Microcrystallites, granularity and agglomerates of detonation nanodiamonds

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Abstract: *Energy-saturated materials are considered to be a source of cheap energy, while detonation synthesis is a new promising form of the basic technology for producing nanodiamonds and other super hard and ceramic nanomaterials. Nanodiamonds is a unique product that combines both the properties of diamond and the advantages of nanostructures. The given work investigated the synthesis products, obtained under industrial conditions, while having detonation of a mixture of trinitrotoluene (TNT) with gecsogen (RDX) and RDX with graphite. The sizes of microcrystallites were, estimated by X-ray diffraction analysis and particle grain size according to the measurement of specific surface area, agglomerate in water suspension after treatment by ultrasound. There was, shown the evolution of nanodiamonds particle sizes and microstructures, both in the primary synthesis products and after enrichment from non-diamond forms of carbon and technological impurities.* Changes in the microstructure indicate a high reactivity of nanodiamonds. *The obtained results can be useful for studying the mechanism of synthesis and practical application of detonation nanodiamonds.*
Keywords*: NANODIAMOND, DETONATION SYNTHESIS, MICROCRYSTALLITES, MICROSTRUCTURE, GRANULARITY, ULTRASOUND, AGGLOMERATE.*

1. Introduction

Energy-saturated materials are considered to be a source of cheap energy, while detonation synthesis is a new promising form of the basic technology for producing nanodiamonds and other super hard and ceramic nanomaterials. Nanodiamonds (ND) is a unique product that combines both the properties of diamond and the advantages of nanostructures [1-3]. At the present, moment science and technology use detonation synthesis ND, obtained both from the carbon of an explosive molecule and from a mixture of explosive with the addition of graphite or soot. In the latter case, the diamonds are larger. 39 years have passed since the discovery of nanodiamonds, there was established certain production not only in Russia but also abroad, however the work as for the research, modification and application of ND continues to be relevant.

The physical and chemical properties of nanomaterials are mainly dependent on the microstructure and the grain size. To put it in practice, ND of detonation synthesis, are produced from both carbon explosive molecule [4,5], and from a mixture of explosives with the addition of graphite or soot [6]. The general technology for ND production in both cases is the same, however, with the use of graphite, diamonds are usually larger in size [7,8]. Experimental experience shows that the size of diamond may also depend on the mass of explosives and the cooling conditions of the detonation products in the chamber [9,10]. In the production process, diamonds go through the stages of crystal nucleation and growth, hardening in the process of expansion of detonation products and enrichment from condensed detonation products, moreover due to surface activity of nanoparticles, the sizes of microcrystallites and grains can vary. The given research paper presents the results of studies as for determination and comparison the sizes of microcrystallites, grain and agglomerates of ND obtained both from explosive molecules and from a mixture of explosives with the graphite addition. It is important to note that the studies were carried out on explosive charges of industrial synthesis and under equal experimental conditions.

2. Research objectives

The detonation synthesis of ND was carried out in an industrial explosive chamber with a volume of 4 m^3 in a buffer cooling medium from its own gaseous detonation products. There were used cast charges of TNT – RDX alloys in a ratio of 40/60 and extruded charges of RDX with graphite in a ratio of 80/20 by weight, respectively. The mass of the explosive charge in the experiments is 0.5-2.0 kg.

There were, estimated the sizes of microcrystallites by means of X-ray diffraction analysis and particle grain size according to the measurement of specific surface area. The crystal structure and crystallite sizes of the samples were determined on a Rigaku Ultima IV X-ray diffractometer. There was used Cu radiation, at a shooting speed of 1 deg./min, with the step of 0.01 deg. and scanning angles of 5-75 deg. The diffraction patterns were, processed using the PDXL software package; the phase composition was determined using the ICDDPDF2 database.

The specific surface area (*S*) was, determined by the BET adsorption method in a stream of nitrogen at the "ASAP-2000" automatic microvolume vacuum unit, Micromeritics. Granularity was calculated according to the formula for spherical particles: $D = 6/ S \bullet \rho$, where ρ is the density of ND.

The size distribution of particles was measured in water suspension (under ultrasound) was determined by the method of a laser diffraction on Horiba LA-950 laser analyzer. The frequency of ultrasound was 20 kHz.

3. Experimental results and discussion

The (Table 1) shows the results of studies of microcrystallites (d_1), granularity (D_1), and specific surface area (S_1) for enriched ND obtained in experiments with different mass and composition of explosives. The sizes of microcrystallites measured in condensed detonation products (d_2) before its enrichment are, shown.

Table 1. *Sizes of microcrystallites and ND grain size for explosives of various mass and composition*

Explosive Composition	The mass of explosives, kg	S_1, sm^2/g	D_1, *nm*	d_1, nm	d_2, nm	S_2, sm^2/g
RDX Graphite	0.5	23.4	75.4	6.55	4.72	47,4
	1.0	32.2	54.8	7.40	5.02	54,5
	1.2	21.0	84.0	6.84	5.24	61,4
RDX TNT	0.5	246.3	7.60	4.90	3.25	315,6
	1.0	232.6	8.10	4.71	3.56	302,5
	2.0	231.3	8.10	4.51	3.44	390,5

The results show that ND from explosives and graphite have similar values in sizes d_1 and d_2, but differ significantly in S_1 and D_1. The sizes D_1 for graphite diamonds are considerably larger. With an increase in the explosive mass, the sizes of microcrystallites and grain size of ND increase. It is interesting to note that for all samples, d_2 is noticeably less than d_1. In the

process of enrichment in a mixture of sulfuric and chloric acids at a temperature of 180-240^{0}C, the sizes of microcrystallites increased. This is possible, since the particle of ND microcrystallites has an amorphous phase at the periphery of the crystal [11]. In the process of enrichment, the amorphous phase recrystallizes with an increase in the size of ND microcrystallites.

It should, be noted that for primary fusion products in the region of 200-400°C, a significant thermal effect is almost always observed on the DTA curve, which is comparable to a number of samples with the heat of combustion. Moreover, no mass loss is, observed on the TGA curve (for example, Fig. 1). This behavior can, be explained by the presence of excess surface energy, the destruction and oxidation of the surface layer. Этот результат также подтверждает о возможной перекристаллизации ND при нагревании. This result also confirms the possible recrystallization of ND during heating.

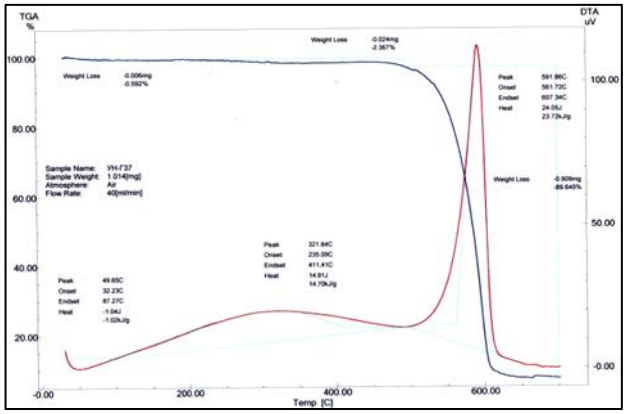

Fig. 1. *DTA and TGA (RDX/TNT, the mass of explosives – 1, 0 kg).*

The results of specially conducted experiments are, presented in (Table 2). Parts of one sample were, heated at different temperatures in the atmosphere. As a sample, primary products of ND.

As can be seen from (Table 2), with the increase in the temperature d_2 and D_2 grow. The proportion of the amorphous phase in the samples decreases. For a sample obtained at 450^{0}C or 530^{0}C, R_2 and D_2 are higher than for a similar sample of ND enriched with acids (Table 1). Thus, it is obvious that the microcrystallites and granularity of diamonds increase in the process of enrichment. Changes in the microstructure indicate a high reactivity of nanodiamonds.

Table 2. *The microcrystallites ND in the world of the temperature*

Explosive Composition	Temperature, ^{0}C	amorphous phase, %	d_2, nm	S_2, см^2/г	D_2, *nm*
RDX /TNT (The mass of explosives, 1,0kg)	25	24,0	3,56	302,5	7,93
	280	26,0	3,70	341,9	7,02
	350	35,0	3,72	287,1	8,03
	450	39,0	7,80	164,8	11,74
RDX Graphite (The mass of explosives, 1,2kg)	25	29,0	5,24	61,4	39,1
	250	31,0	6,30	63,5	39,4
	480	42,0	15,4	19,1	92,4
	530	48,0	22,7	14,8	119,2

Nanomaterials, thanks to the active surface, from a system of units. The looseness of the units grows as they enlarge, and the strength decreases.

Studies of ND units in water suspensions are given on (Fig. 2-5) and in (Table 3).

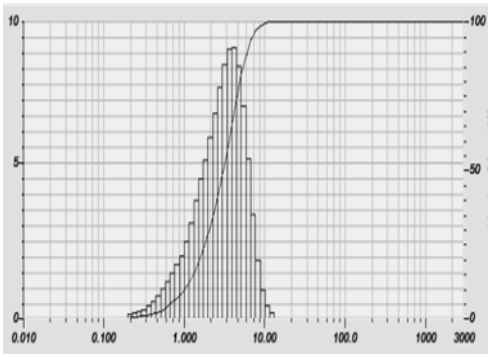

Fig. 2. *Particle Size Distribution for ND (RDX /TNT, the mass - 0.5 kg).*

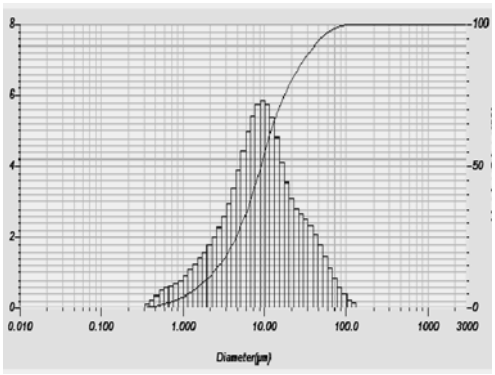

Fig. 3. *Particle Size Distribution for ND (RDX/Graphite, the mass - 1.2 kg).*

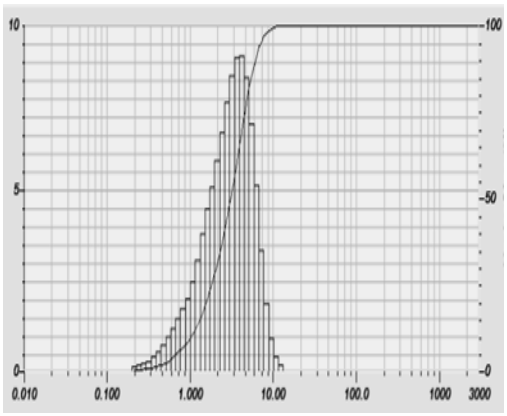

Fig. 4*. Particle Size Distribution for ND (RDX/Graphite, the mass - 1.2 kg, Ultrasound).*

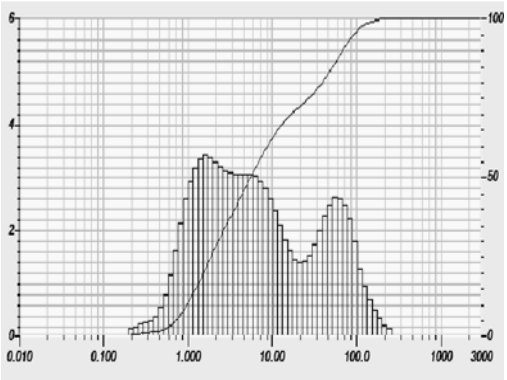

Fig. 5. *Particle Size Distribution for ND (RDX /TNT, the mass - 0.5 kg, Ultrasound).*

Table 3. *The size of the ND particles depending on the time of exposure to ultrasound*

Explosive Composition	The mass of explosives, kg	Time, sec	Mean size, μm	Median size, μm	Mode size, μm
RDX Graphite	0,5	0	14.79	9.54	10.78
		120	9.13	6.14	7.19
	1,2	0	14.71	9.03	9.44
		60	3.39	3.08	4.16
RDX TNT	0.5	0	238.91	180.45	245.20
		125	21.80	5.59	1.62
	1.0	0	63.34	48.80	82.45
		120	2.43	2.03	2.78
	2.0	0	35.09	21.67	54.90
		15	25.55	15.49	12.37

The particle distribution curves are given in size for ND samples obtained using and with, out ultrasound. The frequency of ultrasound was 20 kHz. For all samples, the average size of the units is much lower than the grain of nanodiamonds. There is the following dependence, the smaller the size of the grain, the larger the size of the units. The use of ultrasound reduces the size of stable units by about an order of magnitude. Nanodiamonds from the explosive molecule is more prone to aggregation.

Analyzing of the results, we reached the conclusion that the ND particles from the explosive molecule are a single crystal formation, since d_1 and D_1 have the same size values. Graphite ND particles are polycrystals formed from 8-10 microcrystallites. Particles of ND pass through three stages of formation. The first stage is the condensation, formation and growth of microcrystallites in the area of chemical reactions in the detonation wave and the merging or sintering of microcrystallites (formation D) in the Taylor wave in the second stage. At the third stage (chemical cleaning, drying), microcrystallites, granularity and structure of stable ND agglomerates are finally formed.

4. Conclusion

While conducting the present research there were determined the sizes of microcrystallites and the ND granularity obtained under industrial conditions both from the explosive molecule and from the explosive with the addition of graphite. The sizes of microcrystallites are approximately equal, and the granularity differs significantly. ND particles from explosives have mainly a single-crystal structure with a grain size of 7-8 nm, and ND particles from explosives with graphite are polycrystals with a grain size of 54-84 nm. As the charge, mass increases, the sizes of single crystals and grains increase too. During the chemical cleaning, the size of microcrystallites and the grain of ND increase. Changes in the microstructure indicate a high reactivity of nanodiamonds. After chemical cleaning, stable units with a size from 0.1 to 100 μm are, formed in the water suspension. NA from the explosive molecule is more prone to aggregation.

The obtained results can be useful for studying the mechanism of synthesis and practical application of detonation ND.

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