Nanodiamond graphitization at heating and irradiation

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Abstract. In this work the graphitization and thermal stability of detonation nanodiamonds were studied. Received data showed that the temperature of graphitization of nanodiamond particles lies in wide range and the temperature of graphitization beginning depend on the particle size. It is established the influence of heating rate on the size of nanodiamond conglomerates. The analysis of literature shows that the graphitization processes take place at irradiation. Depending on the type and irradiation dose the point defects, amorphous and graphite phases can form in the diamond structure. Annealing of irradiation samples showed the defect structure restore to ideal lattice and the release of stored energy.

Nanodiamond is quite attractive due to its promising properties. It possesses high heat capacity, heat conduction, density (the density of nanodiamond is 3.51 g/cm³), and so on. The heterogeneous structure of nanodiamond particles, however, causes ambiguities and inconsistencies in its studied properties. A diamond nanoparticle consists of a diamond core and an admixture shell which includes amorphous carbon, adsorbed water, and surface radicals (figure 1). The uncertainties in its properties impact applicability of detonation diamond powder. At present, detonation diamonds have been applied in quite few fields: galvanics, oils and lubricants, fine polishing [1]. In this regard, the search of nanodiamond applications in science and technology continues. This interest is to a large extent determined by the appearance of
high power laboratory installations for producing high pressures and temperatures via non-explosive methods [2]. At present, detonation nanodiamonds remain the most widely produced nanodiamonds. All this determines the experimental and theoretical interest in this problem.

The thermal limits of applicability of detonation nanodiamonds are determined by the conditions of the beginning of phase transformations. With increasing temperature, the diamond sp\(^3\) phase undergoes phase-structural changes and is transformed into a more energy-advantageous sp\(^2\) configuration (graphite). Depending on the methods of impact, detonation nanodiamond particles undergo structural changes, acquiring new properties and losing the diamond uniqueness. The published data on the nanodiamond graphitization temperature under heat treatment in an inert medium under atmospheric pressure vary substantially. Thus, the graphitization temperature is in a range from 670 to 980°C [3–5]. It was established that the phase transition is not instantaneous, but takes place in a certain temperature range. Thus, in [5] detonation nanodiamond particles with a size of 10 nm were reported to be transformed into the onion structure gradually, beginning from 980°C and up to 1600°C. A particle with a size of 2 nm, however, is completely transformed into the onion structure already at 800°C [5]. Therefore, it can be assumed, according to the published data, that the phase transition temperature is a function of the particle size. Graphitization is not a self-maintained process. After the temperature drop the remaining nanodiamonds are stabilized.

At the same time, it is not only the graphitization temperature that is ambiguous, but the very process of nanodiamond phase transformation is dubious. There exist two points of view on the subject. Some researchers [4, 5] assume that onion layers (with carbon atoms in the sp\(^2\) state) are formed on the diamond core surface with increasing temperature, and then, as the temperature grows further, the phase transformation moves inside the particle. Thus, a particle with two carbon phases: graphite shell and diamond core, can exist in a certain temperature range (figure 2). Other researchers [6] state that diamond particles, being heated, are transformed into the amorphous state beginning from a certain temperature. At further heat treatment, the amorphous phase is transformed into the onion structure.

Phase transformations in nanodiamonds are observed at irradiation [7], as well as heat treatment. In the case of irradiation, the following damage can be observed in diamond, depending on the radiation type, dose, and energy: point defects, amorphous phase, and graphite phase (figure 2). Strictly speaking, radiation impact is both a local thermal impact

![Figure 2. Possible development of phase transformations in nanodiamond particles depending on external influence.](image)
and a damage of the crystalline structure. Unlike pure heating, point defects can be formed in nanodiamonds under irradiation. Energy absorption at irradiation is accompanied by the formation of point defects. The absorbed energy is spent for bond rupture, which results in the lattice distortion. Atoms are displaced from the equilibrium position, causing elastic stress around them. Subsequent annealing of irradiated samples results in the restoration of the crystalline lattice to the ideal one. In other words, point defects are restored to an ideal lattice. This process releases a certain amount of energy produced at the lattice deformation.

Another specific feature of irradiation is the creation of two-phase particles, namely, particles with the graphitic core and the diamond shell. At present, publications devoted to the study of radiation damage in nanodiamond are scarce. This can be explained by the cumbersome character of nanodiamond sample preparation. The irradiation study requires the examination of radiation damage for a single nanodiamond particle.

In this paper, we study the thermal stability of detonation nanodiamond using synchronous thermal analysis. Detonation nanodiamond powder was produced by detonation of TNT/RDX (50/50) mixture. The purity of the carbon phase in the nanodiamond powder was about 98%. Heat treatment of the powder was performed in a temperature range from 30°C to 1500°C with a heating rate of 2 and 10°C/min in the dynamic argon environment. The powder was placed in a corundum (Al₂O₃) crucible and the lid was closed. After heat treatment the samples were studied using X ray structural analysis, Raman spectroscopy, and electron microscope.

The thermal stability of detonation nanodiamond at atmospheric pressure in an inert environment was studied in [8–13]. It was found out that detonation nanodiamond powder produced using the TNT/RDX (50/50) mixture is stable to heating up to 600°C. After 600°C the diamond phase in the sample decreased (figure 3, curves 2–5), however, even at 1500°C part of the diamond survived (about 8% of the initial content). The diamond content was determined by the ratio of integral intensities from the diamond base plane (111) in the original powder and the powder after heat treatment (figure 4a). It was noticed that after 600°C the content of the diamond phase decreases, while a new crystalline structure (graphite) is not formed. The formation of a graphitic X-ray amorphous phase was observed after heating to 1500°C (figure 3, curves 4 and 5). This phase gives a broad halo around the X ray line from the base plane (002) (figure 4b) in a Bragg angle range from 20 to 32 degrees, rather than a sharp peak typical for ordered graphite. This phase has a layered structure. Carbon atoms in the plane are in the

![Figure 3](image_url)

Figure 3. Diffractogram of detonation nanodiamond (DND) powder samples before and after heat treatment: (1) original powder; (2) after heating to 600°C at a rate of 10°C/min; (3) after heating to 1000°C at 10°C/min; (4) after heating to 1500°C at a rate of 10°C/min; (5) after heating to 1500°C at a rate of 2°C/min.
Figure 4. (a) Elementary cells of diamond and (b) elementary cells of graphite

sp$^2$ hybrid state, similar to graphite, but the distance between the planes is larger than that in graphite. This is the reason of the halo at the X ray line, instead of the sharp peak. Thus, the question where the diamond phase goes beginning from 600$^\circ$C remains open. It follows from the mass conservation law that the mass of the substances undergoing a reaction is equal to the mass of the substances produced in this reaction. Therefore, the reduction of the amount of diamond is accompanied by the formation of various products that can be observed using certain methods. It was assumed that nanodiamond is transformed to the amorphous phase, which (due to the absence of a crystalline structure) cannot be “visualized” by X rays. It was decided to use Raman spectroscopy for detection of this phase.

Figure 5. Raman spectrum of nanodiamond before and after heat treatment: (a) (1) original sample; (2) after heated to 1500$^\circ$C at a rate of 2$^\circ$C/min and (b) (1) original sample; (2) sample heated to 800$^\circ$C at a rate of 10$^\circ$C/min; (3) sample heated to 1200$^\circ$C at 10$^\circ$C/min; (4) sample heated to 1500$^\circ$C at a rate of 10$^\circ$C/min; (5) sample heated to 1500$^\circ$C at a rate of 2$^\circ$C/min.

In [12], Raman spectra of nanodiamond were studied. A broad peak, about 500 cm$^{-1}$, in figure 5a (curve 1), indicates the presence of amorphous carbon in the sample, atoms of this phase are in the sp$^3$ hybrid state [13]. Amorphous sp$^3$ phase does not have an ordered structure, it consists of fragments of diamond cell bonds. The high peak at 1318.4 cm$^{-1}$ indicates the
presence of nanodiamond in the original sample. The Raman spectrum of the original sample also contains a broad band with intermediate intensity and a maximum at 1553 cm\(^{-1}\) (G peak) corresponding to graphitic carbon. This phase contains carbon in the sp\(^2\) hybrid state and represents a layered structure. With increasing heating temperature, the diamond D peak decreases, while the G peak increases. The published studies on the G peak in Raman spectra of treated nanodiamond, however, do not give an unambiguous idea on the structure corresponding to the peak at offset frequencies of 1550–1600 cm\(^{-1}\). Since the graphite structure corresponds to the peak at 1581 cm\(^{-1}\) \cite{14}, the structure causing the peak offset toward higher frequencies has the sp\(^2\) configuration. In some publications, the peak at this frequency corresponds to the amorphous sp\(^2\) phase \cite{15}. In other sources \cite{16} this peak is said to correspond to the onion structure. The following conclusion can be made from the comparison of the data of X ray analysis \cite{12} and Raman spectra. Since the onion structure has a halo in the X ray spectra near the Bragg angles from 20 to 32 degrees, while the diffractograms of our samples after heating to 600–1000°C do not contain this halo, it can be concluded, based on the Raman spectra, that the diamond structure is transformed into the amorphous sp\(^2\) phase (with the peak at 1612 cm\(^{-1}\)). At further heat treatment, the onion graphitic structure is formed which corresponds to the Raman peak at 1572 cm\(^{-1}\). This assumption was proved by the comparison of the X ray and Raman spectra.

In this study, we propose the method of double heating of detonation nanodiamond powder. The method is as follows. The first heat treatment to 800°C removes surface admixtures from powder particles without impacting the diamond core. Then the sample is cooled to room temperature in an inert environment with a rate of 10°C/min and then heated to 1500°C. The cooling thermogram does not demonstrate any specific features, in other words, no structural or phase changes take place upon cooling. This means that none of the processes in the heated sample is self-maintained. In order to study nanodiamond using the double heating method, it was necessary to select the primary heating temperature in such a way that no phase transformation of the nanodiamond core started. The primary heating temperature was chosen based on the previous studies. The analysis of the available data yielded the conclusion that the powder should be first heated to 800°C.

The comparison of thermograms for detonation nanodiamond samples after primary (to 800°C) and secondary (to 1500°C) heating showed that secondary heating eliminates adsorbed water and some surface radicals. The differential scanning calorimetry (DSC) curve for secondary heating is smoother, as compared to the DSC for primary heating. The study of elemental composition of the powder heated to 800°C demonstrated that the sample did not contain some of the admixtures. This analysis agrees with \cite{17}. In this paper, double heat treated samples were studies using X ray structural analysis. It is planned to involve Raman spectroscopy in the future studies.

An approach to investigation of thermal stability of detonation nanodiamond powder was developed. The study of the nanodiamond graphitization requires at least two diagnostic methods, namely, X ray structural analysis and Raman spectroscopy. The comparison of the data obtained in two different studies yielded the conclusion on the existence of an intermediate amorphous phase in the diamond - graphite phase transition for nanodiamond in the considered temperature range. The secondary heating method proposed earlier was applied for elimination of the influence of water and volatile admixtures in the nanodiamond shell on the beginning of graphitization.

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