Spectroscopic methods of investigation and the thermal stability of detonation nanodiamonds

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Abstract. The behavior of detonation nano- and microdiamonds at increased temperatures is studied by synchronous thermal analysis, X-ray diffraction analysis, and scanning electron microscopy. The X-ray analysis of survived samples shows that a part of the nanodiamond is stable under heating to 1500˚C. At the heating to 600˚C, we see the decreasing of nanodiamond phase. Appearance of graphite phase isn’t observed in the sample up to 1500˚C. However, in the range Bragg angle 20-32˚ after heating to 1500˚C, the x-ray amorphous graphite-like phase is observed. The analysis of microphotographs of samples before and after heating showed the influence of heating rate on the parameters of powder particles. A high thermal stability of detonation microdiamonds (above 1500˚C) is established. Literature data on the radiation stability of diamond are analyzed. It is established that the character of the diamond damage depends on the type and dose of the irradiation.

1. Introduction
Carbon is the key material for the life on the Earth, it remains in the focus of various studies. Due to its special property to form various types of chemical bonds, carbon has many allotropic modifications: cubic and hexagonal diamond, graphite, carbone, and so on. Now, new nanocarbon materials are known: carbon nanotubes, fullerenes, graphenes, and detonation nanodiamonds. These substances possess unique properties. This allows one to use them in various fields.

Detonation nanodiamonds (DND) are obtained by explosion of high explosives. A DND particle has heterogeneous structure. It consists of a diamond core and an impurity shell. The impurity shell...
consists of nondiamond carbon, adsorbed water, and C-O, C-N, C-H radical groups. The model of a DND particle is shown in figure 1.

With decreasing nanoparticle size, the surface fraction of atoms increases. The influence of the surface on the crystal lattice strengthens. The reason is that surface atoms have neighbors on one side only, and the center symmetry of the forces and masses is shifted. The interatomic distances change and the crystalline lattice is distorted [2]. Such structure modifies the properties of DND powder particles, as compared to macrocrystalline diamonds.

![Figure 1. Model of a DND particle.](image)

**Figure 1.** Model of a DND particle.

The published data on the nanodiamond graphitization temperature vary in a wide temperature range from 670°C [3] to 980°C [4]. The graphitization mechanism is also unclear. Either graphitization occurs via the intermediate amorphous phase, or layer-by-layer transformation of a diamond particle into an onion graphite structure takes place. Upon heating, more and more diamond layers are transformed into an sp² structure. The photos of this transformation are shown in figure 2. Therefore, particles with a diamond core and a graphite shell can exist at certain temperatures. Graphitization, like a spherical wave, propagates into the particle. The degree of the graphitization depends on temperature. Thus, if the particle size and the temperature are known, it is possible to determine the amount of graphite and diamond phases in the particle.

The objective for this study is the experimental investigation of the thermal stability of detonation nanodiamond and the analysis of published data on radiation damage of diamond.

### 2. The thermal stability of detonation nano and microdiamond

In this study, the detonation nanodiamond powder is experimentally studied. The powder was obtained by explosion of the TNT/RDX (50/50) mixture [5]. Detonation microdiamond (DMD) is also studied. DMD was obtained by explosion of the TNT/RDX (50/50) mixture in water.

The study of elemental composition of the initial sample revealed the carbon purity of about 98%. The impurity content in the sample is small. Basically, the impurities include the following metals: Fe, Cr and Ti (from 0.3 to 0.2%). The particle sizes in the initial DND powder are from 4 to 7 nm. Detonation microdiamonds were studied in [6]. The typical microdiamond size is about 25 μm.

The DND and DMD heating was performed by synchronous thermal analysis (STA). STA includes thermogravimetry (TG) and differential scanning calorimetry (DSC). The heating was performed at Netzsch STA 409 PC. The samples were put in a corundum crucible (Al₂O₃) and the lid was closed. The heating was performed at ambient pressure in dynamic argon environment at temperature range from 30°C to 1500°C with constant heating rates of 2 and 10°C/min. The survived samples after the heating were studied by X-ray diffraction and scanning electron microscopy.

Detonation nanodiamonds were heated to temperatures of 600, 1000, and 1500°C for a heating rate of 10°C/min and to 1500°C for a heating rate of 2°C/min. The detonation microdiamonds were heated to 1500°C at heating rates of 2 and 10°C/min.

#### 2.1. The thermal stability of detonation nanodiamond

![Figure 2. Layer-by-layer transformation of a diamond particle into an onion graphite.](image)

**Figure 2.** Layer-by-layer transformation of a diamond particle into an onion graphite [4].
The X-ray diffractograms of the studied samples are shown in figure 3. As seen, increase of treatment temperature leads to decrease of diamond sp³ phase (figure 3, lines 1 – 4). The nanodiamond reduction begins at 600°C. A certain number of diamonds, however, can be found in the sample at a temperature of 1500°C. As the sp³ peak from the base plane of the diamond (111) decreases, no graphite component appears. This may be connected with the fact that the nanodiamond structure is transformed to the amorphous phase upon heating. The amorphous phase is transformed into the graphite phase at further heating. The X-ray structural analysis of the sample, heated to 1500°C, revealed a halo in the region of Bragg angles of 2θ=20–32°. This halo corresponds to the X-ray amorphous graphite-like phase. The interplanar spacing in this structure is larger than in graphite. This phase is not graphitized with further heating.

![Graph showing X-ray diffractograms](image)

**Figure 3.** X-ray diffractograms of the samples of DND powder before and after the heat treatment: 1 – the initial powder, 2 – to 600 °C at a rate of 10 °C/min, 3 – to 1000 °C at a rate of 10 °C/min, 4 – to 1500 °C at a rate of 10 °C/min, 5 – to 1500 °C at a rate of 2°C/min. (002) – the base plane of graphite.

![Microstructure of powder nanodiamond](image)

**Figure 4.** Microstructure of powder nanodiamond: a) initial sample; b) after the heat treatment to 1500°C at v=10°C/min; c) to 1500°C at v=2°C/min.

The investigation of DND microstructure showed the influence of the heating rate on the powder particles parameters (figure 4). The heating at a rate of 10°C/min results in powder particles adhesion. As a result, spherical conglomerates with a size of 30 – 40 nm are observed in the sample (figure 4b). The powder heating at a rate of 2°C/min results in the formation of planar structures with a size of about 1 μm (figure 4c).

### 2.2. Thermal stability of detonation microdiamond
Heating of the detonation microdiamond powder was performed in a temperature range from 30 to 1500°C at rates of 2 and 10°C/min in dynamic argon environment. Under heating to a maximum temperature of 1500°C at rates of 2 and 10°C/min the mass loss of the sample was about 2%.

Figure 5. Microstructure of detonation micro and nanodiamond powder: 1 – initial microdiamond; 2 – microdiamond after treatment to 1500°C at a rate 10°C/min; 3 – initial nanodiamond; 4 – nanodiamond after treatment to 1500°C at a rate 10°C/min.

X-ray analysis of the DMD powder before and after the heating is shown in figure 5. As seen, the amount of the diamond phase has not changed even after the heating to a maximum temperature of 1500°C (figure 5, lines 1 and 2) [6]. No graphitization in the sample is observed upon heating. This indicates that the microdiamond is more stable to heating at atmospheric pressure than nanodiamond. The peak from the base plane of diamond (111) for nanodiamond is wider than that for microdiamond (figure 5, lines 1 and 3). The peak broadening results from the distortion of the crystalline lattice with decreasing particle size. The distortion of the crystalline lattice changes the substance properties. The X-ray peak from the base plane of diamond (111) for microdiamond is nearly the same as that for monodiamond. This indicates similarity of properties of the micro- macrocrystalline diamond.

At present, the graphitization mechanism of detonation nanodiamond is not completely clear. The graphitization temperature needs further study. For this purpose, it is necessary to study various impacts on the DND substance. The available published data were analyzed prior to begin the experimental study.

3. Radiation stability of diamond phase
Point defects, amorphous and graphite phases can be formed in the diamond, depending on irradiation type and dose. Irradiation changes the substance structure. Its properties are changed. Thus, it is possible to obtain a material with unique properties that do not exist in nature.

Figure 6. The samples of irradiated single crystal diamond by ions Si⁺ with 1MeV, at a dose 1*10^{15} Si⁺/cm² a) before heating, b) after heating to 1350°C during 24 hours. The black arrows show the surface; the gray arrows show damage bend; c-diamond – the bulk diamond. [7].
Thus, if single diamond is irradiated by 1 MeV Si ions at a dose of $1 \times 10^{15}$ Si$^+$/$\text{cm}^2$ at the room temperature [7], point defect formation is observed (figure 6a). Annealing of the irradiated sample at 1350°C during 24 hours resulted in the recovery of defects to an ideal diamond lattice (figure 6b). If single crystal diamond is irradiated by 1 MeV Si ions at a dose of $7 \times 10^{15}$ Si$^+$/$\text{cm}^2$, amorphous carbon is formed [7]. The annealing of the irradiated sample at 1350°C during 24 hours results in the formation of graphite from the amorphous phase.

The irradiation modeling of nanodiamond particles shows that the character of damage depends on the particles size [8]. Namely, 5 nm particles, being irradiated by heavy fast ions with an effective stopping energy of 17 keV/nm, are completely transformed into the amorphous phase. Particles with a size of 7 nm have an amorphous track at its center after irradiation. Therefore, nanodiamond with a size of 7 nm has two phases after irradiation: nanodiamond and amorphous diamond. For a particle with a size of 10 nm, point defects are only observed at its center. Thus, the particle size is the function of radiation damage.

![Figure 7. Peak temperature of ND grains as functions of diameter after a 6 keV Xe ion impact (a) and of incident Xe energy in a 3 nm ND (b) [9].](image_url)

The irradiation of the nanodiamond powder (particle size from 2 to 40 nm) by Xe ions with a low energy from 6 to 40 keV showed [9] that 8 nm particles were completely destroyed by a small number of ions (with an energy of about 6 keV). It was found that the damage depends on the impact character. Central collisions completely destroy the particle. Non-central collisions result in lesser damage. Particles with a size larger than 8 nm are more stable to irradiation. The simulation of nanodiamond irradiation with the help of molecular dynamics showed (figure 7) that a 3 – 4 nm nanodiamond particle is heated to very high temperatures (over 3000K). The heating temperature decreases with increasing particle size. So, a particle with a diameter of about 10 nm, being irradiated by 6 keV Xe ions, is heated to less than 1000K.

4. Conclusions

It was found that the thermal stability of a part of the detonation nanodiamond is higher than 1500 °C. The analysis of the published data showed a wide spread of data on the nanodiamond powder graphitization temperature. According to our results, the basic process of graphitization of the nanodiamond powder occurs above 800 °C. However, the content of the diamond phase decreased after the sample heating. This is connected with the transformation of the diamond into the amorphous phase. The linear size of the powder particles increased after the heat treatment. The dependence of the limiting stability of nanodiamonds on the physical properties of particles requires further investigation. The graphitization temperature of the detonation microdiamond is above 1500°C. This value is higher than that for nanodiamonds. So, the properties of microdiamonds are close to those of macrocrystalline diamond. The solid-state transition sp$^3$ to sp$^2$ and the corresponding changes in the diffraction pattern is promising for experimental diagnostics. The combination of the diamond structure, the nanoscale size, and the porosity simplifies radiation release from the studied region. Such targets with the known thermophysical transition conditions can be used for WDM (Warm Dense Matter) diagnostics.
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