Journal of Non-Crystalline Solids 386 (2014) 1–7

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Quantitative analysis of the local atomic structure in disordered carbon☆

A.D. Rud *, I.M. Kiryan

G.V. Kurdyumov Institute for Metal Physics of NASU, 36 Academician Vernadsky blvd., 03680 Kiev-142, Ukraine

ARTICLE INFO

Article history:
Received 12 September 2013
Received in revised form 1 November 2013
Available online xxxx

Keywords:
Amorphous carbon;
Reverse Monte Carlo modeling;
Voronoi polyhedra;
Medium-range order;
Local atomic structure

ABSTRACT

The quantitative characteristics of a short- and a medium-range order in amorphous carbon synthesized by electric discharge treatment of hydrocarbons are determined by a combined application of X-ray diffraction analysis, Reverse Monte Carlo modeling and Voronoi diagram method. The obtained characteristics exhibit a graphite- or a mixed graphite–diamond-like type of short-range order and, at the same time, a large portion of carbon atoms within chemical bond lengths is combined into 3-fold rings of the tetrahedral structures. Statistical analysis of Voronoi polyhedra has revealed a wide distribution of their topological and metric characteristics that are inherited by disordered materials with predominated 5-fold faces which are typical for amorphous structures. The regular configuration polyhedra (clusters) are virtually absent in the synthesized carbon nanomaterials.

1. Introduction

The attention to carbon has been focused for a long time owing to its unique properties connected to the features of its electronic and atomic structures [1–3]. It is known that carbon exists in various allotropic modifications. Under the classification scheme of Heimann and coworkers [4], the basic forms of carbon allotropes are diamond, graphite and carbine with integer degree of bond hybridization sp^3, sp^2 and sp, respectively. The new spatial forms of carbon (fullerenes and nanotubes) have non-integer degree of bond hybridization sp^{2+x} $(x < 1)$. A center of the scheme is occupied by a very big class of disordered carbon materials designated as transitional carbon which consists of randomly arranged carbon atoms in various hybridization states, i.e. amorphous carbon, soot, vitreous carbon, diamond-like carbon, carbon spheres, cokes, coals etc. [4]. In spite of the series of works devoted to the investigation of the structural state of disordered carbon (DC), there are no so many studies in which local atomic arrangements in a DC structure were analyzed [5–8]. In this regard, the paper of professor Ilinskii with coworkers should be noted [9]. This paper describes a short-range order in a structure of different type of coals. A list of atomic coordinates obtained on the basis of experimental data is necessary for this analysis [10]. Reverse Monte Carlo (RMC) method based on the procedure proposed by Metropolis [11] is widely and successfully used to solve similar structural problems [12,13]. The list of atomic coordinates allows applying of Voronoi diagram method for analysis of disordered structures [14–16].

A list of atomic coordinates using RMC modeling in disordered carbon nanomaterials (CNM) was obtained for the determination of the local atomic order by Voronoi–Delauney method without detailed quantitative analysis [17]. The aim of this work is to find out the local structure of disordered carbon with the quantitative characteristics of the topological order in its atomic arrangement.

2. Experimental details and modeling procedure

The studied CNM are synthesized in the Institute for Pulse Research and Engineering of National Academy of Science of Ukraine by high-frequency electrical discharge treatment of propane–butane mixture in the ratio of 0.5:0.5 (CNM-1) and acetylene (CNM-2) [18,19]. X-ray diffraction studies are carried out on a standard diffractometer with monochromated MoK_α radiation in the Debye-Scherrer geometry. The experimental curves of structure factors (SF) and the pair radial distribution functions (RDF) are calculated by the procedure described in [9]. Spectrally pure graphite (99.99%) and detonation nanodiamonds (99.9%) have been used as the standard samples. Transmission electron microscopy (TEM) study was performed using the high-resolution microscope JEOL JEM-2100F.

The simulated atomic configurations are reconstructed from experimental curves of the structure factors by RMC method using RMCPOW v.2.4 software (for crystalline samples of graphite and nanodiamond) and RMCA v.3.1 one (for disordered CNM) [20]. The configurations consist of 4096 and 4000 carbon atoms for diamond and graphite, respectively. For disordered CNM, it consists of 10,000 atoms located in a cubic box with a half-length of edge $L = 2.221$ nm with periodic boundary conditions. At the first stage of the simulation, carbon atoms are randomly placed in a model box. To eliminate the inevitable overlap of atoms, the minimal value of their approach are fixed in the place of intersection of the left slope of the first RDF peak with the x-axis: $r_{(C-C)} = 0.12$ nm. At

---

☆ Dedicated to the memory of Prof. Ilinskii.

* Corresponding author. Tel.: +380 44 4243210; fax: +380 44 4242561.
E-mail address: rud@imp.kiev.ua (A.D. Rud).

0022-3093/$ – see front matter © 2013 Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.jnoncrysol.2013.11.010

the second stage, a pair radial distribution function $g^c(r)$ of the atoms and a structure factor $A^c(q)$ were calculated for the generated configurations according to the Eqs. (1) and (2), respectively [12]:

$$g^c(r) = \frac{n^c(r)}{4\pi r^2 \Delta r \rho_0}, \tag{1}$$

where $n^c(r)$ is a number of atoms at a distance between r and r + Δr from a central atom, ρ_0 is an atomic number density,

$$A^C(q) - 1 = \frac{4\pi\rho_0}{q} \int_0^{R_{max}} r\left(g^c(r) - 1\right) \sin(qr) dr, \tag{2}$$

where R_{max} is a distance to which is calculated $g^c(r)$, $q = \frac{4\pi \sin(\theta)}{\lambda}$ is the absolute value of the diffraction vector, 2θ is the scattering angle.

A difference between the model $A^C(q_i)$ and the experimental $A^E(q_i)$ structural factors has been calculated for each iteration:

$$\chi^2 = \sum_{i=1}^{K} \frac{\left[A^C(q_i) - A^E(q_i)\right]^2}{\sigma^2(q_i)}, \tag{3}$$

where $\sigma^2(q_i)$ is an experimental error.

A random displacement of one atom of the modeling system is performed during the next step of the calculations. The pair radial distribution function $g^c(r)$, structure factor $A^c(q)$, and coefficient of convergence χ^2 are calculated for the new atomic configuration. RMC process is iterated at decreasing χ^2.

The local characteristics of the atomic arrangements are calculated for generated ensembles of atomic configurations of the synthesized CNM, graphite and diamond. For this purpose, the 1-st coordination number (N_1) [21] and the bond angle value (Θ_{ijk}) [22] have been used according to Eqs. (4) and (5):

$$N_1 = \int_0^{R_{min}} dr 4\pi r^2 \rho(r) g(r), \tag{4}$$

$$\Theta_{ijk} = \cos^{-1}\left(\frac{r_{ij}^2 + r_{ik}^2 + r_{jk}^2}{2 r_{ij} r_{ik}}\right), \tag{5}$$

where R_{min} is the first minimum on a $g^c(r)$, r_{ij}, r_{ik} and r_{jk} are the bond lengths between the nearest atoms ij, ik and jk, respectively.

Taking into account $\Theta_{ijk,}$ the bond angle distributions P(Θ) were calculated by the following equation [22]:

$$P(\Theta) = \frac{1}{\sum_{i=1}^{N} N_i(N_i - 1)} \sum_{i=1}^{N} \sum_{j=1}^{N_i} \sum_{k=j+1}^{N_i} \delta\left(\Theta - \Theta_{ijk}\right), \tag{6}$$

where N is the total number of atoms, N_i is the number of the neighbors for the i-th atom.

Quantitative characterization of the medium-range order was conducted according to S. King criterion [23] using program RINGS included into the RMCA software package [20]. It allows obtaining the typical atomic configurations for disorder materials in the form of closed rings in the ensemble of atoms. The rings are formed due to the arrangement of atoms in polygons (in the general case of irregular shape) with the limited maximal length of the chemical bond. A ring size *n* of the network is determined by a number of angles in a closed polygon [24]. Statistical and geometrical analyses of the local atomic arrangements in the synthesized CNM are conducted by application of Voronoi tesselation using the software package developed by V. Voloshin [25,26].

3. Results and discussion

The studies have shown that the materials synthesized by electric discharge treatment for acetylene and the mixture of propane–butane are typical amorphous carbon (AC). It is confirmed by the presence of a broad asymmetric halo in the X-ray diagrams and electron microdiffraction patterns (Fig. 1a,b). TEM displays that the CNM possesses a globular structure with the size of individual particles of 15–20 nm characterized by the disordered structure which are typical for onion-like and turbostratic amorphous carbons (Fig. 1 c and d, respectively). The synthesized CNM does not contain impurities practically according to the chemical analysis.

3.1. Reverse Monte Carlo modeling

Based on the experimental structure factors, configurations of atoms are generated by RMC procedure for the synthesized CNM as well as graphite and nanodiamond (ND). The agreement of the experimental and simulated structure factors indicates adequacy of the generated atomic configurations to the real structure of the studied objects (Fig. 2). For the simulated atomic configurations of amorphous carbon, the local characteristics (a coordination number in the first coordination sphere (N_1) and a bond angle (Θ)) are calculated by Eqs. (4) and (5), respectively. Table 1 shows that the experimentally determined values of the radii of the 1st coordination sphere r_1, coordination numbers N_1, bond angles Θ for graphite and ND agree prety well with the literary data [27]. So, the first coordination numbers N_1 for graphite and nanodiamonds equal to 3.0 and 3.89, respectively. N_1 values of different samples of amorphous carbon are in the range of 3.02–3.56. An increase of the coordination number indicates that the synthesized materials possess more close-packed structure than graphite [28].

Fig. 3 shows a bond angle distribution for synthesized amorphous carbon and standard carbon samples. In the case of AC, there is a broad intensive peak in the region of ~60° which is absent in the bond angles distribution calculated for graphite and ND. From the crystal–chemical point of view, this fact can be interpreted as breaking the six-membered graphene layers and formation of a randomly arranged close-packed structure. The less intensive and very broad maximum which occupies the intermediate position between the peaks of graphite (120°) and ND (109°) is also presented on the bond angle distribution of CNM-1 and CNM-2 samples what indicates a significant disordered structure of the material.

According to the literature [29–32], the structure features of disordered materials can be more correctly characterized by the medium-range order which extends not only to the first coordination sphere as in the short-range order approach, but also it follows to the coordination spheres with the size up to 1–2 nm. The statistical analysis of *n*-fold rings has shown that the ring size distribution (Fig. 4) is in a good agreement with the bond angle distribution for the studied carbon materials (Fig. 3). It allows explaining the formation of the fragments of the curved graphene planes from the different *n*-fold rings with carbon atoms in their vertex. So, in the cases of graphite and diamond (Fig. 4), 6-fold rings dominate. The interior angle for regular hexagon equals 120°. It is seen from Fig. 3 and Table 1 that the value of a valence bond angle for graphite is 120° which indicates the formation of graphene planes from the ideal 6-fold rings. However, the peak for ND is positioned at 109° that corresponds to the diamond ring.

At the same time, the three-fold rings dominate in the structure of amorphous carbon (Fig. 4) that explains the presence of the intensive peak in the region of 60° at Fig. 3. The four-, five- and ten-fold rings are presented in a very small amount. Moreover, they have a distorted shape that is due to the width and asymmetry of the second peak at ~114° in the bond angle distributions (Fig. 3). The dominance of 3-fold rings indicates the presence of a randomly close-packed structure in the synthesized amorphous carbon that agrees with