PROPERTIES OF NANODIAMONDS OF INDUSTRIAL DETONATION SYNTHESIS

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Abstract: *Detonation synthesis nanodiamonds have been widely used in modern science and technology. Such kind of nanodiamonds can be obtained either from the carbon explosive molecule (DND) or from a mixture of explosives with the addition of graphite or soot (DALAN). Possessing nanoscale and high surface energy, diamonds have a structural and dispersion-strengthening effect being in contact with any materials. In many ways, the applications of nanodiamonds are determined by their dispersion, reactivity, and aggregative state in various environments. The given scientific research investigated the properties of industrial DND and DALAN produced by JSC RPE "SIDAL", being one of the leading manufacturers in Russia. There were estimated the following properties: crystallites sizes; elemental composition; thermal stability; specific surface area; unit sizes.*

Keywords: NANO DIAMONDS, DETONATION SYNTHESIS, REACTIVITY, CRYSTALLITES, DISPERSION, UNITS

1. Introduction

Artificial diamonds are considered to be strategic materials all over the world, as they play a vital role in the development of the industry. With the establishment of a new detonation method for the synthesis of diamonds, there appeared fundamentally new opportunities for the implementation of advanced technologies [1,2]. The synthesis is carried out by detonation of explosives in an explosion chamber, while nanocarbon and nanodiamonds are formed in condensed detonation products with a high mass yield. Detonation synthesis is a fundamentally new and productive type of basic technology for producing nanostates and nanomaterials. Nanodiamonds (ND) of detonation synthesis is a unique material that combines the properties of diamonds and the advantages of nanostructures. Industrial development of the given method made it possible to actually reach large-volume production and consumption of ND in a number of industries [3,4]. ND is currently applied as anti-friction additives to motor, industrial oils and greases; in pastes and suspensions for super finishing material polishing; in wear-resistant electrochemical and chemical metal-diamond coatings; as dispersion-strengthening additives in composite materials based on polymers, metals, alloys and rubbers; as effective sorbents, catalyst carriers, biomarkers, transporter of medicinal substances, etc [5].

Science and technology are prone to use detonation synthesis, obtained both from carbon explosive molecules (DND) and from a mixture of explosives with the addition of graphite or soot (DALAN). In the latter case, they are larger.

The applications of ND are mainly determined by the dispersion of crystallites and particles, the reactivity and the aggregative state of ND powders in various environments. The given scientific research investigated the properties of industrial DND and DALAN produced by JSC RPE "SIDAL", being one of the leading manufacturers in Russia.

2. Preconditions and Means for Resolving the Problem

Detonation synthesis of DND and DALAN was carried out in industrial explosion chambers with a volume of 4 m^3 in a buffer cooling environment out of their own detonation products. In order to obtain DND there were used cast charges from TNT – RDX alloys in a ratio of 40/60 by weight, respectively; as for DALAN there were used pressed charges of hexogen and graphite in a ratio of 80/20 by weight, respectively. The mass of the explosive charge was 0.5-2.0kg. The following DND and DALAN properties were evaluated: elemental composition; crystallite sizes and specific surface; thermal stability; particle size distribution according to the unit sizes in powders and water environment. The elemental composition (C, N, H, O) was determined on an elemental analyzer FlashEATM 1112 manufactured by ThermoQuest at the incineration temperature of 900°C. The crystal structure and crystallite sizes of the samples were determined by means of wide-angle X-ray dispersion on a Rigaku Ultima IV X-ray diffractometer. There was used Cu radiation at a shooting speed of 1 deg/min, at a step of 0.01 deg and scanning angles of 5-75 deg. Processing of the obtained diffraction patterns was carried out by using the PDXL software package, the phase composition was determined by using the ICDDPDF2 database.

The specific area of the surface (S_{BET}) was determined by the BET adsorption method in a stream of nitrogen at the "ASAP-2000" automatic microvolume vacuum unit, Micromeritics.

The reactivity of the samples was determined by heating up to 800°C in the atmospheric environment with a heating rate of 10°C per minute by the method of simultaneous thermal analysis of DTA / TGA on a Shimadzu-60 device. There were estimated the initial temperature of intense mass loss, the temperature of the maximum and the thermal effect of samples combustion.

The size distribution of particles was measured in an Olympus OMEC DC130 microscope. The data were analyzed using OLYMPUS Particle Image Processor (PIP 9.0) software. In aqueous suspensions with the usage of ultrasound and without it the distribution was determined by the method of a laser diffraction on Horiba LA-950 laser analyzer. The frequency of ultrasound was 20 kHz.

3. Results and Discussion

Due to the fact that NDs are formed in fractions of microseconds under strongly different conditions, they possess a number of properties specific to nanomaterials. As for nanoparticles, the surface in terms of their volume is significantly larger in comparison with large crystals, that is why there can be spectated the physicochemical properties of the surface layers. According to IR spectroscopy and polarography, the surface of ND is saturated with hydrocarbons, functional groups, and carbon structures with which these groups are directly connected. They contain hydroxyl, carboxyl and carbonyl groups, as a result of which the carbon content in the products decreases [6]. The results of studies of DND and DALAN properties are shown in table 1.

According to elemental analysis, ND powders contain C, H, N, O with a basic substance content of 86 ... 95% and an ash content of not more than 0.3%. The carbon content in DND samples is noticeably lower than for DALAN, the content of hydrogen, nitrogen, and oxygen is higher. It should be noted that there is no nitrogen in DALAN and this may be due to different kinetic conditions for the nucleation and growth of ND crystallites in the detonation wave. The crystallite sizes (the region of coherent scattering of the lattice) for DALAN are 1.5 times larger than for DND, while S_{BET} differs dramatically. DND particles are single-crystal formations, since the crystallite sizes coincide with the sizes

of particles, calculated by S_{BET}. A slight difference in values can be explained by the presence of distortions and defects inside the grain. This increases the width of the diffraction lines and decreases the crystallite size. DALAN particles are polycrystalline formations collected at the stage of synthesis from 6.8-7.4 nm crystallites into 58-89 nm particles.

Table 1*: *Main Properties of DND and DALAN

TITLE	DND	DALAN
Crystallites size [nm]	**4,7-5,2**	**6,8-7,4**
Specific surface (S_{BET}) [m^2/g]	**220-246**	**21-32**
Particle size (calculation) [nm]	**7,6-8,5**	**58-89**
Elemental composition [%]:		
C	**86-88**	**93-95**
H	**0,8-1,2**	**0,3-0,9**
N	**1,7-2,1**	**0,0**
O	**9,7-10,3**	**3,7-4,6**
ash content	**0,1-0,3**	**0,1-0,3**
Density [g/sm^3]:		
bulk	**0,21-0,31**	**0,78-0,85**
pycnometric density	**3,05-3,21**	**3,35-3,48**
temperature oxidation [°C]:		
initial	**540-580**	**630-650**
maximum	**590-614**	**693-714**
Heat of combustion [kJ/g]	**13,7-26,7**	**13,0-17,1**
Unit diameter in powder [mkm]:		
mass average	**2,5-3,3**	**2,6-3,2**
median	**2,2-5,6**	**2,5-3,2**
Unit diameter in suspension [mkm]:		
average	**35,2-63,4**	**14,1-21,2**
median	**21,3-48,3**	**9,1-11,3**
Unit diameter in suspension after ultra sound processing [mkm]:		
average	**2,3-4,7**	**3,4-6,1**
median	**1,8-5,6**	**3,0-6,1**

The presence of a large number of uncompensated bonds on the surface of the particles leads to the appearance of "stored energy" and an increase in reactivity. The oxidation of DND and DALAN in air begins at 540-630°C, and occurs intensively at 590-714°C. For catalytic diamonds of static synthesis, the temperature of the oxidation onset is 670-850°C. Judging by the temperatures of the onset and maximum oxidation, the reactivity for DND is higher than for DALAN; in general, the heat of combustion is also higher. It is known that the formation enthalpy for crystalline diamond is 158 KJ/kg, for ND is in the range of 2560-2950 KJ/kg and may be higher according to calculations [3,6,7]. In our case, the heat of combustion for DND and DALAN reaches 26 and 17 KJ/g, respectively.

It should be noted that for DND and DALAN in the region of 300°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 (fig. 1,2). This behavior can be explained by the presence of excess surface energy, the destruction and oxidation of the surface layer.

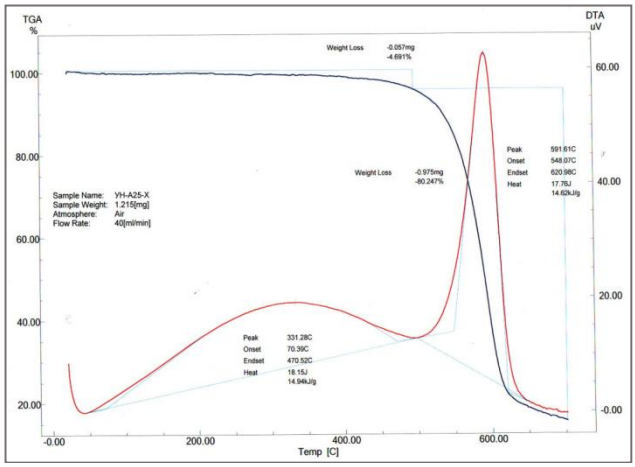

***Fig.1** DTA and TGA curves for DNA*

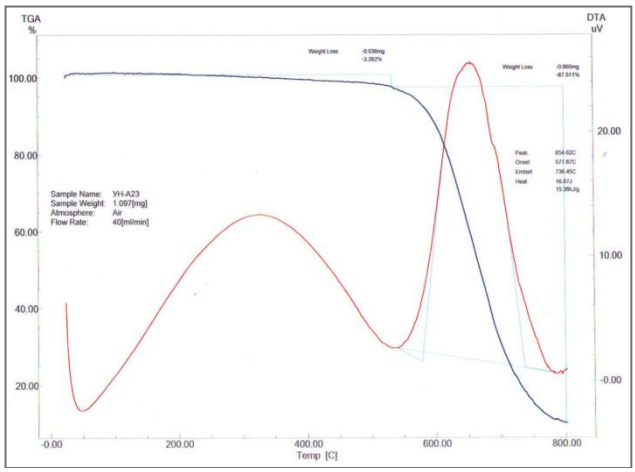

***Fig.2** DTA and TGA Curves for DALAN*

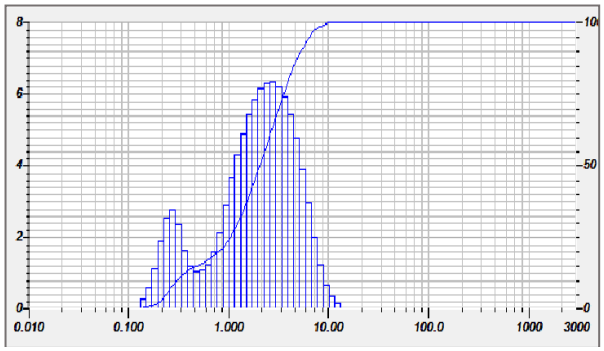

***Fig.3** DND particle size distribution*

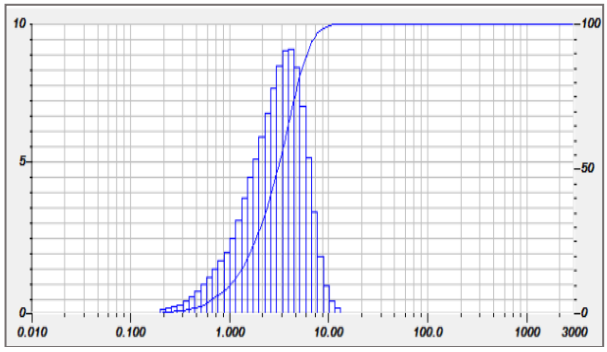

***Fig.4** DALAN particle size distribution*

Unsaturated surface bonds and surface energies lead to ND aggregation, forming a consistent hierarchical system of primary, secondary, and further units. The friability of units increases as they become larger while the density decreases.

The charging of DND and DALAN powders measured on a helium auto Picnometer is significantly lower than the X-ray density. In DND and DALAN powders, previously ground in an agate mortar, the unit sizes are approximately equal. In suspensions, without exposure to ultrasound, there are formed larger units. On the differential curves there observed two- and for DNDs also a three-modal size distribution of units. With ultrasonic processing, the dimensions of the units reduce and after 120 seconds they practically do not change. The unit sizes for DALAN and DND become comparable, however, for DND, the two-modal distribution of particles is sometimes preserved on the differential curve (fig. 3,4).

4. Conclusion

Studies have shown that the main difference between DND and DALAN is the crystal structure and particle size. DALAN has a polycrystalline structure with a particle size of 58-89nm, DND is a single-crystal structure with a particle size of 7.1-8.5nm. This explains other differences: carbon content; reactivity; energy saturation and propensity to form the units. The elemental and phase composition of nanomaterials is reproducible and stable. Crystallite sizes and granularity, energy intensity within the detonation production method can be controlled. As industrial nanomaterials, DND and DALAN are promising for use in materials science and nanoindustry.

The study was carried out with the financial support of the Russian Federal Property Fund in the framework of a scientific project No. 18-29-19070 MK.

5. Literature

[1] A. I. Lyamkin, E. A. Petrov, A. P. Ershov, G. V. Sakovich, A. M. Staver, and V. M. Titov, “The way to produce diamonds from explosives,” Dokl. Akad. Nauk SSSR 302(3), 611–613 (1988).

[2] F. E. Griener, B. S. Phillips, J. D. Johnson, and F. Volk, “Diamonds in detonation soot,” Nature 333(172), 440–442 (1988).

[3] G. V. Sakovich, V. F. Komarov, and E. A. Petrov, “Synthesis, properties and application of nanosized synthetic diamonds. Part 1. Synthesis and properties,” Superhard. Materials., No. 3, 3–18 (2002).

[4] G. V. Sakovich, V. F. Komarov, and E. A. Petrov, “Synthesis, properties and application of nanosized synthetic diamonds. Part 2. Application and manufacturing,” Superhard. Materials., No. 4, 8–23 (2002).

[5] Sakovich G.V., Zharkov A.S., Petrov E.A., “Results of research into the physicochemical processes of detonation synthesis and nanodiamond applications”, Nanotechnologies in Russia, 8 (9-10), 581-591 (2013)

[6] A. L. Vereschagin, G. V. Sakovich, V. F. Komarov, and E. A. Petrov, “Properties of ultrafine diamond clusters from detonation synthesis,” Diamond and Relater Materials, No. 3, 160–162 (1993).

[7] E.A. Petrov, “Achievements and actual tasks of the development of detonation synthesis of nanodiamonds”: Proceedings of the 22nd Seminar on New Trends in Research of Energetic Materials, Pardubice, Czech Republic April 10–12, 2019. pp. 588-592.