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The X-ray diffraction study of three-dimensional disordered network of nanographites: experiment and theory

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Abstract

The average sizes of nanographites (the structure units of activated carbon fibers) have been determined by fitting experimental X-ray diffraction profile by theoretical curves, calculated using Warren-Bodenstein equations. The structure parameters of nanographites obtained by this way are different from ones determined by standard Scherrer equation. The result indicates that the shape factor of the Scherrer equation for the considered ensemble of nanographites differs from generally accepted value.

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1. Introduction

The number of studies in physics, chemistry and technology of nanosystems is constantly increasing. One of the topical problems in nanotechnology still remains acquirement of information on structure parameters of nanoscale particles. The direct-imaging techniques (such as TEM) or X-ray powder diffraction are primarily used for solving this problem. A wide class of nanoscale systems, which is of interest to both fundamental and applied science, is formed by activated carbon materials including activated carbon fibers (ACFs).

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* Corresponding author. Tel.: +7-423-268-1329; fax: +7-423-231-1889.
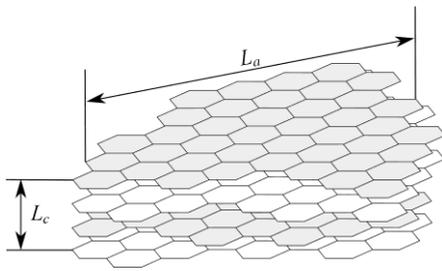*E-mail address*: saenko@ich.dvo.ru.

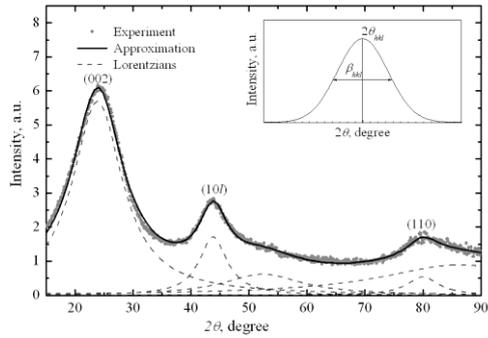Fig. 1. The schematic image of nanographite particle.

Fig. 2. The approximation of corrected experimental profile of X-ray diffraction for ACFs. In the inset the determination of peak parameters are shown.

ACFs may be considered as a three-dimensional disordered network of nanographites with the ordered or turbostratic stacking structure. Fig. 1 shows schematic image of the graphite nanoparticle and its sizes: in the basal plane L_a and perpendicular to the basal plane L_c.

The conventional way to obtain the average size D_{hkl} of microscopic powder particle in the [hkl] direction is to apply the Scherrer equation:

$$D_{hkl} = \frac{K \lambda}{\beta_{hkl} \cos(\theta_{hkl})},$$

(1)

where h, k, l are Miller indices, K – the shape factor, λ – the wavelength of the diffraction beam, $2\theta_{hkl}$ and β_{hkl} – the position and the full width at half maximum of the (hkl) line, respectively. The values of the shape factor K for different (hkl) peaks were estimated to be 1.84 for L_a from position and FWHM of (hk) peaks and 0.9 for L_c from position and FWHM of (00l) peaks [1]. However, it was relatively recently shown [2] that K value is not a constant; it depends on the graphite domain size. This dependence becomes particularly apparent for the graphite domains of nanometer size. The foregoing indicates the importance of elaboration of the procedure for finding the true sizes of carbon nanoparticles from the X-ray powder diffraction data taking into account mentioned above K value dependence.

2. Results and discussion

The typical experimental X-ray diffraction profile (corrected by atomic form factor, absorption factor and Lorentz-polarization factor) of commercial polyacrylonitrile based ACFs is presented in Fig. 2. A very good agreement with experimental data has been obtained by approximation of the line shape by five Lorentzian curves. Using values β and 2θ for (002) peak and (10l) peaks (see the inset of Fig. 2), and also corresponding values of the shape factor K from [1], it is easy to determine values L_a = 2.56 nm and L_c = 0.74 nm by equation (1). The interlayer distance 0.37 nm was obtained by Bragg's law using 2θ value of (002) peak. Thereby the average number of graphene layers in ACFs domains was estimated to be 3.

Then the analysis of the diffraction profile of the ACFs was performed in terms close to procedure of the X-ray diffraction profile simulation proposed by Fujimoto for powder of nanoscale graphite particles [2]. The coherent scattering intensity of system consisting of M parallel layers with N atoms in each layer

can be expressed by

$$I_{coh}(s) = I_{Intra}(s) + I_{Inter}(s).$$

The terms $I_{Intra}(s)$ and $I_{Inter}(s)$ give inlayer and interlayer interference, correspondingly. For powder of nanoscale graphite particles with turbostratic stacking structure Warren and Bodenstein have obtained following equations [3]:

$$I_{Intra}(s) = f^2 \left(\frac{1}{N} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{\sin(2\pi s\, r_{ij})}{2\pi s\, r_{ij}} \right), \quad I_{Inter}(s) = f^2 \left(\frac{2}{N} \sum_{p=1}^{M-1} (1 - \frac{p}{M}) i(p) \right),$$

$$i(p) = \frac{2N}{\pi A_c s} \int_{p d_{002}}^{r_m} \left(\arccos(u) - u\sqrt{1-u^2} \right) \sin(2\pi s\, r) dr, \quad r_m = \sqrt{L_a^2 + (p d_{002})^2}, \quad u = \frac{\sqrt{r^2 - (p d_{002})^2}}{L_a},$$

where $s = 2\sin\theta / \lambda$, r_{ij} is the distance between two atoms, i and j, the value f^2 is the atomic form factor multiplied by Debye-Waller factor, A_c is the area of a carbon layer and d_{002} is the interlayer distance. In order to calculate the term $I_{Intra}(s)$, i.e. to obtain all values r_{ij}, the benzene-coronene model of carbon layer plane was applied [4]. The basal plane size L_a was calculated using Belenkov's equation [5].

In the real sample there is a size distribution of particles. Hence, the total scattering intensity from the experimental sample can be expressed by the sum of the theoretical scattering intensities from q nanographites with different L_a and L_c [4]:

$$I(s) = G(s) \sum_{i=1}^{q} w_i \left(I_{coh}(s) + I_{inc}(s) \right)_i + v(s),$$

(2)

where I_{inc} is the incoherent scattering intensity in Hajdu's approximation [6], w_i is the intensity scale factor for particle i, $v(s)$ is the difference between the fit and the observed data, the factor $G(s)$ is the product of absorption factor and Lorentz-polarization factor. A least-square refinement was performed to minimize the sum of $v(s)^2$ over all s by adjusting values w_i [4].

The experimental X-ray diffraction profiles of ACFs have been approximated using equation (2) for a number of interlayer distances: from 0.335 nm (interlayer distance in macroscopic ordered graphite) to 0.405 nm (apparent interlayer distance in nanographites of ACFs). For a given d_{002} value the nanographite ensemble was constructed from the particles characterized by variation of the basal plane size L_a and the number of layers M. The limits of parameter variations have been established using the conventional X-ray diffraction data analysis as follows: $0.23 \le L_a \le 5.1$ nm and $1 \le M \le 5$. According to this procedure, the best approximation was achieved with $d_{002} = 0.345$ nm (Fig. 3) which corresponds to the average values $L_a = 2.67$ nm and $L_c = 0.53$ nm.

As previously mentioned, the value of shape factor depends on domain size and hence the standard value of shape factor can not be used for powder with distribution of nanoparticles. Firstly, there is a difference between average shape factor value in considered ensemble of graphite particles and value of corresponding parameter traditionally used. Secondly, (002) peak angle position in X-ray diffraction profile shifts with changing the number of layers (at fixed distance between them) in the graphite domains. Therefore, the values of the structural parameters of nanographites, calculated by Scherrer
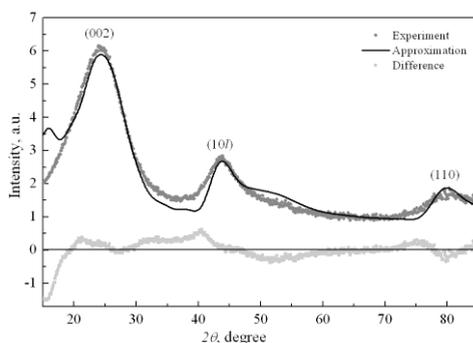
Fig. 3. The approximation of experimental X-ray diffraction profile for ACFs by equation (2).

equation are different from ones obtained by procedure used in our study. The conventional analysis of X-ray diffraction profile provides estimation of upper bounds for L_c and d_{002}; the difference of the basal plain size L_a is an object of further study.

3. Conclusion

The X-ray diffraction profile simulation procedure for the powder of turbostraticly stacked nanographite particles has been modified by Belenkov's equation for basal plane size. Using Warren-Bodenstein equations the procedure for determination of the nanographite particle average sizes with the interlayer distance variation was developed to obtain more precise results from X-ray diffraction data than those from the Scherrer equation. The possible reasons of difference between structural parameters calculated by conventional way and new one have been suggested. The verification of X-ray diffraction profile analysis proposed in this work by the powder of calibrated nanographites and comparison with the Scherrer equation results is an aim of further investigations.

Acknowledgements

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