Elemental composition and crystallography of detonation nanodiamonds (DND)

Dolmatov V.Yu.

FGUP «SCTB «Technolog», 192076 St.-Petersburg, Russia

The improved method of determination of elemental composition of DND (preliminary keeping of a DND-sample under vacuum of 0,01-10Pa at temperature of 200°C during 3-5 hours, then its combustion at 1200°C during 40-50 seconds) showed actually technologically “dry” detonation nanodiamonds (being dried at 150°C to constant weight) contain 10-12wt.% volatile compounds (H_2O, gases, components of mixtures for chemical purification of DND) [1]. The volatile compounds are tightly restrained in DND-nanopores.

That is why all previous methods of determination of elemental composition gave understated data on carbon and overstated ones on oxygen (Table).

Table. Elemental composition and crystallography data of DND

Producer (reducing agent)	Elemental composition of DND (without regard to incombustible impurities)				Content of incombustible impurities, wt.%	Crystal lattice parameter, E**	Basic sizes of mono-crystals, nm **
	C	H	N	O			
2	3	4	5	6	7	10	11
1. FGUP «SCTB «Technolog», usual synthesis in water	93.3 (89.6) *	1.2 (2.4)*	2.5 (2.2)*	3.0 (5.8)*	0.9	3.565	2.1; 5.4; 4.8
2. JSC «ALIT», Ukraine, synthesis – water spray	91.7	0.5	1.8	6.3	0.34	3.565	
3. Shenzhen industrial company», People's Republic China	93.4	0.4	1.8	4.4	0.26	3.5667	
4. FGUP «SCTB «Technolog» (hydrazine)	95.2	0.7	2.3	1.6	0.45		
5. FGUP «SCTB «Technolog» (urotropine)	96.0	0.4	2.6	0.7	0.07	3.584	2.4; 7.0
6. FGUP «SCTB «Technolog» (urea)	94.3	1.6	2.7	0.8	0.6	3.5667	2.1;5.4; 10.2
7. FGUP «SCTB «Technolog» (ammonia)	92.7	2.4	2.9	1.3	0.7		2.4; 7.0; 9.4

** elemental composition of DND was determined by standard method*
*** Prof.Yuryev data (Institute of Inorganic Chemistry, t. Novosibirsk)*

Addition of a reducing agent - urotropine into the water shell of a charge at detonation synthesis of DND results in considerable decrease in content of incombustible impurities to 0,07wt.% (urotropine is a strong complexing agent with metals being contaminants of DND) [1].

Crystallographic analysis showed that when using of a reducing agent – urea perfect crystal lattice parameters (a=3,5667) are obtained. It was also determined that a basic part of DND-crystals have a set of two and more basic unit sizes, not mono-size of 4-6 nm.

[1] V.Yu. Dolmatov. *Journal Prikladnoi Khimii* **81**(10), 1620 (2008).

Investigation of properties of chrome-nanodiamond coatings based on detonation nanodiamonds (DND) of different producers

Burkat G.K.*, Dolmatov V.Yu.*, Osawa E.+, Orlova E.A.*

** FGUP «SCTB «Technolog»,192076 St.-Petersburg, Russia*
+NanoCarbon Research Institute Ltd, Ueda, Japan

Electrochemical deposition of metals along with DND is related to more наиболее producible and controlled processes. One of the widespread processes is deposition process of chrome-nanodiamond coatings (CDC). The work purpose is investigation of the possibility of using DND of different producers and different quality to obtain qualitative CDC from a standard chrome-plating electrolyte, g/litre: CrO_3 – 250, H_2SO_4 – 2.5, every thing else – water. DND of the following producers were investigated: 1) DND-TAH, FGUP «SCTB «Technolog», Russia; 2) DND-OS (NanoAmando®), NanoCarbon Research Institute Ltd, Japan; 3) DND-M, NPO «Sinta», Byelorussia; 4) DND-B, NPO «Altay», Russia; 5) DND-L, Complex «Electrokhimpribor», Russia.

Microhardness. Experiments being realized *in hard chrome-plating conditions* (45±1^{0}C) showed that addition of DND-OS and DND-TAH results in an increase in microhardness by 36% (12500 MPa) and 29% (11500 MPa), respectively, as against a pure chrome coating. The use of DND-M, DND-B and DND-L gave a practically equal increase in microhardness by 13-19% (it should be noted that a quantity of incombustible impurities of these three samples amounts to 2-5%, that is much more than for DND-OS and DND-TAH). *In wear-resistant chrome-plating conditions* (55±1°C) the use of DND-TAH resulted to the largest microhardness whereas DND-OS showed unstable microhardness data.

Wear-resistance. *In wear-resistant chrome-plating conditions* (55±1°C, 40 A/dm^2 and 50 A/dm^2) wear-resistance of CDC increases 2.4-2.8 times in the presence all DND under investigation in comparison with a pure chrome coating. CDC based on DND-TAH has the best microhardness. *In hard chrome-plating conditions* (45±1°C, 40 A/dm^2) the use of DND-TAH results in the largest wear-resistance (1.7-1.8–fold increase as against a pure chrome coating). Addition of DND-OS did not practically change the wear-resistance of a chrome coating. At current density of 50 A/dm^2 wear-resistance increases when using all DND under investigation, but DND-TAH are found to be the best ones.

Corrosion resistance. *In hard chrome-plating conditions* (45±1°C, 40 A/dm^2) corrosion resistance of CDC slightly increases (1.25 time) only in the presence of DND-TAH (5 g/l). An increase in current density to 70 A/dm^2 allowed the corrosion resistance to be increased 1.4-2.4 times in the presence of all DND under investigation. *In wear-resistant chrome-plating conditions* at 40 and 70 A/dm^2 the use of all DND under investigation decreases corrosion resistance 1.5-2.0 times since DND increase internal stress in CDC, as a result, fissuring and a number of pores.

So, it is shown that CDC based on DND has the best results on a complex of properties.

Detonation nanocarbons. From explosion to composition

Gavrilov A.S., Voznyakovsky A.P.

FSUE Lebedev Research Institute for Synthetic Rubber, St.-Petersburg, Russia

Detonation nanocarbons (DNC) have been known for more than 20 years. First experiments provided evidence that DNC was a composite material comprising a few allotropic forms of nanocarbon. The most studied one is crystal component - detonation nanodiamonds (DND). The major effort was made to develop an explosion technology that would ensure the best of crystal structure of the diamond component. Meantime DNC, named «diamonds-containing carbon black», found promising use in making polymeric materials. Strong incentive arose to characterize DCB by both DND content and amorphous constituent composition. On the bases of reported data on the presence of Sp^1, Sp^2, Sp^3-hybrid carbons in DCB[1] we assumed that fullerenes could also be present in DCB.

Jamples from divers producers were selected for study (RF Nuclear Center – Snezhinsk town, closed corp. "Synta" – Byelorussia, "Electrohimpribor" – town Lesnoye). They were found to show different modifying activity in polymeric compositions. X-ray crystal analysis showed that DND samplesof different make differ in their crystal features [2]. Possible presence of fullerenes in DCB was studied as well, but we failed to isolate fullerenes even via prolonged extraction at (10-50) °C combined with US fields application. On the other hand, fullerene absorption in DCB is almost irreversible, as evidence attempts to artificially introduce fullerenes into DCB, absorption time being influenced by DCB origin. Research into fullerene absorption by DND provide evidence that a limited specific amount of absorbed fullerenes exist and absorption irreversibility does persist. Polydispersity profiles have been drawn using dynamic light scattering for original DND and fullerenes-modified ones in non-polar hydrocarbon media. It has been stated that DND modification enables to markedly shift mass part distribution toward nano-region. The present work offers simulated mechanisms of fullerene - DND link formation. The development of specific grade of DCB for application is thought to be expedient for use in making polymeric materials.

[1] V.V. Danilenko, Sintez I spekanie almaza vzrivom, M.: Energoatomizdat, 2003, 272 p.
[2] A.Y. Vul, private communication

Detection and identification of nitrogen centers in nanodiamonds: EPR studies

Ilyin I.V.*, Soltamova A.A.*, Baranov P.G.*, Vul' A.Ya.*,
Kidalov S.V.*, Shakhov F.M.*, Mamin G.V.+, Orlinskii S.B.+,
Salakhov M.Kh.+

**Ioffe Physical-Technical Institute, 194021 St- Petersburg, Russia*
+Kazan State University, Federal Center of Shared Usage for Physicochemical Measurements, 420008 Kazan, Russia

The properties of carbon nanostructures are of the great interest. Nanodiamond (ND) doping processes, formation and structure of intrinsic and impurity defects differ from those in bulk diamonds. In particular, the theoretical studies have shown that nitrogen impurities in ND are metastable in contrast to bulk diamonds.

Continuous-wave (cw) electron paramagnetic resonance (EPR) and electron-spin echo (ESE) at both X-band (9.3 GHz, cw) and W-band (94 GHz, cw and ESE) were used to study nitrogen impurities in natural nanodiamond powder with characteristic size of a particles of about 150 nm and detonation nanodiamonds (after pressure sintering) with a size of ~ 8.5 nm.

Observed X-band EPR signals in natural nanodiamond powder were similar to previously observed in natural diamond microcrystals. The EPR spectrum consists of a strong central line of surface centers and small intensity satellites. A number of the EPR signals in microdiamond powder occur in approximately the same magnetic fields, and the EPR signal of the surface centers masks the main EPR lines. The interpretation of the satellite lines remains contradictory even in diamond microcrystals and this was not yet discussed in nanodiamonds.

In this report the problem was solved by measuring the EPR and especially ESE spectra at high frequency. In the ESE experiments central line of the surface centers was suppressed due to short relaxation time and all the EPR lines of two types of nitrogen centers: isolated nitrogen donor N^0 (P1 in bulk diamond) and nitrogen pair N_2^+ (W24) have been observed in the natural nanodiamond powder with spin Hamiltonian parameters $g_{\parallel}=g_{\perp}= 2.0024$, $A_{\parallel}= 40.7G$, $A_{\perp}= 29G$ (N^0) and $g_{\parallel}=2.00245$, $g_{\perp}=2.0030$, $A_{\parallel}=55.38G$, $A_{\perp}=29G$ (N_2^+).

EPR studies in detonation nanodiamonds showed the presence of N0 centers for the fist time. The appearance of the EPR signals related to N0 center suggests that single nitrogen atoms occupy stable position inside nanodiamod particles with a size of less then 10 nm produced by pressure sintering of nanodiamond powder.

This work was supported by the Programs of RAS: Spintronics; Support of Innovations and Elaborations and by the FASI under Contract No 02.513.12.3031.

Morphology and properties of polymer-nanodiamond composites

Karbushev V., Vasil‘ev G., Konstantinov I., Semakov A., Kulichikhin V.

Topchiev Institute of Petrochemical Synthesis RAS, Leninskii pr. 29, 119991 Moscow, Russia

Nanodiamonds of detonational synthesis (ND) are one of the most interesting materials from both a fundamental and practical points of view due to their unique combination of properties. However, a homogeneous dispersion of nanodiamonds in a polymer matrix is a very difficult task due to their great tendency to agglomeration.

It was shown, that for achievement of good dispersion of ND particles in the case of mechanical melt processing is necessary to provide conditions of elastic turbulence. Above this method obtained composites based on amorphous polymers: polysulfone (PSF) and styrene-acrylonitrile copolymer (SAN). For estimation of nanodiamond distribution in the polymer matrix the methods of optical and transmission electron microscopy were used. In order to reduce ND particles tendency to aggregation some attempts have been offered to change their functional cover by chemical and physical-chemical modification.

The average diameters of initial and modificated NDs in different liquids are measured on CPS Disc Centrifuge. Measurements of rheological properties of composite melts were performed on rheometer RheoStress RS600 (ThermoHaake) and capillary viscosimeter of melt-indexer type. Introduction of small additives of ND leads to increasing of polymer strength and modulus as in melt state (method of uniaxial tension) as in the solid state (tension tests). The sliding friction coefficient and wear resistance of composites on nichrome was measured, the wear resistance of modified by ND polymers increases essentially in comparison with neat polymers. Standard measurements of Brinell hardness and Izod impact strength showed its essential increase at introduction of ND particles. It was shown that modification of polymers by ND leads to improvement of wide complex of functional properties of thermoplasts.

Do primary particles of detonation nanodiamond form a secondary structure?

Korobov M.V.[1], Efremova M.M.[1], Avramenko N.V.[1], Ivanova N.I.[1], Rozhkova N.N.[2], Ōsawa E.[3]

[1]*Department of Chemistry, Moscow State University, 119991 Moscow, Russia*
[2]*Institute of Geology, Karelian Research Centre RAS, Petrozavodsk, Russia*
[3]*NanoCarbon Research Institute, AREC, Faculty of Textile Science and Engineering, Shinshu University, 3-15-1 Tokita, Ueda 386-8567, Japan*

Commercial samples of Detonation Nanodiamond (ND) consist of tight agglomerate particles having 100-200 nm in diameter, called *agglutinates.* An agglutinate is composed of primary particles – diamond crystals with the diameter of 4-5 nm. Primary particles are bound with each other by multitudes of C–C covalent bonds [1] or according to the other theory by means of coherent attractive Columbic interactions [2]. In this study we examined the material produced by disintegrating of agglutinates. It was made by means of stirred-media milling in water. The resulting water dispersion demonstrated sharp distribution of ND particles with the maximum at d = 5 nm [1]. This material will be referred to as Single-Nano Buckydiamond (SNBD). SNBD was studied as dried powder (flakes), gel and water dispersion by means of Differential Scanning calorimetry, nitrogen adsorption, isopiestic method, dynamic desorption of water and Dynamic Light Scattering.

The results obtained revealed that gel and dried powder of SNBD material exist in close-packed structures rather than in chaotic and weakly bonded mixtures of the primary particles. Strong cohesive interaction between neighboring carbon nanoparticles (e.g. carbon nanotubes), caused by large surface area to volume ratios is a well-known fact. The perfectly dispersed state of SNBD particles is likely to happen only in dispersions. We found that in gel and dried powder the primary ND particles form one and the same reproducible porous *network* with voids larger than the primary ND itself. The volume of the voids may range from 47 to 63% of the total volume of the material. This free volume is readily available for water, some organic solvent molecules, nitrogen at low temperatures. Measured characteristic parameters of the network are well retained and do not depend on the way of preparation of the samples, hence we consider them as *fingerprints* of SNBD material. With the help of these fingerprints SNBD was easily distinguished from non-milled commercial samples of detonation NDs.

This work was supported by the RFBR grant 06-03-32446.

[1] E. Ōsawa, *Pure Appl. Chem.* **80**, 1365 (2008).
[2] A.S. Barnard, *J. Mater. Chem.* **18**, 4038 (2008).

Infrared absorption studies of surface functional groups of chemically modified nanodiamonds

Osipov V.Yu.[*], Volgaev A.S.[*], Aleksenskiy A.E.[*], Shames A.I.[+], Vul' A.Ya.[*]

[*]*Ioffe Physical-Technical Institute, 194021 St.-Petersburg, Russia*
[+]*Department of Physics, Ben-Gurion University of the Negev, Beer Sheva 84105, Israel*

Detonation nanodiamonds (DND) with chemically modified surface are the most interesting class of hybrid nanomaterials among other promising recently developed nanomaterials. The use of DND suppose to be very promising for synthesis of new types of metallic catalysts, design of nano-sized bioprobes and biocompatible fluorescent markers. The main reason for such an interest originates from unique properties of the pristine DND surface partially terminated by carboxyl groups to be further chemically modified and re-functionalized by various atomic groups and metal ions.

In this research we study DND particles whose surface was chemically modified by copper. Chemical modification has been made by mixing a suspension of nanodiamond particles with a water solution of copper acetate. The resulting mixture was subjected to an ultrasonic irradiation, promoting deaggregation of the nanodiamond particles and ion exchange in water solution between Cu^{2+} ion and two protons of the nearest neighboring surface carboxyl groups. We studied a series of DND samples: A1 - initial highly purified and dried DND, A2 and A3 modified by 0.06 wt% and 0.6 wt.% of copper, respectively; another samples, A3-1 and A3-2, were prepared by annealing of the A3 sample at 550 and 900°C in a stream of hydrogen for 2 hours.

IR spectra of A1, A3 and A3-1 samples reveal hydroxyl (-OH), carbonyl (C=O) and C–H groups. Observation of carbonyl and hydroxyl groups evidences the presence of carboxyl groups –COOH. Narrow absorption peaks at 2850 and 2920 cm^{-1} due to $C(sp^3)$ –H stretching modes show that a part of surface carbon atoms is saturated by hydrogen. The absorption band at 900-1550 cm^{-1} consists of a number of distinct absorption lines. Pronounced lines at 1048, 1120 and 1164 cm^{-1} may be attributed to various modes of stretching vibrations in C-O and C–O–C groups. The latter appear in quantities on the DND surface at drying when two neighboring surface carboxyl groups react forming an anhydride group and a water molecule. Therefore the ether-like C–O–C bridge fragment in the anhydride O=C–O–C=O chain is apparently responsible for the lines mentioned above. The same lines in the spectral range 900-1200 cm^{-1} observed in cellulose and some other compounds undoubtedly evidences the presence of bridging C–O–C groups in the system under study.

Since there are only insignificant differences in the overal IR spectra within the series A1-A3-A31-A32, one can suppose that the ion exchange process yields a small substitution of protons of the surface carboxyl groups by Cu^{2+} ions. Rough estimation shows that for the A3 sample the amount of the surface carboxyl groups substituted by divalent copper ions does not exceed 2%.

This work was supported by the Russian Foundation for Basic Research (project 09-02-92477-MNKS_a).

Apatite-nanodiamond composite as a functional coating of stainless steel implants

Pecheva E.*, Pramatarova L.*, Tanaka Y.+, Sakamoto H.+, Doi H.+, Tsutsumi Y.+, Vul' A.#, Hanawa T.+

* *Institute of Solid State Physics, Bulgarian Academy of Sciences, 1784 Sofia, Bulgaria*
\+ *Institute of Biomaterials and Bioengineering, Tokyo Medical and Dental University, 101-0062 Tokyo, Japan*
\# *Ioffe Physical-Technical Institute, 194021 St. Petersburg, Russia*

Biological apatite is the main component of human bones, highly bioactive and biocompatible inorganic material. However, it has insufficient mechanical parameters and adhesion to surfaces. Diamond is the hardest known material, it is biologically compatible, chemically inert, and resistant to chemical corrosion and wear. Carbon-based coatings, such as diamond-like carbon, carbon nanotubes and amorphous carbon are found to significantly improve the mechanical properties of apatite, increase its adhesion, prevent metal ion release from metal implants and inhibit the formation of fibrous tissue and blood clotting upon implantation.

In this study, diamond nanoparticles with grain size of 4-6 nm were used in a co-deposition experiment with apatite. Composite coatings of apatite with embedded nanodiamond particles were prepared by potentiostatic mode electrodeposition on austenitic stainless steel substrates from nanodiamond-containing electrolyte (simulated body fluid was used as the electrolyte). Results revealed the formation of dense and homogeneous, non-stoichiometric apatite-nanodiamond composite coatings, containing CO_3 and HPO_4 groups, similar to the biological apatite. The composite coatings were characterized by ductility, improved hardness and adhesion to the steel surface in comparison to the pure apatite. We consider that the nanodiamond-reinforced apatite coatings represent a significant improvement for the stability of bioactive coatings, and thus can be considered as an attractive surface modification for medical device materials.

This study was supported by two National projects: with the Ministry of Education and Science, Bulgaria (TK-X 1708/2007) and with the Agency of Innovation, Bulgaria (02-54/2007). The support of a NATO grant CBP.EAP.RIG.982693 is also acknowledged.

Properties of high pressure sintered nanodiamonds and its composites

Kidalov S.V., Shakhov F.M., Vul' A.Ya., Ozerin A.N.*,
Kurkin T.S.*, Smirnov A.N.

Ioffe Physical-Technical Institute, 194021 St.-Petersburg, Russia
**Institute of synthetic polymer materials of the Russian Academy of Sciences, Russia*

New composites produced from nanocarbons are attractive materials for many applications, for example for heat-sink. In this report we inform about the new results on structure and thermal conductivity of the composites produced from detonation nanodiamonds (DND).

The composites have been sintered from DND and DND modified by fullerene C_{60} at high pressure (up to 7 GPa) and high temperature (up to 2000°C) [1].

Thermal conductivity, X-ray diffraction, Raman spectra and sound velocity of the composites have been characterized.

According to the X-ray diffraction measurements, coherent scattering region of nanodiamond cores increased from 5,5 nm in starting DND to 12 nm after sintering process. Possible mechanism of the sintering process is discussed.

Thermal conductivity of nanodiamond composites increased from 5 W/(m·K) to 50 W/(m·K) [2]. Only small amount of nondiamond phase was detected by the X-ray diffraction. Calculations based on experimental X-ray patterns demonstrate that nanodiamond particles' size distribution is not monotonic and consists of two maxima. We believe that it is a result of orientation of neighboring particles [3].

The experimental data on size distribution of nanodiamond particles' size and the thermal conductivity of the samples, allow us to calculate the nanodiamond boundary thermal conductance. The value of boundary thermal conductance is 1-4 GW/(m^2·K).

Measured sound velocity in the sintered DND is was 8.4 km/s. At the same time the sound velocity in the samples sintered from 10-14 μm natural diamond particles at different temperatures is equal 8-12 km/s. Increasing of sintering pressure results in increasing of the sound velocity.

Acknowledgments to RFBR grant 09-08-01200-a.

[1] S.V. Kidalov, F.M. Shakhov, A.Ya.Vul'. *Diam. Rel. Mat.* **17**, 844 (2008).
[2] S.V. Kidalov, F.M. Shakhov, A.Ya. Vul'. *Diam. Rel. Mat.* **16**, 2063 (2007).
[3] M. Niederberger, H. Cèlfen. *Phys. Chem. Chem. Phys.* **8**, 3271 (2006).

Highohmic nanocrystalline diamond films

Blaut-Blachev A.N., Bouilov L.L., Zolotarevsky V.I., Spitsyn B.V.

Frumkin Institute of Physical Chemistry and Electrochemistry RAS,
119991 Moscow, Russia

The nanocrystalline diamond films with thickness up to 3 micrometer was grown in anomalous dc-glow discharge from CH_4/H_2 gaseous mixture of using CVD technique. The velocity of gases flow for H_2 was – 10 L/h and 0.25 L/h for CH_4. The total gas pressure during growth supported at 70-75 Torr level. The film growth rate was equal to order of 1 mkm/h. The study of structure and properties of the films were carried out by methods of Raman spectroscopy, AFM, electro physical measurements, and XRD. The data analysis revealed a nanostructural films constitution with individual crystallites from 20-25 nm. Measured electrical resistivity of films exceeded up to 10^8 Ohm.

The research was performed under partial support from Presidium RAS Program No 18P(2).

Heat transfer in forced convective flows of water-based nanofluids with nanocrystalline diamonds of detonation synthesis

Kidalov S.V., Bogomazov I.E., Vul' A.Ya.

Ioffe Physical-Technical Institute RAS, 194021 St.-Petersburg, Russia

Investigations of heat transport properties dependency on concentration of nanodiamonds of detonation synthesis in water suspensions are undertaken in case of forced laminar flow in a closed cooling system.

Samples of nanofluids with low particle concentrations are probed in whole temperature range where a phase transition does not take a place. Alterations of effective heat transfer and of heat energy adsorption on solid state – fluid interface are shown with different values of a flow velocity and dissipation power.

Only nanodiamonds of detonation synthesis, which was firstly industrially synthesized in Russia, is used in a role of nanometer phase. The characteristic size of nanodimonds aggregates in suspensions amounts to 120 – 150 nm. Water suspensions are solely taken into account.

In last seven – ten years an interest to a heat dissipation problem has been constantly increasing and research of heat transport properties of nanofluids takes a specific place in this field. Regardless to a few new works as theoretical and the ones containing new experimental data as well, any common point of view on a possible mechanism of nanometer particles influence on nanofluids heat conductivity characteristics does not exist nowadays.

Investigations of heat conduction in forced convective systems, which are difficult to be described analytically, are of special interest. Far less works are carried out in this direction comparing to investigations concerned with stationary medium systems, and contradiction results has been reported.

This study is supported by the RFBR grant 09-08-01200-a.

The aggregation of the particles in the purified detonation nanodiamond

Aleksenskiy A.E., Dydeikin A.T., Shvidchenko A.V., Vul’ A.Ya., Sakseyev D.A., Baidakova M.V.

Ioffe Physical-Technical Institute RAS, 194021 St.-Peterburg, Russia

The aggregation of the particles in detonation nanodiamond (DND) is a significant factor, which restricts the application area of this promising nanomaterial. The average size of the aggregates in usual samples of the industrial detonation nanodiamond amounts about 200-400 nm.

In our previous work we have found that that the average size of the aggregates can be reduced by removing the magnetic impurities (ferromagnetic metals) from the water suspension of DND up to the value of 100 nm [1]. According to the acknowledged representation it corresponds to the hard initial aggregates formed at final stages of the detonation synthesis. Till now only Osawa.[2] could overcome the hardness of the mentioned initial aggregates by steering milling with zirconia’s balls and obtain the single digit nanodiamond suspension. This way sill remains the only one in spite of the contamination of the surface of nanodiamond particles by the residuals of zirconia and partial graphitization due to the enormous local pressure that occurs during milling.

However, according to our recent results, the reducing of the size of the initial aggregates can be obtained just by further deep purification including sequential washing and sedimentation the suspension in centrifuge. The average size of the nanodiamond particles aggregates determined by the dynamic light scattering (DLS) in the suspension purified by abovementioned method is 40 nm. The high resolution SEM image of the DND deposited from the purified suspension to the smooth surface of silicon substrate confirms completely this result. In the image the great amount of the smaller (up to 18 nm) particles can be clearly observed. The results of the element X-ray micro analysis give the ratio between C and O concentrations witch corresponds specially to DND due to the concentration of the carboxyl functional groups at the surface of each nanodiamond particle.

The obtained results are in good agreement with the idea about the role played by the ions of metals in the initial aggregation of DND particles.

The authors are grateful for the partial financial support from RFBR grants 08-024-00983 and 09-02-92477.

[1] A.E. Aleksensky, M.A. Yagovkina, A. Ya Vul. Method of nanodiamond purification. Patent of the Russian Federation 2322389 with priority date 13.10.2006.

[2] M. Ozawa, M. Inaguma, M. Takahashi, F. Kataoka, A. Krüger, E. Osawa. *Adv. Mater.* **19**, 1201 (2007).