Russian Chemical Reviews **76** (4) 339 – 360 (2007) © 2007 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2007v076n04ABEH003643

Detonation-synthesis nanodiamonds: synthesis, structure, properties and applications

V Yu Dolmatov

Contents

I.	Introduction	339
II.	Detonation synthesis of nanodiamonds: mechanisms	339
III.	Detonation synthesis of nanodiamonds: key features and regularities	341
IV.	Novel method of synthesis and revised elemental compositions of nanodiamonds and diamond blend	343
V.	Chemical purification of nanodiamonds: theory *vs.* practice	345
VI.	Industrial synthesis of nanodiamonds	346
VII.	Properties of nanodiamonds	346
VIII.	Fields of application of nanodiamonds	350

Abstract. The review outlines the theoretical foundations and industrial implementations of modern detonation synthesis of nanodiamonds and chemical purification of the nanodiamonds thus obtained. The structure, key properties and promising fields of application of detonation-synthesis nanodiamonds are considered. The bibliography includes 135 references.

I. Introduction

Detonation-synthesis nanodiamonds (ND) were first synthesised by researchers from the USSR in 1963 by explosive decomposition of high-explosive mixtures with negative oxygen balance in a non-oxidising medium.[1,2] Nanodiamonds are characterised by nanoscale particle sizes and have chemically inert cores and reactive peripheral regions called shells. A micrograph of a typical ND particle is shown in Fig. 1.

The detonation synthesis offers the following advantages over the static synthesis of ND: (1) high performance due to the lack of limitations associated with the size and the weight of charges; (2) no need for expensive and scarce expendable materials (hard alloys, alloy steels) and metal catalysts (nickel, manganese); and (3) possibility of preparation of unique polycrystalline ND powders under strongly non-equilibrium conditions.

A drawback of the technique consists in potential explosion risk when carrying out blasting operations, fabrication and transportation of charges.

II. Detonation synthesis of nanodiamonds: mechanisms

No commonly accepted theory of the detonation synthesis of ND is available at the moment. Different authors propose different (sometimes, significantly different) ND formation mechanisms. In this Section we will consider a number of theoretical models for ND formation.

A mechanism of ND formation from TNT – hexogen (RDX) mixtures is as follows.[3,4] In the zone of the detonation wave the explosive molecules disintegrate into atoms. Carbon atoms thus released are condensed into an amorphous carbon phase by means of diffusion and liquid droplet coalescence. Subsequently, amorphous carbon particles undergo a phase transition to diamond. It is believed that the degree of conversion increases from 0% to 100% in the pressure range 17 – 23 MPa. The formation of the diamond phase in this pressure range (it corresponds to the region of chemical peak of the detonation wave) was confirmed in other studies.[5–7] According to the data mentioned above, the formation of ND takes a time of 0.2 to 0.5 μs.

The diamond phase repeatedly experiences the action of reflected shock waves, and the ND temperature increases. As a

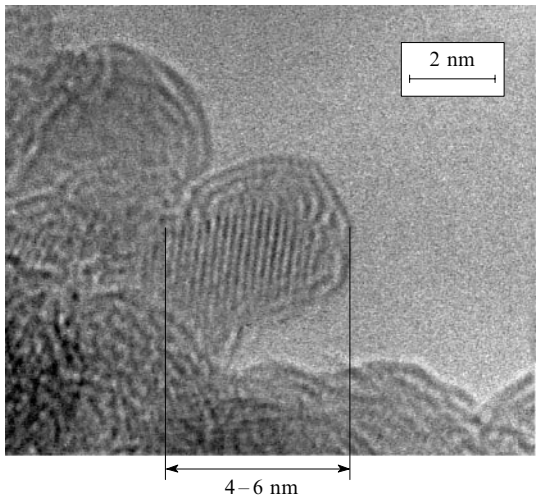


Figure 1. Micrograph of a single nanodiamond particle.
Courtesy of Professor A Ya Vul' (Ioffe Physico-Technical Institute, Russian Academy of Sciences, St Petersburg).

V Yu Dolmatov Federal State Unitary Enterprise Special Design-Technology Bureau (FSUE SDTB) 'Tekhnolog' at the St Petersburg State Institute of Technology (Technical University), Sovetskii prosp. 33A, 192076 St Petersburg, Russian Federation. Fax (7-812) 700 38 98, tel. (7-812) 700 38 98, e-mail: alcen@peterstar.ru

Received 18 January 2007
Uspekhi Khimii **76** (4) 375 – 397 (2007); translated by A M Raevskiy

consequence, the thermodynamic state of detonation products corresponds to the graphite stability region and partial graphitisation of ND occurs.

A study of the isotopic composition of the condensed products formed upon detonation of a TNT/octogen (HMX) mixture (TNT was labelled with ^{13}C at methyl group) showed that detonation-synthesis ND are mainly formed from the carbon atoms of TNT.[8] Similar conclusions were made in the studies of ND synthesis from a mixture of RDX with TNT labelled with ^{14}C at position 1 of the benzene ring.[9,10] It was also established that the yield of condensed carbon linearly decreases as the TNT content in the mixtures decreases, while the ND content in the diamond blend (DB), an intermediate product of ND synthesis, monotonically increases and reaches a constant value (for mixtures with RDX and HMX denoted TNT/RDX and TNT/HMX, respectively).[11]

The addition of heterocyclic and aliphatic nitramines has a little effect on the formation of ND. The role of the additives is to produce the necessary pressure and temperature for the phase transition to occur.[12]

The dispersion of ND depends on the nature of the carbon source.[13] For instance, the average particle size of the diamond phase formed upon detonation of mixtures of HMX with liquid organic additives varied from 1.8 (for glycerol) to 4.1 nm (for ethanol).

The maximum yield of ND was obtained using TNT/HMX or TNT/RDX mixtures containing 60 mass % to 70 mass % of TNT (density 1630 kg m^{-3}).[11]

According to Lin,[14] the key step in ND formation is the appearance of cyclohexane molecules (nuclei of the diamond structure). Collisions between the nuclei cause their aggregation into small clusters followed by growth of mesoscopic structures with long-range crystal order. Subsequent interaction of the mesoscopic structures with one another and with nuclei causes the formation of ND.

Anisichkin [15] put forward an original hypothesis, according to which the initial decomposition stages of explosive materials occur with the release of hydrogen as methane and carbon in the diamond phase. Then, these products are oxidised. The extent of carbon conversion to the diamond phase is determined by the detonation parameters.

It was shown that the chemical reaction zone extends as the dimensions of the explosive charge increase and that energy release also continues behind the Chapman–Jouguet plane.[16] Carbon coagulation and crystallisation can occur upon adiabatic expansion of detonation products. This was established in the studies [2,17] of the effect of the mass of the charge and the heavy shell surrounding it on the ND particle size. For instance, an increase in the charge mass from 0.6 to 10 kg using a water shell causes the particle size to increase from 4 to 6 nm (specific surface area is reduced from 330 to 200 $m^2\ g^{-1}$, see Ref. 2). The detonation of a 140-kg charge in water shell afforded ND particles with an average size of about 8 nm and individual polycrystals of size up to 85 μm.[17]

According to Danilenko,[18] the formation of ND can proceed by the known mechanism of homogeneous condensation of ultradisperse phases in highly supersaturated vapour (vapour–liquid–crystal mechanism) and result in spherical particles. Because of rapid exhaustion of the gas-vapour medium the average particle size does not increase with increasing duration of existence of the particle-growth conditions.

Crystallisation from vapour usually gives spherical nanoparticles of size $\leqslant 20$ nm, which also holds for ND.[19]

Additionally, Danilenko reported [18] that the assumption of ND crystallisation from the liquid phase was substantiated by the fact that the shape of the ND particle size distribution is typical of liquid droplet coalescence.[20]

The most probable values of the detonation pressure and temperature in the Chapman–Jouguet plane are listed in Table 1. The Chapman–Jouguet parameters of TNT/RDX alloys correspond to liquid nanocarbon.[18] At higher densities of explosive materials (ρ), carbon condensed in the reaction zone consists of nanodroplets only.

Table 1. Parameters of the ideal detonation in the Chapman–Jouguet plane.[18]

Explosive	ρ /kg m^{-3}	P /GPa		T /K	
		experiment	calculations	experiment	calculations
TNT	1600–1640	18–19	18.3–20.1	3700 [a]	3500–3618
RDX	1780–1800	34.5–35.4	34.7–35.0	4500 [b]	4200
TNT/RDX					
36:64	1713–1730	27–29.2	27.4–29.3	—	3931–4063
50:50	1670–1680	24.6	24.4.–25.5	—	3225–3900
Tetryl	1700	—	23.9–25.4	3700, 4300 [c]	3991–4063

ρ = 1510,[a] 1660 [b] and 1610 [c] kg m^{-3}.

The formation of ND in the detonation wave involves the following processes:[18]

— condensation of carbon in the reaction zone with the formation of primary clusters ($d < 1$ nm);

— cluster–cluster interaction (liquid droplet coalescence) with the formation of nanodroplets;

— crystallisation of nanodroplets with formation of ND provided a sufficiently long period of cooling by turbulent detonation products or amorphisation of nanodroplets and clusters resulting in free and bound soot.

Possible reasons for soot release in DB are (i) imperfect detonation in certain regions of the charge volume (initiation zone, boundary regions) characterised by low P and T values and leading to carbon condensation by the vapour–amorphous carbon mechanism and (ii) formation of methane,[15] which decomposes to soot upon detonation according to the reaction

$$CH_4 \rightleftharpoons C + 2H_2.$$

Detonation in real systems occurs in non-ideal and non-steady-state regimes. Here, carbon is oxidised to CO rather than CO_2. The process is characterised by lower pressures and temperatures and, correspondingly, by lower content of free carbon in detonation products and a decrease in the yield of ND. For instance, calculations [21] showed that the $P_{50}:P_{100}$ and $T_{50}:T_{100}$ ratios are respectively equal to 0.337 and 0.546 at 50% conversion, *i.e.*, the pressure decreases about twice faster than the temperature.

As the mass of the water shell surrounding the charge increases, the ND yield increases and reaches a maximum value at the shell mass equal to ten charge masses.[22,23] Optimum conditions for the synthesis of ND require the use of explosive charges with minimum porosity (highest density) and the blast conditions that provide the minimum possible imperfection of detonation.

The general conditions for optimum synthesis resulting in the maximum ND yield and the corresponding experimental methods are listed below.

Synthesis conditions	Implementation methods
Condensation of maximum possible, for a given explosive, amount of free carbon.	Detonation of explosive charges with the minimum porosity and imperfection.
Carbon condensation in the liquid nanocarbon region.	Use of TNT/RDX or TNT/HMX alloys with pressures higher than 22 GPa in the Chapman–Jouguet plane.
Maximum possible times of existence of liquid nanocarbon conditions in the detonation products and crystallisation of nanocarbon at pressures higher than 10 GPa in detonation products.	Detonation of explosive charges heavier than 5 kg in a water shell weighing more than ten charges.
Blasting under conditions that ensure the absence of amorphisation, oxidation and graphitisation.	Blasting charges in a massive water shell.

Thus, the chemical reaction zone of the detonation wave involves formation of carbon nanodroplets, which then crystallise into ND upon adiabatic expansion of detonation products in the pressure range from 16.5 to 10.0 GPa and in the temperature range from 3400 to 2900 K (ND stability region).[18] When the charge is surrounded by a water shell, the unloading (pressure drop) in this pressure interval slows down and the temperature of detonation products is halved. As a consequence, the degree of oxidation of ND decreases and the effect of chamber walls on the yield of ND becomes less pronounced. Soot in the resultant mixture is treated as the product of amorphisation of carbon nanodroplets rather than graphitisation of ND. In the case of adiabatic expansion of detonation products, crystallisation of nanodroplets with $d < 1$ nm is impossible at all, amorphisation of nanodroplets with $d < 2$ nm occurs under conditions corresponding to the diamond region in the phase diagram of carbon, while amorphisation of nanodroplets with $d > 2$ nm, under conditions corresponding to the graphite region.

Another model for ND formation was proposed by Breusov.[24] A comparison of the energy released upon detonation of explosives with the energies of chemical bonds in the starting (explosive) molecules revealed impossibility of release of free carbon. Indeed, the energy released upon detonation is at most 809 kJ mol^{-1} for TNT and 1240 kJ mol^{-1} for RDX.[25]

The energies of some chemical bonds (in kJ mol^{-1})[26] are listed below.

C–H	CC	C–N	C=N	N=O	N–N
413.6 (in alkanes) 421.9 (in benzene)	346.1 (in alkanes) 487.7 (in benzene)	305.0	615.9	188.6 (in nitro compounds)	163.4

Cleavage of all C–H and C–N bonds in the molecule requires a total of 3000 kJ mol^{-1} for TNT and 3071 kJ mol^{-1} for RDX; *i.e.*, the energy released upon detonation of each explosive or their mixture is several times lower than that needed for intermediate formation of elemental carbon. Therefore, a fraction of volatile chemically bonded components should not be consumed in the initial stages of the process.

In the shock-wave front zone certain bonds in the starting molecules can break down. According to Breusov,[24] radicals thus produced favour the formation of the carbon cage to which many molecules of volatile products are chemically bonded in the initial stages. Depending on the $P-T$ detonation conditions and corresponding electronic hybridisation of carbon atoms, one can deal with either a graphite-like or a diamond-like frame.

Nucleation and growth of diamond particles are accompanied by accumulation of volatile low-molecular-mass detonation products (nitrogen, hydrogen, CO, CO_2, N_xO_y, H_2O, *etc.*) in the interparticle space, which precludes the delivery of carbon-containing 'building' material to the growing particles and finally the growth ceases.

It is believed[24] that methane and methyl radical are most suitable for growth of diamond particles and 'healing' their structural defects.

III. Detonation synthesis of nanodiamonds: key features and regularities

The design of the blast chamber is of great importance for the synthesis of nanodiamonds. Roughly, 1 to 4 m^3 of the chamber volume are required per kg of explosive.[2]

In design of large blast chambers (> 50 m^3) one should allow for the fact that the larger the chamber volume the lower the mechanical strength of the chamber.[2] The effect of the scale factor can be explained by brittle fracture of large items made of plasticised steel in the elastic deformation region. The thicker the chamber walls the more probable the appearance of structural defects that reduce the fracture stress.

The effect of the scale factor can be significantly reduced using blast chambers with multilayer walls made of, *e.g.*, steel strips or glass fibre. This significantly increases the crack resistance of the material.

Industrial blast chambers are usually relatively small and have a volume of 2 m^3 [FSUE 'Federal Research and Production Centre (FRPC) Altai', FSUE 'Elektrokhimpribor' Integrated Plant, FSUE SDTB 'Tekhnolog', facilities in China]. They have long operating life (failure-free operation since mid-1980s). The mass of the explosive charges varies from 0.5 to 1.0 kg; this allows up to 2.5 kg of nanodiamonds to be synthesised over a period of 8 h. These chambers are reliable and simple in operation.

Larger blast chambers, *e.g.*, 11 m^3 in volume, are also used [RPA 'Sinta', Belarus; Russian Federation Nuclear Centre–All-Russian Research Institute of Technical Physics (RFNC–ARITP), Snezhinsk, Russia]. Here, the explosive charges have a mass of 2 kg and therefore such blast chambers are characterised by higher performance. However, they are unreliable in service.

The Closed Joint-Stock Company (CJSC) 'Alit' (Kiev, Ukraine) successfully employs for more than a decade a 100 m^3 blast chamber (mass of explosive charge is 10 kg), which provides a high performance with respect to ND. However, the blast chamber has a complex hand-driven charging system; sometimes, ice armour weighing at least 60 kg is used. The blast chamber looks like a railway tank and is rail tracked. The charge is blasted at the centre of the 'tank'. The action of the shock waves on the blast chamber walls is non-uniform and the undesired effects are quenched by spraying water in the chamber upon explosion. As a result, the content of incombustible impurities (products of chamber wall corrosion) in the condensed carbon is rather high (16 mass % to 26 mass %).[2]

Thus, in choosing the volume and design of industrial blast chambers one should allow for not only the performance, but also simplicity and safety of operations with explosives and the content of impurities in the condensed carbon.

Nanodiamonds can be synthesised using various individual explosives and high-explosive mixtures. The type of the explosive governs the detonation characteristics and the composition of detonation products. In the case of adiabatic (isentropic) expansion of detonation products the temperature drop rate also depends on the type of the explosive, the state of the charge surface and the charge shape and on the atmosphere in the blast chamber. The key parameters affecting the final temperature and the corresponding rate constant (and, hence,

Table 2. Yields of diamond blend (M_{DB}) and ND (M_{ND}) as functions of the type of explosive.[27]

Explosive	$M_{Expl.}$ /g (see [a])	ρ /kg m^{-3}	$M_{DB}/M_{Expl.}$ (%)	M_{ND}/M_{DB} (%)	$M_{ND}/M_{Expl.}$ (%)
z-Takot	153.2	1603	18.4	19.2	3.34
z-Takot : HMX (80 : 20)	250.7	1580	14.3	30	4.3
z-Takot : HMX (70 : 30)	294.5	1740	12.3	69	8.6
HNAB	263.5	1630	9.47	71	6.63
TATB : HMX (70 : 30)	324.6	1850	9.9	54	5.3
TNT [b]	280	1605	18.1	15.7	2.8
TNT/HMX (70 : 30)	310	1700	12.5	65.7	8.2

[a] $M_{Expl.}$ is the charge mass. [b] Data taken from Refs 10 and 28.

the yield of ND) include the heat capacity, the content and the reactivity of the medium. An increase in the volume of the gas, its initial pressure and heat capacity in the blast chamber favour efficient reduction of the residual temperature and improves the yield of ND. The most pronounced effect is attained using CO_2.

A general rule is as follows: the larger the ratio of the mass of the medium surrounding the blasting charge to the mass of the explosive charge, the higher the yield of ND.

The possibility of synthesis of ND upon detonation of the following aromatic nitro compounds: 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), bis(2,4,6-trinitrophenyl)diazine (HNAB) and 2,4,8,10-tetranitro-5*H*-benzotriazolo[2,1-*a*]benzotriazolium (*z*-Takot) was studied.[27] To improve the detonation parameters, in some cases the explosives were mixed with HMX and then used in the experiments.

Analysis of experimental data (Table 2) showed that the syntheses of ND upon detonation of the explosives under study and TNT obey the same pattern. Indeed, if the detonation parameters of an explosive and TNT are similar, the ND yields are also similar. The data for *z*-Takot show that, similarly to the TNT/RDX and TNT/HMX compositions, the content of the diamond phase in the DB released increases as the HMX proportion in the charge increases.

In the case of HNAB the thermodynamic parameters produced are sufficiently high to efficiently form ND without HMX additives. However, in this case the overall yield of DB is nearly halved compared to that obtained using TNT and *z*-Takot; therefore, the yield of ND is somewhat lower than the yields reached using optimum TNT/RDX compositions.

The results obtained using TATB deserve particular attention. Despite the higher detonation pressure (compared to *z*-Takot and TNT), the content of the diamond phase in DB was lower. This is probably due to the lower detonation temperature, which hampers efficient growth of the diamond particles.

Nanodiamonds are also formed upon detonation of hexanitrostilbene,[29] picric acid,[30] tetryl [31] and TNT/nitroguanidine, RDX/polybutadiene and RDX/aluminum mixtures.[32]

Long experience in industrial synthesis of ND has shown that TNT/RDX mixtures remain the most appropriate explosives. Indeed, these substances have well-known characteristics and are produced on a large scale. Processing of these explosives faces no problems, charges are castable and mouldable and can be shaped in any desired fashion. The yield of industrially synthesised ND can be as high as about 14%.

The synthesis of ND in the presence of organic admixtures to high explosives (RDX or HMX) is of considerable interest. The yield of ND produced in the presence of benzene, benzyl alcohol, allyl alcohol, allylamine, acetonitrile, nitrobenzene, propargyl alcohol and aniline admixed to HMX ($\sim$25 vol.%) is 6% – 10% per unit mass of the mixture. Lower yields ($\sim$3%) were obtained with paraffin admixtures (hexane, decane), alcohols (pentyl and octyl alcohols) and the lowest yield ($\sim$2%) was obtained using tetradecane.

The temperature and pressure developed upon detonation of explosives reach up to 4000 K and 30 GPa, respectively.

Table 3 lists the yields of diamond blend and ND obtained under different detonation synthesis conditions, namely, in the atmosphere of gaseous detonation products or an inert gas; in a water shell surrounding the explosive charge; and in an ice armour.[33, 34] High yield of ND in the presence of a water shell or ice armour is due to prolonged action of pressure in the diamond stability region.

As shown above, the process affords the raw carbonaceous material (DB) consisting of ND, graphite-like particles and contaminants (metals and metal compounds).

The yields of ND and DB also depend on the charge mass-to-chamber volume ratio and on the site where the explosion is initiated. The ND content in diamond blend is plotted *vs*. water shell thickness at different charge geometries (TNT : RDX = 40 : 60) in Fig. 2. In the case of long cylindrical charge ($l/d > 2$) the amount of ND is much higher compared to those obtained

Table 3. Yields of DB and ND under different detonation synthesis conditions.[33, 34]

Quality parameters of final product	Synthesis conditions		
	intert gas medium	aqueous medium	ice armour
DB yield (mass %)	3 – 8	6 – 12	8 – 14
ND content in DB (mass %)	20 – 40	40 – 63	55 – 75
ND yield calculated with respect to explosive	0.6 – 3.2	2.4 – 7.6	4.4 – 10.5

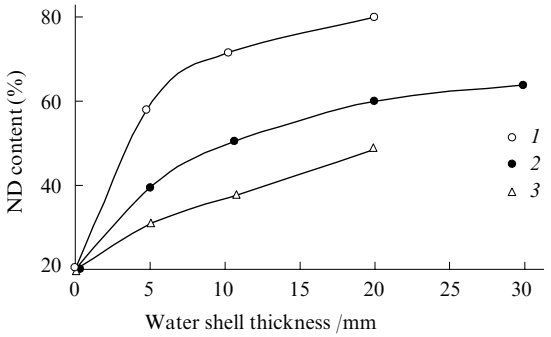


Figure 2. ND content in diamond blend plotted *vs*. water shell thickness at different charge geometries (TNT : RDX = 40 : 60 charge, mass 100 g).[35]
Charge shape: cylinder (*1*), disc (*2*) and sphere (*3*).

with disc-like of spherical charges under identical explosion conditions.[35]

To obtain the maximum possible yield of ND and DB, one should use long cylindrical charges of the highest possible density, a water shell or an ice armour surrounding the charge and a hardest booster pulse.

The yield of ND and DB also depends on the procedure used for cooling of detonation products in the blast chamber. If the charge is surrounded by a water shell or ice armour (so-called 'wet' synthesis), intense cooling of detonation products is due to transformation of their energy to heat (heating and vapour formation) and the kinetic energy of water and turbulent mixing with water. Additionally, water and ice are convenient substances, because they do not damage the walls of the blast chamber and ice does not require a container.

'Wet' synthesis (in water) can be carried out in optimum manner using a TNT/RDX charge with a TNT content of 40%. The composition produces a high synthesis temperature, while rapid cooling with water provides a higher degree of conservation of ND.

The so-called 'dry' synthesis involves blasting of a charge in gaseous medium. Here, carbon dioxide is the most efficient coolant of ND. Detonation products of a preceding blast can be used as coolant gas. A TNT/RDX charge containing 60% of TNT is optimum for the 'dry' method. Since for this alloy the detonation pressure and detonation temperature are lower than those reported for the composition with 40% of TNT, the yield of ND is nearly halved.

As the number of blasts in unventilated chamber increases, the composition of the gaseous atmosphere significantly changes. Namely, the concentrations of carbon dioxide, nitrogen and oxygen decrease, while the concentration of carbon monoxide increases, which makes the cooling of detonation products less efficient.[35] Therefore, it is desired to introduce carbon dioxide into the chamber after each series of four or five blasts.

The synthesis takes at most 0.5 μs, which approximately corresponds to the time of chemical reaction (or chemical peak) in the detonation (explosive) decomposition of TNT.[6]

The elemental composition of DB is governed by heterophase endothermic processes of gasification of the blend with carbon dioxide and water vapour

$$C + CO_2 \longrightarrow 2CO - 172.4 \text{ kJ mol}^{-1}, \quad (1)$$

$$C + H_2O \longrightarrow CO + H_2 - 130.1 \text{ kJ mol}^{-1}, \quad (2)$$

which can be described by the overall reaction

$$2C + CO_2 + H_2O \longrightarrow 3CO + H_2 - 151.3 \text{ kJ mol}^{-1}. \quad (3)$$

At high temperature, two competing processes proceed in the chamber, namely, gasification of DB (first of all, gasification of the non-diamond carbon as the more reactive DB component) and graphitisation of ND.

In the course of chemical purification (on going from DB to ND) the texture of the material changes non-monotonically (in stepwise fashion), which distinguishes the DB from other carbonaceous materials.[36] This is due to the fact that DB is an organised three-dimensional structure formed as a result of multistage aggregation of primary particles rather than a mixture of ND and non-diamond carbon.

IV. Novel method of synthesis and revised elemental compositions of nanodiamonds and diamond blend

A novel method of synthesis of ND[37,38] permits significant improvement of the qualitative and quantitative characteristics of ND and DB. Namely, it allows one to change the elemental composition towards higher content of carbon as the major element, to considerably increase the yield of ND and DB and to reduce the content of incombustible impurities.

A charge made of TNT – RDX alloy containing 40 mass % of TNT (TNT/RDX 40) was blasted in a blast chamber surrounded by a water shell (chamber volume 1 m^3, charge mass 0.6 kg, blast atmosphere: products of previous detonations). The explosive : water mass ratio was maintained at 1 : 6. A number of readily oxidisable reducing agents (hydrazine hydrate, urotropin, urea, ammonia) were added to water, the explosive : reducing agent ratios being 1 : (0.1 – 10.0). The DB was purified to ND by dilute nitric acid at 513 K and a pressure of ~80 atm.[39]

Additionally, a new procedure for elemental analysis of DB and ND was elaborated. It differs from conventional procedure by more severe conditions.[37,38] Namely, a weighed sample is kept *in vacuo* (0.01 – 10.0 Pa) at 120 – 140 °C (DB) or 423 – 453 K (ND) for 3 – 5 h and then treated with oxygen passing at a flow rate that ensures complete combustion of the sample at 1323 – 1473 K over a period of 40 – 50 s. Subsequent determination of the elemental composition is carried out by conventional analytical techniques.

According to published data,[36,40] the detonation synthesis of ND involves four stages. In the first stage, the detonation transformation of the explosive mainly occurs within the volume occupied by the charge. When using a condensed shell (water or ice), the detonation products are for some time confined within this volume, which favours a more complete transformation of carbon into the diamond prastructure.

Completion of the detonation process requires rapid gas-dynamic cooling of products to protect ND formed in the chemical reaction zone (or behind this zone[18]). The second stage consists in adiabatic expansion of gaseous detonation products.

The third stage of the detonation synthesis of ND involves circulation of the shock wave reflected from the chamber walls and turbulent mixing of detonation products with the medium in the chamber.

The fourth stage of the process involves intense cooling of the blast-heated medium surrounded (and thus confined) by the cold shell. In addition to various gaseous products (CO_2, CO, O_2, H_2, N_2, CH_4, NO, NO_2, NH_3, H_2O), the blast chamber contains highly disperse suspension of carbon particles possessing high radiating capacity. Therefore, cooling of this medium occurs through simultaneous heat transfer by convection and radiation.

The retention of condensed carbon is governed by heterophase gasification reactions with carbon dioxide and water vapour. Two competing processes proceed in the blast chamber in the third and fourth stages at the high residual temperature. These are gasification of condensed carbon (first of all, non-diamond carbon as the most reactive component) and graphitisation (or amorphisation[18]) of ND.

At a constant composition and density of the explosive, it is impossible to influence the first stage of the synthesis (*i.e.*, the formation of ND) by adding various admixtures to the condensed phase (water, ice) surrounding the charge. The processes occurring in the second stage can also hardly be affected by the substances in the condensed phase even with allowance for non-ideal character of gas-dynamic cooling of detonation products upon expansion. On the contrary, the addition of more readily oxidisable compounds (reducing agents) in the third stage (turbulisation of products), where condensed carbon reacts with CO_2, H_2O and other corrosive (under these conditions) compounds, will strongly affect the results of the synthesis. Of course, the oxidising agents (CO_2, H_2O, O_2, NO_2, N_2O_3) first of all react with more readily oxidisable reducing agents (in our case, hydrazine hydrate, urotropin, urea, ammonia) rather than with hardly oxidisable

Table 4. Elemental compositions and the DB and ND yields upon blasting of TNT/RDX 40 charges surrounded by water shell with different reducing agents.[38]

Reducing agent	Explosive : reducing agent ratio (mass to mass)	Elemental composition of DB (mass %)				Content of incombustible impurities in DB (mass %)	Content of ND in DB (mass %)	DB yield calculated with respect to explosive (mass %)	ND yield calculated with respect to explosive (mass %)
		C	H	N	O				
Hydrazine hydrate	1 : 0.1	90.2	3.3	3.0	0.4	3.1	51.1	14.4	7.36
	1 : 0.5	90.5	3.0	2.9	0.8	2.8	54.7	15.8	8.64
	1 : 2.0	90.1	3.7	3.2	0.4	2.6	53.8	16.0	8.61
Urotropin	1 : 0.25	94.1	1.6	2.2	0.5	1.6	51.6	12.4	6.4
	1 : 0.5	91.2	3.0	2.6	0.9	2.3	51.7	12.2	6.3
	1 : 1	92.7	2.8	2.8	0.3	1.4	51.9	16.3	8.46
Urea	1 : 0.5	90.1	3.6	3.1	0.5	2.7	51.2	14.1	7.22
Ammonia	1 : 0.5	91.1	3.0	2.8	0.9	2.2	51.0	13.4	6.83
No additive	–	84.2	0.9	8.3	3.1	3.5	45.0	7.2	3.24

carbon, especially ND. Therefore, one should expect an increase in the yield of DB and, hence, ND and quantitative changes in the elemental composition.

Additionally, the presence of readily oxidisable reducing agents among the detonation products also affects the fourth stage of the process, Namely, the temperature of the products decreases due to decomposition of a fraction of the reducing agent, which favours protection of ND and a decrease in the extent of its graphitisation.

The elemental compositions of DB and the content of the major impurity (incombustible metal oxides and carbides) are listed in Table 4. As can be seen, introduction of organic or inorganic reducing agents (at least 10 mass %, calculated with respect to the initial explosive) causes a significant increase (by ~4 mass % – 7 mass %) in the content of carbon in DB. The content of hydrogen remains almost unchanged, but those of nitrogen and oxygen decrease dramatically (3- to 10-fold). The amount of incombustible impurities also decreases 1.5 – 2-fold, which makes the DB thus produced suitable for immediate use in plating, finish polishing, polymer chemistry, oil composites, *etc*. Additionally, this DB can be much more readily purified, which leads to high-quality ND.

The content of ND in the DB synthesised in the presence of reducing agents increases by about 5 mass % – 7 mass %, whereas the overall mass of the DB is doubled and therefore the yield of ND calculated with respect to the starting explosive increases 2.5-fold.

The elemental compositions and amount of impurities in the ND isolated by chemical purification of the DB produced by the novel method are listed in Table 5. The content of the major component (carbon) in the detonation-synthesis ND prepared by the new technique is considerably larger (by 4 mass % – 6 mass %) and amounts to 96.0 mass %. Irrespective of the synthesis conditions, the content of nitrogen varies in a narrow region, from 2.2 to 2.9 mass %, which indicates a quite uniform distribution of this element within all ND layers. Contrary to this, the amounts of hydrogen and oxygen change considerably (from 0.4 mass % to 2.4 mass % and from 0.7 mass % to 2.3 mass %, respectively). This points to accumulation of H and O in the outer layers of ND particles and to strong dependence of the contents of these elements on the synthesis conditions.

The lowest amount of incombustible impurities was found in the ND produced in the presence of urotropin. This is due to the fact that urotropin is a strong complex-forming agent, which reacts with metal impurities (Fe, Ni, Cr, Cu, *etc*.) to form soluble complexes which can be easily removed during chemical purification (upon treatment with nitric acid).

Because of the low content (0.1 mass % – 0.3 mass %) of incombustible impurities (metal oxides and carbides) ND thus produced can be used in all technologies. At the same time the content of the non-diamond carbon in ND is almost constant (0.8 mass % – 1.4 mass %) and has no effect on the technologies that use ND. The content of the diamond phase in the purified ND can be as high as 99.1 mass %

The elemental compositions of a large number of ND samples produced at different facilities in Russia, China, Ukraine and Belarus were determined using the recently proposed procedure.[37, 38] The contents of the constituent elements in ND vary within the following limits (in mass %):

Table 5. Elemental composition and purity of ND isolated by nitric-acid purification from DB prepared using different types of reducing agents.[37]

Reducing agent	Explosive : reducing agent (mass to mass ratio)	Elemental composition of ND (mass %)				Content of incombustible impurities in ND (mass %)	Content of oxidisable carbon in ND (mass %)	ND purity (ND content in the solid phase) (mass %)
		C	H	N	O			
Hydrazine hydrate	1 : 0.1	93.6	1.2	2.3	1.7	1.2	1.0	97.8
	1 : 0.5	94.4	0.4	2.5	2.3	0.4	1.1	98.5
	1 : 2.0	95.2	0.7	2.3	1.6	0.2	1.0	98.8
Urotropin	1 : 0.25	94.9	1.1	2.5	1.4	0.1	0.8	99.1
	1 : 0.5	95.2	1.0	2.2	1.5	0.1	1.0	98.9
	1 : 1	96.0	0.4	2.6	0.7	0.3	0.9	98.8
Urea	1 : 0.5	94.3	1.6	2.7	0.8	0.6	1.4	98.0
Ammonia	1 : 0.5	92.7	2.4	2.9	1.3	0.7	0.9	98.4
No additive [41]	–	88.5	1.1	2.2	8.2	–	–	–

90.3–93.8 for C, 0.4–4.8 for H, 1.5–2.3 for N and 2.3–4.5 for O.

The actual elemental composition of ND is as follows:

Element	C	H	N	O
Content (mass %)	93–95	1–2	~2.5	2–3.5

V. Chemical purification of nanodiamonds: theory *vs.* practice

The specific features of DB include high dispersion, defectness of the carbon structures, developed active surface and, as a consequence, enhanced reactivity.

Besides, the detonation blend contains metal particles resulting from wear of the operating surfaces of the blast chambers and foreign impurity particles.

All the known ND purification techniques are based on the use of different stability of the diamond and non-diamond forms of carbon to oxidants.[42] Liquid-phase oxidants offer an undoubtful advantage over gas–solid systems, because they allow one to obtain higher reactant concentrations in the reaction zone and, therefore, provide high reaction rates.

Nevertheless, a method of oxidation of the non-diamond carbon by ozone was reported.[43] The ozone–air mixture is passed through DB at 120–400 °C. Despite quite a high degree of purification of DB from the non-diamond carbon, it still contains unburnt impurities (mainly iron oxides and carbides, up to 25 mass %; CJSC 'Alit', Ukraine). These impurities can be dissolved using liquid oxidants (strong acids).

The liquid-phase oxidation proceeds at sufficiently high rates at high temperature. Therefore, the oxidising mixtures are prepared using high-boiling acids ($HClO_4$, H_3PO_4, H_2SO_4) and oxidising agents (HNO_3, nitrogen oxides, H_2O_2, $NaClO_4$, CrO_3, $K_2Cr_2O_7$, *etc.*). Initially, perchloric acid was widely used as the high-temperature single-component oxidising agent. However, this is a hazardous substance (operation with and storage of this acid are expensive) and therefore it is no longer used for isolation of ND despite the unique properties.

There are three conventional ND purification techniques used in industry:

(1) action of chromium anhydride (CrO_3) solution on DB in concentrated sulfuric acid (RFNC–ARITP; FSUE 'Elektrokhimpribor' Integrated Plant, Lesnoy, Russia; CJSC 'Alit', Ukraine; facilities in China);

(2) use of nitric acid/oleum mixtures ('FRPC Altai', Biysk, Russia); and

(3) use of dilute nitric acid (FSUE SDTB 'Tekhnolog', St Petersburg, Russia; CJSC 'Sinta', Minsk, Belarus; Beijing Technological Institute, China).

In particular, DB was mechanically filtered, treated with concentrated sulfuric acid, then heated and the non-diamond carbon was removed by adding oxidising agent (aqueous chromium anhydride solution) to the mixture of DB with concentrated sulfuric acid.[44] After the oxidation, ND were washed with water. The primary treatment of DB with sulfuric acid was carried out at 105–110 °C for 1.0–1.5 h. Nanodiamonds were first washed from acid treatment products with water to pH 5–6 at 60–70 °C and then with hot distilled water until negative reaction for chromium ions in rinse water. As a result, the amount of metal impurities in ND reduced to 0.9 mass % and the content of the major component increased to 98.5 mass %. This multistage chemical purification technique [44] is complex and expensive and produces very toxic waste.

The main advantages of the nitric acid/oleum oxidising systems consist in the availability and cheapness of the components. They are also simple in design and technological operation.[45] The drawbacks of the technique include low quality of purified ND (ND content is ~90 mass %), large consumption of the acids (up to 57 kg per kg of DB), complexity of the regeneration and utilisation of the multicomponent mixture and contamination of the diamond surface with sulfur and nitrogen compounds.

Yet another group of methods of liquid-phase purification of ND is based on the principle of free dispersion of carbonaceous material in all stages of treatment.[46] The reaction suspensions of DB in liquid oxidising mixtures are homogeneous, colloidally stable (no ND precipitate), highly disperse and characterised by low viscosity. During the reaction, the oxidising agent has unrestricted access to the solid particles, which practically removes the diffusion limitations on the reaction rate.

High reactivity of DB allows the following oxidising systems to be used for purification:

$$C + x[O] \longrightarrow [CO_x] \longrightarrow CO_2\uparrow$$

Oxidation system	Reaction products
$HNO_3-H_2SO_4-SO_3$ $HNO_3-H_2SO_4$ $HNO_3-H_2SO_4-H_2O$	$CO_2 + H_2O + NO_x + SO_y$
HNO_3-H_2O $HNO_3-H_2O-H_2O_2$	$CO_2 + H_2O + NO_x$
$H_2O_2-H_2O-$catalyst O_2-H_2O-catalyst	$CO_2 + H_2O$

The total concentration of acids, specific consumption of reactants, amount and toxicity of gaseous reaction products and corrosion activity of the reaction medium decrease while the economic and environmental characteristics of technological processes are improved along the arrow.

Hydrogen peroxide is an attractive oxidising agent. Indeed, its reaction with carbon results in only two products, carbon dioxide and water.[47] The reaction also causes the development of a specific surface of the diamond material, which is free from sulfo and nitro derivatives. The use of hydrogen peroxide based oxidising systems for purification of ND significantly simplifies the process infrastructure, first of all the environmental protection system and waste reclamation. The main drawbacks of the technique include the impossibility of removal of unburnt impurities, the need of using equipment for high-pressure operation and incomplete removal of the non-diamond carbon.

These problems can be solved on going to aqueous nitric acid solutions. This fundamentally improves the quality of ND purification, because sulfur-containing derivatives cannot be formed on the diamond surface.[39] The process is carried out at elevated pressure. The equipment operating at high temperature is made of corrosion resistant materials.

High-purity ND (carbon content $\geqslant$ 98.5 mass %) can be obtained from DB upon 30–40 min of its residence in hot zone under high pressure. This process has been implemented in Russia, China and Belarus.

The use of complicated but efficient method of high-temperature oxidation with nitric acid under pressure makes it possible to implement a high-performance process characterised by low content of hazardous waste. The dissolution of metal-containing impurities and their transformation into water-soluble products are combined with oxidation within this method.

The simplest and the most readily available oxidising agent is atmospheric oxygen. Using specific features of the detonation blend, the non-diamond carbon was selectively oxidised by blowing air through an aqueous DB suspension in the presence of catalysts.[46] The procedure offers all advantages of the liquid-phase ND purification techniques and has the same

drawbacks as the method based on purification with hydrogen peroxide.

Analysis of the simplest, convenient and environmentally safe purification methods unambiguously shows that only dilute nitric acid should be used in large-scale production.

At present, the two-step ND purification technique based on treatment of DB with aqueous nitric acid solutions is practically implemented at some facilities. The first stage involves treatment of DB with concentrated (50–99)% nitric acid at 80–180 °C. In the second stage the material is treated with (10–40)% nitric acid at 220–280 °C.[39]

A novel promising method of chemical purification of ND by combined treatment of DB with (2–40)% nitric acid and atmospheric oxygen at 200–280 °C under pressure (5–15 MPa) was developed.[37] The treatment involves renewal of the outer boundary layer of ND particles and has almost no effect on the structure of the diamond core. Therefore, purification is the key stage in the formation of the application characteristic of ND, because it is this stage that determines the possibility of preparation of various modifications of the product.

VI. Industrial synthesis of nanodiamonds

Technologically, production of ND involves the detonation synthesis, chemical purification and washing of ND from acids and conditioning of the product,[34, 36] recovery and utilisation of acid vapours and gases, pretreatment and recycling of nitric acid and water treatment.

Usually, industrial detonation synthesis (Fig. 3) is a periodic process. Every time an explosive charge equipped with electric detonator is manually loaded through a top hatch (not shown) of a hermetically closed blast chamber. Depending on the process used at the plant, a cylindrical charge (either non-armoured or surrounded by a water shell or ice armour) is suspended on strips to a hook welded at the top of the blast chamber. The charge is blasted from a distant explosion-proof room by applying an electric pulse to the detonator. The blast chambers of volume ~ 2 m^3 are used most often.

In addition to DB, 60% nitric acid, air and desalinated water are used. The process results in ND as the end product in the form of either thickened stabilised suspension in distilled water or dry powder.

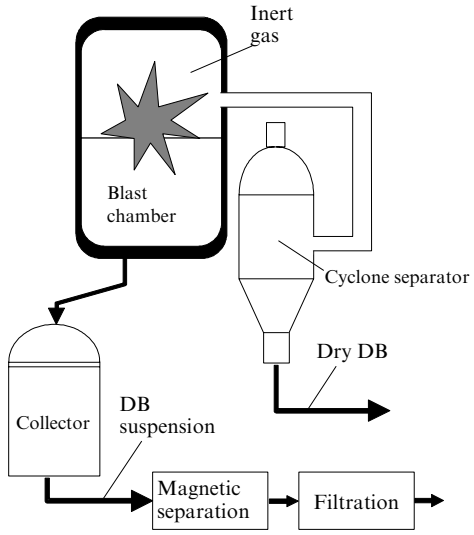


Figure 3. Detonation synthesis of nanodiamonds: flow chart of the process.[3]

A simplified scheme illustrating the key stages of purification process is shown in Fig. 4. Generally, the ND purification procedure involves the following steps.[36]

1. Preparation of DB.
2. Preparation of aqueous nitric acid solutions.
3. Preparation of thin homogenated suspensions of DB in aqueous nitric acid solutions.
4. Continuous thermal-oxidation treatment of DB suspensions under pressure (~ 500 K, 8–10 MPa). This is the key stage, which requires the use of tailor-made equipment. The process is carried out in a flow reactor cascade with a particular temperature profile (smooth variation of the temperature along the reactor cascade) under equilibrium pressure.
5. Separation of thermal-oxidation treatment products.
6. Recycling of nitric acid.
7. Washing of ND from acids.
8. Waste processing.
9. Preparation of stabilised ND suspensions in distilled water.
10. Preparation of ND in the form of dry uniform powder.

Modern technology of ND purification by thermal oxidation using liquid-phase high-temperature oxidation of nitric acid provides high and stable characteristics of purification and is readily scalable and best practically implemented.

VII. Properties of nanodiamonds

Nanodiamonds are complex objects usually having a three-layer structure [48, 49] comprised of

— a diamond core 4–6 nm in size, containing from 70% to 90% of the total number of carbon atoms;

— a transient carbon shell (intermediate layer) surrounding the core and consisting of X-ray amorphous carbonaceous structures 0.4–1.0 nm thick, containing from 10% to 30% of the total number of carbon atoms; and

— a surface layer comprised of carbon atoms and other heteroatoms (N, O, H) that form various functional groups; the nitrogen atoms are quite uniformly distributed among all layers.

Detonation-synthesis ND are chemically inert and hardly oxidisable.[49] The diamond core can be partially decomposed by prolonged etching under severe conditions (in strong acids or acid mixtures, *e.g.*, conc. HNO_3, $HNO_3 + HCl$, $HNO_3 + H_2SO_4 + SO_3$, *etc.* at corresponding boiling temperatures for 50–100 h). Oxidation (etching) of ND has a complex character because the process does not involve a conventional layer-by-layer removal of the non-diamond and diamond phases (*i.e.*, their oxidation to gaseous products). Etching of the carbon matrix (up to the diamond phase) proceeds at structural defects within the intermediate layer. When the process involves the diamond core (mass loss of 30 mass % and more with respect to starting ND), not only the chemical composition of the surface functional groups, but also the structure of the intermediate layer is reproduced. It was shown that highly etched ND particles (mass loss of 40 mass %–60 mass %) possess nearly the same properties as the starting detonation-synthesis ND. The formation of almost the same intermediate shell was proved in many studies by various analytical methods. The oxidation processes first of all affect unstable (excited) atoms in the material. The most excited carbon atoms are on the surface of particles near structural defects. Thus, here we deal with selective etching of the most defect fragments of the near-surface structures near the most excited carbon atoms, resulting in the formation of nearly identical intermediate layer.

It should be noted that the greatest difficulties during chemical purification of detonation-synthesis ND by oxidation of DB are encountered in the oxidation of the 'last'

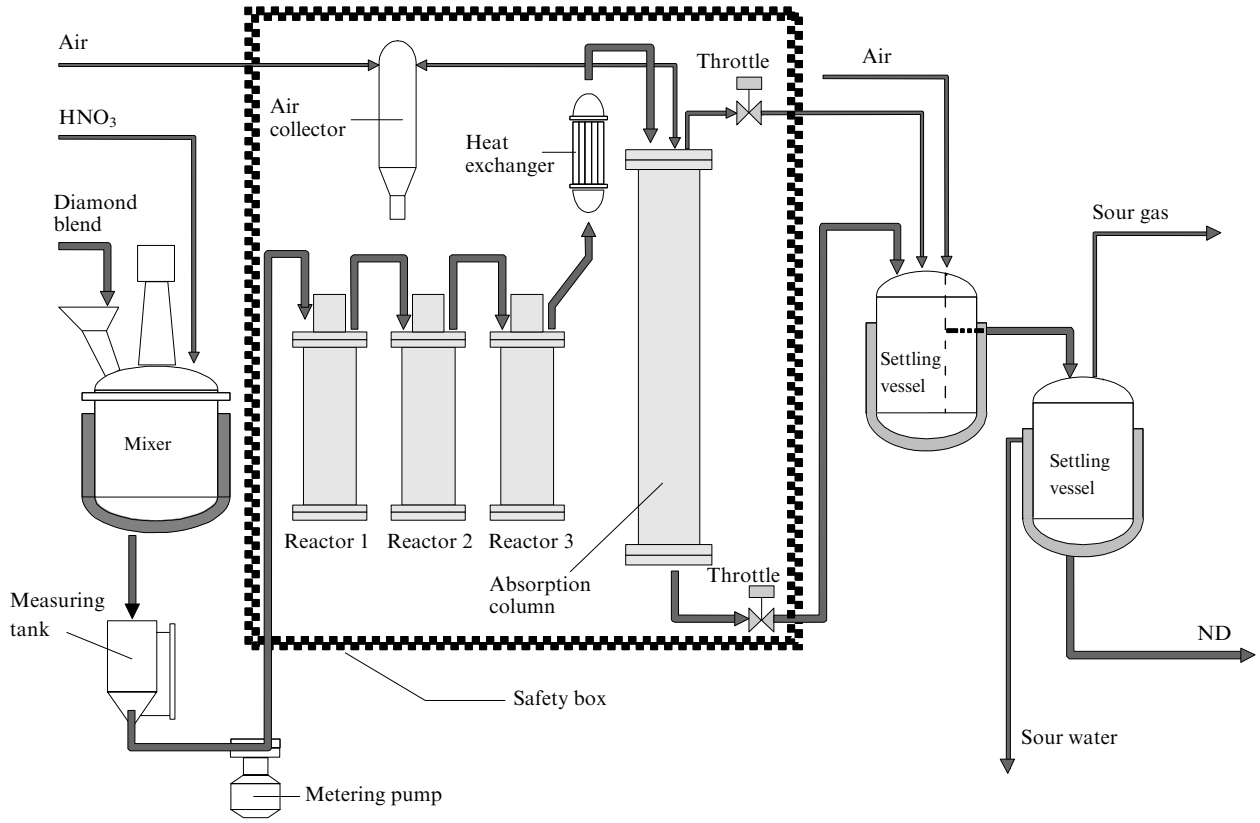


Figure 4. Simplified nanodiamond purification flow chart.[36]
The mixer is filled with DB and HNO_3 . A suspension thus formed is fed to the measuring tank and then to Reactor 1. The ND suspension in spent HNO_3 passes through the heat exchanger and then is delivered to the adsorption column where gas separation occurs. Gases are absorbed by water and by alkali solution and the sour suspension is fed to the system of settling vessels and subsequent washing. The air collector is used to smooth pressure surges and to produce prepressure at the start-up in the operating mode, thus acting as a high-pressure throttle.

18 mass % – 20 mass % of the non-diamond carbon, *i.e.*, in this case the residual carbon also shows a diamond-like behaviour.

The intermediate layer of purified ND has inhomogeneous structure. The inner sphere of the intermediate shell, which is adjacent to the diamond core, is comprised of continuous onion-like carbon (OLC) layers formed by hexagons.[48] The intermediate layer also contains graphite-like monolayers localised in peripheral regions. However, the overall structure of the intermediate layer is still to be clarified.

The complex structure of the intermediate layer is due to incomplete transformation of the carbon component of the ND particle to the diamond under the synthesis conditions. During the action of the detonation wave and in the course of the unloading step, when detonation products expand and reflected shock waves pass through them at rapidly dropping pressure but still at a very high temperature, structural fragments of the molecules of initial explosives chaotically combine with one another in the chemical reaction zone.[1, 2, 10, 28, 36] Secondary processes, namely, graphitisation of detonation-synthesis ND and amorphisation of the crystalline phase are also highly probable under these conditions.

It is likely that the structure of the intermediate layer is comprised of a randomly combined praunits of those chemical compounds that release from ND upon extraction and thermal desorption. However, it is still unclear what these units and compounds made of them look like and how they are bonded to one another, embedded into the intermediate-layer cage and stabilised.

Undoubtedly, it is vast variety and high reactivity of chemically bonded prastructures (in addition to the reactivity of functional groups on the surface of ND particles) that are responsible for the high reactivity of detonation-synthesis ND. Amazingly, the bulk mass concentrated in the diamond core remains chemically inert. Therefore, the behaviour of detonation-synthesis ND in various systems is hard to predict.

The average ND particle size is 4.2 nm. A simplified model for the surface of an ND particle with different functional groups is shown in Fig. 5. The number of atoms in such a particle is quite difficult to estimate owing to imperfection of the crystal, complication in the determination of the actual number and types of functional groups and uncertainty associated with characteristics of the intermediate carbon shell of the nanocrystal.

The number of carbon atoms in 4.2-nm ND particles reported by different authors varies from 300 to 20 000.[36, 50] (Usually, the elemental composition was calculated for a perfect crystal.) The average number of atoms (including heteroatoms) in octahedral ND crystal (edge length 4.4 nm) is $\sim$20 000.[51]

A spherical ND particle of 4.2 nm size comprises nearly 7000 carbon atoms. The results of some calculations of the elemental composition of ND are listed in Table 6. According to Shenderova, the number of surface carbon atoms is $\sim$1000 or $\sim$15% of the total number of atoms.

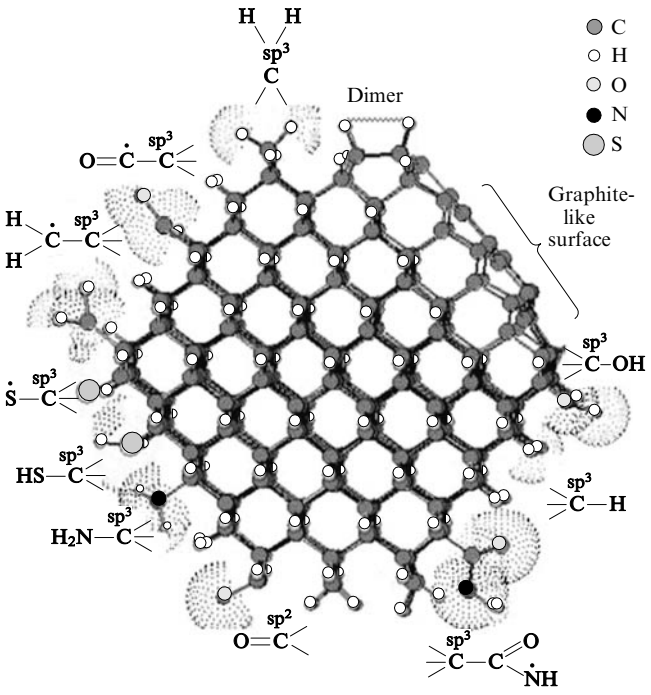


Figure 5. Nanodianond particle with different surface functional groups (according to Shenderova, International Technology Center, USA). The structure was optimised by the semiempirical quantum-chemical method PM3.

Most often, functional groups appear on the surface of ND particles during purification of DB with strong oxidising agents. All oxygen and hydrogen atoms belong to the surface groups of ND.[36, 50, 52–55] Nitrogen atoms are incorporated not only into the diamond lattice, but also the surface groups (amide groups [53] and nitro groups [54, 56]).

The surface functional groups were analysed by IR spectroscopy,[53–59] temperature-programmed desorption,[53] chemical titration,[59, 60] polarography [36, 60] and X-ray photoelectron spectroscopy.[58]

The surface groups were identified as hydroxyl groups (OH) in the form of sorbed water, carboxyl group and tertiary alcohol;[53–57, 61] amide groups [NC(O)–H];[53] hydrocarbon groups (C–H) in the form of CH, CH_2 and CH_3;[53, 56, 58, 62, 63] carbonyl groups (C=O) in the form of ketone, carboxyl group, acid anhydride, ester and lactone;[53, 55–58, 63] C–O–C groups in the form of ether, acid anhydride, lactone and epoxy group.[54–57, 62]

A study of fluorinated ND revealed the presence of surface CF, CF_2 and CF_3 groups.[58]

The electrokinetic potential (ξ-potential) is one of the key characteristics of the ND surface, which strongly depends on the surface state. Different fractions of the same ND sample and, moreover, of ND samples purified and surface-modified in different manner are usually characterised by different ξ-potentials.

The ξ-potentials of three fractions (precipitate, intermediate and aqueous suspension) of the ND produced at the RFNC–ARITP were +16, +32 and +39 mV, respectively.[64] The ξ-potential of non-fractionated ND (UDD-TAH brand) produced at the FSUE SDTB 'Tekhnolog' is +33 mV (aqueous medium).

Three types of modified ND (UD-HP, UD-SO and UD-M brands) are produced at the RPA 'Sinta'.[65] The ξ-potentials of their aqueous suspensions equal −16 (UD-HP), −87 (UD-SO) and +24.9 (UD-M) mV.

Dry ND is a light-grey polydisperse powder with a bulk density of about 0.5 g cm^{-3}. It is comprised of agglomerates of size from a few to hundreds of micrometres. Two main types of impurities in ND are incombustible and oxidisable carbon (the latter remains on the surface of ND particles after chemical purification). The admissible content of each of the two impurities is at most 1.0 mass %. Well-purified ND contains at most 0.5 mass % of each type of impurity. Practical applications of ND are mainly interfered with the presence of incombustible impurities; their compositions for three commercially available ND brands is presented in Table 7.[50, 66]

An aqueous suspension of pure ND in water cannot be neutral (Fig. 6); the ND particles should behave in water like

Table 6. Contents of chemical elements (%) with allowance for various functional groups on the surface of spherical diamond particle 4.2 nm in diameter.

Surface composition		$C_{diamond}$	H	O	N	C–X (hetero-atom)	C_{tot}
atom or group	content (%)						
H	100	98.7	1.3				
OH	100	81.9	1.0	17.1			
OH	50	89.5	1.2	9.3			
H	50						
COOH	50	77.0	1.0	16.0		6.0	83.0
H	50						
H	63.8	88.7	1.17	5.68	2.34	2.09	90.79
OH	10						
COOH	5						
CO	10						
NH_2	11						
NO_2	0.1						
NO_3	0.1						

Note. All surface groups provide a 100% 'coverage' of unsaturated bonds. (Calculated by Shenderova, International Technology Center, USA).

Table 7. Contents of incombustible impurities (mass %) in ND samples according to atomic emission spectroscopy data (analysed by Chukhaeva, RFNC–ARITP).[50, 66]

Impurity	Aqueous ND suspension [a]		Typical ND [b]
	UDD-SWS powder	UDD-TAH powder	
Fe	0.15	0.1	0.1
Cr	0.07	0.05	0.5
Xi	0.3	0.1	0.15
Al	0.005	0.001	0.01
Na	0.03	0.003	0.05
K	0.002	0.002	0.002
Cu	0.005	0.002	0.003
Ca	0.002	0.002	0.01
Mg	0.005	0.003	0.005
Mn	0.001	see [c]	0.001
Ti	0.01	0.005	0.002
Pb	0.001	0.001	0.001
Total	0.58	0.27	0.84
Incombustible residue (%)	0.95	0.4	1.4

[a] Produced at FSUE SDTB 'Tekhnolog'. [b] Produced at RFNC–ARITP. [c] Undetected at a sensitivity of 5×10^{-4} mass %.

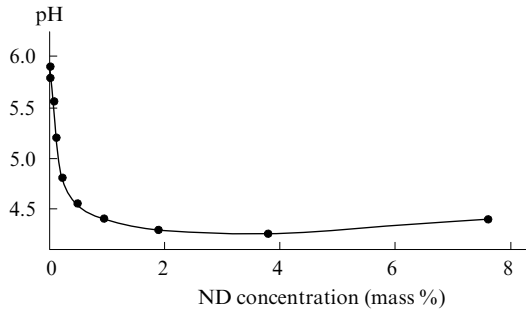


Figure 6. The pH values of a washed aqueous ND suspension plotted *vs.* ND content.[67]

an acid due to the presence of surface carboxyl groups.[67] Indeed, they do behave as poorly soluble weak organic acids. The rapid coagulation threshold of ND particles, *i.e.*, the loss of sedimentation stability, corresponds to a pH value of 5.5.

Earlier (see, *e.g.*, Ref. 68), it was shown that the phase transition occurs on heating of ND from 720 to 1400 K in inert atmosphere.

The lines in the Raman spectra of ND coincide with maxima of the phonon state density functions of diamond and graphite. This indicates the presence of small amounts of amorphous diamond and graphite in the ND material. Nanodiamond clusters exist only in the form of aggregates;[69] the amorphous phase is likely to occur in the interior. The presence of the amorphous phase is also confirmed by X-ray diffractometry data; the characteristic size of this phase was estimated at about 1.5 nm.

According to X-ray diffractometry data, nucleation of the graphite phase occurs only at $T > 1200$ K. The diamond–graphite structural phase transition occurs on anneling in inert atmosphere and begins at the surface of ND clusters; the graphite phase nucleates in the form of equidistant nanoplates.

The phase transition onset temperature correlates with the electron microscopy data,[70] according to which the decrease in the size of the ND core begins only at $T > 1300$ K. The process is accompanied by transition of the outer carbon atoms to the OLC phase.

Later on, it was found that graphitisation of diamond can be induced by heat treatment and by the action of reactive gases and maintained using metal catalysts and also by emission from various sources.[71] On the one hand, graphitisation sets limitations on the temperature range and conditions for efficient use of diamond. On the other hand, it provides the possibility of design of novel nanoscale carbonaceous materials. It was shown[71] that annealing of 2–5-nm ND particles gives rise to the OLC phase,† whereas the annealing of micrometre-size diamond particles leads to formation of closed bent graphite-like structures, such as nanotubes, nanohelices, *etc.* Based on the results of molecular modeling by the molecular mechanics, molecular dynamics and Hartree–Fock methods, it was assumed that the formation of the OLC and closed bent graphite-like structures on the surface of diamond particles exhibits specific features of self-assembly processes.

Nanodiamond particles have a large specific surface area and therefore their physical and chemical properties are strongly affected by the surface groups. Controlled functionalisation provides a powerful tool of specific modification of ND particles. Using this approach, one can involve ND in various chemical reactions, enhance their interaction with solvents, components of composite materials, polymers and catalysts. The surface groups stabilise the surface of ND particles and preclude their graphitisation. Decomposition of the surface groups causes graphitisation of ND and formation of bucky-diamonds (intermediates of the transformation of ND to OLC) and, finally, to OLC. With allowance for high stability of the hydrocarbon groups the most thermally stable ND can be prepared by surface hydrogenation.

Various graphitisation mechanisms were reported for the 'low'- and 'high'-temperature regions.[71] In the high-temperature region, the rate of graphitisation is controlled by the detachment of a single atom from the diamond surface. In the low-temperature region, the mechanism of graphitisation involves incomplete detachment of carbon atoms from the surface of diamond particles and the external planes (faces) of diamond crystal are gradually transformed into the graphite planes. These temperature regions are separated by the Debye temperature of diamond (1910 K).

By varying the ND graphitisation rate it is possible to prepare diamond/nanographite composites with different ratios between the diamond core and bent graphite shells (so-called sp^2/sp^3-nanocomposites). The presence of interfaces between the nanoscale diamond cores and graphite shells and, probably, high concentrations of the open graphite edges can predetermine unusual electronic properties of these composites.

Selected characteristics of the static-synthesis diamonds and detonation-synthesis ND are listed in Table 8. The differences between the particle size, specific surface area and content of volatile impurities are most pronounced.

Table 9 lists selected properties of ND and technological parameters of large-scale production of ND for three leading manufacturers of detonation-synthesis ND in the CIS.[72] The maximum yield of ND is obtained using the novel method of synthesis at the FSUE SDTB 'Tekhnolog'. Additionally, the content of incombustible impurities even in DB is minimum and their content in pure ND is very low.

Table 8. Characteristics of detonation-synthesis nanodiamonds and static-synthesis diamonds.[72]

Parameter	Nanodiamonds	Diamonds
Phase composition	cubic diamond, $a = 0.3565$	cubic diamond, $a = 0.3567$
Picnometric density /g cm^{-3}	3.30	3.51
Particle size /nm	4–15	30–2000
Specific surface area /m^2 g^{-1}	200–450	13.5
Content of incombustible impurities (mass %)	<1.5	<0.2
Content of volatile impurities (mass %)	10–12	1–2
Temperature corresponding to the onset of intense oxidation in air /K	800	780
Maximum exothermic effect in air /K	960–1000	900
Temperature corresponding to the onset of graphitisation *in vacuo* /K	1373	1373
Electrical resistivity /Ω m	7.7×10^9	1×10^{10}
Specific magnetic susceptibility, $10^8 \chi$ /m^3 kg^{-1}	<1.0	0.5
Surface functional groups	OH, C=O, CO_2H NH_2	HO, C=O, CO_2H

† Complete annealing results in OLC particles while partial annealing affords diamond/OLC core–shell particles.

Table 9. Technological parameters and properties of samples produced by the leading manufacturers of detonation-synthesis ND in the CIS area.[72]

Parameter	FSUE SDTB 'Tekhnolog', St Petersburg, Russia	CJSC 'Alit', Kiev, Ukraine	'FRPC Altai', Biysk, Russia
Blast conditions in chamber	water shell (3 kg) of complex composition	water shower/water shower + ice armour (100 kg)	gaseous atmosphere
Mass of explosive charge /kg	0.6	10.0	0.6
Explosive charge composition (TNT/RDX mixture) (mass % of TNT)	40%	40%	60%
ND yield relative to the mass of explosive (%)	10 – 14	5 – 7/8 – 12	4 – 5
ND content in diamond blend (mass %)	55 – 75	50 – 60/ ~ 70	30 – 40
Content of incombustible impurities in DB (mass %)	1.5 – 3.0	16 – 26	5 – 12
Chemical purification procedure and its parameters	55% – 60% HNO_3, 513 K, ~ 8 MPa	1) HCl (boiling) 2) $H_2SO_4 + H_2Cr_2O_7$ (boiling) 3) $HCl + HNO_3$ (boiling)	$H_2SO_4 + SO_3 + HNO_3$, 523 K
ND size (coherent scattering range) /nm	4 – 5	6 – 8	4 – 6
ND specific surface area /$m^2\ g^{-1}$	330	200	250 – 350
Content of incombustible residue in ND (mass %)	0.1 – 0.6	2.5 – 3.0	4 – 5
Content of oxidisable carbon in ND (mass %)	0.5 – 0.8	0.8 – 1.5	4 – 5

VIII. Fields of application of nanodiamonds

Nanodiamonds incorporated into materials act as powerful structure-forming agents that ensure dispersion strengthening of composites.

In search for optimum cost – quality relation for ND-containing products one should allow for the following:

— simple ND synthesis technology makes it possible to establish large-scale production of cheap ND the cost of which is mainly determined by the cost of explosives;

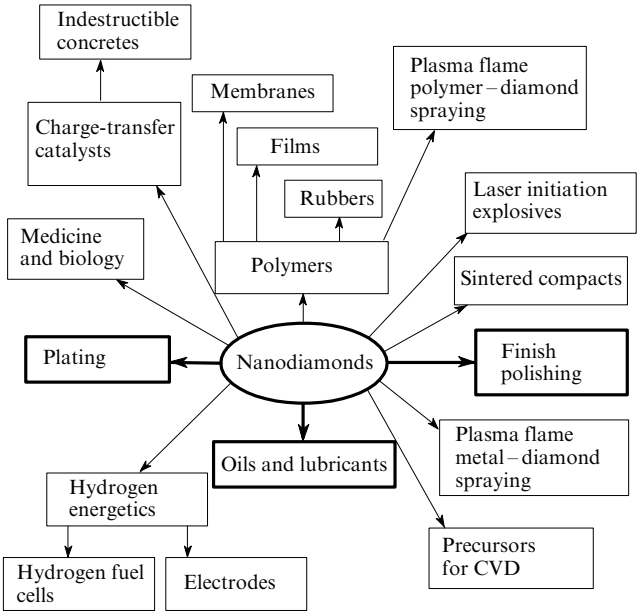


Figure 7. Fields of application of nanodiamonds.
Thick and thin arrows denote the current and future fields of application, respectively.

— in many fields of application ND can be replaced by crude DB, which is much cheaper than purified ND;

— positive effect is attained upon introduction of (0.1 mass % – 1.0 mass %) of ND additive into the material.

Nanodiamonds have a broad spectrum of applications (Fig. 7), three of them being the major ones. These are finish polishing (~ 70% of the total amount of ND), metal plating (~ 25%) and oil composites (~ 5%). In the nearest future, production of polymer – diamond composites, charge-transfer catalysts and modified biologically stable concretes can develop into large-scale industries.

1. Metal plating

Nanodiamonds present in the electrolyte of a galvanic bath should be in the suspended state. To this end, an aqueous ND suspension is added to the electrolyte. In the preparation of metal – diamond composite electrochemical coatings, the suspended state of ND is maintained by gas evolution and thermal convection.

The introduction of ND into electrochemical coatings significantly improves their microhardness, wear resistance, corrosion resistance, throwing power, makes the visual appearance of goods more attractive and reduces porosity. The main reason for these changes consists in reduction of the size of metal domains in the coatings. Nanodiamond particles are small and therefore sufficiently dense and uniform distribution over the coating can be attained even at very low content of these species (few tenth of a per cent).

A number of ND-containing composite electrochemical coatings based on chromium, nickel, tin, zinc, copper, gold, silver, aluminium, iron and various alloys were developed. Selected physicomechanical characteristics of such coatings are listed in Table 10.

a. Chromium plating

Investigations on metal – diamond coatings began with the studies of electrochemical deposition of chromium and ND.[73 – 75] Later on, they attracted the greatest interest because chromium coatings are most often used to provide for high wear resistance of tools and workpieces.

Table 10. Physicomechanical characteristics of metal – diamond coatings.

Coating	Wear resistance increases by a factor of n, where n is	H_V /kg mm^{-2} (see [a])	Porosity decreases by a factor of m, where m is	Corrosion resistance increases by a factor of p, where p is
Cr + ND	2 – 12	up to 2300	2 – 3	3 – 6
Ni + ND	5 – 6	up to 600	no pores	2 – 5
Cu + ND	9 – 10	160	the same	no corrosion
Au + ND	2 – 5	200	6	the same
Ag + ND	10 – 15	180	8	"
Zn + ND	–	–	6 – 8	2 – 4
Sn + ND	4 – 5	150	7	1.5
Al + ND	10 – 13	600 – 700	3	no corrosion
Fe + ND	6 – 8	800	8 – 10	3 – 4
Ni + B + ND	6	8000	–	no corrosion
Sn + Pb + ND	–	31	no pores	5 – 7
Sn + Sb + ND	2.5	25	5 – 6	2 – 3
Ag + Sb + ND	1.5 – 1.7	150	–	–

[a] Microhardness.

Either solid chromium plating electrolytes or buffer electrolytes are used as chromium/ND plating electrolytes. The content of ND in the coating is 0.3 mass % – 1.0 mass %.

The content of ND in the chromium coating is analysed as follows. A chromium – diamond coating (CDC) 55 – 60 μm thick is deposited on a stainless steel plate. Then, the CDC is electrolytically dissolved in 10% aqueous NaOH solution at a cathode current density (i_c) of 10 A dm^{-2} and a temperature of 303 K. A sodium chromate solution containing the ND suspension is passed through a preliminarily weighed Schott filter. The ND precipitate on the filter is successively washed with hot water, 10% H_2SO_4, water, 20% HCl and again water. The filter with the precipitate is dried at 423 – 473 K, the absolute amount of ND is determined from the mass difference and then the ND concentration in CDC is calculated (knowing the mass of the dissolved coating).

The microhardness of chromium coating depends on the ND concentration in the electrolyte, namely, the microhardness increases as the ND concentration increases.[76] As i_c increases, the microhardness also increases. The most impressive results were obtained using a composite diamond additive comprised of detonation-synthesis ND and static-synthesis diamonds (Fig. 8).[77]

In Fig. 9 the wear of various chromium coatings is compared with that of titanium nitride coatings.[77]

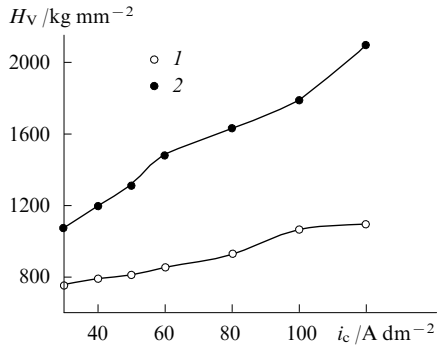


Figure 8. Microhardness of solid Cr-ND-ASM-coating plotted *vs.* cathodic current density (standard electrolyte).[77]
No ND additives (*1*) and in the presence of ND (ND : ASM = 5 : 5) (*2*); ASM brand is synthetic diamond nanopowder.

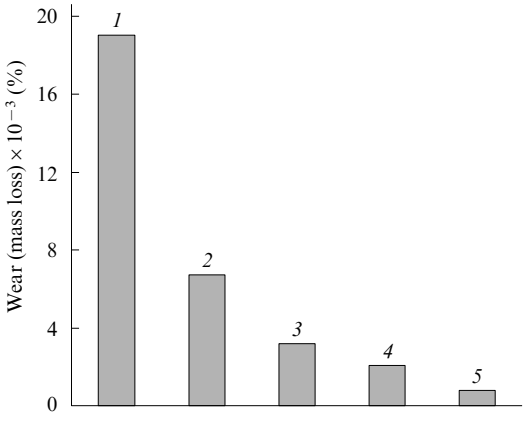


Figure 9. Wear of titanium nitride (TiN) and chromium coatings.[77]
TiN (*1*), hard Cr (*2*), wear-resistant Cr (*3*), Cr + ND (*4*) and Cr + ND + ASM (*5*).

Chromium plating using ND is widely used in Russia, USA and South Korea.

b. Nickel plating

Analysis of the data listed in Table 11 and the plots shown in Fig. 10 reveals a positive effect of ND on the quality of nickel – diamond coatings.[76, 78, 79]

Table 11. Effect of ND content on microhardness, wear resistance and porosity of nickel coatings at different cathodic current densities.[76, 78]

ND content /g litre^{-1}	H_V /kg mm^{-2}			Porosity /number of pores per cm^2		Wear resistance (rel.u.)
	1.0 [a]	1.5 [a]	5.0 [a]	1.0 [a]	1.5 [a]	5.0 [a]
No additives	251	286	308	20	15	1.0
0.5	301	312	330	15	10	1.8
1	320	331	354	15	5	2.3
2	359	380	378	15	5	3.8
5	370	408	472	10	5	5.7
10	395	467	583	6	4	6.4

[a] The i_c values (in A dm^{-2}).

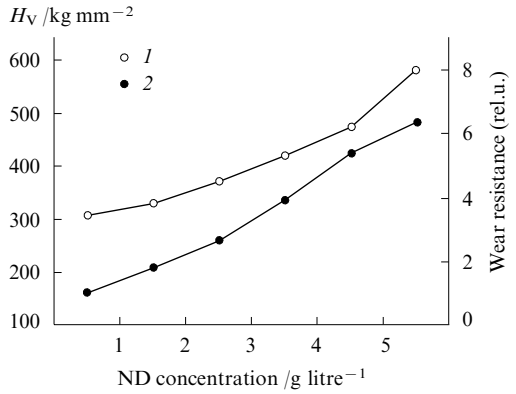


Figure 10. Microhardness (*1*) and wear resistance (*2*) of nickel coating plotted *vs.* ND concentration in sulfuric acid electrolyte.[36]
i_c = 5 A dm^{-2}.

The content of ND in the coating increases from 0.1 mass % to 0.7 mass % as the ND concentration in the electrolyte increases from 0.5 to 10.0 g litre^{-1}. At a 5 g litre^{-1} ND concentration in the electrolyte, the microhardness of the coating becomes nearly doubled (see Fig. 10) and the wear resistance shows a nearly sixfold increase. The coating thus prepared is fine-grained, dense and has a low porosity.

c. Gold plating

If the ND concentration in the electrolyte varies from 0.1 to 10.0 g litre^{-1}, the ND content in the gold coating changes from 0.2 mass % to 0.8 mass %. The microhardness of the coating reaches a value of 200 kg mm^{-2} and the wear resistance increases two- to five-fold.[36, 80–82]

The structure and properties of the coating vary non-monotonically. Figures 11 and 12 show bimodal plots.[65] The first peak appears at low ND concentrations and its intensity depends on both the electrolyte composition and the type of the co-deposited diamond-containing additive. The second peak appears at higher ND concentrations. Nanodiamonds can be incorporated into the coating in the form of individual particles or as large aggregates depending on their colloidal state in the electrolyte. The second peak appears in the concentration range corresponding to co-deposition of gold with ND aggregates. In this region some technological characteristics (*e.g.*, sedimentation rate and the yield of gold calculated with respect to electric current) are deteriorated.

The gold plating process has been implemented on a large scale.

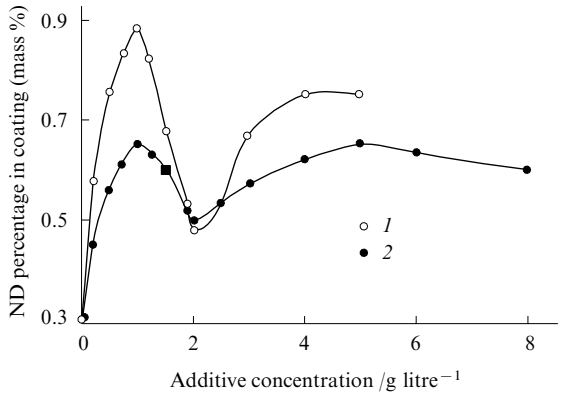


Figure 11. Mass percentage of co-deposited ND particles in gold coating plotted *vs.* concentration of the diamond-containing additive in the electrolyte for two types of additives: DB (*1*) and ND (*2*).[65]

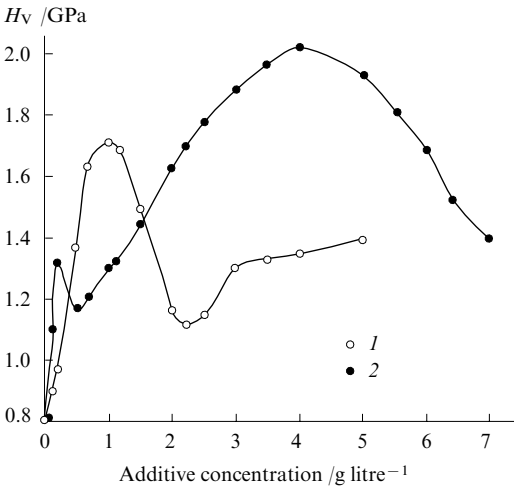


Figure 12. Microhardness of gold coating plotted *vs.* concentration of the diamond-containing additive in the electrolyte for two types of additives: DB (*1*) and ND (*2*).[65]

g. Silver plating

Using ND, it is possible to prepare dense, fine-grained semi-bright silver coatings containing up to 1.0 mass % of ND.[36, 80, 83]

Depending on the electrolysis conditions, composition and type of electrolyte, the microhardness of the silver–diamond coating increases by 200–700 MPa compared to that of microhardness of pure silver. The wear resistance of the coatings shows a ten- to fifteen-fold increase (Fig. 13), the solderability of this coating is identical to that of pure silver. The silver plating process has been implemented on a large scale.[36]

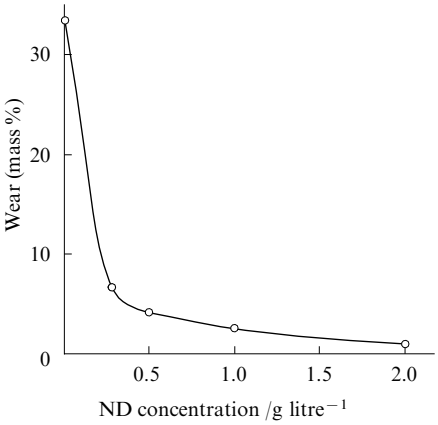


Figure 13. Wear resistance (mass loss) of silver–diamond coating plotted *vs.* ND concentration in electrolyte.[36, 80]

d. Zinc plating

The optimum concentration of ND in the zinc plating electrolyte is 10 g litre^{-1}, which corresponds to the ND content in the coating of 0.7 mass %.[36, 76, 84] As the amount of ND in the electrolyte increases, the precipitates become more finely grained.

Passivation of zinc/ND coatings thus obtained by conventional chromium plating or phosphating significantly increases

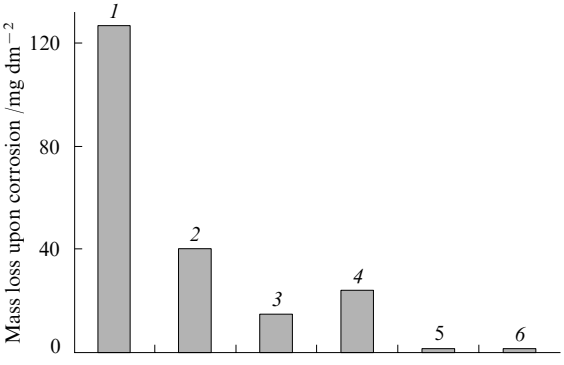


Figure 14. Corrosion resistance (mass loss) of zinc coatings compared to that of unprotected steel and cadmium coating (NaCl fog, 60 h).[36, 76, 84] Unprotected steel (*1*), Zn-coating (*2*), Cd-coating (*3*), Zn + ND (*4*), Zn + ND + chromating (*5*) and Zn + ND + phosphating (*6*).

their corrosion resistance (Fig. 14). Phosphating was found to be much more efficient and environmentally safe.

e. Anodic oxidation of aluminium

Anodic oxidation is the main method of corrosion protection, and increasing the strength and wear resistance of aluminium and aluminium alloys.

During oxidation, the ND particles fill pores and remain in them due to mechanical and van der Waals forces. The mass of the filled oxide film increases two- to four-fold.[36, 76, 85] The wear resistance of such a film increases to a much greater extent (by 10 to 13 times; see Fig. 15) and so do its corrosion resistance and dielectric properties. The film turns grey.

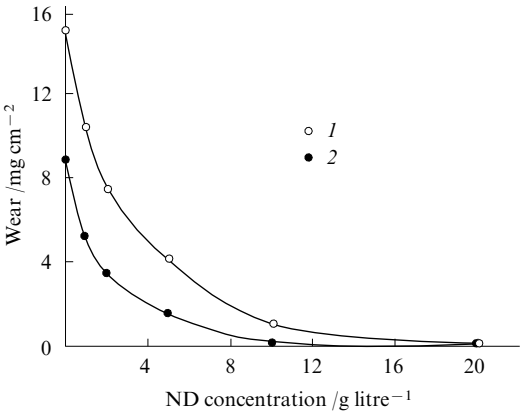


Figure 15. Wear of anodically oxidised aluminium film based on D-16 alloy (Germany) plotted *vs.* ND concentration in anodic oxidisation electrolyte (i_a = 1.5 A dm^{-2}).[36, 76, 85]
At 10 °C (*1*) and at 20 °C (*2*).

g. Iron plating

The hardness of electrochemical iron coating approaches that of steel. Such coatings become even harder when using ND.[86] For iron plating, it is more appropriate to use DB rather than purified ND. The best results were obtained using partially oxidised DB prepared following a known procedure.[87]

The effect of ND and partially oxidised DB on the microhardness and wear of iron coatings is illustrated in Figs 16 and 17. The advantage of using the cheaper product (DB) is clearly seen.

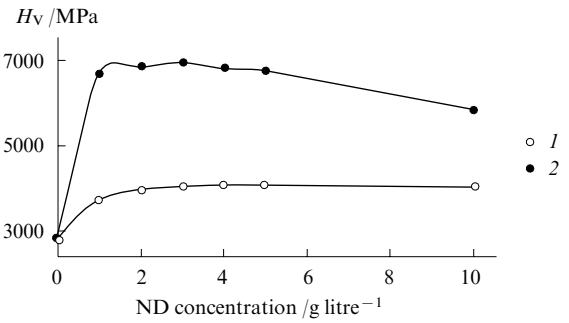


Figure 16. Effect of ND (*1*) and DB (*2*) concentration on microhardness of iron coating (i_c = 4 A dm^{-2}).[86]

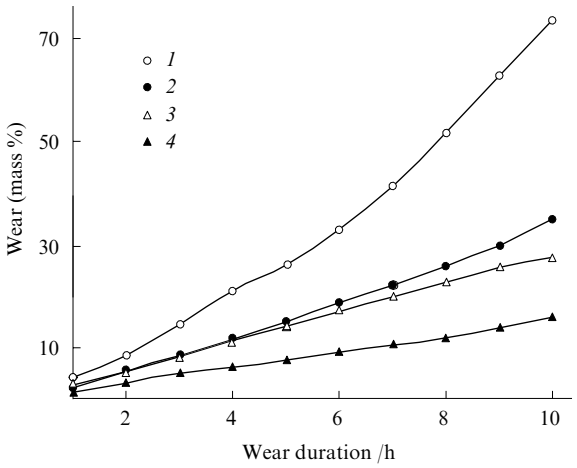


Figure 17. Effect of various diamond-containing additives on wear of an iron coating (concentrations of all additives were 5 g litre^{-1}, i_c = 4 A dm^{-2}).[86]
No additives (*1*), ND (*2*), conventional DB (*3*) and oxidised DB (*4*).

2. Polishing

Introduction of ND into polishing composites improves the characteristics of chemicomechanical polishing and the efficiency of the overall surface treatment.[36, 50, 88–93]

The colloidal, sedimentation and mechanical properties of ND clusters aggregated into complex fractal structures depend on the procedure for preparation and on the composition of the liquid dispersion medium. Nanodiamonds introduced into the liquid (ND content of 0.1 mass % – 0.3 mass %) act as powerful structure-forming agent. Using low-filled aqueous, organic and aqueous-organic ND dispersions, one can obtain ideally smooth surfaces of materials processed, in which the microroughness is comparable in size with interatomic distances.

The fractal structure of ND favours efficient relief of local stress produced as the working surfaces approach each other. Large loose ND aggregates easily break down upon slightest action on the suspension and appear again also easily.

The fractal ND aggregates act as a kind of damper, which makes rigid point-to-point interactions between the working surfaces less probable. This prevents the material being processed from deformations and stress in the near-surface layer.

When the polishing pads and treatment regimes on most buffing machines were chosen appropriately, all materials showed smoothing of relief and formation of flat mirror surfaces without macroscopic defects.

Preparation of polycrystalline micropowders with different nanostructures of porous particles seems to be promising for polishing. Powders are prepared by milling large aggregates formed upon compaction of ND powder.

Polishing using ND is employed to improve the operating characteristics of almost all materials, namely, composites, semiconductors, dielectrics and conductors having a crystal, polycrystal, glassy or some other structure.[92]

The key parameters of polishing are the rate of removal of material, surface roughness, plateness and plane-parallel arrangement of surfaces of working pieces. They are determined by the properties of ND and to a great extent by the design of buffing mashines, types of polishing pads, their pretreatment and other factors. Therefore, a particular ND powder (or polishing composite) should be 'tuned' to a technology of treatment of a material in hand or working pieces made of it.

Table 12. ND-containing polishing compositions.[94]

State	Medium	ND content (mass %)
Suspension	water, ethylene glycol, aqueous KOH or $FeSO_4$ solution, petroleum oil	3 – 5
Polishing compound	lipids, polymers	3 – 5
Solids of specified shape	cured silicone, nitrile, *etc*. rubbers	2 – 3
	cured formaldehyde and epoxy resins	2 – 5
	metal (aluminum, nickel)	< 50

Nanodiamond-containing polishing compositions can provide a high plateness (to 1 μm) and reproducible surface roughness from a few fractions of a nanometre to a few nanometres for more than thirty crystalline substances. The number of such materials increases and the polishing quality is improved, which indicates a versatile character of this technology.

Table 12 lists the components of some polishing compositions.[94] The results of treatment of materials characterised by different hardness and plasticity are listed below.[94]

Material	Surface roughness /nm
Hard alloy	1 – 5
Steel	5 – 6
Sapphire	5 – 6
Quartz	0.5 – 1.5
Molten silica	0.5 – 1.0
Silicon	0.5 – 1.5
NaCl crystal	2 – 3
KBr crystal	2 – 3

A decrease in the diamond particle size from 1 μm to 3 – 5 nm is accompanied by a decrease in the relief roughness and by the change in the mechanism of mass transfer on the surfaces of alloys and composite materials from anisotropic (plastic deformation) to isotropic (nanoscratching) removal of material.

3. Oils and lubricants

Nanodiamonds, as modifiers of the friction surfaces, offer the following advantages over other types of surface modifiers:[36, 50, 95 – 97]

— efficiency at very low concentrations in the base oil;

— compatibility with various types of synthetic and mineral oils; and

— environmental safety of the carbon additive to oils compared to metal particles or fluorocarbons.

The addition of diamond blend containing a large number of ultrasmall graphite-like particles and ND causes the properties of lubricants and the character of the interaction between the friction surfaces to change. Namely, the viscosity of the liquid, the strength of the lubricating film and, as a consequence, the loading capacity of tribomating increase. Selected characteristics of diamond-containing lubricant compositions and their efficiency are listed below.

Parameter	Numerical value
ND content (mass %)	0.01 – 0.3
Particle concentration /cm^{-3}	$\sim 10^{14}$
Reduction of temperature in the contact zone (%)	16 – 20
Reduction of the friction coefficient (%)	20 – 30
Increase in limiting load of a friction pair (steel – bronze) /MPa	from 16 to 72 (approximately fourfold)
Reduction of wear of mating components by a factor of n	n = 1.5 – 3.0
Combustion engines	
Engine run-in time reduction by a factor of m	m = 10 – 12
Fuel economy (%)	3 – 6
Power increase (%)	4 – 8
Cylinder compression increase (%)	10 – 17
Cooling-lubricating liquids (CLL)	
Cutting torque reduction (%)	20 – 30
Increase in operating life of tools by a factor of p	p = 1.5 – 4.0

The most interesting parameters are the very low content of ND, considerable increase in the limiting load, reduction of wear of mating components, engine run-in time reduction and an increase in the operating life of tools. ND-containing lubricant compositions can be based on mineral or synthetic oils and CLL.

The DB in a lubricant composition produces a complex effect consisting in:

— filling of dips on the friction surfaces with carbon clusters and subsequent reduction of boundary friction and wear;

— an increase in viscosity of the lubricant composition in thin films due to dispersion structuring of carbon clusters;

— a decrease in viscosity of the lubricant composition at low temperatures due to reduction of glass transition threshold of the dispersion-filled medium;

— after-effect (duration over 60 h) upon replacement of the lubricant composition by the base oil; the effect is due to strong mechanical, adsorption and diffusion immobilisation of carbon clusters on the friction surfaces;

— operation of ND clusters as microscopic antifriction bearings under high load at maximum displacement of the liquid phase between friction surfaces, which permits an increase in the limiting load of the friction pair.

The content of DB in the lubricant composition depends on the character and operation mode of a particular device.

Diamond blend has a strong effect on most structural-mechanical and operating characteristics of almost all types of lubricants. The use of preservation greases reduces the chemical and electrochemical metal corrosion because many additives (usually, corrosive substances) are no longer used. The use of sealing greases and thread lubricants improves the tightness of joints, reduces corrosion of the contact surfaces and stabilises and reduces the shear stress and torque.

Cooling-lubricating liquids are most efficient in screw cutting and holemaking in hard-to-machine materials.[98 – 100] Introduction of DB (1 mass % – 5 mass %) into lubricants used in plastic metal working significantly reduces the friction coefficient and improves the quality of the surface of goods.[101]

Diamond blend-containing oil compositions are used in Russia, Germany, Italy, Turkey and China.

4. Polymer – diamond composites

Numerous studies showed efficiency of the introduction of ND and DB into polymeric composites and films based on poly(flouroelastomers), perfluorocarbons, polysiloxanes, poly(isoprenes), butadiene – styrene rubbers, polyurethanes, polyimides, *etc.*[36, 50, 91, 102 – 107]

The introduction of ND improves the overall elasticity and strength characteristics and in some cases provides polymers with unique tribotechnical properties.

The introduction of DB significantly reduces the permeability of fluoroelastomer films.[103 – 105] Based on some optimisation parameters, poly(vinylidene fluoride-*co*-perfluoropropyl ether) (CVPE) filled with DB to different extent (from 2 to 50 parts by mass) was chosen as the elastomeric component. A comparative analysis of mass thermograms of the elastomer and nanocomposites based on it showed an increase in the thermal degradation onset temperature, on average, by 40 °.

At a DB content of 5 mass %, the tear resistance of the fluoroelastomer is doubled (Fig. 18). The physicomechanical characteristics of the fluoroelastomers based on this DB measured in the course of thermal ageing at 522 K are identical to or better than those of non-aged conventional vulcanisates.

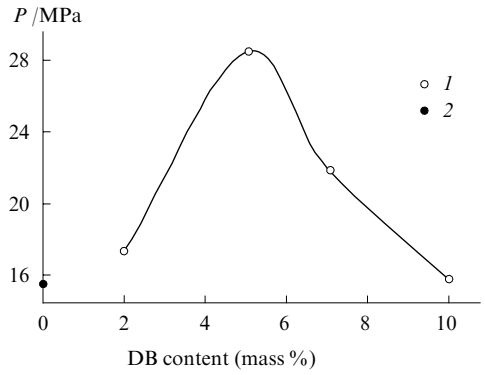


Figure 18. Tensile strength of perfluorinated polymer (film) CVPE plotted *vs*. additive concentration. Additives: diamond blend (*1*) and carbon black (*2*).[105]

A fluoropolymer filled with DB (2 parts by mass) demonstrated a decrease in the coefficient of sliding friction at the metal – rubber interface to 7.0×10^{-3}. Rubber mixtures based on DB-modified fluoroelastomers showed an increase in the abrasive wear resistance by a factor of 1.5 – 2.0.

Thus, DB is the most reactive filler of fluoroelastomers and provides a highly cross-linked vulcanisation network, minimum thermal ageing, low friction coefficient of film coatings and extends their operating life by 25% – 40% in the friction units.

a. Polyisoprene and butadiene – styrene copolymer

The modifying action of DB was demonstrated in relation to conventional filled polymer blends based on polyisoprene and butadiene – styrene rubbers, which are widely used in Russia.[108]

Diamond blend-modified rubbers are characterised by higher degree of vulcanisation, a 35% higher conditional tensile strength at 300% elongation and a 30% lower degree of swelling in toluene. Such rubbers have better strength characteristics (about 30% higher than those of conventional rubbers) under normal test conditions and better wear endurance. The addition of DB to rubber in a (2 – 4) : 100 ratio (by mass) is optimum from the standpoint of the overall effect on the physicomechanical characteristics of rubbers.

As the DB content increasees, the cohesion strength of rubbers increases by a factor of 1.3 – 2.0. The maximum cohesion strength is attained at the DB content of 7.5 parts (by mass). The introduction of DB into polyisoprenes causes the tear strength to increase by a factor of about 1.5.

To determine the effect of the rubber matrix on the modifying activity of DB, the latter was introduced in excess (2, 3 and 4 parts by mass) into a conventional rubber blend based on butadiene – styrene copolymer containing 30% of styrene units. The rubber blends containing 3 and 4 parts (by mass) of DB showed an increase in the cohesion strength by a factor of 1.5 to 2.0 compared to the reference samples. The tear resistance of DB-containing vulcanisates is doubled compared to that of the reference samples (Fig. 19). Thus the modifying action of DB introduced into rubber matrices of different nature manifests itself in different manner.

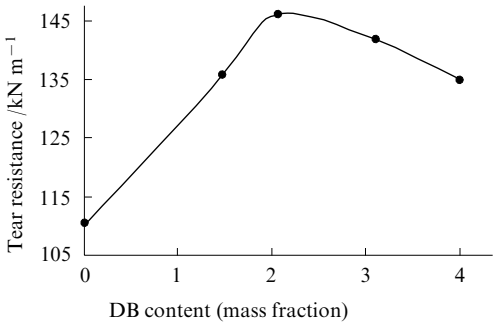
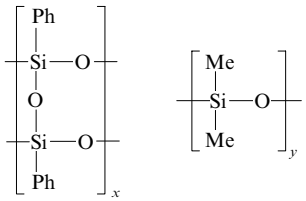


Figure 19. Tear resistance of butadiene – styrene rubber CKCM-30 APK (Russia) at different diamond blend content.[108]

b. Polysiloxanes

Polysiloxanes were studied using a polyblock copolymer of ladder phenylsesquisiloxane and poly(dimethylsiloxane) (LPS-PDMS) as the polymer matrix.[106]



This copolymer is cold-resistant to 200 K and thermally stable to 673 K. It can be used as the basic component of film-forming materials having a broad spectrum of applications from protective coatings to selectively permeable membranes.

Nanodiamond powders were pre-calcined and the ND particle surfaces were modified using the silylation reaction (Fig. 20).

When the modified fillers were used in their individual state, the strength parameters of the modified films increase by 20% – 30% in the practically valuable interval of deformations and their elastic properties remain reasonably good. The effect is attained at filling degrees of less than 5 mass %.

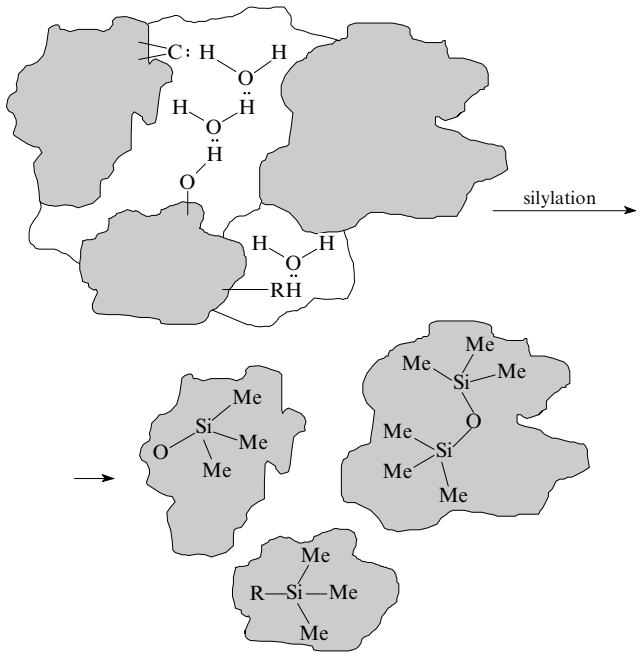


Figure 20. Modification of ND surface with silylating agents.[106]
The following silylating composites were used: Me_3SiCl : $(Me_3Si)_2NH$ = 1 : 1, $(CH_2{=}CH)_2SiCl_2 : Me_3SiNH_2$ = 1 : 1; R is the functional group containing 'reactive' proton (OH, NH_2, COOH, *etc.*).

c. Polyurethanes

The introduction of DB (0.2 mass %) into polyurethanes causes the conditional strength to increase by a factor of 3 upon an increase in the polymer elasticity by a factor of 1.5.

The introduction of DB (0.3 mass %) into polyurethane foams leads to an increase in the compression strength by a factor of 1.5 and improvement of process performance in the preparation of this polymer.

d. Cold-resistant butadiene – nitrile rubber

Introduction of DB (to 1 mass %) into cold-resistant butadiene – nitrile rubber causes a significant (up to 70%) increase in the relative ultimate elongation of the rubber. Additionally, the wear resistance increases and the friction coefficient is halved compared to that of gum rubber.[109,110] At 223 K, the cold resistance increases by 50%.

The resistance of rubbers in hydrocarbon media increases by 20% upon introduction of DB. The addition of DB (0.1% – 0.5%) improves the key operating characteristics, namely, the friction coefficient decreases and the wear resistance, elasticity and cold resistance of the materials increase. Additionally, the rubbers studied had lower hysteresis losses under dynamic loading; this is responsible for longer operating life.

e. Explosive decompression-resistant rubbers

The introduction of DB (0.1 mass % to ~2 mass %) into commercially available, explosive decompression-resistant rubbers based on various polymers having an elastic modulus of up to 8 MPa causes the tear resistance and wear resistance to increase by 60% and 40%, respectively.[111]

f. Plasma-flame-spraying polymeric coating

A process was developed for plasma flame spraying of single- and multilayer polymeric coatings containing disperse ND.[112]

Bilayer metal – polymer coatings containing 0.5 mass % of ND prepared by plasma flame spraying technique provide reliable protection of immersion pump bearings and rotors and other parts from combined action of corrosion and wear, which allows them to retain high operating characteristics over a long period of time.

5. Diamond sintered samples and compacts

Experience in sintering of diamond micropowders has shown that a decrease in the grain size causes deterioration of the physicomechanical properties of sintered polycrystals. The reason lies in high back pressure of desorbed gases at $T > 1773$ K and at pressures > 5 GPa.[113–115]

Desorption of gases physisorbed on the surface of ND particles was achieved by heat treatment of compacts *in vacuo* for 2 h at 773 K and a residual gas pressure of 10^{-3} Pa.[116]

As the sintering temperature increases, the degree of graphitisation increases. Removal of carbonyl and hydroxyl groups from the surface of diamond particles as a result of its chemical modification decreases the degree of graphitisation of ND on sintering. Here, raising the temperature is accompanied by densification of the sintered polycrystals; as a consequence, their strength and hardness increase (maximum hardness is 28 GPa).[116]

By cold pressing of ND one can prepare compacts with a density of 1830 (at 4.5 GPa) and 1950 kg m^{-3} (at 8 GPa). At the pressing temperature of 1773 K, the density slowly increases and at 2273 and 2573 K it decreases.[117] The samples prepared at 1273 K and higher temperatures showed graphitisation of ND, which develops at the grain boundaries. The optimum sintering duration is 36 s. The sintering of ND is governed by two parameters, the initial density of ND and the quality of purification of the particle surfaces.

The data on the ND sintering conditions and the characteristics of their structural state are listed in Table 13.[115] Two processes occur during the sintering of ND, that is, transformation of the structural state of ND and the diamond → graphite phase transition.

A possible method of counteracting the effect of desorbed gases on the sintering of ND involves the introduction of getters (elements or compounds that form chemical bonds with gas molecules) into the reaction volume.[118] For instance, by modifying the surface of ND particles with cobalt and nickel, a fraction of volatile oxides was replaced by non-volatile ones; as a consequence, gas evolution in the course of hot compaction reduced and the density and hardness of the compacts increased.[119]

The approach involving the introduction of compounds favouring glass formation into the ND powder proved to be fruitful.[120] In particular, the addition of B_2O_3, SiO_2, CaO or B (1 mass % to 3 mass %) made it possible to reduce the sintering pressure from 7 to 5 GPa and to increase the temperature and duration of sintering; graphitisation and recrystallisation of diamond slowed down.

The density and hardness of sintered ND samples can also be increased by sintering mixtures of ND with static-synthesis diamond micropowders produced on a large scale. The drawing dies for metal cord fabrication showed a halved wear compared to the dies sintered from static-synthesis diamond micropowders only.

By introducing DB into copper – graphite collectors one can eliminate the wear problems of both the collector and the copper wire (minimum wear).

Rolled tungsten + aluminium + ND composite (thickness 4 mm) is used for production of body armour.[2]

Table 13. Characteristics of starting ND and ND-based compacts prepared under different conditions of heat treatment under pressure.[115]

Treatment conditions			Phase composition	Composition of the diamond component					
				polycrystaline particles		aggregates		single-crystal grains	
P /GPa	T /°C	τ /s		size	content (%)	size /Å	content (%)	size /Å	content (%)
1	–	–	starting diamond	I	90				
				II	10				
4.5	1000	36	diamond + graphite	I + II	100	–		–	
4.5	1500	36	the same	I + II	80	100 – 150	20		
8	750	36	diamond	I + II	100	–		–	
8	1000	36	diamond + graphite	I + II	100	–		–	
8	1500	36	the same	I + II	80	100 – 150	20	–	
8	2000	12	"	I + II	20	100 – 200	70	100 – 300	10
8	2000	36	"	–		100 – 500	70	100 – 500	30
8	2300	12	"	–		100 – 500	20	500 – 1500	80

Note. Notations used in this Table are as follows: 'I' for particle size from 3 to 50 Å and 'II' for particle size from 100 to 150 Å.

6. Biological activity of nanodiamonds

Modern antioxidants used for chemotherapy of cancer patients are very toxic compounds. This makes the search for novel antioxidants of low toxicity topical.

Diamonds are non-toxic and non-tumourigenic species, possess no mutagenic properties and are insoluble in biological liquids. The biological activity of ND has not been studied as yet.

An ND crystal has a chemically inert classical diamond core (almost round or oval in shape) and a quite reactive surface 'fringe' comprised of functional groups that are safe for living organism and impart the surface with hydrophilic properties.[121, 122] Additionally, each ND crystal has a large number of unpaired electrons, being in essence a multiradical.[123]

Nanodiamonds belong to fundamentally novel antitumour agents.[124, 125] They can be treated as polyfunctional supramolecular structures bearing polar groups [OH, NH_2, $C(O)NH_2$] that govern the antioxidant activity and the ability to participate in free-radical processes in living cells.

A large number of functional groups on the surface of ND particles can provide both additional generation and quenching of excess radicals in metabolic processes. It is the ability to control free-radical processes under the action of ND that can appear to be a basis for their antitumour action.

In all studies, ND showed a marked beneficial effect, which manifests itself in the extension of life of cancer patients compared to predictions. Figure 21 shows the initial and final stages of the attack of ND on malignant cells in human body.

Generally, the results obtained using aqueous ND suspensions are as follows: significant or even complete relief of severe pain; normalisation of intestinal peristalsis, including recovery of gut permeability; improvement of blood characteristics; significant activation of the immune system and the mental status of patients (incredible eagerness for life was observed).

It is possible to design ND-based pharmaceuticals for activation of the enzymatic subsystem of the antioxidative cell protection system.[126, 127]

Thus, the results of a few available studies of biological activity of ND are as follows.

1. At present, ND have no analogues, with allowance for their physical state (insoluble solid powder), from the standpoint of complex action on human organism.

2. The use of ND along with chemotherapy and radiotherapy can appear to be promising in treatment of malignant neoplasms.

3. ND are highly efficient for normalisation of gastrointestinal function.

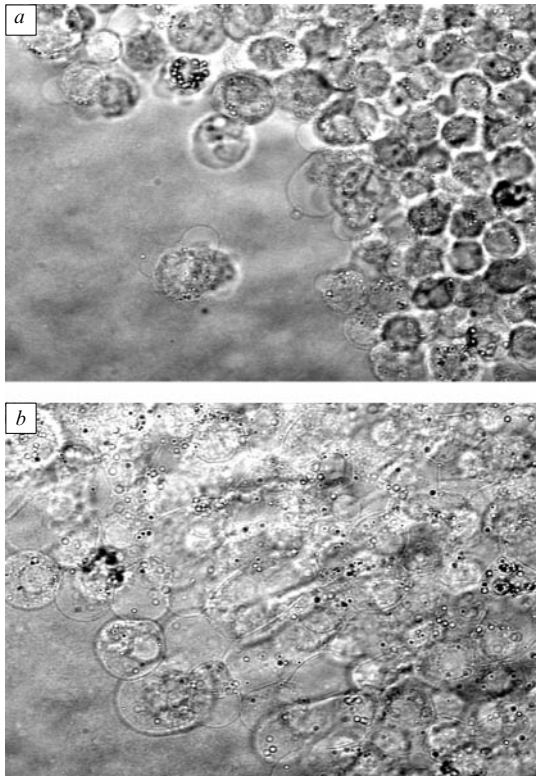


Figure 21. Initial (*a*) and final (*b*) stage of ND attack on malignant cells in human organism.[126]

Nanodiamonds are also of great interest for biochemistry as a novel kind of sorbents suitable for separation and purification of proteins.[128 – 131] Nanodiamonds can selectively adsorb recombinant apoobelin from the protein extract of the cells of *Escherichia Coli*. It was found that ND particles also can adsorb phytoprotein on their surface.[129] An ND – obelin composition was grafted onto the surface of aluminium substrate and a prototype of planar luminescent sensors (biochips) was created.[128]

Recently, a highly sensitive test method for determination of the presence and type of antibodies and antigen markers of different nosology using ND has been developed. The technique does not require any equipment and solutions other than analysed one.

7. Other fields of application of nanodiamonds

A novel initiation composition VS-2 based on 5-hydrazinotetrazolylmercury(II) and poly(methylvinyltetrazole) containing ND (Table 14) was developed.[132, 133] The substance is sensitive to low-temperature laser radiation.

Table 14. Parameters of VS-2 explosive initiation with a laser pulse.

VS-2 charge + additive		Initiation energy /μJ
additive	additive content (%)	
No additive	–	310
Soot	0.5	2450
	1	2550
	2	3050
	3	3250
Nanodiamonds	0.5	260
	1	200
	3	180
	5	340
Fullerenes	1	630
	3	830
	5	730
Nanotubes	0.5	640
	1	590
	2	640
	3	850

Laser initiation is a relatively new safe procedure for blasting explosives. It provides a high degree of isolation of the light-initiated detonator from a false pulse because of the lack of powerful random light sources suitable for blasting the detonator in the optical region. The additives to the VS-2 composition, namely, finely disperse soot, fullerenes or nanotubes (1% – 3%) increase the threshold of initiation by a single pulse of a neodymium laser. On the contrary, the introduction of detonation-synthesis ND (0.5% – 3%) reduces this threshold.

The composition provides simultaneous enhancement of sensitivity to the laser pulse by a factor of 1.5 – 1.7 and high adhesion to the contact surface due to improvement of the adhesive properties of poly(methylvinyltetrazole) caused by the presence of ND. The minimum initiation energy drops from 310 to 180 μJ for the ND-containing material.

To protect architectural monuments made of white Carrara marble, ND-containing organic – silicate coatings were developed and evaluated.[134, 135] Nanodiamonds present in such coatings inhibit the growth of the most abundant, in urban environment, fungi and bacteria that destroy the structure of stone materials. The coatings are prepared from tetraethoxysilane-based sols containing ND. They can be used to modify the surface of particles of the powder components of cements and concretes. This permits a significant extension of the operating life of buildings, motorways, hydroelectric power plants and other facilities made of concrete.

References

1. K V Volkov, V V Danilenko, V I Elin *Fiz. Goreniya Vzryva* **26** (3) 123 (1990) [a]
2. V V Danilenko *Sintez i Spekanie Almaza Vzryvom* (Synthesis and Caking of Diamond by Explosion) (Moscow: Energoatomizdat, 2003)
3. Yu A Babushkin, A I Lyamkin, G A Chiganova *Ul'tradispersnye Poroshki, Nanostruktury, Materialy* (Ultradispersed Powders, Nanostructures and Materials) (Krasnoyarsk: Krasnoyarsk State Technological University, 1996) p. 10
4. A Yu Babushkin, A I Lyamkin *Fizikokhimiya Ul'tradispersnykh Sistem (Sb. Nauch. Tr. IV Vseros. Konf.)* [Physicochemistry of Ultradispersed Systems (Proceedings of the IVth All-Russian Conference)] (Moscow: Moscow Engineering Physics Institute, 1999) p. 125
5. S V Pershin, D N Tsaplin *V Vsesoyuznoe Soveshchanie po Detonatsii* (The Vth All-Union Meeting on Detonation) (Chernogolovka: Small-scale Enterprise Imtekh, 1991) Vol. 2, p. 237
6. A M Staver, A P Ershov, A I Lyamkin *Fiz. Goreniya Vzryva* **20** (3) 79 (1984) [a]
7. E E Lin *Fizikokhimiya Ul'tradispersnykh Sistem (Sb. Nauch. Tr. IV Vseros. Konf.)* [Physicochemistry of Ultradispersed Systems (Proceedings of the IVth All-Russian Conference)] (Moscow: Moscow Engineering Physics Institute, 1999) p. 40
8. V F Anisichkin, B G Derendyaev, V A Koptyug, Yu I Mal'kov, N F Salakhutdinov, V M Titov *Fiz. Goreniya Vzryva* **24** (3) 121 (1988) [a]
9. N V Kozyrev, G V Sakovich, S Ch Su, M S Shtein *V Vsesoyuznoe Soveshchanie po Detonatsii* (The Vth All-Union Meeting on Detonation) (Chernogolovka: Small-scale Enterprise Imtekh, 1991) Vol. 1, p. 176
10. N V Kozyrev, P M Brylyakov, S Ch Su, M S Shtein *Dokl. Akad. Nauk SSSR* **314** 889 (1990) [b]
11. N V Kozyrev, E S Golubeva *Fiz. Goreniya Vzryva* **28** (5) 119 (1992) [a]
12. A L Vereshchagin *Detonatsionnye Nanoalmazy* (Detonation-synthesis Nanodiamonds) (Barnaul: Altai State Technological University, 2001)
13. Yu I Mal'kov *Fiz. Goreniya Vzryva* **27** (5) 136 (1991) [a]
14. E E Lin *Fizikokhimiya Ul'tradispersnykh Sistem (Sb. Nauch. Tr. V Vseros. Konf.)* [Physicochemistry of Ultradispersed Systems (Proceedings of the IVth All-Russian Conference)] (Moscow: Moscow Engineering Physics Institute, 2000) p. 40
15. V F Anisichkin *Fiz. Goreniya Vzryva* **30** (5) 100 (1994) [a]
16. B G Loboiko *Fiz. Goreniya Vzryva* **36** (6) 45 (2000) [a]
17. B A Vyskubenko, V V Danilenko, E E Lin, V A Mazanov, T V Serova, V I Sukharenko, A P Tolochko *Fiz. Goreniya Vzryva* **28** (2) 108 (1992) [a]
18. V V Danilenko *Fiz. Goreniya Vzryva* **41** (5) 104 (2005) [a]
19. V V Danilenko *Fiz. Goreniya Vzryva* **41** (4) 110 (2005) [a]
20. V M Titov, V F Anisichkin, I Yu Mal'kov *Fiz. Goreniya Vzryva* **25** (3) 117 (1989) [a]
21. C L Mader *Numerical Modeling of Explosives and Propellants* (New York: CRC Press, 1998)
22. A L Vereshchagin, G V Sakovich, L A Petrova, V V Novoselov, P M Brylyakov *Dokl. Akad. Nauk SSSR* **315** 104 (1990) [b]
23. RF P. 2230702; *Byull. Izobret.* (17) (2004)
24. O N Breusov *Khim. Fiz.* **21** (11) 110 (2002) [c]
25. L V Dubnov, N S Bakharevich, A N Romanov *Promyshlennye Vzryvchatye Veshchestva* (Industrial Explosives) (Moscow: Nedra, 1973)
26. A N Nesmeyanov, N A Nesmeyanov *Nachala Organicheskoi Khimii* (Principles of Organic Chemistry) (Moscow: Khimiya, 1969) Vol. 1, p. 344
27. V F Anisichkin, I Yu Mal'kov, F A Sagdiev *V Vsesoyuznoe Soveshchanie po Detonatsii* (The Vth All-Union Meeting on Detonation) (Chernogolovka: Small-scale Enterprise Imtekh, 1991) Vol. 1, p. 27
28. A M Staver, N V Gubareva, A I Lyamkin, E A Petrov *Fiz. Goreniya Vzryva* **20** (5) 100 (1984) [a]
29. V V Odintsov, S A Gubin, V I Pepekin, L N Akimova *Khim. Fiz.* **10** 687 (1991) [c]
30. S V Pershin, V N Tsaplin, A N Dremin, A G Antipenko *Fiz. Goreniya Vzryva* **27** (4) 117 (1991) [a]

31. S V Pershin, V N Tsaplin, A G Antipenko *V Vsesoyuznoe Soveshchanie po Detonatsii* (The Vth All-Union Meeting on Detonation) (Chernogolovka: Small-scale Enterprise Imtekh, 1991) Vol. 2, p. 233
32. F Volk *Philos. Trans. R. Soc. London, Ser. A* **339** 335 (1992)
33. V Yu Dolmatov *Sverkhtv. Mater.* (4) 38 (2003) [d]
34. V Yu Dolmatov, M V Veretennikova, V A Marchukov, V G Sushchev *Fiz. Tv. Tela* **46** 596 (2004) [e]
35. A M Staver, A I Lyamkin *Ul'tradispersnye Materialy. Poluchenie i Svoistva (Mezhvuzovskii Sbornik)* [Ultradispersed Materials. Production and Properties (Intercollegiate Collection)] (Krasnoyarsk: Krasnoyarsk Polytechnic Institute, 1990) p. 3
36. V Yu Dolmatov *Ul'tradispersnye Almazy Detonatsionnogo Sinteza* (Ultradispersed Detonation-snthesis Diamonds) (St Petersburg: St Petersburg State Pedagogical University, 2003)
37. Appl. PCT WO 000686 (2005)
38. Appl. PCT WO 000685 (2005)
39. RF P. 2109683; *Byull. Izobret.* (12) 215 (1998)
40. V A Mazanov *Fiz. Tv. Tela* **46** 614 (2004) [e]
41. US P. 5916955; *Chem. Abstr.* **121** 208474 (1994)
42. A A Putyatin, A V Nikol'skaya, Ya A Kalashnikov *Sverkhtv. Mater.* (2) 2 (1982) [d]
43. RF P. 2019502; *Byull. Izobret.* (17) 79 (1997)
44. RF P. 2077476; *Byull. Izobret.* (11) (1997)
45. RF P. 1770271; *Byull. Izobret.* (39) (1992)
46. T M Gubarevich, R R Sataev, V Yu Dolmatov *V Vsesoyuznoe Soveshchanie po Detonatsii* (The Vth All-Union Meeting on Detonation) (Chernogolovka: Small-scale Enterprise Imtekh, 1991) Vol. 2, p. 272
47. T M Gubarevich, V Yu Dolmatov, V F Pyaterikov, I S Larionova *Zh. Prikl. Khim.* **65** 2512 (1992) [f]
48. A E Aleksenskii, M V Baidakova, A Ya Vul', V I Siklitskii *Fiz. Tv. Tela* **41** 740 (1999) [e]
49. V Yu Dolmatov *Sverkhtv. Mater.* (1) 28 (2005) [d]
50. V Yu Dolmatov *Usp. Khim.* **70** 687 (2001) [*Russ. Chem. Rev.* **70** 607 (2001)]
51. E Osawa *Proceedings of the NATO ARW 'Synthesis, Properties and Applications of Ultrananocrystalline Diamond'* (Dordrecht: Springer, 2004) p. 231
52. V F Loktev, V I Makal'skii, I V Stoyanova, A V Kalinkin, V A Likholobov, V N Mitkin *Carbon* **29** 817 (1991)
53. T Jiang, K Xu *Carbon* **33** 1663 (1995)
54. V L Kuznetsov, M N Aleksandrov, I V Zagoruiko, A L Chuvilin, E M Moroz, V N Kolomichuk, V A Likholobov, P M Brylyakov, G V Sakovich *Carbon* **29** 665 (1991)
55. F Cataldo, A P Koscheev *Fullerenes, Nanotubes, Carbon Nanostruct.* **11** 201 (2003)
56. E Mironov, A Koretz, E Petrov *Diamond Relat. Mater.* **11** 872 (2002)
57. L-C L Huang, H-C Chang *Langmuir* **20** 5879 (2004)
58. Y Liu, X Gu, J L Margrave, V N Khabashesku *Chem. Mater.* **16** 3924 (2004)
59. I I Kulakova *Phys. Solid State* **46** 636 (2004)
60. G Post, V Yu Dolmatov, V A Marchukov, M V Veretennikova, A E Sal'ko *Zh. Prikl. Khim.* **75** 773 (2002) [f]
61. S Ji, T Jiang, K Xu, S Li *Appl. Surf. Sci.* **133** 231 (1998)
62. A Dandekar, R T K Baker, M A Vannice *Carbon* **36** 1821 (1998)
63. X Xua, Z Yua, Y Zhub, B Wang *Diamond Relat. Mater.* **14** 206 (2005)
64. S I Chukhaeva, P Ya Detkov, A P Tkachenko, A D Toropov *Sverkhtv. Mater.* (4) 29 (1998) [d]
65. T M Gubarevich, L E Chernukho *Proceedings of the NATO ARW 'Synthesis, Properties and Applications of Ultrananocrystalline Diamond'* (Dordrecht: Springer, 2004) p. 345
66. V Yu Dolmatov, V G Sushchev, V A Marchukov, M V Veretennikova *Porodorazrushayushchii i Metallo-obrabatyvayushchii Instrument — Tekhnika i Tekhnologiya ego Izgotovleniya i Primeneniya (Nauchnye Trudy ISM im. V N Bakulya NAN Ukrainy, Kiev, 2004)* [Rock-destroying and Metal-working Instrument: Technique and Technology of Its Production and Application (Proceedings of V N Bakul Institute for Superhard Materials of National Academy of Sciences of Ukraine, Kiev 2004)] No. 7, p. 176
67. V Yu Dolmatov, T Fujimura *Proceedings of the NATO ARW 'Synthesis, Properties and Applications of Ultrananocrystalline Diamond'* (Dordrecht: Springer, 2004) p. 217
68. A E Aleksenskii, M V Baidakova, A Ya Vul' *Fiz. Tv. Tela* **39** 1125 (1997) [e]
69. G V Sakovich, V D Gubarevich, F Z Badaev *Dokl. Akad. Nauk SSSR* **310** 402 (1990) [b]
70. V L Kuznetsov, A L Chuvilin, Yu V Butenko *Proceedings of Symposium 'Science and Technology of Fullerene Materials'* Vol. 359 (Pittsburg: Materials Research Society, 1995) p. 105
71. O A Shenderova, D M Gruen *Ultrananocrystalline Diamond: Synthesis, Properties and Applications* (New York: William Andrew Publishing, 2006)
72. V Yu Dolmatov *Proceedings of the 4th International Conference on Materials Processing for Properties and Performance (MP^3-IV), Tsukuba Science City, Ibraki, Japan, 2005* p. 284
73. Appl. PCT WO 89/07668; *Chem. Abstr.* **111** 242622 (1989)
74. USSR P. 1694710; *Byull. Izobret.* (44) 91 (1991)
75. Jpn P. 05106195; *Chem. Abstr.* **116** 141825 (1992)
76. G K Burkat, V Yu Dolmatov *Fiz. Tv. Tela* **46** 685 (2004) [e]
77. Korean P. 10-0634125 (2006)
78. V Yu Dolmatov, G K Burkat *Sverkhtv. Mater.* (1) 84 (2000) [d]
79. Yu V Timoshkov, T M Gubarevich, T I Orekhovskaya, I S Molchan, V I Kurmashov *Gal'vanotekh. Obrab. Poverkhn.* **7** (2) 20 (1999)
80. V Yu Dolmatov, G K Burkat, V Yu Saburbaev, A E Sal'ko, M V Veretennikova *Sverkhtv. Mater.* (2) 52 (2001) [d]
81. RF P. 2191227; *Byull. Izobret.* (29) 345 (2002)
82. E N Loubnin, S M Pimenov, A Blatter, F Schwager, P Ya Detkov *New Diamond Front. Carbon Technol.* **9** (4) 273 (1999)
83. USSR P. 1668490; *Byull. Izobret.* (29) 123 (1991)
84. RF P. 2169798; *Byull. Izobret.* (18) 279 (2001)
85. RF P. 2169800; *Byull. Izobret.* (18) 279 (2001)
86. Appl. RF 2005 131916 (2005)
87. RF P. 2046094; *Byull. Izobret.* (29) 189 (1995)
88. T M Gubarevich, V Yu Dolmatov *Zh. Prikl. Khim.* **66** 1878 (1993) [f]
89. RF P. 2082738; *Byull. Izobret.* (18) 141 (1997)
90. A A Zakharov, V A Yuzova, N V Eristova *Ul'tradispersnye Materialy. Poluchenie i Svoistva (Mezhvuzovskii Sbornik)* [Ultradispersed Materials. Production and Properties (Intercollegiate Collection)] (Krasnoyarsk: Krasnoyarsk Polytechnic Institute, 1990) p. 170
91. G V Sakovich, V F Komarov, E A Petrov *V Vsesoyuznoe Soveshchanie po Detonatsii* (The Vth All-Union Meeting on Detonation) (Chernogolovka: Small-scale Enterprise Imtekh, 1991) Vol. 2, p. 273
92. A S Artemov *Fiz. Tv. Tela* **46** 670 (2004) [e]
93. T Kurobe, T Fujimura, H Ikeda *Fiz. Tv. Tela* **46** 730 (2004) [e]
94. V F Komarov *Tekhn. Mashinostr.* **4** (14) 106 (1997)
95. A I Lyamkin, V E Red'kin *Nauka — Proizvodst.* **3** (28) 59 (2000)
96. Appl. RF 87/00249 (1987)
97. Appl. RF 4923749 (1992)
98. V M Sannikov, Yu M Koreibo *Ul'tradispersnye Materialy. Poluchenie i Svoistva (Mezhvuzovskii Sbornik)* [Ultradispersed Materials. Production and Properties (Intercollegiate Collection)] (Krasnoyarsk: Krasnoyarsk Polytechnic Institute, 1990) p. 155

99. A P Shangin, V E Red'kin, E D Rakshin, S V Seligeev *Ul'tradispersnye Materialy. Poluchenie i Svoistva (Mezhvuzovskii Sbornik)* [Ultradispersed Materials. Production and Properties (Intercollegiate Collection)] (Krasnoyarsk: Krasnoyarsk Polytechnic Institute, 1990) p. 165
100. RF P. 2009186; *Byull. Izobret*. (5) 124 (1994)
101. V N Istomin, E D Rakshin, Yu D Akimov *Ul'tradispersnye Materialy. Poluchenie i Svoistva (Mezhvuzovskii Sbornik)* [Ultradispersed Materials. Production and Properties (Intercollegiate Collection)] (Krasnoyarsk: Krasnoyarsk Polytechnic Institute, 1990) p. 161
102. A P Voznyakovskii, L F Shelokhneva, V Yu Dolmatov, V S Bodrova *Kauchuk Rezina* **6** 27 (1996)
103. RF P. 2100389; *Byull. Izobret*. (36) 295 (1997)
104. V Yu Dolmatov, A P Voznyakovskii, M V Veretennikova *Sverkhtv. Mater*. (6) 81 (2001) [d]
105. A P Voznyakovskii, V Yu Dolmatov, E A Levintova, T M Gubarevich *Doklady Mezhdunarodnoi Konferentsii po Kauchuku i Rezine* (Reports of International Conference on Rubber) (Moscow: Moscow State University, 1994) Vol. 2, p. 80
106. A P Voznyakovskii, V Yu Dolmatov, M V Veretennikova *Sverkhtv. Mater*. (4) 27 (2003) [d]
107. N V Sirotinkin, A P Voznyakovskii, A N Ershova *Fiz. Tv. Tela* **46** 725 (2004) [e]
108. V Yu Dolmatov, A P Voznyakovskii, K A Shevtsova, V S Kutyanina, M V Veretennikova *Porodorazrushayushchii i Metalloobrabatyvayushchii Instrument — Tekhnika i Tekhnologiya ego Izgotovleniya i Primeneniya (Nauchnye Trudy ISM im. V N Bakulya NAN Ukrainy, Kiev, 2005)* [Rock-destroying and Metal-working Instrument: Technique and Technology of Its Production and Application (Proceedings of V N Bakul Institute for Superhard Materials of National Academy of Sciences of Ukraine, Kiev 2005] No. 7, p. 160
109. O A Adrianova, M D Sokolova, S N Popov *Kauchuk Rezina* **6** 11 (1999)
110. RF P. 2129132; *Byull. Izobret*. (11) 375 (1999)
111. L A Akopyan, M N Zlotnikov, B V Rumyantsev, N L Abramova, M V Zobina, T L Mordvintseva *Fiz. Tv. Tela* **46** 722 (2004) [e]
112. P A Vityaz' *Fiz. Tv. Tela* **46** 591 (2004) [e]
113. A A Shul'zhenko, V G Gargin, V A Shishkin, A A Bochechka *Polikristallicheskie Materialy na Osnove Almaza* (Polycrystalline Materials Based on Diamond) (Kiev: Naukova Dumka, 1989)
114. A A Bochechka *Fiz. Tv. Tela* **46** 652 (2004) [e]
115. A A Bochechka *Sverkhtv. Mater*. (4) 10 (1998) [d]
116. A A Shul'zhenko, A A Bochechka, L A Romanko, A M Kutsai, V G Kargin *Sverkhtv. Mater*. (6) 50 (2000) [d]
117. V V Danilenko, I A Petrusha, G S Oleinik, N V Danilenko *Sverkhtv. Mater*. (4) 53 (1998) [d]
118. A A Shul'zhenko, A A Bochechka, V G Gargin, A G Gontar', L A Romanko, V N Tkach *Sverkhtv. Mater*. (4) 46 (1998) [d]
119. V B Shipilo, I M Starchenko, T M Gubarevich *Poroshk. Metall*. **18** 126 (1995) [g]
120. V B Shipilo, I M Starchenko, E V Zvonarev, V T Senyut' *Materialy, Tekhnologii, Instrumenty* **2** (4) 61 (1997)
121. I I Kulakova, V Yu Dolmatov, T M Gubarevich, A P Rudenko *Sverkhtv. Mater*. (1) 46 (2000) [d]
122. A L Vereshchagin, L A Petrova, V V Brylyakov *Sverkhtv. Mater*. (1) 14 (1992) [d]
123. T A Nachal'naya, V G Malogolovets, G A Podzerei, Yu I Nikitin, N V Novikov, Yu A Polkanov *Sverkhtv. Mater*. (1) 36 (2000) [d]
124. V Yu Dolmatov, L N Kostrova *Sverkhtv. Mater*. **3** 82 (2000) [d]
125. RF P. 2203068; *Byull. Izobret*. (12) 72 (2003)
126. A P Puzyr, D A Neshumayev, S V Tarskikh, G V Makarskaya, V Yu Dolmatov, V S Bondar *Diamond Relat. Mater*. **13** 2020 (2004)
127. A P Puzyr, V Yu Dolmatov, I V Shigalei, S V Tarskikh, G V Makarskaya, V S Bondar *Proceedings of NATO ARW 'Innovative Superhard Materials and Sustainable Coating'* (Dordrecht: Springer, 2004) p. 155
128. K V Purtov, V S Bondar', A P Puzyr' *Dokl. Akad. Nauk* **380** 411 (2001) [b]
129. V S Bondar', A P Puzyr' *Dokl. Akad. Nauk* **373** 251 (2000 [b]
130. V S Bondar', I O Pozdnyakova, A P Puzyr' *Fiz. Tv. Tela* **46** 737 (2004) [e]
131. A P Puzyr', I O Pozdnyakova, V S Bondar' *Fiz. Tv. Tela* **46** 740 (2004) [e]
132. Appl. RF 2004134657 (2004)
133. M A Ilyushin, I V Tselinsky, I A Ugryumov, V Yu Dolmatov, I V Shugalei *Cent. Eur. J. Energ. Mater*. **2** (1) 21 (2005)
134. O V Frank-Kamenetskaya, T Fujimura, O A Shilova, V Yu Dolmatov, D Yu Vlasov *Proceedings of the 10th International Conference on New Diamond Science and Technology (ICNDST-10), Comenius University, Bratislava, 2005* p. 170
135. A M Marugin, M A Arkhipova, O V Frank-Kamenetskaya, D Yu Vlasov, V Yu Dolmatov, O A Shilova, V P Chelibanov, T Fujimura *Proceedings of International Conference SREN 2005, Florence, Italy, 2005* p. 130

[a] — *Comb. Explos. Shock Waves (Engl. Transl.)*
[b] — *Dokl. Phys. (Engl. Transl.)*
[c] — *Chem. Phys. Rep. (Engl. Transl.)*
[d] — *J. Superhard Mater. (Engl. Transl.)*
[e] — *Phys. Solid State (Engl. Transl.)*
[f] — *Russ. J. Appl. Chem. (Engl. Transl.)*
[g] — *Power Metall. Met. Ceram. (Engl. Transl.)*