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Interrelation between the Structural Parameters of Polyacrylonitrile-based Carbon Fiber

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Abstract—Interrelation between the structural parameters of polyacrylonitrile-based carbon fiber is studied. Correlation is established between the interplanar spacings d_{002} and d_{110}, as well as between the average dimensions of the coherent scattering regions L_c, $L_{a\|}$, and $L_{a\perp}$.

Carbon fibers (CFs) are prepared by high-temperature (1500–3100°C) treatment of carbon-containing polymer fibers [1, 2]. The crystal structure of CFs can be characterized by five main parameters: periods of translation along the crystallographic axes *a* and *c* (or interplanar spacings $d_{002} = c/2$ and $d_{110} = a/2$) and the corresponding average dimensions of coherent scattering regions (CSRs), L_c, $L_{a\|}$, and $L_{a\perp}$ (Fig. 1). The main parameter conventionally used for characterizing the structure of carbon materials is the easily measurable interplanar spacing d_{002} [3, 4]. In view of correlation between the structural parameters of carbon materials it is possible to use other characteristics as the main parameter [3, 4]. To choose among them, it is necessary to elucidate the interrelations between the structural characteristics. In this work, we study the interrelation between the structural characteristics of CFs based on polyacrylonitrile (PAN).

EXPERIMENTAL

Our studies were concerned with a CF whose structural characteristics were studied earlier but were not analyzed for interrelations [5]. Twenty-two samples of the carbon fiber were synthesized by high-temperature dynamic treatment of the VMN-4 fiber in a vacuum at 3000–3100°C; the bundle load was 1.5, 0.75, 0.375, and 0.125 kg. We also studied the initial fiber obtained by carbonization of a polymeric PAN fiber at 2500°C.

The samples for X-ray diffraction analysis were prepared in the form of small joists of rectangular cross section by pressing fiber bundles arranged parallel to each other and impregnated with epoxy resin. The diffraction maximum profiles were recorded on a DRON-3 X-ray diffractometer. The average interplanar spacing d_{002} and the CSR dimensions were determined using the 002 diffraction maxima recorded when irradiating the lateral surface of the fibers. The d_{110} and $L_{a\|}$ parameters were determined using the 110 diffraction line recorded when irradiating the end surfaces of the fibers. Because of the high degree of orientation of the crystallites and interatomic bonds in the CF obtained from PAN the 110 plane families are oriented predominantly at angles of 30° and 90° with respect to the fiber axis (Fig. 2).

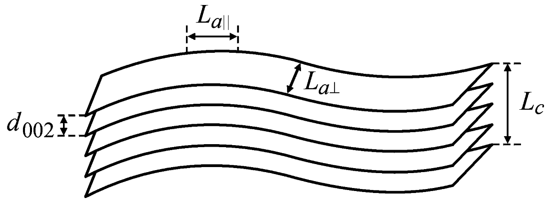

Fig. 1. Scheme of a stack of band layers constituting the CF crystallites.

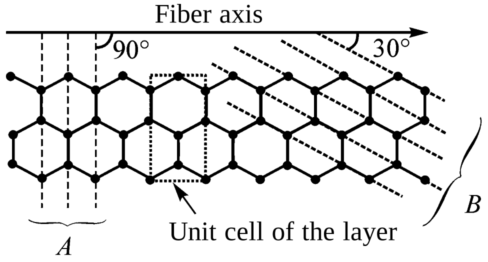

Fig. 2. Preferred orientation of the atomic layers with respect to the axis of the CF obtained from PAN. Families of the atomic planes responsible for the 110 reflection exist only in the case when the cross-section surface is located at an angle of (*A*) 90° and (*B*) 30° with respect to the fiber axis.

Therefore, the dimensions of the CSR in the direction perpendicular to the fiber axis were determined using the 110 line recorded in the case when the cross-section surface was oriented at an angle of 30°C to the fiber axis. To this end, we used the formula

$$L_{a\perp} = L_{110-30^\circ}\cos 30^\circ.$$

The average dimensions of the CSR were estimated from the integral width of the line, and the interplanar spacings, from the center of gravity of the maximum [6]. Silicon and silicon carbide served as references.

Because of high degree of orientation of the crystallites with respect to the fiber axis, the reflection intensities are strongly dependent on the orientation angle between the cross-section surface and the fiber axis, as well as on the Miller indices of the reflection observed. Therefore, the diffraction maximum 110 obtained for the orientation of the cross-section surface at 90° to the fiber axis does not overlap with the closely located lines 006 and 112 (their intensities are close to zero). The analogous maximum 110 recorded at an angle of orientation of the cross-section surface to the fiber axis of 30° overlaps with the maximum 112 (the intensity of the line 006 is close to zero). Therefore, before mathematical processing, the experimental diffraction maximum was resolved into components corresponding to the lines 110 and 112 [7] (Fig. 3). Because of the low intensity of the diffraction maximum 110_{30^0} and resolution procedure, $L_{a\perp}$ was determined with a large error (~15 %). The $L_{a\|}$ parameter was determined more accurately (~3–5%). Analysis of the interrelation between $L_{a\|}$ and $L_{a\perp}$ showed their linear correlation

$$L_{a\|} = kL_{a\perp} \qquad (1)$$

with the coefficient $k = 2.0 \pm 0.1$.

A better accuracy of determining $L_{a\|}$ compared to $L_{a\perp}$ sent us in a search for the dependences of other structural parameters on $L_{a\|}$. The plots of other parameters vs. $L_{a\|}$ also contain the axis corresponding to $L_{a\perp}$, as specified by equation (1). Figures 4–6 show the dependences obtained. It is found that the interplanar spacing d_{002} is inversely proportional to the dimensions of the crystallites along the crystallographic axis (Fig. 4). For example, for $L_{a\|}$ = 10 nm ($L_{a\perp}$ = 5 nm) d_{002} ~ 0.347 nm; increase of $L_{a\|}$ to 20 nm ($L_{a\perp}$ = 10 nm) decreases d_{002} to ca. 0.344 nm. The interplanar spacing d_{110}, on the contrary, tends to increase with increasing L_a. For $L_{a\|}$ = 10 nm ($L_{a\perp}$ = 5 nm) d_{110} ~ 0.1223 nm, and with $L_{a\|}$ (and, correspondingly, $L_{a\perp}$) increasing twofold d_{110} increases to ca. 0.1229 nm (Fig. 5). Extrapolation of the $d_{002} = f(L_a)$ and $d_{110} = f(L_a)$ dependences to large dimensions shows that with crystal dimensions tending to infinity the interplanar spacings tend to values typical of graphite.

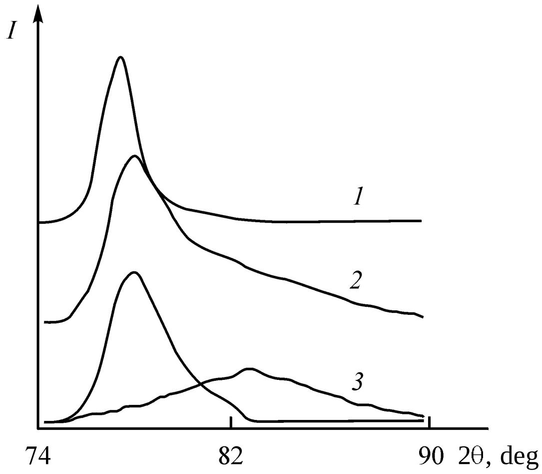

Fig. 3. Profiles of reflection 110 at different orientations of the cross-section surface with respect to the CF axis. (*I*) Intensity and (2θ) Bragg angle. Orientation angle (deg): (*1*) 90, (*2*) 30, and (*3*) 30 (as determined by resolution into components).

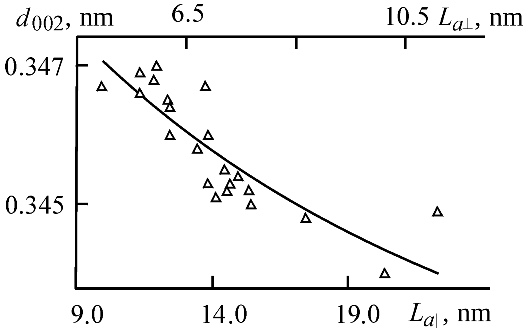

Fig. 4. Average interplanar spacing d_{002} as a function of the CSR dimensions $L_{a\|}$ and $L_{a\perp}$.

Another experimentally observed correlation between the CSR dimension along the crystallogrpahic axis *c* L_c and the dimensions of the crystallites $L_{a\|}$ and $L_{a\perp}$ is shown in Fig. 6. It is seen that L_c tends to increase with L_a. This correlation can be closely described by the equation

$$L_c = 0.54L_{a\perp} + 3.6 \text{ nm (or } L_c = 0.27L_{a\|} + 3.6 \text{ nm).} \qquad (2)$$

It follows from equation (2), however, that when the dimension of the crystallites along the crystallographic axis *a* is equal to zero, their dimension

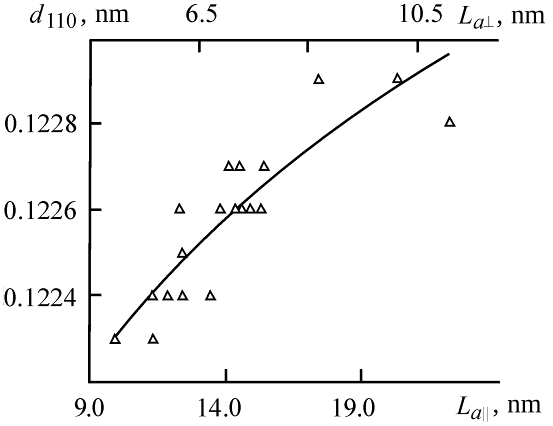

Fig. 5. Average interplanar spacing d_{111} as a function of the CSR dimensions $L_{a||}$ and $L_{a\perp}$.

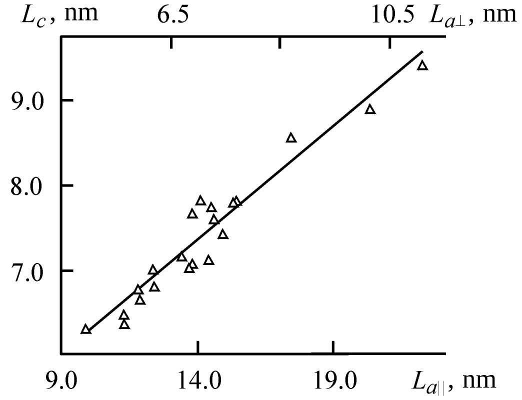

Fig. 6. Correlation between the CSR dimensions L_c and the dimensions of the crystallites $L_{a||}$ and $L_{a\perp}$.

along the axis c will be equal to 3.6 nm, which makes no sense. Therefore,

$$L_c = 1.06L_{a\perp} \text{ (or } L_c = 0.53L_{a||}). \tag{3}$$

will be more appropriate.

Let us analyze the reasons for this correlation. According to the structural model of carbon fiber proposed by Ruland [2], the crystallites of the fiber are composed of stacks of band layers of carbon atoms with infinite length and small width and height (ca. 2–10 nm; Fig. 1). The stacks of band layers are wave-like bended and oriented predominantly along the fiber axis. The atoms inside the layer are arranged similarly to graphite layers and linked by strong covalent bonds. The layers are bound by weak van der Waals interactions. Let us consider the bond energy of the atoms constituting one stack. We will designate the total number of atoms in the stack as N and assume that the bands are so long that the contribution of the end surfaces to the total energy is negligible:

$$E = nE_l + E_{il}, \tag{4}$$

where E_l is the energy of bonds inside one layer, E_{il} is the energy of interaction of the layers, and n is the number of layers in the stack.

As each layer is characterized by regular arrangement of the atoms, it can be represented by a set of unit cells (Fig. 2) whose periodic translation along the fiber axis can yield the whole layer. Then, we will designate the number of unit cells in the layer as N_{uc}, the energy of covalent bonds of the atoms in one unit cell as E_{cuc} and thus obtain for the energy of the bonds for one layer

$$E_l = N_{uc}E_{cuc}. \tag{5}$$

The energy of the bonds for one unit cell can be written as

$$E_{cuc} = N_{at}E_c f, \tag{6}$$

where N_{at} is the number of atoms in the cell; E_c is the energy of one covalent bond; and f is the function determining the average number of covalent bonds per atom.

For carbon fiber synthesized from PAN

$$f = 1.5 - 1/N_{at}. \tag{7}$$

In view of $N = nN_{uc}N_{at}$, it follows from (5)–(7) that

$$E_l = (1.5 - 1/N_{at})(E_c N/n). \tag{8}$$

Under assumption that only the energy of interaction of the neighboring layers is significant, we will find the energy of the van der Waals interaction

$$E_{uc} = NE_v(1 - 1/n), \tag{9}$$

where E_v is the van-der-Waals interaction energy for one atom.

Then, using (4), (8), and (9) we will find the total energy of interaction for a stack of carbon layers

$$E = N(1.5E_c + E_v) - N(E_c/N_{at} + E_v/n). \tag{10}$$

The first term in the latter equation is independent of the dimensions of the crystallites and represents the bond energy for atoms in a graphite crystal of infinite size.

Let us determine the shape of the stack with a minimal surface energy. To this end, let us assume that the number of atoms in the stack cross section is constant:

$$M = N/2N_{\mathrm{uc}} = \mathrm{const.} \tag{11}$$

Then $N_{\mathrm{at}} = 2M/n$. The stacks of layers with identical cross sections can differ in the number of layers; therefore, we will find the energetically preferred shape from the condition

$$\mathrm{d}E/\mathrm{d}n = 0. \tag{12}$$

We will introduce the designation $F = E_{\mathrm{v}}/E_{\mathrm{c}}$ and find that the minimum of the interaction energy corresponds to the number of layers in the stack

$$n = (2FM)^{1/2}. \tag{13}$$

Hence, we will find the height of the stack

$$L_c = [(2FM)^{1/2} - 1]d_{002} \tag{14}$$

and the width of the stack

$$L_{a\perp} = 1.5R_{\mathrm{C–C}}[M/(2FM)^{1/2} - 1]. \tag{15}$$

Here, $R_{\mathrm{C–C}}$ is the smallest distance between the atoms in the layer.

From (14) and (15) we will find that

$$L_c/L_{a\perp} = 2d_{002}/3R_{\mathrm{C–C}}\{1 + (2F - 1)/[1 - (2F/M)^{1/2}]\}. \tag{16}$$

As the minimal value of M is no lower that 10, and $2F$ is ca. 0.2 [3], we can neglect the $(2F/M)^{1/2}$ parameter. As a result, we obtain

$$L_c/L_{a\perp} = 4d_{002}F/3R_{\mathrm{C–C}}. \tag{17}$$

Thus, L_c and $L_{a\perp}$ indeed should correlate by the dependence determining the equilibrium faceting of the CF crystallites. This dependence can be considered as linear to the first approximation (under assumption that d_{002}, $R_{\mathrm{C–C}}$, and F are constant). Let us estimate the equilibrium ratio of the dimensions of the crystalites in the approximation that the structure of the fiber corresponds to that in graphite: $F = 0.1$ [3], $d_{002} = 0.3354$ nm, and $R_{\mathrm{C–C}} = 0.1422$ nm. In this case, $L_c = 0.314L_{a\perp}$. Even if we take $d_{002} = 0.346$ nm and $R_{\mathrm{C–C}} = 0.141$ nm, as observed experimentally for the fibers studied, in this case also the correlation equation obtained, $L_c = 0.327L_{a\perp}$, is inconsistent with equation (3). Therefore, the shape of the crystallites in the CF substantially differs from the equilibrium and energetically preferred shape. The transverse dimensions of the carbon layers $L_{a\perp}$ prove to be underestimated, and the height of the stacks of layers L_c, overestimated, as seen from equation (2) as well. All this suggests a low intensity of mass transfer of carbon atoms. As a result, the shape of the crystallites cannot take the equilibrium faceting. As growth of $L_{a\perp}$ is hindered, the corresponding change in the interplanar spacings d_{002} and d_{110} toward values characteristic for graphite becomes impossible (Figs. 4, 5) [8]. As a result, the structure of the fiber remains different from that of graphite even after heat treatment at above 3000°C, while in other carbon materials (e.g., in oil cokes) polycrystalline graphite is formed at temperatures of 1700–2500°C [3, 9, 10].

CONCLUSIONS

(1) In the polyacrylonitrile-based carbon fiber subjected to heat treatment at 3000–3100°C the interplanar spacings d_{002} and d_{110} are functions of the CSR dimension L_a.

(2) The L_c-to-$L_{a\perp}$ ratio (1.06 : 1) differs from the equilibrium and energetically preferred value (1 : 3.18), which indicates a low intensity of mass transfer in carbon fibers.

(3) Small dimension of the crystallites $L_{a\perp}$ is responsible for the difference in the interplanar spacings from the analogous characteristic of graphite and, consequently, for poor graphitization ability of carbon fiber.

REFERENCES

1. Varshavskii, V.Ya., *Khim. Volokna*, 1994, no. 3, pp. 9–16.
2. *Handbook of Composites*, Lubin, G., Ed., New York: Van Nostrand Reinhold, 1982, vol. 1.
3. Shulepov, S.V., *Fizika uglegrafitovykh materialov* (Physics of Carbon–Graphite Materials), Moscow: Metallurgiya, 1990.
4. Iwashita, N. and Inagaki, M., *Carbon*, 1993, vol. 28, no. 7, pp. 1107–1113.

5. Belenkov, E.A., Tyumentsev, V.A., Podkopaev, S.A., *et al.*, *Zh. Prikl. Khim.*, 1998, vol. 71, no. 8, pp. 1379–1383.
6. Umanskii, Ya.S., Skakov, Yu.A., Ivanov, A.N., and Rastorguev, L.N., *Kristallografiya, rentgenografiya i elektronnaya mikroskopiya* (Crystallography, X-ray Diffraction Analysis, and Electron Microscopy), Moscow: Metallurgiya, 1982.
7. Belenkov, E.A., Tyumentsev, V.A., and Fotiev, A.A., *Izv. Ross. Akad. Nauk, Neorg. Mater.*, 1995, vol. 31, no. 5, pp. 651–654.
8. Belenkov, E.A., *Vestn. Chelyabinsk. Univ., Fizika*, 1998, no. 1, pp. 42–53.
9. Tyumentsev, V.A., Belenkov, E.A., Shveikin, G.P., and Podkopaev, S.A., *Carbon*, 1998, vol. 36, no. 7–8, pp. 845–853.
10. Tyumentsev, V.A., Belenkov, E.A., Saunina, S.I., *et al.*, *Izv. Ross. Akad. Nauk*, *Neorg. Mater.*, 1998, vol. 34, no. 4, pp. 418–423.