Thermal stability of detonation-produced micro and nanodiamonds

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Abstract. Detonation nanodiamonds are produced at utilization of high explosives. When an explosive blasts in a water environment, the detonation products contain microdiamonds, and in a gaseous medium, nanodiamonds. It is known that with decreasing size the influence of the surface energy of particles on their properties increases. Thus, it is interesting to compare the properties of detonation nano and microdiamonds. In this study, we have examined the thermal stability of diamond materials by synchronous thermal analysis. The experiments were performed at atmospheric pressure in argon flow for different heating rates in a range from room temperature to 1500 °C. Samples of initial and annealed micro and nanomaterials were studied using electron microscopy, x-ray and x-ray-fluorescence analysis. It was established that thermal and structural properties of micro and nanodiamonds differ substantially.

1. Introduction

Industrial technologies for producing detonation diamonds are based on utilization of explosives. This method provides direct production of powder carbon mixtures containing diamonds from nano to microsize, depending on initial conditions of the explosion. Thus, if an explosive mixture blasts in a water environment, the condensed products contain micron-size diamonds, and in a gaseous medium, nanodiamonds.

Nano and microdiamonds have a diamond crystalline lattice. Nanodiamonds, however, have an inhomogeneous structure. Their particles consist of the diamond core and the admixture shell from non-diamond carbon \cite{1}. Study of the surface chemistry of the detonation nanodiamond (DND) showed that the admixture shell contains different functional groups: C–H, C–O, C–N \cite{2}. These groups substantially influence the properties of the DND powders. The structure of microdiamond particles is more perfect and close to the macrocrystalline diamond. The microdiamond surface does not have an admixture shell or radical groups. It is known \cite{3,4} that with decreasing particle size the influence of the surface energy on the thermodynamic parameters (in particular, enthalpy and entropy) of diamond particles, and therefore, the properties of the diamond powder, increases.
One of the most important properties is the temperature of the beginning of graphitization of diamond. The graphitization process is the solid-state phase transition during which carbon atoms are transformed from $sp^3$-hybridization to $sp^2$-hybridization. It is known [4] that the graphitization temperature decreases with decreasing size of diamond particles. It was discovered in [5] that if a nanodiamond is annealed in vacuum, graphitization begins at about 900 °C. Nanoparticles consisting of the diamond core and the onion-shaped multilayered graphite shell [6] are formed at a temperature of 1130–1630 °C. In the case of annealing in the inert argon environment at atmospheric pressure the phase transition in diamond nanoparticles completes at 1600 °C [7]. In different heating regimes, the temperature of the beginning of the phase transition in the nanodiamond is ambiguous. This circumstance is connected with the inhomogeneous structure of nanoparticles and the presence of the surface shell. The microdiamond graphitization begins above 1500 °C [8]. This is much higher than the initial nanodiamond graphitization temperature. There exist other methods for diamond destruction. For example, phase transition in the diamond can take place under irradiation [9].

This implies that the properties of micro and nanodiamonds differ from the properties of macrocrystalline diamond and from each other. Thus, it is interesting to compare the two types of diamonds for possible practical application in various fields of industry.

Possessing high density (3.51 g/cm$^3$), hardness, heat conduction, heat capacity, and so on, nano and microdiamonds are a promising material in different fields of science and technology. Thus, possessing high surface energy and the presence of radical groups, nanodiamonds may serve as a good filler in a composite material. Nanoparticles allow one to reduce the porosity of the final product and increase its hardness. The properties of detonation nanodiamond powder, however, are ambiguous, and sometimes even contradictory. This is connected with the complex structure of nanoparticles. The properties of detonation microdiamond are closer to macrocrystalline ones.

Nonetheless, unlike nanodiamonds, the production of microdiamond requires more effort and costs more. Thus, nanodiamond production is several tons a year, while microdiamonds are produced in an amount of several dozens of kilograms a year. Taking into account the above considerations, the question on the most promising diamond material for wide application is still open. In this study, we compare the thermal stability and examine the thermal behavior of detonation-produced micro and nanodiamond powders.

### 2. Experiment

The detonation microdiamond powder was obtained by utilization of an explosive in water [10]. The nanodiamond powder is produced in trotyl–hexogen (50 : 50) explosion in argon atmosphere [11]. The initial carbon micro and nanomaterials were tested using electron microscopy, x-ray and x-ray-fluorescence methods. The initial data for the detonation nanodiamond powder were obtained in our previous studies [12–14].

The elemental composition of the microdiamond sample is given in table 1. According to the elemental analysis, the microdiamond powder contains more than 99.3% of diamond carbon. The remaining part is the admixture elements, mainly Al and Fe. It was shown in [10], that microdiamond particles represent almost defect-free crystals with a typical size of 1–25 µm.

The thermal stability of carbon materials was studied using synchronous thermal analysis (thermogravimetric (TG) analysis) and differential scanning calorimetry (DSC) at Netzsch STA 409 PC. The studied powder was placed in the corundum crucible (Al$_2$O$_3$), then covered by a lid and put in a furnace at atmospheric pressure and an initial temperature of 30 °C. The reference line was measured in the same conditions (heating rate, exposure time, gas flow rate, etc) as the sample prior to the sample measurement. Taking into account reference lines in experiments allows one to reject readings that are not connected with the thermal behavior of the sample. The experiments were performed at atmospheric pressure in argon at a temperature from room
temperature to 800, 1000, 1200, 1500 °C with a heating rate of 10 °C/min and up to 1500 °C with a heating rate of 2 °C/min. All samples were studied after cooling to room temperature using the x-ray structural analysis and the scanning electron microscope.

The phase composition of annealed nanodiamond samples was studied by x-ray fluorescence analysis at DRON-2 (CuKα radiation). The crystalline lattice parameter, the average size of the coherent scattering region, and the volume per cent of the phase were measured for the diamond phase in all samples. The amount of the diamond phase in the samples after the experiment was determined with respect to the initial content of this phase in the main material. The integral intensities of the diffraction peak in the diamond x-ray line (111) for the samples before and after the experiment were measured.

The microstructure of the carbon powder after thermal processing was studied using the scanning electron microscope Nova NanoSEM 650 with the standard procedure.

3. Discussion

The microdiamond powder did not change color and structure after annealing to 800, 1000, 1200, 1500 °C. This result differs substantially from the behavior of the powder of detonation nanodiamond. After annealing to 800 °C the powder changed visibly. The nanodiamond color changed from grey to greyish-black. The x-ray structural analysis, however, shows the absence of phase transition in this temperature range [13]. This circumstance may testify the change of the particle conglomerate size.

Figure 1 shows the thermograms for powders of detonation microdiamond (curves 1 and 2) and nanodiamond (curves 3 and 4). The sample heating rate was 10 °C/min. It can be clearly seen in the TG curves that the mass loss rate differs for nano and microdiamonds. The mass of the microdiamond sample remains almost unchanged (the mass loss is less than 2%), unlike the nanodiamond sample (the mass loss is about 16%). Radicals present on the surface of nanoparticles are removed during thermal processing with production H₂, CO, and CO₂. This process results in the sample mass loss by 10–20% [2]. It was already noted that nanodiamonds have a complex heterogeneous structure. This is important at increased temperatures. The DSC curve for nanodiamond (curve 4) shows that certain processes take place in the sample upon heating (see arrow 4a). It is known from published data that nanodiamond graphitization begins at about 600 °C [15]. This process goes with energy release, since the lattice energy of diamond is larger than that of graphite. The x-ray structural analysis of the powder of detonation nanodiamond shows that the nanodiamond phase in the sample somewhat reduced after heating to 600 °C [13]. The sp² phase was not produced. Therefore, energy release at 600 °C is not connected with graphitization. The exothermal peak near 600 °C may be connected with the removal of lacton groups from the surface of nanodiamond particles. This process goes with release of a certain amount of heat and production of CO₂ [6]. In the case of nanodiamond annealing, above 800 °C two processes go in parallel: nanodiamond particles are transformed into the graphite phase, and sintering takes place with increasing temperature. It is possible that further reduction of the thermal flux (the drop in the DSC curve 4 in figure 1) is connected with heat absorption during sintering (agglomeration) of nanodiamond particles. This is probably connected with the fact that the energy absorbed during sintering exceeds the energy released during graphitization. There are no peaks related to the change of thermal flux in the DSC (curve 2) for microdiamonds.

The diffractograms of the powders of microdiamond (figure 2, curves 1 and 2) and nanodiamond (figure 2, curves 3 and 4) before and after heating to 1500 °C with a rate of 10 °C/min are shown in figure 2. The microdiamond peak intensity in the X ray line from the diamond base plane (111) before (curve 1) and after (curve 2) heating to 1500 °C with a rate of 10 °C/min nearly coincide. This indicates high thermal stability of microdiamond. The diffraction pattern of the initial nanodiamond sample has a broader diamond peak in the x-ray line from the same
Table 1. Element structure of the cleared DND.

| Chemical element | C   | Al  | Si  | P   | S   | Cl  | Ca  |
|------------------|-----|-----|-----|-----|-----|-----|-----|
| %                | 99.36 | 0.14 | 0.06 | 0.06 | 0.09 | 0.05 | 0.02 |
| Measurement uncertainty | — | 0.004 | 0.004 | 0.006 | 0.004 | 0.004 | 0.004 |

| Chemical element | Ti  | Cr  | Fe  | Ni  | Cu  | Zn  | Mo  |
|------------------|-----|-----|-----|-----|-----|-----|-----|
| %                | 0.08 | 0.03 | 0.23 | 0.002 | 0.003 | 0.001 | 0.002 |
| Measurement uncertainty | 0.006 | 0.003 | 0.01 | 0.001 | 0.003 | 0.003 | 0.001 |

Figure 1. Termograms of the samples: 1—TG curve of microdiamond; 2—DSC curve of microdiamond; 3—TG curve of nanodiamond; 4—DSC curve of nanodiamond.

base plane (111). This is connected with the small size and imperfect structure of nanoparticles. As the particle size decreases, the fraction of surface atoms increases, which results in the larger root mean square displacement of atoms and violation of the spatial symmetry of lattice atoms [16]. This results in the growth of the crystal surface energy, and thus, compression of crystallographic planes and spatial deformation of the crystalline cell parameter (the results of x-ray structural analysis for nanodiamond with the crystalline cell parameter \( a = 0.3569 \) nm and for microdiamond with \( a = 0.3571 \) nm). After nanodiamond thermal processing to 1500 °C with a rate of 10 °C/min min the x-ray line (figure 2, curve 4) demonstrates a noticeable reduction of the peak intensity of the base plane (111). This indicates the smaller amount of nanodiamond particles after thermal processing. Curve 4 in figure 2 also demonstrates a halo corresponding to the x-ray amorphous graphite-like structure near the Bragg angles \( 2\theta = 20–32^\circ \). This phase consists of graphite planes. Atoms in the plane are in the state of sp\(^2\)-hybridization, similar to graphite. The distance between planes, however, larger than in graphite.

The photos of annealed microdiamond samples are shown in figure 3: the diamond powder microstructure after thermal processing to 1500 °C at a heating rate of 10 °C/min in figure 3(a) and at a heating rate of 2 °C/min in figure 3(b). Cubic structures with pronounced interfaces between particles can be clearly see in the photos. Particles with a homogeneous size of about
Figure 2. The XRD pattern of the powder: 1—the initial detonation microdiamond; 2—after the heat treatment detonation microdiamond up to 1500 °C with rate 10 °C/min; 3—the initial detonation nanodiamond; 4—after the heat treatment of detonation nanodiamond up to 1500 °C with rate 10 °C/min.

Figure 3. The microstructure of the detonation microdiamond powder after heat treatment to temperature 1500 °C: (a) heating rate 10 °C/min and (b) heating rate 2 °C/min. 100 µm are observed in the photos of the microdiamond sample after thermal processing to 1500 °C with a rate of 10 °C/min. Particles of other sizes also appear in the photos, this is
Figure 4. The microstructure of the nanodiamond powder: (a) before the heat treatment and (b) after the heat treatment to temperature 1500 °C at heating rate 10 °C/min.

Figure 5. The microstructure of the nanodiamond powder after heat treatment to temperature 1500 °C at heating rate 2 °C/min.
connected with solid inhomogeneous structure of some particles with a size of about 20 µm, figure 3(b). Particles with this size dominate in the sample after thermal processing to 1500 ºC with a rate 2 ºC/min, figure 3(b).

The reduction of the heating rate for detonation powder of microdiamond results in fragmentation into finer particles. As the heating rate decreases, the total heating time increases. As a consequence, microdiamond particles are at high temperature during a longer time, i.e., the time of particle interaction with each other increases.

The initial nanodiamond powder consisted of nanoparticles with a size of 6–8 nm, figure 4(a). After heating with a rate of 10 ºC/min to 1500 ºC particles acquired the spherical shape with a size of 30–40 nm, figure 4(b), [12]. In other words, the typical powder particle size increased with increasing temperature. It is possible that glueing of separate nanoparticles with each other took place. Sintered conglomerates can be observed in figure 4(b).

The study of the nanodiamond powder after thermal processing to 1500 ºC with a rate of 2 ºC/min showed that the sample consisted of loose agglomerates with a size of 0.5–3 µm (figure 5). Particles with a size of 6–8 nm were observed on the agglomerate surface. Separate large, up to 1 µm, plane formations were also observed in the sample (figure 5). Spherical particles with a size of about 100 nm were formed on the surface of separate microparticles after thermal processing of microdiamond powder in the same conditions.

The sample volume grew upon annealing of detonation nanodiamond with a heating rate of 2 ºC/min to 1500 ºC, it was accompanied by the lid rise in the crucible. The sample mass reduction was about 30%. The volume of microdiamonds did not grow for the same temperature mode, however, microdiamond particles were fragmented into finer parts.

4. Conclusion
In this study, we compared the thermal stability of detonation nano and microdiamond powder. The thermal and phase stability of microdiamond substantially exceeds the nanomaterial stability. The thermal stability was compared in a temperature range from room temperature to 1500 ºC. It was found that that the mass of the heated powder of detonation nanodiamond changed mass by about 16%, while the mass change of microdiamond was about 2%. After annealing with a rate of 10 ºC/min to 1500 ºC powder conglomerates of detonation diamond became more homogeneous, and their effective size increased from 6–10 to 30–40 nm. The change of the heating rate results in the change of the type of destruction of nanodiamond powder conglomerates. After annealing with a rate of 2 ºC/min to 1500 ºC new plane carbon structures with a size of about 1 µm were discovered in nanodiamond. It is assumed that these structures began to form at 1300 ºC. In the case of the same annealing of microdiamond powder the sample fragmented into finer fractions. The data obtained for thermal stability of micro and nanodiamond particles can be useful for development of new composite materials and optimization of ion plasma hardening of steel component surfaces.

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