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HIGH-PRESSURE REORGANIZATION OF THE FRACTAL PORE STRUCTURE IN DETONATION NANODIAMOND POWDERS

Diamond nanoparticles have significant prospects for technological applications, so their manufacture and subsequent disaggregation are a challenging task. In this paper, the porous structure of aggregates in detonation nanodiamond powders has been analyzed using small-angle neutron scattering. The influence of high pressure allowed the contributions to the small-angle scattering from micro- and nano-sized pores to be separated. The type of fractal clusters formed by nanopores was determined. The possibility of a partial mechanical disaggregation of nanodiamond particles at a pressure of 1.5 GPa is confirmed.

K e y w o r d s: detonation nanodiamonds, porosity, fractal clusters, high pressure, small-angle neutron scattering, X-ray diffraction analysis.

1. Introduction

Nowadays, various carbon nanomaterials find a number of important applications [1, 2]. In particular, nanodiamonds combine unique mechanical, thermodynamic, and optical properties of diamonds with the features characteristic of the colloidal size scale and wide possibilities for their surface to be chemically modified [3–5]. Therefore, nanodiamonds are used as an important element in advanced developments of abrasives, anti-corrosion coatings, lubricants, electronics, local drug delivery systems, and so forth.

Among the synthesis methods, the detonation technique aimed at obtaining the nanodiamonds from ex-

plosives without additional carbon sources occupies a special place [3, 6]. This method can be used to produce the required material on the industrial scale. However, the powders obtained in such a way are characterized by the multilevel aggregation, which is realized through covalent bonds as well. The aggregation core on the submicron scale is composed of the so-called agglutinates, which contain nanodiamond particles sintered together via non-diamond components. The latter are mainly amorphous carbon and other carbon-containing chemical groups, which are the explosion by-products [7]. There are several disaggregation methods based on the dispersion in polar liquids [3, 8]. However, the research of detonation nanodiamond powders is continued in order to optimize the existing methods and to develop new
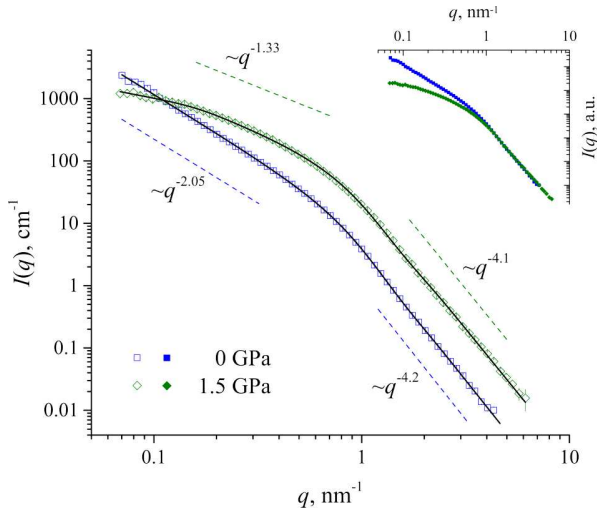
Fig. 1. Experimental curves of small-angle neutron scattering (symbols) for detonation nanodiamond powder before (0 GPa) and after (1.5 GPa) the pressure application, and their approximations using form factor (1) (solid curves). The dashed lines mark the intervals with the power-law scattering dependence. The data normalized at large q's are shown in the inset

approaches to the production of non-aggregated diamond nanoparticles for practical applications.

In this work, the porous structure in detonation nanodiamond powders has been analyzed by studying the influence of a high pressure on the pore reorganization. This approach allows the micro- and nanoscopic aspects of the structure to be separated. Small-angle neutron scattering (SANS) is a non-invasive method with high permeability [6, 9, 10]. It allowed us to trace the changes in the agglomeration-porous structure. The fractal concept [11, 12] was applied to describe nanopores in agglutinates, which allowed new unique information about the examined system on a scale of 1–100 nm to be obtained.

2. Materials and Methods

Commercial powder of detonation nanodiamonds of the DND-STP brand (Federal State Unitary Enterprise "Technolog", St.-Petersburg, Russian Federation) was studied. The maximum amount of non-combustible residues was less than 1.2%. A pressure of 1.5 GPa (a hydraulic press GHP-10, GIGANT, Chengdu, China) was applied for 1 min. As a result, the pressed sample acquired the form of a cylinder 8 mm in diameter and 1.5 mm in height.

SANS experiments were performed at room temperature on a time-of-flight diffractometer YuMO lo-

cated at the 4th channel of the pulsed neutron source IBR-2 (Dubna, Russia) [13]. The differential scattering cross-section of thermal neutrons per unit volume of the sample, $I(q)$, was isotropic over the radial angle in the detector plane. It was registered with the help of two 8-ring detectors located at distances of 4.5 and 13 m from the sample. Corrections were made to account for the presence of the fast-neutron background, which was measured separately. The quantity $I(q)$ was calibrated in absolute units, cm^{-1}, using a vanadium standard. The absolute value of the transmitted wave vector, $q = 4\pi \sin(\theta/2)/\lambda$, was calculated knowing the scattering angle θ and the de Broglie wavelength λ of neutrons. The uncompressed powder was measured in a flat Hellma quartz cuvette with an optical path length of 1 mm, whereas the pressed sample was arranged perpendicularly to the neutron beam.

The measurements of the X-ray diffraction in a nanodiamond powder were carried out on an EMPYREAN diffractometer (Malvern PANalytical, Malvern, UK) using Cu-Kα radiation (0.154 nm). The size of crystallites was determined using the Scherrer formula by the (111) line at $k = 0.9$ [14].

3. Results

In the experimental SANS curves depicted in Fig. 1, one can see a manifestation of a two-level structure. The both levels are described by power laws for scattering, so they can be easily traced in the form of linear dependences on the log-log scale. The slopes of both dependences change under the action of a static pressure, but the scattering reacts to such influence more strongly at small q. The magnitude of the power exponent at $q > 1$ nm^{-1} exceeds 4. This fact testifies that the scatterers have a diffuse rather than smooth surface [15]. According to the earlier studies [9, 10], this is a result of the presence of nano-sized pores in the dense structure of diamond agglutinates rather than nanodiamond particles themselves. At the same time, the power exponent values are less than 3 at $q < 1$ nm^{-1}, which testifies to a mass fractal organization of clusters formed by the scatterers. The scattering of this type can be described using the Beaucage unified exponential/power-law scattering form factor [16–18],

$$I(q) = G_1 \exp\left(-\frac{q^2 R_{g1}^2}{3}\right) + B_1 q_1^{-P_1} \exp\left(-\frac{q^2 R_{g2}^2}{3}\right) +$$

$$+ G_2 \exp\left(-\frac{q^2 R_{g2}^2}{3}\right) + B_2 q_2^{-P_2}, \qquad (1)$$

where R_{g1} and R_{g2} are the gyration radii for clusters and constituent particles, respectively; P_1 and P_2 are the power-law exponents; G and B are parameters that are proportional to the neutron contrast and concentration; $q_{1,2} = q[\mathrm{erf}(qR_{g1,2}/\sqrt{6})]^{-3}$; and $\mathrm{erf}(x)$ is the error function. At the mass-fractal level, P_1 coincides with the fractal dimension D. At the level of pore surface, $P_2 = 4 + 2\beta$, where β is the diffusivity parameter describing a certain power-law modulation of the scattering length density at the nanodiamond-pore interface [15]. For a smooth surface, the parameter β equals zero.

One can see that the scattering curve obtained for the unpressed powder of detonation nanodiamonds using the available equipment configuration does not demonstrate the characteristic size of clusters. A plateau, which is typical of the Guinier regime, is not observed, and the power-law of scattering is satisfied up to $q_{\min} \approx 0.07$ nm^{-1}. In this case, when approximating the experimental data, one may omit the first term in Eq. (1) and put $q_1 \to q$. As a result, only the minimum estimate of the size can be obtained in the form $R_{g1} \geq \pi/q_{\min}$.

The pressure-induced changes of the most informative structural parameters are presented in Table. A pronounced effect is observed for the fractal dimension of clusters, D, which diminishes from 2 to 1.3, if the pressure is applied. The structural level of nanopores demonstrates a much weaker response in the form of a reduction in the gyration radius and the diffusivity parameter $\beta = (P_2 - 4)/2$.

Small β-values testify to the presence of the nondiamond component on the surface of detonation nanodiamond particles, which are associated with graphene states [19]. This assumption is confirmed by the data of X-ray diffraction (Fig. 2), which detects a region of crystalline scattering (the coherence volume) that is smaller than the region observed at SANS in suspensions of disaggregated nanodiamond particles [18, 19].

4. Discussion

Let us first consider the small-angle scattering at large q-values, which occurs at the surface of nano-sized pores. The curve profile changes weakly with the application of a high pressure. The inset in Fig. 1
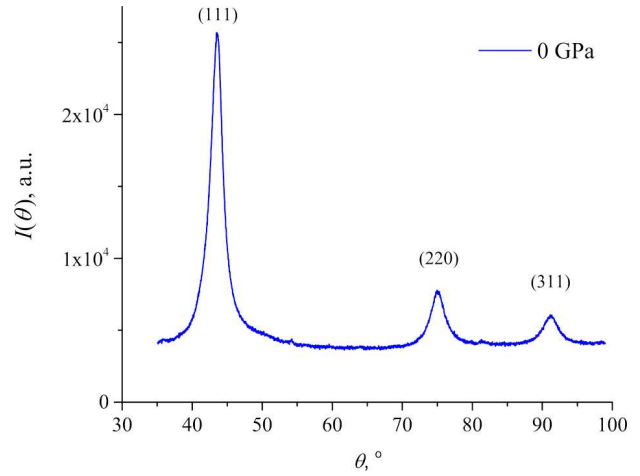

Fig. 2. X-ray diffraction pattern of detonation nanodiamond powder. The corresponding Miller indices are indicated. The crystallite size is 2.7 nm

illustrates the data that confirm the numerical closeness of the structural parameters of the diamond-pore interface at various pressures. Therefore, the difference between the spectra of the compressed and uncompressed powders at the level $q > 1$ nm^{-1} is only determined by the contrast factor, which, in turn, depends on the microporosity. Of course, the size of micropores is beyond the resolution of the SANS method. However, the ratio between the volume fractions of those pores and agglutinates affects the scattering signal in the form of a constant multiplier. Hence, the proportional growth of the scattering curve tail is associated just with the ordinary compression effect. In this case, the parameter B_2 becomes 6 times larger, which points to a corresponding growth in the volume fraction of agglutinates. In other words, the number and the size of micro-sized pores decrease, and the average density of the system increases.

However, it should be noted that if the issue only concerns this effect, then no changes would occur on a scale of 1–100 nm, to which SANS is sensitive. The

**Structural parameters
of detonation nanodiamond powders
according to small-angle neutron scattering**

p, GPa	R_{g1}, nm	R_{g2}, nm	D	β	$B_1(R_{g1})^D/G_1$
0	≥ 45	2.40	2.047	0.095	–
1.5	25.9	2.19	1.326	0.05	2.29

stable internal structure of agglutinates would only be reflected in the proportional growth of the scattering curve in the whole interval of scattering vectors. Nevertheless, experiments demonstrate the opposite for $q < 1$ nm^{-1}. A reduction of the fractal dimension testifies to the pore recombination [9]. The branched porous structure in the agglutinates in the form of fractal clusters becomes less branched. Together with a decrease of the diffusivity parameter β, this fact testifies that the pressure of an order of 1 GPa leads not only to a more compact packing of aggregates on the micronic scale, but to substantial changes in the internal structure of nanodiamond agglutinates.

Besides the collapse of nano-sized pores, the important trend is the interface smoothing due to the elimination of amorphous sp^3-carbon, which is always present in systems of the detonation genesis. Nevertheless, a smooth interface between the phases, which corresponds to $\beta = 0$ ($P_2 = 4$, the Porod law), is not reached even at 1.5 GPa. In other words, the β-values in a vicinity of $\beta = 0.05$ comprise a fundamental characteristic of detonation nanodiamond particles. Those values are associated with the presence of carbon sp^2-states on the nanoparticle surface, which cannot be removed with the help of a mechanical treatment [15, 17, 19]. A reduction in the characteristic size of nanopores, R_{g2}, also testifies to a reorganization under pressure.

An important feature of the current experiment in comparison with previous study [9] consists in that, owing to the extension of the examined q-interval, we managed to detect the size of agglutinates in the pressed powder. Since it turned out smaller than the size estimated for the uncompressed sample, this reduction also evidences their partial destruction already at a pressure of 1.5 GPa.

The parameter of fractal dimension alone cannot completely describe all features in the structural organization of a fractal cluster. In particular, the gyration radii of the clusters, R_{g1}, and their structural units, R_{g2}, determine the size interval, where the fractal properties manifest themselves in the form of a power-law behavior of the density autocorrelation function. In particular, R_{g1} is related to the correlation length ξ, which is a parameter of the cutoff fractal correlation function $f(r, \xi)$. This dependence affects some of the macroscopic physical properties of the systems with fractal clusters. Every cutoff function corresponds to certain physico-chemical condi-

tions for the synthesis of natural fractals [20], which allows their detailed classification to perform. Small-angle scattering of neutrons or X-rays makes it possible to determine the type of $f(r, \xi)$ on the basis of the combined dimensionless parameter $B_1(R_{g1})^D/G_1$ [20–23]. According to the literature data, the parameter value obtained for nanodiamonds corresponds to the model of the first order exponential decay of the density autocorrelation function [24]. Its Fourier transform is a fractal scattering function described by the parameter

$$\frac{B_1(R_{g1})^D}{G_1} = \frac{\sin{(D-1)\pi/2}}{D-1} \left(\frac{D(D+1)}{2}\right)^{D/2}. \quad (2)$$

At $D = 1.326$, Eq. (2) gives a theoretical value of 2.01, which is close to the value obtained experimentally (see Table). In this case, the correlation length is determined by the formula

$$\xi = R_{g1} \left(\frac{2}{D(D+1)}\right)^{1/2}, \quad (3)$$

and equals 20.83 nm.

5. Conclusions

In this research, the structural organization of submicron aggregates of detonation nanodiamonds, agglutinates, has been analyzed. It is shown that the application of a high pressure differently affects micro- and nanoscale porosity. Large pores between agglutinates almost disappear, which is typical of the pressing. At the same time, the branched system of nano-sized pores in agglutinates demonstrates fractal properties. A comprehensive consideration of the pressure effect on the fractal dimension, the diffuseness of the diamond-pore interface, as well as the size of pores and agglutinates, testifies to the motion of crystallites with respect to one another and the partial destruction of agglutinates. The fractal clusters, which were observed in this work, belong to the type of fractals with the cutoff function of fractal correlations in the form of the first-order exponent.

The study of the pressure effect on the nanostructure of ultrafine detonation diamond powders provides important information for the development of protocols for disaggregation and production of separate diamond nanocrystallites.

1. O.A. Shenderova, V.V. Zhirnov, D.W. Brenner. Carbon nanostructures. *Crit. Rev. Solid State Mater. Sci.* **27**, 227 (2002).

2. O.V. Tomchuk, M.V. Avdeev, A.T. Dideikin *et al.* Revealing the structure of composite nanodiamond–graphene oxide aqueous dispersions by small-angle scattering. *Diamond Relat. Mater.* **103**, 107670 (2020).

3. E. Osawa. Monodisperse single nanodiamond particulates. *Pure Appl. Chem.* **80**, 1365 (2008).

4. V.N. Mochalin, O. Shenderova, D. Ho *et al.* The properties and applications of nanodiamonds. *Nat. Nanotechnol.* **7**, 11 (2012).

5. O. Tomchuk, V. Ryukhtin, O. Ivankov *et al.* SANS analysis of aqueous dispersions of Eu- and Gd-grafted nanodiamond particles. *Fuller. Nanotub. Carbon Nanostr.* **28**, 272 (2020).

6. O.V. Tomchuk, L.A. Bulavin, V.L. Aksenov *et al.* Small-angle scattering in structural research of nanodiamond dispersions. In: *Modern Problems of the Physics of Liquid Systems. Selected Reviews from the 8th International Conference "Physics of Liquid Matter: Modern Problems", May 18–22, 2018, Kyiv, Ukraine.* Edited by L.A. Bulavin, L. Xu (Springer, 2019), p. 201.

7. A. Kruger, F. Kataoka, M. Ozawa *et al.* Unusually tight aggregation in detonation nanodiamond: Identification and disintegration. *Carbon* **43**, 1722 (2005).

8. A.T. Dideikin, A.E. Aleksenskii, M.V. Baidakova *et al.* Rehybridization of carbon on facets of detonation diamond nanocrystals and forming hydrosols of individual particles. *Carbon* **122**, 737 (2017).

9. M.V. Avdeev, V.L. Aksenov, L. Rosta. Pressure induced changes in fractal structure of detonation nanodiamond powder by small-angle neutron scattering. *Diamond Relat. Mater.* **16**, 2050 (2007).

10. O.A. Kyzyma, A.V. Tomchuk, M.V. Avdeev *et al.* Structural researches of carbonic fluid nanosystems. *Ukr. J. Phys.* **60**, 835 (2015).

11. B.B. Mandelbrot, *The Fractal Geometry of Nature* (Freeman, 1982).

12. O.V. Tomchuk. The concept of fractals in the structural analysis of nanosystems: A retrospective look and prospects. *Ukr. J. Phys.* **65**, 703 (2020).

13. A.I. Kuklin, A.V. Rogachev, D.V. Soloviov *et al.*, Neutronographic investigations of supramolecular structures on upgraded small-angle spectrometer YuMO. *J. Phys.: Conf. Ser.* **848**, 012010 (2017).

14. P. Scardi, M. Leoni. Diffraction line profiles from polydisperse crystalline systems. *Acta Crystallogr. A* **57**, 604 (2001).

15. O.V. Tomchuk, L.A. Bulavin, V.L. Aksenov *et al.* Small-angle scattering from polydisperse particles with a diffusive surface. *J. Appl. Cryst.* **47**, 642 (2014).

16. G. Beaucage. Approximations leading to a unified exponential/power-law approach to small-angle scattering. *J. Appl. Cryst.* **28**, 717 (1995).

17. M.V. Avdeev, N.N. Rozhkova, V.L. Aksenov *et al.* Aggregate structure in concentrated liquid dispersions of ultrananocrystalline diamond by small-angle neutron scattering. *J. Phys. Chem. C* **113**, 9473 (2009).

18. O.V. Tomchuk, M.V. Avdeev, A.E. Aleksenskii *et al.* Sol–gel transition in nanodiamond aqueous dispersions by small-angle scattering. *J. Phys. Chem. C* **123**, 18028 (2019).

19. M.V. Avdeev, V.L. Aksenov, O.V. Tomchuk *et al.* The spatial diamond–graphite transition in detonation nanodiamond as revealed by small-angle neutron scattering. *J.Phys.: Cond. Matt.* **25**, 445001 (2013).

20. C.M. Sorensen. Light scattering by fractal aggregates: A review. *Aerosol Sci. Technol.* **35**, 648 (2001).

21. O.V. Tomchuk. Some aspects of small-angle scattering by fractal chains. *AIP Conf. Proc.* **2163**, 020006 (2019).

22. O.V. Tomchuk, M.V. Avdeev, L.A. Bulavin. About the size cut-off effect on small-angle scattering by stochastic mass fractals. *J. Surf. Invest.* **14**, S231 (2020).

23. O.V. Tomchuk, M.V. Avdeev, V.L. Aksenov *et al.* Temperature-dependent fractal structure of particle clusters in aqueous ferrofluids by small-angle scattering. *Colloids Surf. A* **613**, 126090 (2021).

24. T. Freltoft, J.K. Kjems, S.K. Sinha. Power-law correlations and finite-size effects in silica particle aggregates studied by small-angle neutron scattering. *Phys. Rev. B* **33**, 269 (1986).

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РЕОРГАНІЗАЦІЯ ФРАКТАЛЬНОЇ
СТРУКТУРИ ПОР У ПОРОШКАХ ДЕТОНАЦІЙНИХ
НАНОАЛМАЗІВ ЗА ВИСОКОГО ТИСКУ

Алмазні наночастинки мають значні перспективи технологічних застосувань, тому їх виготовлення та подальша деагрегація є актуальною задачею. В даній статті за допомогою малокутового розсіяння нейтронів проаналізовано пористу структуру агрегатів у порошках детонаційних наноалмазів. Вплив високого тиску дозволив розділити внески у малокутове розсіяння від мікро- та нанорозмірних пор. Визначено тип фрактальних кластерів, утворених нанопорами. Підтверджено можливість часткової механічної деагрегації наноалмазних частинок за тиску 1,5 ГПа.

К л ю ч о в і с л о в а: детонаційні наноалмази, пористість, фрактальні кластери, високий тиск, малокутове розсіяння нейтронів, рентгеноструктурний аналіз.