -9006.5$ J/mol at $L_{a\perp} = \infty$.

The results of the computations at $\mathbf{S} \neq 0$ are listed in Table 2 and shown in Figs. 3b and 4. It is established that at layers width less than 3 nm, the vector of the relative displacement at which the energy of layer interactions is minimal differs from the analogous value for the graphite structure. Thus, at $L_{a\perp} \approx 0.5$ nm, the value is $|\mathbf{S}| \approx 0.164$ nm for the HC structure and 0.123 nm, for the PAN structure, whereas for graphite, the corresponding value equals 0.142 nm. With an increase of the layer width, $|\mathbf{S}|$ gradually changes, so that at $L_{a\perp}$ tending to infinity, the relative displacement of the layers is the same as for the graphite structure.

Thus, it has been established that, similar to the situation in disperse carbon [11, 12], different values of interlayer spacings d_{002} in a carbon fiber and graphite are provided by small dimensions of crystalline regions in carbon fibers. The fine-crystalline structure of a carbon fiber does not allow the formation of a threedimensional order in the arrangement of the constituent graphite-like layers. The structure of small crystalline regions with the interlayer spacing d_{002} different from the analogous spacing in graphite cannot be considered as a defect structure. On the contrary, this structure is equilibrium and energetically advantageous. Therefore, the most adequate model of graphitization is the tutbostrate model.

The main arguments for the defect-induced increase of the interlayer spacing in graphite are provided by the experiments on graphite grinding and its irradiation with high-energy neutrons [3, 4]. In these studies, nonmonotonic variations of the d_{002} spacing depending on the fragment dimensions and the irradiation dose were recorded. However, the phenomenon seems to be explained by a more or less stepwise variation of the average crystal dimensions during grinding and irradiation rather than by defects located between the layers.

The transformation of the turbostrate structure of a carbon fiber into the graphite structure is possible only for larger crystals. Therefore, the weak graphitization of carbon fibers is explained by small dimensions of the crystals, which, in turn, is explained by small dimensions of fibrils formed still in the starting polymeric fibers.

The process of carbon-fiber graphitization also depends on the type of its structure. For the HC structure having the same $L_{a\perp}$ values as the PAN structure,

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Fig. 4. Specific energy of van der Waals interactions (in J/mol) as a function of the mutual layer arrangement and the transverse dimensions of the layer: (a–c) HC structure (2, 6, and 12 atoms), (d–f) PAN-structure (2, 6, and 12 atoms).

the interlayer spacings d_{002} and the mutual arrangement of the layers-bands forming the crystals of carbon fibers are closer to those characteristic of graphite.

CONCLUSIONS

The differences observed in the interlayer spacing d_{002} and the mutual arrangement of graphite-like lay-

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ers-bands forming the crystalline regions in carbon fibers from those characteristic of graphite are explained by small transverse dimensions of the crystalline regions in the fibers.

The transformation of the carbon-fiber structure into the graphite structure is provided by the process of crystal growth. Weak graphitization of carbon fibers is explained by almost constant dimensions of the crystalline regions in the fibers.

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