The structure of detonation nanodiamond particles

V. A. Plotnikov, S. V. Makarov, D. G. Bogdanov, and A. S. Bogdanov

Citation: AIP Conference Proceedings **1785**, 040045 (2016); doi: 10.1063/1.4967102
View online: http://dx.doi.org/10.1063/1.4967102
View Table of Contents: http://scitation.aip.org/content/aip/proceeding/aipcp/1785?ver=pdfcov
Published by the AIP Publishing

The Structure of Detonation Nanodiamond Particles

Plotnikov V.A.[1, a)], Makarov S.V. [1, a)], Bogdanov D.G. [1, b)] and Bogdanov A.S. [1, a)]

[1]*Altai State University, Barnaul, Altai, Russia.*

[a)]Corresponding author: plotnikov@ phys.asu.ru
[b)] bogdanov.d.g@mail.ru

Abstract. A model of particles of detonation nanodiamonds is discussed. The model is based on the analyses of experimental data obtained from transmission electron microscopy, X-ray diffraction, smallangle X-ray scattering and simultaneous thermal analysis. This model considers the diamond particle as a crystalline diamond nanokernel coated by an impurity shell.

INTRODUCTION

Nanodiamonds obtained by explosion synthesis are now attracting increasing attention of investigators. The particular interest expressed by researchers to nanosized objects stems from the fact that their properties differ significantly from those of bulk materials. The detonation synthesis of nanodiamonds has been performed under nonequilibrium conditions at high pressures and temperatures in the region of the existence of the stable diamond phase [1].

It is believed that each nanodiamond particle is a particle that consists of a single-crystal diamond kernel surrounded by a shell consisting of functional groups [2, 3]. But currently there is no general opinion about the structure of nanocrystals of detonation diamond. Some data say that nanodiamonds have a highly defective structure. In other studies, it was demonstrated that the single-crystal kernel of nanodiamond is free of defects and only the shell of diamond particles is distorted. Also, there is no general model of impurity shell surface of detonation nanodiamond. Thus, the difficulty is the principal obstacle on the way to substantial broadening of their wide application in various areas. The information about the shell structure and properties is important for understanding the processes of interaction of nanodiamond particles both among themselves and with other substances. The widespread use of diamond powders requires continuous improvement of the synthesis procedures, postprocessing techniques, and current control methods. It is impossible without a study of particle structure.

The purpose of this study was to examine the specific features revealed in the structure of the nanokernel and impurity shell particle of detonation nanodiamonds.

SAMPLES AND EXPERIMENTAL TECHNIQUE

The objects of the study were detonation nanodiamonds samples prepared by the standard explosive technique. [1]. All measurements were made on standard powder samples. The detonation nanodiamond particles were susceptible to aggregation with the formation of chain structures, both primary and secondary.

The analysis of the crystal structure of detonation nanodiamonds was obtained from the results of electron microscopy investigations. Microphotographs of the samples were obtained with a JEM-2200FS transmission electron microscope.

The kinetics of thermodesorption measurements was performed on a Luxx 409 derivatograph linked with an Aelos 403 mass spectrometer (both from Netzsch GmbH, Germany). The samples were heated to 900–950 °C in argon at a rate of about 10 °K/min.

Mechanics, Resource and Diagnostics of Materials and Structures (MRDMS-2016)
AIP Conf. Proc. 1785, 040045-1–040045-4; doi: 10.1063/1.4967102
Published by AIP Publishing. 978-0-7354-1447-1/$30.00

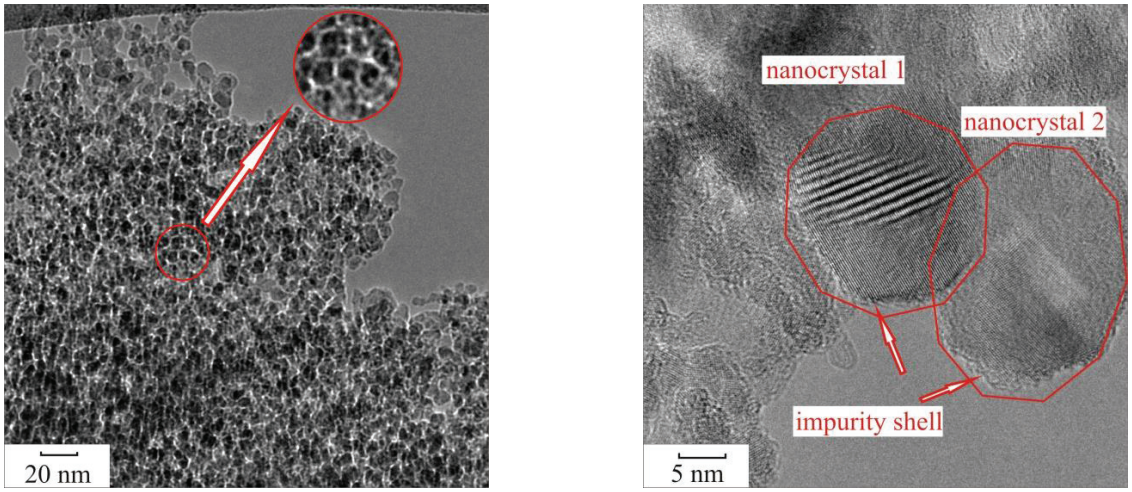
The X-ray diffraction was studied with an XRD-6000 (Shimadzu) diffractometer. Cu radiation (λ=1.54183 Å) was used. The current and the accelerating voltages in the X-ray tube were 60 mA and 40 kV.

The elemental composition of the detonation nanodiamonds was derived from REM (REM Quanta-200-3D equipped with an EDAX analyzer). The instrument permits identification of elements starting with boron.

DESCRIPTION OF THE RESULTS

Figure 1 presents electron microscopy images of nanocrystals of detonation nanodiamonds [4]. The TEM image obtained with a magnification makes it possible to examine a sufficiently large number of nanoparticles (Fig. 1a) and reveals that the diamond nanocrystals have similar sizes. The faces of crystals are clearly visible. The forms of crystals shown in the figure are close to the form of hexagon. The size of most of the crystals is 5 to 10 nm. The analysis of the atomic structure of detonation diamond crystals indicates that the nanoparticles are quite perfect single crystals. At the same time, some single crystals contain crystallographic defects, such as stacking faults and subgrain boundaries with torsion. Figure 1b shows crystals containing structural defects (nanocrystal 1, nanocrystals 2).

It is also clearly seen in the figure that the shell on the surface nanoparticles does not have crystalline structure (Fig. 1b).



(a) (b)

FIGURE 1. a) Electron microscope images of particles of detonation nanodiamonds. b) A high-resolution electron microscope image of the structure of nanocrystals

Thus, the results of the electron microscopy investigations have allowed us to distinguish and refine the structure of the nanokernel and impurity shell of the detonation nanodiamond crystals.

The crystalline lattice parameters of nanokernel were investigated by X-ray diffraction analysis. Figure 2 a presents an X-ray diffraction pattern of detonation nanodiamonds.

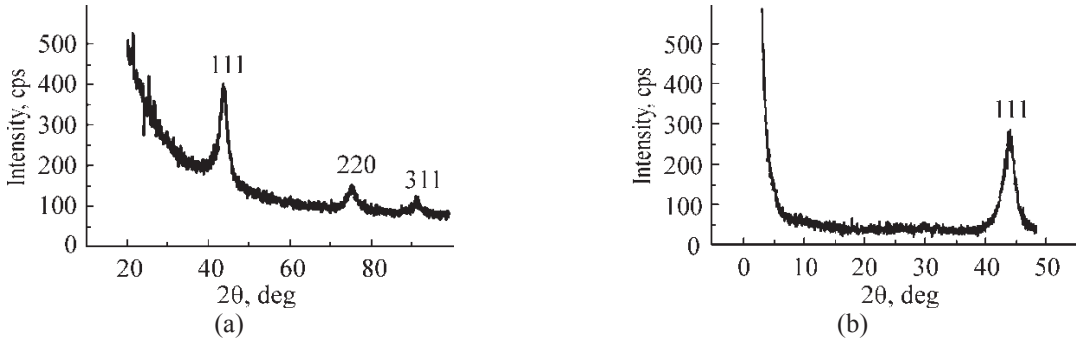


FIGURE 2. a) X-ray diffraction of a detonation nanodiamond sample. b) Diffuse smallangle X-ray scattering from a sample of detonation nanodiamonds

The figure shows that all reflections in the X-ray diffraction patterns of detonation nanodiamonds exhibit anomalously high broadening. Table 1 gives a summary of X-ray diffraction data, including the positions and width of the main reflections for the detonation nanodiamonds [5].

TABLE 1. Physical broadening (β) and positions (2θ) of main reflections in the X-ray diffraction patterns of detonation nanodiamonds and bulk single-crystal diamond

Diamond				Detonation nanodiamonds			
Reflection	**d, Å**	**2θ, deg**	**a, Å**	**2θ, deg**	**d, Å**	**β, deg**	**a, Å**
111	2.060	43.93		43.61	2.07	2.11	
220	1.261	75.34	3.56	75.13	1.26	2.45	3.5
311	1.075	91.53		91.15	1.07	2.78	

As it can be seen from these data, positions (2θ) of main reflections (111), (220), (311) and sizes of the interplanar spacings of the nanocrystal of detonation diamond are considered to coincide with crystal diamond grains. Thus, it is clear that the crystal structure of nanodiamond remains unchanged with decreasing grain size.

Using the data on the broadening (β) and positions (2θ) of the main reflections presented in Table 1, we have calculated the dimensions of coherent scattering domains in these samples. The coherent scattering domain size D was calculated using a simplified formula; according to it, the diffraction line broadening β is determined entirely by the degree of dispersion as follows:

$$D = \frac{\lambda}{\beta \cos \Theta}, \tag{1}$$

where λ is the radiation wavelength. As it follows from these calculations, the size of nanocrystals is small, amounting to about 4.5nm.

Thus, the data obtained from transmission electron microscopy and X-ray diffraction indicate that the nanokernel of detonation diamond have a perfect crystalline structure.

Diffuse smallangle X-ray scattering from a sample of detonation nanodiamonds (Fig. 2b) is formed from molecular complexes without crystalline structure [6]. The size and structure of the molecular complexes are different.

The size of the molecular complexes is determined by the Guinier formulas as

$$I(s) = I_0 \exp(\frac{-s^2 r^2_q}{3}). \tag{2}$$

The calculation gives the following sizes of molecular complexes of detonation nanodiamond: 2.2 nm and 1.2 nm.

The elemental analysis shows that nanodiamonds contain carbon that occurs predominantly in the diamond phase. The other main elemental components are aluminum, silicon, iron, calcium, copper and chromium.

Figure 3 presents typical experimental curves of the temporal variations of the sample weight (TG curves) and enthalpy (DSC curves), measured with detonation nanodiamond powder.

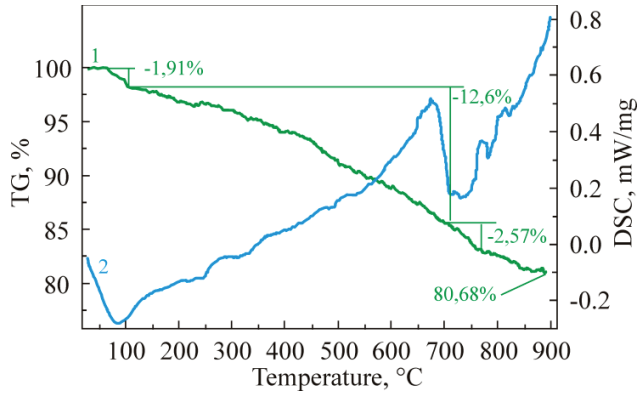


FIGURE 3. Variation of (1) sample weight (TG curves) and (2) enthalpy (DSC curves) measured during the heating of samples of detonation nanodiamond powder

As it can be seen from Figure 3, the heating leads to a significant monotonic decrease (reaching up to ~20 %) in the sample weight. This monotonic change in weight is accompanied by a clearly pronounced nonmonotonic variation of the enthalpy. At temperatures ranging between 530 °C and 700 °C, the DSC curve shows an exothermal effect with a maximum at 675 °C; on heating above 700 °C and up to 900 °C, this curve displays local exothermicities that are indicative of the further evolution of the impurity shell [7].

The process of thermodesorption of the volatile compounds extends over the entire temperature range studied (30 °C to 950 °C). Several intervals in which the TDS process is especially intense can be separated. They include low- (40 °C to 200 °C), middle- (180 °C to 320 °C and 530 °C to 780 °C), and high-temperature (680 °C to 900 °C) intervals.

As it follows from the data of massspectrometric measurements, the main volatile impurities of nanodiamond are water, hydrogen, nitrogen, methane, carbon dioxide, and sulfur dioxide.

CONCLUSIONS

Thus, on the basis of experimental data, it is possible to make a model describing the structure of detonation nanodiamond particles. The nanoparticle consists of the diamond nanokernal with a perfect crystalline structure and the impurity shell. The impurity shell possesses an intricate hierarchical structure. Each layer of the shell has a different binding energy connected with the nanodiamond kernel. On the surface of the nanokernel there is a heteroatom layer consisting of aluminum, silicon, iron, calcium, copper, and chromium. The heteroatoms are strongly bound with the kernel. The upper layer impurity shell consists of volatile molecular complexes that have a Van der Waals interaction with the nanokernel. The heteroatoms and molecular clusters form an impurity subsystem of detonation nanodiamond [6]. It can be argued that the impurity subsystem determines the physical and chemical properties of detonation nanodiamond. It is necessary to consider the existence of an impurity subsystem of detonation nanodiamond in applied tasks.

REFERENCES

1. A. M. Staver, N. V. Gubareva, A. I. Lyamkin, E. A. Petrov, Combustion, Explosion and Shock Waves **20**, 567–570 (1984).
2. A. E. Aleksenskii, M. V. Baidakova, A. Ya. Vul', V. I. Siklitskii Physics of the Solid State **41**, 668–671 (1999).
3. D. S. Volkov, M. A. Proskurnin and M. V. Korobov, Carbon **74**, 1–13 (2014).
4. V. A. Plotnikov, B. F. Demyanov, S. V. Makarov, Basic Problems of Material Science **4**, 521–526, (2012).
5. V. A. Plotnikov, B. F. Demyanov, S. V. Makarov, Applied Physics Letters **35**, 473–475 (2009).
6. V. A. Plotnikov, S. V. Makarov, D. G. Bogdanov, Basic Problems of Material Science **12**, 183–187 (2015).
7. D. G. Bogdanov, S. V. Makarov, V. A. Plotnikov, Applied Physics Letters **38**, 199–202 (2012).