Investigation of the Morphology and Atomic Structure of Nanopowder Particles Obtained by Grinding Natural Diamond and by the Method of Detonation Synthesis

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Abstract. By a complex of high-resolution methods, it has been shown that the nanopowder particles obtained by grinding natural diamonds have a wide range of sizes and are predominantly lamellar in contrast to the detonation synthesis nanopowder, which consists mainly of similar in size and isometric particles. The primary particles of the nanopowder obtained by grinding, as well as detonation synthesis nanodiamonds, consist of diamond cores with cubic crystal lattices surrounded by shells with complex structures formed from carbon atoms in the sp² state and impurities. A noticeable increase in the interatomic distances in nanodispersed diamond crystals is observed compared to those for bulk diamond crystals.

1. Introduction

Due to the unique physical-chemical and mechanical properties, nanodiamonds are of great interest to science and industry. As authors [1-4] note, the areas of their application are extensive - from additives to lubricating oils and composite materials to quantum dots and drug carriers.

The most used approach in the synthesis of diamond nanoparticles is the so-called bottom-up approach based on the process of joining carbon atoms into diamond nanocrystals during detonation of carbon-containing explosives in a closed volume with a negative oxygen balance [5–7]. However, the detonation synthesis method has several disadvantages associated with the use of expensive explosive chambers and no less costly and complex technological processes for extracting and purifying diamond nanoparticles from the accompanying synthesis products. Authors [5-8] consider that an alternative top-down approach, based on grinding bulk diamonds of natural origin or static synthesis, in combination with centrifugation methods, is a relatively simple and controlled method for manufacturing diamond nanoclusters. It can ensure the production of diamond nanoparticles with controlled and reproducible characteristics. When grinding, it is preferable to use natural diamonds as source material since they contain a small amount of metallic or other impurities and defects compared to synthetic diamonds.
The purpose of the present work is the investigation and comparative analysis of the morphology and structural characteristics of primary particles of nanopowders obtained by two methods: mechanical grinding of natural diamond and the method of detonation synthesis.

2. Research objects and methods
In the work of Sharin P.P. [9], the nanopowder of natural diamond (NND) was obtained by grinding in a vibrating mill (in the wet grinding mode). Steel balls 6–11 mm in diameter served as grinding elements. A fraction (−40 µm) of natural diamond micropowder was used as a raw material. Our study [10] describes the method of obtaining nanopowder from a natural diamond in detail.

The structural characteristics of the primary particles of the nanopowder were investigated by scanning electron microscopy (SEM) on a JSM-6480LV device (JEOL, Japan) and high-resolution transmission electron microscopy (TEM) on a Titan 80-300 device (FEI, USA) with a resolution of STEM; HREM ~ 0.08nm. Digital processing of images obtained on TEM (Fourier transform, Fourier filtering, determination of interplanar distances on FFT spectra) was performed using the GMS-2.3.2 software package (GATAN, USA).

The phase composition (XRD) and structural parameters of the nanodiamond powder sample were studied on an ARL X'Tra powder diffractometer (Thermo Fisher Scientific, Switzerland) using CuKα radiation (λ = 1.541 Å). X-ray diffraction measurements were accomplished in the range of angles from 3 to 80° with a scanning step of 0.02°. The processing and qualitative analysis of the measurement data were performed using the WinXRD and Crystallographica Search-Match programs.

The Raman spectra (RS) of nanodiamond powder samples were investigated using a Solar TII Raman spectrometer, which is part of the INTEGRA SPECTRA measuring complex (ZAO NT-MDT, Zelenograd). The spectrometer is equipped with a microscope with a 100x objective with a numerical aperture of NA = 0.7, a TV camera, and a cooled (-70 ° C) CCD detector. To excite Raman spectra, a He-Ne laser with a radiation wavelength of 632.8 nm and a power of 3 mW was used. A diffraction grating with a density of 600 lines / mm was used to register Raman spectra in a spectrometer. The Raman spectra of the samples were measured in the signal accumulation mode at room temperature.

The measurements and analysis of the size distribution of the primary particles of the nanopowder were performed by small-angle X-ray scattering (SAXS) on a Rigaku Ultima IV diffractometer (Japan) equipped with a small-angle scattering module and Nano Solver 3.1 special software. The specific surface area of the samples was determined by the BET method (Brunauer-Emmett-Teller) according to the measurements of the low-temperature adsorption of nitrogen molecules (77 K) using a SORB-I-MS instrument (ZAO Meta, Novosibirsk) equipped with a standard GSO 7912-2001 (Ssp = 98.42 m2 / g), developed at the Institute of Catalysis. G.K. Boreskov SB RAS. The density of diamond nanopowders was determined by the pycnometric method.

3. Results
The obtained dry NND nanopowder has a light gray color, while the detonation synthesis nanopowder (DND) of the UDA-S-GO grade produced by the Altai Federal Research and Production Center, used as a sample in comparative studies, is brown.

The densities of NND and DND nanopowders were ~ 3.05 and ~ 2.95 g/cm³, respectively. It is much lower than the theoretical density of diamond (3.5154 g/cm³) and bulk natural diamond crystals, which ranges from 3.30 to 3.60 g/cm³ depending on the content of impurities in them, as authors [1,3] note. The specific surface areas of NND and DND nanopowders were ~ 33.4 and ~ 338.6 m²/g, respectively.

The sizes of the primary particles of nanopowders measured by XRD and SAXS were equal to ~25.9 and ~ 24.0 nm for NND particles, respectively, and ~ 5.0 and ~ 5.6 nm for DND particles. Depending on the method of determination, the average size of NND primary particles is ~ 4.29 times (SAXS) or ~ 5.18 times (XRD) larger than the size of DND particles. The values of their specific surface area differ by more than ten times, which indicates a significant difference in the shape of their primary particles. Analytical processing of the direct images of nanopowder samples obtained using
high-resolution TEM and SEM have revealed that NND contains particles with a wide range of sizes, and predominantly platelet shape (~74% of all particles subjected to treatment). In contrast, DND nanopowder consists of particles of uniform size (~84% of all the processed particles) and has an isometric form (sphere or cube). An assessment according to the heuristic formula \( D = \frac{k}{\rho S_{\text{BET}}} \), which links the particle size \( D \), the specific surface area \( S_{\text{BET}} \), and the density \( \rho \) with a coefficient \( k \) equal to 2 (for lamellar particles) or 6 (for particles with a spherical shape) gives for \( D \) results that agree with the average particle sizes of NND and DND determined by XRD and SAXS.

Figure 1 demonstrates the diffraction spectra. The observed clear peaks in the spectrum of the NND nanopowder at angles of \( 2\theta \sim 43.89^\circ \) and \( \sim 75.25^\circ \) and in the spectrum of the DND nanopowder at angles of \( 2\theta \sim 43.62^\circ \) and \( \sim 75.21^\circ \) correspond to the diffraction of X-ray radiation on the (111) and (220) atomic planes of the crystal diamond lattice.

![Figure 1. Diffraction patterns of (a) NND and (b) DND powders.](image)

Table 1. Values of scan angles (2\(\theta\)), interplanar distances (\(d_{hkl}\)), physical broadening (\(\beta\)), lattice parameters (\(a\)) for a bulk diamond crystal, NND and DND nanocrystals.

| Miller indices | Massive diamond crystal | NND | DND |
|---------------|------------------------|-----|-----|
| 111           | 43.93 2.059 3.567      | 43.89 2.061 0.37 3.569 43.62 2.073 1.84 3.581 |
| 220           | 75.29 1.261 3.567      | 75.25 1.262 0.38 3.569 75.21 1.262 2.05 3.581 |

Figure 2 shows the images (a) NND and (b) DND nanocrystals obtained by high-resolution TEM in bright field mode. The middle insertion in Figure 2a presents SEM images of NND particles, which predominantly have a platelet shape.
Figure 2. Images of the atomic structure of the primary particles of (a) PNA and (b) DND nanopowders, obtained using a high-resolution TEM in the bright field mode at various magnifications. The numbers indicate No. of nanocrystals, the structural parameters of which are given in Table 2.

The TEM images clearly show and resolve the series of (111) and (220) atomic planes of NND and DND nanocrystals, which are constituent elements of the system of planes that form the cubic crystal lattice of a diamond. Obtaining high-quality TEM images allows determining the structural parameters of nanocrystals, revealing, and identifying the presence of defects in them. Table 2 shows the structural parameters of NND and DND nanocrystals determined from the TEM images in Figure 2.
Table 2. Average values of $d_{hkl}$ interplanar distance, the number of atomic planes, and their spatial arrangement (Miller indices) in NND and DND nanocrystals shown in Figure 2, a, b.

| Crystal No. | $d_{hkl}$, Å | NND | Miller indices | $d_{hkl}$, Å | DND | Miller indices |
|-------------|--------------|-----|---------------|--------------|-----|---------------|
| 1           | 2.062        | 154 | (111)         | 2.071        | 107 | (111)         |
| 2           | 1.262        | 191 | (220)         | 2.071        | 25  | (111)         |
| 3           | 1.262        | 41  | (220)         | 2.071        | 16  | (111)         |
| 4           | 2.062        | 10  | (111)         | 1.262        | 8   | (220)         |
| 5           | 2.062        | 14  | (111)         | 2.071        | 21  | (111)         |
| 6           | 2.062        | 20  | (111)         | 2.071        | 10  | (111)         |

Note that the average $d_{hkl}$ values of NND and DND nanocrystals determined from their TEM images agree with the data obtained from the analysis of their diffraction spectra. As follows from Table 2, the average values of $d_{hkl}$ between the rows of carbon atoms and, consequently, the lattice parameters of DND nanocrystals are noticeably larger than those of NND nanocrystals. In turn, NND lattice parameters also significantly exceed the structural parameters of the lattice of a bulk diamond crystal. It indicates a noticeable increase in $d_{hkl}$ in the nanodiamond lattices compared to $d_{hkl}$ for a large diamond crystal and experimentally confirms the results obtained by authors [12, 13]. It is conceivable that an increase in $d_{hkl}$ of nanodiamonds contributes to the observed decrease in the density of NND and DND nanopowders in comparison with the density of bulk diamond crystals. However, according to Baitinger E.M. et al. [14], the decrease in the density of nanopowders in comparison with the density of a bulk diamond crystal is mainly due to the presence of shells. These shells are inevitably formed on the surface of primary nanodiamond particles during their production and have a density lower than the crystalline diamond core of nanopowder particles. As it is seen in Figure 2, NND and DND nanocrystals are covered with shells (some of them are highlighted by black arrows in the Figure), consisting mainly of carbon atoms with $sp^2$-hybridization, which is confirmed by their Raman spectra. Figure 3 demonstrates that, in the Raman spectra of both nanopowders, in addition to clearly pronounced D lines at a frequency near 1332 cm$^{-1}$, which are related to carbon with $sp^3$-hybridization and indicate the diamond structure of their lattices, two broadband peaks G and G' appear, corresponding to modes of carbon atoms in the $sp^2$ state.

Figure 3. Two-dimensional (2D) images of the Raman spectra map of (a) NND and (b) DND nanopowders and the view of the spectra at four arbitrary points marked with numbers on the map.

A line known as the D-peak of graphite (as Bulakov S.S. et al. (2006) points, D stands for the “disorder”) appears in the Raman spectrum at a frequency centered at ~1350 cm$^{-1}$ near the D-line of a diamond. As Figure 3 shows, in the Raman spectrum of NND nanopowder, the D-peak of graphite
looks like a broadband base with a half-width of up to 90 cm\(^{-1}\), from which a narrow intense D-line of diamond with a half-width of \(\sim 14\) cm\(^{-1}\) protrudes. In the spectrum of DND, a narrow D-line of diamond barely noticeable against the background of the broadband D-peak of graphite. According to Bulakov S.S. et al. [15], shells of carbon atoms with sp\(^2\)-hybridization, containing various impurity atoms and functional groups and being located along the boundaries, serve as chemically active matrices that connect neighboring diamond nanocrystals. Study and analysis of a large number of high-resolution images (more than 40 pictures of NND and DND particles), similar to those presented in Figure 2, made it possible to reveal that the most common defects in nanocrystals of both NND and DND are the edge dislocations (see inserts in Figure 2).

Thus, the particles of the nanopowder obtained by grinding, as well as the nanodiamonds of detonation synthesis, consist of diamond cores with cubic crystal lattices surrounded by shells with complex structures formed from carbon atoms in the sp\(^2\) state and impurities. A noticeable increase in the interatomic distances in nanodispersed diamond crystals in comparison with those for large diamond crystals has been established.

4. Conclusion

The paper studies the features of the morphological and structural characteristics of nanopowder particles obtained by grinding bulk natural diamonds and by the method of detonation synthesis. High-resolution TEM and SEM, as well as small-angle X-ray scattering, have revealed that the particles of natural nanopowder have a predominantly lamellar shape and a wide range of size in contrast to the detonation synthesis nanopowder, which consists of isometric nanoparticles of uniform size. Using X-ray phase analysis and Raman spectroscopy, used in addition to the above-mentioned methods, it has been established that the structure of nanodiamonds obtained from natural diamond is similar to the structure of nanodiamonds of detonation synthesis. Each particle of natural nanopowder, as well as nanodiamond of detonation synthesis, consists of a diamond core with a crystal lattice related to the cubic system and a shell. The shell contains mainly non-diamond forms of sp\(^2\)-hybridized carbon with a complex structure. The results of estimating the average particle size of nanopowders obtained by three methods, including the BET method, based on the effects significantly different in physical nature, demonstrated satisfactory agreement among themselves. The average size of nanoparticles of a powder of natural origin is about 24 nm, and it is close to 5.6 nm for the detonation synthesis nanodiamonds of UDA-S-GO grade produced by the “Altai” Federal Research and Production Center. An insignificant but noticeable increase in the interatomic distances in diamond nanocrystals has been established in comparison with bulk diamond crystals. It is shown that the most common defects in NND and DND nanocrystals are stacking faults, that is, edge dislocation.

5. References

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