Studying Ultradisperse Diamond Structure within Explosively Synthesized Samples via X-Ray Techniques

M D Sharkov¹, M E Boiko¹, S N Ivashevskaya² and N S Belyakova³

¹Ioffe Physico-Technical Institute of the RAS, 26 Politekhnicheskaya Ul., St. Petersburg, Russian Federation
²Geology Institute, the Karelian Research Center of the RAS, 11 Pushkinskaya Ul., Petrozavodsk, Russian Federation
³St. Petersburg Polytechnical State University, 29 Politekhnicheskaya Ul., St. Petersburg, Russian Federation

E-mail: mischar@mail.ioffe.ru

Abstract. XRD (X-Ray Diffraction) and SAXS (Small-Angle X-Ray Scattering) data have been measured for a pair of samples produced with the help of explosives. XRD peaks have shown the both samples to contain crystal diamond components as well as graphite ones. Basing on SAXS analysis, possible presence of grains with radii up to 30–50 nm within all the samples has been shown. Structure components with fractal dimension between 1 and 2 in the sample have been detected, this fact being in agreement with the assumption of diamond grain coating similarity to onion shells. In order to broad rocking curves analysis, the standard SAXS treatment technique has been complemented by a Fourier filtering procedure. For the sample #1, rocking curve components corresponding to individual interplanar distances with magnitudes from 5 nm up to 15 nm have been separated. A hypothesis relating these values to the distances between concentric onion-like shells of diamond grains has been formulated.

1. Introduction

Ultradisperse diamonds (UDD), or diamond nanoparticles, belong to the set of the most frequently synthesized modern materials. Such strong interest is due to the fact that they have a series of special features, i.e. high adsorption capacity, high thermal conductivity, hydrophoby, large specific surface. These properties provide multiple prospects of UDD applicability.

The spatial size magnitude of a stable diamond nanoparticle is situated within a wide range of values, from 5 to 50 nm typically. The nanoparticle can be described as a diamond core surrounded by the shell consisting of two phases. These are, namely, the diamond one (constituted by sp³-hybridized carbon atoms) and the amorphous graphite phase with carbon atoms in the sp² state [1]. According to published data, UDD particle shells differ in the both chemical composition and thickness [2]. The images of individual UDD clusters obtained by the method of transmission electron microscopy (TEM) showed the nanoparticles to have a well-faceted polyhedral shape. Digital modeling stated this polyhedral shape to influence the surface of small-size particles [3]. Diamond nanoparticles tend to form primary (up to 100 nm) and secondary (more than 100 nm) aggregations with fractal structure.
Within the number of materials containing big quantities of UDD there is the primary product of diamond detonation synthesis (the procedure of obtaining nanodiamonds using explosives). This primary product is represented by a black powder consisting of 30–60 per cent of UDD, 40–60 per cent of non-diamond carbon, and impurities containing metals (15% or less). Non-diamond carbon can include ultradisperse graphite, amorphous carbon, and also unstable carbon structures like carbines [4]. Presence of different carbon-based substances within the primary diamond detonation synthesis product confines its usefulness in chemically active media and compositions and, besides, results in enhanced adsorption of non-polarized compounds as well as low sensitivity to polarized and ionic ones. Therefore, the substance produced by diamond detonation synthesis is subject to diverse purification procedures, particularly, ones based on thermal treatment [5].

One of main tasks in studying finely grained materials (similar to UDD produced by detonation synthesis) is their domain structure investigation. A special role is played by the techniques that do not destroy the analyzed sample. Within the number of such methods there is the technique of small-angle x-ray scattering (SAXS).

SAXS is usually applied to tasks of determining spatial sizes for clusters, crystallites, powder and polycrystalline grains, layer thicknesses and superlattice periods, all these values being able to have order of magnitude from nanometers to hundreds of nanometers. The method of SAXS allows one to solve a triple problem constituted by defining sizes of large sample structure homogeneities (grains and pores), determining geometrical properties of the sample atomic matrix (so-called fractal dimension), and estimating lattice parameters for superstructures presented within the sample [6].

2. Experiments

The measurements have been performed for two samples of UDD obtained by detonation synthesis and received from the company JSC Sinta (Minsk, Belarus). The sample denoted #2 hereafter was subject to heat treatment unlikely another sample (#1). The both ones have been characterized by a set of physical and chemical techniques: powder x-ray diffraction (Thermo Scientific ARL X’TRA Powder X-ray Diffraction System, $\lambda_{Cu} = 1.54$ Å), scanning electron microscopy (the microscope VEGA II LSH, TESCAN Ltd., with a module for microprobe analysis), mass-spectrometry (the mass-spectrometer with inductively coupled plasma ICP-MS Xseries2, ThermoFisher Scientific). SAXS data have been obtained within the frames of several sequences of experiments at the laboratory set DRON-8 of the company Bourevestnik (St. Petersburg, Russia) at the $K_{\alpha 1}$ Cu beam wavelength.

The standard procedure of SAXS analysis [6] includes data treatment in three different data ranges. The angular scale is transformed initially into the scale of wave vector magnitudes $q = 4\pi \sin \theta/\lambda$ (with $\theta$ being one half of the scattering angle). In the vicinity of the incident beam direction the SAXS curve is broadened; the FWHM (full width at half maximum) of this SAXS peak allows one to estimate homogeneity sizes in the sample. At the slopes of the small-angle peak the SAXS curve can be described as a power function explained by the Porod’s model [7]. The power magnitude is related to the so-called fractal dimension of the sample structure indicating the atomic matrix geometry. For 3D dense dispersed media, the power magnitude is to be 4 (the Porod law), whereas its value for a low-dimensional matrix is close to the dimension itself. Finally, when the sample contains some layering or superlattice the wide interplanar distances will be represented at the SAXS curve as Bragg peaks whose positions will then obey to the Bragg law $qd = 2\pi n$ ($d$ is an interplanar distance here, and $n$ is an integer).

3. Results and discussion

The both samples consist generally of carbon (about 80%). Analyses of micro-impurities in the samples showed them to contain enlarged quantity of copper. There were also detected unessential fractions of Zn, Pb, Ti, Cr, Ni, Mn, La, Fe, P, Mg, Al, Si, Ca, Na, K, Cl, S. Figure 1 represents the powder XRD data for both the samples #1 and #2.

On processing these data the two samples appeared to be constituted by nano-diamond (Num. 00-058-1638 in the ICDD database) and graphite (Num. 00-041-4187 in the ICDD database). A series of
intensive peaks (2\(\theta\)/deg: 43.7, 75.5, 91.4, 120.5, 141.1) corresponding to diamond lattice reflections of Cu K\(\alpha\) photons can be observed at figure 1, as well as a separate peak at 2\(\theta\)=26.6\(^{\circ}\) which must correspond to the graphite peak at 26.4\(^{\circ}\). Also the XRD data of the both samples contain a set of five intensive peaks representing the copper spinel reflections (2\(\theta\)/deg: 30.2; 35.5; 54; 56.5; 62), this fact being completely consistent with the results on the samples chemical composition. It can also be concluded from the data at figure 1 that the sample #1 thermal treatment did not give rise to substantial decay of non-diamond carbon forms. The sizes of coherent scattering regions calculated with the help of the Scherrer model (from the FWHM of the most intensive peak, for the (111) reflection here) happened to be about 4 nm. These results derived from modeling are consistent with the data obtained from direct SAXS measurements.

**Figure 1.** The XRD signals for the samples #1 and #2.

SAXS data analysis has led to following results. Different specimens have appeared to contain grains with spatial sizes up to 30–50 nm. Particularly, the sample #1 SAXS data (figure 2a) treatment has demonstrated the central peak to correspond to particles with the size of about 30 nm. The meaning of 50 nm has been obtained on processing the specimen #1 SAXS data recorded after the sample had been deformed (figure 2b). In turn, SAXS data for the sample #2 have resulted in the grain radius estimation of 40 nm approximately (figure 3).

Low-dimensional structural components have also been detected within the samples. This fact is consistent with the hypothesis of onion-like UDD grain coverage. Particularly, the deformed sample #1 SAXS data have turned out to contain fragments with power dependence whose power values are close to 1.5 and 1.8. Besides, the sample #2 SAXS function has been shown to include parts with power decrement characterized by power magnitudes of about 1.8 and 4. The value 4 is typical of 3D dense grained substance (that is the Porod law [7]) whereas power exponents about 2 must describe a 2D component presented within the sample under investigation.

For the sake of clarifying the specimen #1 SAXS data it was suggested to expand the standard SAXS processing technique by a procedure of Bragg peak Fourier filtering. This procedure consists of several steps. The data subject to filtering are Fourier transformed initially, then the image is divided by a typical Fourier transformed signal shape, and this result is treated using the inverse Fourier transform. Such processing has given rise to splitting the broad Bragg peak into a variety of separate contributions. Each of them is to represent an individual interplanar distance in the sample matrix. The distance values (situated in the current case within the interval from 5 nm to 15 nm) may describe differences between particular pairs of concentric onion-like shells.

SAXS analysis has thus yielded estimations for UDD grain sizes in two UDD samples produced via detonation synthesis and confirmed the assumption of onion-like concentric shells of UDD grains.
Figure 2a. Recorded SAXS data for the UDD sample #1 before its deformation.

Figure 2b. Recorded SAXS data for the sample #1 before its deformation.

4. Conclusions
The SAXS data for two UDD samples produced by detonation synthesis have been obtained and treated. SAXS data processing for two DC samples has given appreciations for nanodiamond spatial sizes about 40–50 nm. The model of UDD grains surrounded by onion-like shells has been confirmed, with double Fourier transformation being the first time used for this purpose.
Figure 3. Measured SAXS data for the sample #2 (which was earlier subject to heat treatment).

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