Russian Chemical Reviews **70** (7) 607 – 626 (2001) © 2001 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2001v070n07ABEH000665

Detonation synthesis ultradispersed diamonds: properties and applications

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Abstract. Published data on the properties of a novel nanomaterial *viz*., detonation synthesis ultradispersed diamonds (UDD), are summarised and systematised for the first time. Certain properties of UDD synthesised under different conditions are compared. Particular attention is drawn to substantiation of the cluster model of UDD and the fractal nature of their aggregates. The potential application fields of UDD are considered. Operating parameters of new materials are presented. The bibliography includes 110 references.

I. Introduction

Detonation synthesis ultradispersed diamonds (UDD or nanodiamonds) pertain a class of nanomaterials the fabrication, modification, and application of which attract the attention of scientists and engineers from different countries. This area of science and technology is at the boundary of solid-state physics and chemistry and thus becomes the world's most rapidly growing field as regards fundings provided for its development.

At present, a wide spectrum of nanoparticles is studied which differ in both their nature (metals, non-metals, chemical compounds) and the technologies for their production (gas-phase and plasmochemical syntheses, precipitation from colloidal solutions, thermal decomposition and reduction, mechanical synthesis, electrical-detonation and detonation syntheses) and the unique properties of particles and materials and articles manufactured on their basis. The latter aspect is of prime importance in view of the development of novel industrial technologies which include miniaturisation of facilities.

We believe that, among all types of nanomaterials, UDD represent the most interesting subject. Indeed, first of all, even a bulk diamond (*e.g.*, natural diamond) exhibits a unique combination of chemical, physicochemical (particularly, thermophysical) and mechanical properties. Second, diamonds resulting from miniaturisation or, more precisely, prepared in a form of nanoparticles (mean size 4 – 6 nm) from a plasma upon detonation of powerful explosive mixtures (EM), acquire more pronounced anomalous properties.

Whereas ordinary (natural) diamonds are applied in practice, as a rule, as abrasives and cutting tools and substrates for microelectronics, the application sphere of UDD is much wider. By chemical, barochemical and thermal treatment of UDD one can impart to them different surface properties. In this connection, the attention of scientists is focused on detailed studies of characteristics and properties of diamonds and a search for new application fields.

In Russia, UDD are used as a composite material in electrochemical and chemical metal – diamond coatings, polymeric films and membranes; in different kinds of rubbers; as anti-friction and anti-wear additives to lubricants of different purposes; in finishing and super-finishing polishing compositions; in abrasives. Nanodiamonds serve in fabrication of magnetically soft and hard input media, anti-friction tribotechnological diamond-containing compositions based on thermoplastic materials (used in friction joints), abrasion-resistant structure materials based on ethylene thermoplastic co-polymers and in manufacture of radiation- and ozone-resistant rubbers. Moreover, they are most important components in the reprocessing of worn tire rubber. Studies are launched on sintering of UDD under high dynamic and static pressures (for manufacture of cutting tools, abrasives, substrates for microelectronics), on using them in medicine (as anti-cancer drugs and a component of such drugs, an effective gastroenteritis

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Received 28 February 2001
Uspekhi Khimii **70** (7) 687 – 708 (2001); translated by T Ya Safonova

remedy, an immobiliser of biologically active substances, a super-effective sorbent for purification of blood and lymph, *etc*.).

In Russia, particularly, at SDB 'Tekhnolog' industrial technologies are developed for the detonation synthesis of UDD, which allow production of diamonds (as powders and suspensions) in amounts that run into tons.

In this review, for the first time, an attempt is undertaken to describe the properties of detonation synthesis diamonds in sufficient detail. All the available literature on UDD is analysed for the last 15 years including publications by the author.

Inasmuch as UDD are extremely complex materials and their characteristics are largely determined by the methods of preparation, chemical purification and surface modification, the properties of nanodiamonds reported in different studies can differ. The literature data reviewed do not exhaust the subject, because the approaches of different authors were different, the UDD samples used differed from one another and the studies were carried out under different conditions and often were sporadic.

II. Synthesis and morphology

Detonation-induced transformations of powerful explosives and their mixtures with the composition $C_aH_bN_cO_d$ with a negative oxygen balance (*i.e*., with the oxygen content lower than the stoichiometric value) in a non-oxidising medium yields a condensed carbon phase which involves ultradispersed diamonds.[1,2] The pressure and temperature in the detonation wave ($P-T$ parameters) correspond to the region of thermodynamic stability of diamonds ($P \geqslant 10$ GPa, $T \geqslant 3000$ K).[3,4] Such condensed carbon, which is commonly named a diamond blend (DB), can contain up to 75% UDD. Calculation and experimental methods have shown[5,6] that the primary UDD particles with diameter of $\sim$4 nm form fractal cluster structures (of 30–40-nm size) from which larger aggregates (of an order of magnitude of hundreds of nanometers) are formed. The clusters are built of a limited number of atoms (from several tens to several thousands) and, with regard to their properties, occupy an intermediate position between individual atoms and bulk solids.[7,8]

In the liquid-phase oxidation of condensed carbon, non-diamond structures gradually decompose, the most sophisticated method of chemical purification of DB being their treatment by dilute nitric acid at elevated temperature and pressure.[9,10]

According to the literature data,[11] purified UDD contain no intermediate amorphous phase. This is indicated by the shape of the (111) band in X-ray diffraction spectra and the results of electron microscopy. Depending on the conditions of the detonation synthesis, the mean size of UDD grains varies from 2 to 20 nm.

Diamond grains with sizes up to 100 nm are shown to exhibit highly defective block structures (1–3-nm blocks were observed in dark-field images).[12] With an increase in the grain size, the crystalline structure becomes more perfect. These results are confirmed in studies by high-resolution electron microscopy.[13]

It was found[14] that UDD are single-phase materials and contain no Lonsdalite, graphite and other admixtures. The size of subgrains (mosaic blocks) was found to be 4 nm by the method of diffractometry of co-ordination spheres,[15] no lattice microdistortions were revealed and the dislocation density determined from the value of subgrain size by the Williamson–Smallman relationship $N = 3/z^2$ was found to be equal to 1.8×10^{17} m^{-2}.

An X-ray diffraction pattern for UDD powders[16] also characterises UDD as a diamond phase containing no admixtures of Lonsdalite and graphite.

The coherent-scattering regions (CSR) were found to be of a mean size of 4.2 ± 0.2 nm and represent the proper UDD grains of diamond-lattice structure and an insignificant amount of aggregates of carbon atoms dispersed throughout the bulk which form no lattice and are mainly spaced at $\sim$0.15 nm from one another.[16] Along intergrain boundaries, carbon-atom aggregates are located for which the distribution in interatomic distances is close to Gaussian. The latter fact indicates that the structure of intergrain boundaries is amorphous.

Sizes of UDD crystals were estimated based on the so-called phonon confinement model.[17–19] It was shown that the nanocrystal size is 4.3 nm, which coincides with the results X-ray diffraction analysis of the same samples.[20]

In their usual state, UDD represent a powder of a specific surface area of 250–350 m^2 g^{-1} and a pore volume of 0.3–1.0 cm^3 g^{-1} (see Ref. 21). Heating of samples to 1273 K does not result in any decrease in the specific surface area. In a suspension, the size of UDD particles reaches 0.05×10^{-6} m; in a dried form, nanodiamonds represent a polydispersed powder. On heating above 873 K in an inert atmosphere, UDD particles begin to grow and acquire spherulitic shapes which measure up to $(150-200) \times 10^{-6}$ m and disintegrate at a load of 10–15 kg mm^{-2}. No polycrystals are formed in this case.

Due to the non-equilibrium conditions of their synthesis, UDD particles display a high density of defects, an active and well-developed surface (reaching 450 m^2 g^{-1}) and an excess enthalpy of formation.

III. Elemental composition and admixtures

Ultradispersed diamonds are characterised by the presence of a substantial amount of difficultly removable volatile and solid admixtures. The former include adsorbed gases (CO, CO_2, N_2), water and acids remaining after chemical purification (HNO_3, H_2SO_4). The latter group of admixtures involves non-diamond carbon, insoluble metal compounds (oxides, carbides) and salt admixtures. Powders of UDD can be considered as a certain diamond-containing composite material that consists of different carbon forms (80%–89%), nitrogen (2%–3%), hydrogen (0.5%–1.5%), oxygen (up to 10%), and an incombustible residue (0.5%–8.0%). Carbon represents a mixture of proper ultradispersed diamond (90%–97%) and non-diamond carbon (3%–10%). In detonation synthesis nanodiamonds, the impurity percentage is higher compared with other artificial diamonds (diamonds prepared by steady-state synthesis contain no less than 96% carbon); and, therefore, the effect of impurities on physical and chemical properties should be more pronounced for UDD compared with other diamonds.

Impurities present in UDD can be arbitrarily divided into the following groups:

(1) water-soluble ionised (free electrolytes);

(2) chemically bonded to the diamond surface and prone to hydrolysis and ionisation (salt forms of functional surface groups);

(3) water insoluble (mechanical impurities, non-dissociating salt and oxide forms of surface impurities);

(4) incorporated into the diamond lattice and encapsulated.

The impurities of the first and second groups are formed in the stage of chemical purification of UDD by acids.[9] Major water-soluble admixtures (first group) are removed by washing UDD with water. To make the removal more efficient, the suspensions are additionally treated by ion-exchange resins.

Surface functional groups (the second group of impurities) of the COOH, OH, SO_3H, NO_3 and NO_2 types can be considered as ionogenic with the diamond itself as the ion-exchange material.[22] In this case, treatment of UDD aqueous suspensions by ion-exchange resins, which involves demineralisation of surface groups, is also the most efficient.

Water-insoluble impurities (the third group) represent both individual microparticles of metals, oxides, carbides, salts (sulfates, silicates, carbonates) and surface compounds of salts and metal oxides incapable of dissociation. For their removal, *i.e*., transformation into soluble forms, UDD are treated by acids.

By using different methods of UDD purification, one can remove 40%–95% of the impurities of these three groups. All attempts to obtain individual UDD have failed. This is explained by the fact that the impurities of the fourth group are virtually

impossible to remove by chemical methods; moreover, the transition of third-group impurities into a soluble state is incomplete.

The main admixed elements are silicon, calcium, iron and sulfur; titanium, copper, chromium, and potassium are present virtually always in small amounts. Having an active and well-developed surface, nanodiamonds can sorb solution impurities. Hence, the presence of certain impurities, namely, silicon, potassium and, partially, iron can be attributed to the hardness of water employed in UDD purification.

Being among the major technological impurities in UDD, iron in concentrations of no less than 0.1 mass% – 0.5 mass% (which corresponds to the presence of insoluble iron compounds, preferentially on the surface) is difficult to remove.

Powders of UDD also contain substantial amounts of volatile admixtures ($\sim$10 mass%);[23] thermal treatment of UDD in vacuum (0.01 Pa) allows one to either remove the volatile impurities or substantially decrease their content. The optimum temperature of annealing is 673 K.

Ultradispersed diamonds studied in Ref. 21 were of the following composition: carbon, up to 88%; hydrogen, up to 1%; nitrogen, up to 2.5%, oxygen, up to 10%. The same ratio of elements remains after a thermal treatment up to 1273 K in either reductive (hydrogen) or neutral (argon) atmosphere. The carbon content in UDD samples passes through a maximum in a range of 973 – 1073 K, whereas hydrogen and nitrogen contents remain virtually unchanged. The maximum density of UDD was reached after heating in an argon atmosphere at 1073 K and amounted to 3.21×10^3 kg m^{-3}.

Scientists from the Russian Federation Nuclear Centre — All-Russian Research Institute of Technical Physics (RFNC-ARITP, Snezhinsk) have determined the contents of admixed elements in UDD samples manufactured at SDB 'Tekhnolog' and RFNC-ARITP (Table 1).

Table 1. Content (mass %) of admixed elements in UDD samples (AES data).

Admixture	UDD powder of UDD-STP brand [a]	Aqueous UDD suspension of UDD-TAH brand [a]	Typical UDD [b]
Fe	0.150	0.100	0.100
Cr	0.070	0.050	0.500
Si	0.300	0.100	0.150
Al	0.005	0.001	0.010
Na	0.030	0.003	0.050
K	0.002	0.002	0.002
Cu	0.005	0.002	0.003
Ca	0.002	0.002	0.010
Mg	0.005	0.003	0.005
Mn	0.001	see [c]	0.001
Ti	0.010	0.005	0.002
Pb	0.001	0.001	0.001
Total	0.580	0.270	0.840
Incombustible residue	0.950	0.400	1.400

[a] Produced at SDB 'Technolog' in accordance to specification TU 05121441-275-95. [b] Produced at RFNC-ARRITP. [c] Undetected at a sensitivity of 5×10^{-4} mass %.

Due to the fact that the time of synthesis of UDD is very short, surface carbon atoms have no time to stabilise by closure of all the bonds in the newly formed diamond lattice. They form a bond or two bonds with other elements of explosive materials, *viz*., hydrogen, nitrogen and oxygen. Hence, it is of great importance to assess the changes in the relative contents of heteroatoms that stabilise surface carbon atoms on the interface as a function of chemical treatment conditions and the degree of oxidative decomposition of DB.[24] For this purpose, an original diamond blend is treated by oxidising systems based on nitric acid and also by organic solvents, hydrocarbons and alcohols in the temperature interval of 358 – 578 K. Table 2 shows the results of the analysis as arbitrary molecular formulas calculated per 100 carbon atoms. Generally, the relative content of heteroatoms varies in a wide interval: from 5 to 35 hydrogen atoms and from 4 to 32 oxygen atoms per 100 carbon atoms. The nitrogen content varies from 2 to 4 atoms per 100 carbon atoms and is independent of the treatment conditions.

Table 2. Elemental composition of DB.[24]

Treatment conditions	Arbitrary molecular formula	Number of heteroatoms per 100 carbon atoms
DB sample		
Original, $\alpha = 0$	$C_{100}H_{5.3}N_{2.84.1}$	12.2
Treated by hydrocarbons C_nH_{2n+2}	$C_{100}H_{13.8}N_{2.94.6}$	21.3
Treated by alcohols $C_nH_{2n+1}OH$	$C_{100}H_{15.5}N_{2.68.0}$	26.1
Oxidative decomposition, $\alpha = 26.3\%$	$C_{100}H_{25.4}N_{2.922.5}$	50.8
Oxidative decomposition, $\alpha = 31.8\%$	$C_{100}H_{34.9}N_{2.923.1}$	60.9
UDD sample		
Original, $\alpha = 55.0\%$	$C_{100}H_{11.2}N_{2.29.1}$	22.5
Oxidative decomposition, $\alpha = 64.9\%$	$C_{100}H_{19.3}N_{2.123.5}$	44.9
Oxidative decomposition, $\alpha = 74.4\%$	$C_{100}H_{18.7}N_{2.022.8}$	43.5
Oxidative decomposition, $\alpha = 75.6\%$	$C_{100}H_{23.7}N_{2.422.9}$	48.8

Note: α is the degree of oxidative decomposition determined from the expression

$$\alpha = \frac{[C_{ox}] - [C_{ox}]'}{[C_{ox}]},$$

where $[C_{ox}]$ and $[C_{ox}]'$ are the mass fractions of the oxidisable carbon in original DB and UDD and in treated (oxidised) samples, respectively.

Non-oxidative treatment of DB by organic solvents (hydrocarbons C_nH_{2n+2} and alcohols $C_nH_{2n+1}OH$) does not affect the carbon skeleton of particles, but causes changes in the composition of surface functional groups. In this process, the elemental composition of DB changes regularly: relative concentrations of hydrogen and oxygen increase owing to the addition of hydrocarbon- and hydroxyl-containing fragments. The total number of heteroatoms is doubled.

In the oxidative decomposition of DB, the spectrum of carbon-to-heteroatom ratio in the products may be wider. As the action of oxidants on DB is stronger (increase in temperature, acid concentration, *etc*.), carbon gradually transforms into carbon dioxide.

First of all, the most disordered amorphous part of carbon is oxidised, next comes the turn of micrographite structures. After practically complete removal of non-diamond carbon forms from DB, the resulting UDD represent a chemically inactive material difficultly susceptible to further oxidation. Nonetheless, the author has succeeded in decomposing partially the diamond substance by long-term etching. The etching degree was 45% of UDD mass or 75.6% of the mass of original DB. The dependence of DB composition on the degree of oxidative decomposition (Fig. 1) has a complicated shape.

The minimum contents of heteroatoms correspond to both the original DB and purified UDD, the maximum values (53.5 and 44.9 heteroatoms per 100 carbon atoms) are typical of partially oxidised DB ($\alpha = 26\% - 31\%$) and etched UDD

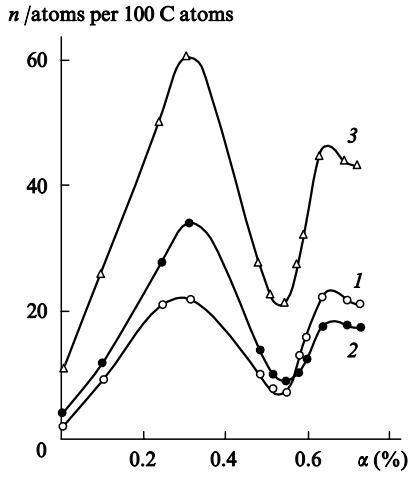


Figure 1. Elemental composition of DB as a function of the degree of oxidative decomposition (α).[24]
Relative content (n) of (*1*) oxygen, (*2*) hydrogen, (*3*) all heteroatoms.

($\alpha = 65\% - 75\%$), respectively. The concentrations of hydrogen and oxygen bonded to the surface vary in parallel. This makes it possible to assume that the chemical composition of surface functional groups is constantly reproduced.

For metastable structures, like partially oxidised DB and products of UDD etching, the recovery of surface-group composition results from active interactions with the reaction medium and the formation of a maximum number of heterobonds. The more stable forms, *viz*., the original DB and UDD, contain the smallest numbers of heteroatoms, which however is higher compared with that in the well-known diamond micropowders of steady-state synthesis ($C_{100}H_{1.1}O_{2.2}$) and soot ($C_{100}H_{5.1}O_{4.1}$).

From the chemical standpoint, the curves obtained allow the process of oxidative decomposition to be interpreted as two consecutive stages: (1) preferential etching of the carbon matrix at structural defects and along links between species, in the course of which the reaction surface increases and is enriched with oxidation intermediates; (2) etching of the loosened surface, gas formation and removal of surface oxidation products. A cyclic nature of these stages suggests that decomposition affects only structurally heterogeneous materials, whereas the oxidation selectively involves different structural forms.

Inasmuch as the concentrations of heteroatoms in DB and UDD are very high, a question arises of a possible location of these heteroatoms and the nature of their bonds with carbon. Calculations show that a 4-nm diamond particle consists of $\sim 12 \times 10^3$ carbon atoms, nearly 3×10^3 of which are located on the surface. For example, for UDD, we can write the following arbitrary molecular formulas: C_{75} for bulk and $C_{25}H_{11.2}N_{2.8}O_{9.1}$ for the surface atoms. Thus almost every carbon atom on the surface should be bonded to a heteroatom.

IV. Surface properties

The concentration of active hydrogen ($[H_a]$) on a UDD surface has been determined.[25] It is commonly agreed that a hydrogen atom bonded to an atom of any other element except carbon is active. For a carbon surface, the quantity $[H_a]$ may serve as a measure of its enrichment by functional groups (hydroxy, carboxy, amine, sulfonic, *etc*.).

In the studies on the reaction of methylmagnesium iodide in anisole with functional surface groups of DB and UDD, three stages can arbitrarily be distinguished, *viz*., (1) the reaction with molecular impurities and the external surface (with functional groups most easily accessible), (2) the reaction with the surfaces of open pores and (3) the reaction with the surface becoming free upon mechanical destruction of UDD aggregates.

Depending on treatment conditions of DB and UDD, the density of protogenic groups in them varies from 0.34 to 2.52 μg-equiv m^{-2}, and the concentration of active hydrogen varies from 0.49 to 7.52 μg-equiv m^{-2}. The proportion of the mobile hydrogen on DB and UDD surfaces amounts to 4% – 22% of the total hydrogen content in the powders.

Surface and electrophysical properties of nanodiamonds of two different specimens (UDD-1 and UDD-2) differing in the content of incombustible residue ([I.r.]) have been studied (Table 3).[26]

Table 3. Characteristics of the nanodiamond powders studied.[26]

Parameter	UDD-1	UDD-2
[I.r.] (%)	0.75	1.16
χ /m^3 kg^{-1}	$-0.35 \cdot 10^{-8}$	0
S_{sp} /m^2 g^{-1}	167	162
C_{BET}	303	814
A /J g^{-1}	400	550
A' /J m^{-2}	2.4	3.4

Note. The parameters are specified in the text.

The amounts of incombustible residues in powders and their specific magnetic susceptibilities (χ) were measured following the procedures developed at the Bakul' Institute of Superhard Materials (Kiev, Ukraine). Adsorption and structural characteristics, *viz.,* the C_{BET} constant, the adsorption potential (A), the specific adsorption potential of UDD (A') and the specific surface area (S_{sp}) were determined by the BET method from isotherms of nitrogen low-temperature adsorption measured on an 'Akusorb-2100' instrument. For UDD samples from both specimens studied, the isotherms of the second kind are typical.

As can be seen from Table 3 the UDD-1 and UDD-2 samples have equal specific surfaces but differ somewhat in the degree of purity and especially in the adsorption potential (for UDD-2 this is 37% larger). According to the values of the C_{BET} constant found, the UDD-2 powder exhibits higher adsorption activity, which suggests that the use of the degree of purity for characterising UDD is ambiguous.

It is found[26] that the absorption band in the IR spectrum of UDD at 1640 cm^{-1} is associated with the deformation vibrations of water, both bound and free. A band at 1750 cm^{-1} corresponds to vibrations of the OH groups.

Drying of UDD powders at 393 K did not result in any noticeable qualitative changes in the spectra. This suggests that the UDD surface bears active functional groups which favour adsorption of water.

On the basis of absorption spectra of UDD powders, it was concluded that the amount of moisture in the form of bound water molecules on the surfaces of nanodiamonds is higher compared with common diamond micropowders obtained in steady-state synthesis. Carboxy and carbonyl groups were also identified. The contents of methyl and methylene groups in UDD powders were insignificant.[26]

An analysis of IR spectra revealed the presence of potassium and aluminium sulfates, chromates and their complex compounds involving silicon in incombustible residues of UDD. Most probably, all these compounds have appeared as a result of a contamination during chemical purification of UDD by chromic anhydride in sulfuric acid.[26]

The changes in the nature of a 'coat' of functional groups on the surface of nanodiamonds upon their treatment in different media, affects the susceptibility of UDD to cold pressing.[27] Table 4 shows the values of limiting pressures during the compaction and the densities of compacted UDD both non-modified and

Table 4. The effect of UDD pretreatment on the limiting compacting pressure (P_{lim}) and the density (ρ) of compacts.[27]

Parameter	Initial UDD	UDD modified by treatment with		
		H_2	CO_2	concentrated HNO_3
P_{lim} /kg cm^{-2}	800–900	300–400	1200	1200
ρ /g cm^{-3}	1.2	1.00–1.15	1.23–1.30	1.3–1.4

modified by treatment with concentrated nitric acid, hydrogen and carbon dioxide.

V. Phase composition, microstructure and surface texture

Depending on the synthesis conditions, the explosion condensed products contain either only a cubic phase of diamond or also Lonsdalite as an admixture (up to 30%).[21] The X-ray diffraction pattern of a UDD sample contains five reflections characterised by the following intensity distribution:

Reflection	(111)	(220)	(113)	(400)	(331)
Fraction (%):					
UDD sample	85.0	14.0	0.5	0.3	0.2
reference sample	44	22	18	4	12

It may be assumed that the predominance of the reflection from the (111) plane in the spectrum is associated with the spherical shapes of UDD particles.

Table 5 shows microstructure parameters of UDD specimens. Nanodiamonds formed during detonation of a trotyl–hexogen melt (60 : 40) [21] exhibit the highest microstresses of the second kind and, as a consequence, have most deformed lattices. It was found that the microstresses of UDD lattice do not change until the onset of graphitisation at 1473 K. Thus, a highly strained structure of UDD is thermally stable. Nonetheless, UDD synthesised by the aforementioned method should be expected to possess an enhanced reactivity.

Table 5. Microstructure of detonation synthesis nanodiamonds.

Coherent scattering region /nm	a/a_0 (%) [a]	Microstresses /GPa	a /nm	Ref.
4–6	1.0	10	0.3562 ± 0.0003	21
5–10	0.42–0.47	4.2–4.7	–	28
5–15	0.1	1.0	0.3572 ± 0.0004	29

Note. [a] Relative lattice distortion (a is the parameter of a real lattice, a_0 is the parameter of the diamond cubic lattice).

Peculiarities of the surface structure were studied for DB, partially oxidised DB and UDD,[30, 31] and the degree of oxidative decomposition was estimated (see footnote to Table 2).

The BET method was used for the determination of the specific surface area (S_{BET}) and the size distribution of pores from the adsorption isotherms of nitrogen. By gradually increasing the degree of oxidative decomposition (α) of DB by acids it was possible to obtain a series of specimens of partially oxidised DB containing different amounts of oxidised carbon, *viz*., from the initial DB (sample *1*) to UDD (sample *12*). Table 6 shows the texture parameters of the specimens.

The dependences of the specific surface area, the volume, and geometrical parameters of pores on the quantity α reach an extremum at $\alpha = 0.63$; at this point, S_{BET} and the volume of pores are a minimum, and C_{BET} is a maximum. At this stage of

Table 6. Parameters of DB and UDD textures.[30]

Sample	$[C_{ox}]$ (%)	α	S_{BET} /m^2 g^{-1}	V_p /cm^3 g^{-1}	C_{BET}	d_a /nm	d_d /nm
1	53.4	0	404	1.2451	108	9.1	8.8
2	44.4	0.17	409	1.0746	112	8.1	8.0
3	38.4	0.28	399	0.9931	107	7.7	7.9
4	36.3	0.32	314	0.7488	109	7.5	7.6
5	27.8	0.48	244	0.6621	133	8.6	6.8
6	27.6	0.49	209	0.5406	136	8.7	8.8
7	23.7	0.56	198	0.5236	155	9.1	9.1
8	19.5	0.63	195	0.5089	182	9.5	9.3
9	9.9	0.81	240	–	–	–	–
10	7.9	0.85	252	–	–	–	–
11	3.4	0.94	276	0.8241	135	9.8	9.6
12	1.2	0.98	290	0.8396	121	9.2	9.2

Note. Here, $[C_{ox}]$ denotes the mass fraction of oxidised carbon; V_p is the limiting volume of the sorption space at $P/P_s = 0.995$ (P is the partial pressure of nitrogen, P_s is the pressure at which the whole internal surface of pores is covered by a nitrogen monolayer); d_a is the size of an open pore; d_d is the critical neck size, *i.e*., the maximum pore size at which the atoms of an adsorbed gas can enter the adsorbent.

decomposition, a partially oxidised DB retains ~20% of non-diamond carbon. In the range of $\alpha = 0.63–0.98$, carbon particles are etched at the stressed and defective areas. Here, a new kind of surface with predominant relaxed diamond-type structures is formed. Thus, when passing from the original DB to UDD, the texture characteristics of the substances change non-monotonically. This distinguishes DB from other carbon phases (technological carbon, coals, carbon fibres) being associated, first of all, with the presence of two carbon phases, *viz*., diamond-type and non-diamond in DB, which differ in their chemical activities and oxidation mechanisms. Comparing the values of S_{BET}, C_{BET} and the volume of pores found for DB and UDD, on the one hand, and those obtained for intermediate oxidation products, on the other hand, we can conclude that the powders of detonation carbon represent organised space structures formed during multistep aggregation of original particles rather than a mechanical mixture of UDD and non-diamond carbon.

In the liquid-phase oxidation, chemical decomposition (etching) of secondary aggregates occurs, which entails regular changes in the surface area and in texture characteristics of the powders. Primary aggregates remain practically unchanged. These data taken altogether point to a structural self-organisation of detonation synthesis ultradispersed carbon.

As was discussed above, the properties of UDD surface strongly depend on the conditions of their chemical pretreatment, which in a number of cases plays a key role in the production of new composite diamond-containing materials with the required characteristics.

VI. Sorption properties and exchange capacity

The sorption properties of DB and UDD, which are extremely important characteristics for different application fields of UDD have been studied.[32]

Oxygen-containing groups present on nanodiamond surfaces [33] impart a charge to UDD aggregates in aqueous solutions; the value and sign of this charge depend on the concentration and the dissociation constant of these groups, the solution pH and the background-electrolyte concentration. Ions H^+ and OH^- are potential-determining. The dependence of the specific adsorption on the solution pH, which is observed for all powders under study, can be attributed to an increase in the degree of dissociation of surface groups with acidic properties.

In the gradual oxidation of the detonation-derived carbon, the specific adsorption changes non-monotonically and passes

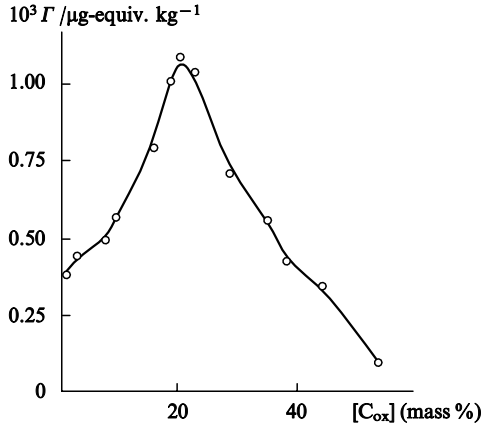


Figure 2. Specific adsorption (Γ) as a function of oxidisable carbon content in DB (pH 11).[32]

through a pronounced extremum (Fig. 2). A low specific adsorption value for the original DB is explained by the fact that this DB has been synthesised in a non-oxidative medium and thus involves a small amount of surface oxygen-containing groups.

When a DB is exposed to oxidants, two processes proceed simultaneously, *viz*., surface enrichement with oxygen-containing groups and etching of carbon. With an increase in the degree of oxidative decomposition, the surface is enriched with oxygen-containing groups, the specific adsorption would have been expected to reach a maximum and then remain constant. However, starting from 18% – 20% of residual oxidisable carbon, the specific adsorption decreases.

The presence of an extremum in the curve (see Fig. 2) reflects qualitative changes in the surface structure of DB upon treatment, namely, a transition from a graphite-like form to a diamond-like form.[31] In this transitional state, the material exhibits the best adsorption properties. The DB subjected to drastic oxidation retains only a stable diamond form. Under the conditions of mild oxidative etching, the boundary between diamond-like and non-diamond carbon shifts. The residual oxidisable carbon (the remaining 18% – 20%) actually represents a diamond-like phase, *i.e*., corresponds to the periphery of a diamond cluster.

For UDD samples listed in Table 1, the sorption capacity with respect to benzene and chloroform vapours was estimated at 292 – 294 K by a weighing method under steady-state conditions close to the isothermal ones. The results obtained are as follows.

1. The sorption capacity of a dry powder of UDD-STP (produced at SDB 'Tekhnolog') amounts to 9 mol kg^{-1} with respect to benzene vapour and 10.5 mol kg^{-1} with respect to chloroform vapour. The observation time was 15 days; 90% – 95% of adsorbate was absorbed in 2 days.

2. The sorption capacities of four fractions isolated from the suspension of UDD-TAH decrease monotonically from 8 mol kg^{-1} for the first fraction to 7 mol kg^{-1} for the fourth fraction with respect to benzene vapour and, correspondingly, from 8.5 to 7.5 mol kg^{-1} with respect to chloroform vapour. The observation time was 13.3 days; 95% – 100% of the adsorbate was adsorbed in 2 days (more quickly for chloroform).

3. For comparison, sorption capacities of certain UDD samples made at RFNC-ARITP were determined, which varied from 12 – 16 to 10 – 14 mol kg^{-1} for benzene vapour and from 14 – 19 to 12 – 17 mol kg^{-1} for chloroform vapour. A distinguishing feature of this type of UDD is that its sorption capacity gradually increases: 55% – 65% of adsorbate is adsorbed in 2 days. The adsorption capacities and rates virtually coincide for DB and diamonds isolated from it (*i.e*., the sorption capacity in fact is independent of the content of non-diamond carbon in the diamonds).

Inasmuch as the adsorption phenomenon forms the basis of many technological processes, the degrees of adsorption of heavy-metal ions on the UDD surface were estimated. For this purpose, an electrochemical technique of cathodic potentiodynamic pulses was applied.[34]

Table 7. Results on the adsorption activity studies of UDD-1 and UDD-2 powders with respect to heavy metal ions.[26]

M^{n+}	$[M^{n+}]$ in electrolyte /mol kg^{-1}	θ (%)	
		UDD-1	UDD-2
Fe^{2+}	0.1	18.0	26.5
Fe^{2+}	10	80.6	82.5
Ni^{2+}	0.1	16.0	33.0
Ni^{2+}	10	75.0	80.0
Cr^{6+}	0.1	12.0	40.0
Cr^{6+}	10	48.0	53.3

It was shown that the adsorption activities of UDD powders with respect to metal ions (iron, nickel, chromium) differ substantially (Table 7). In all experiments, the surface coverages (θ) of UDD-2 were higher. On the whole, the adsorption activity of nanodiamonds with respect to the ions under study decreases in the following order: $Fe^{2+} > Ni^{2+} > Cr^{6+}$ (Ref. 26). However, at low concentrations of metal ions (0.1 mol kg^{-1}), this sequence for UDD-2 is reversed: $Cr^{6+} > Ni^{2+} > Fe^{2+}$. With an increase in the ion concentrations from 0.1 to 10 mol kg^{-1}, the degree of surface coverage of diamond particles increases 3 – 4-fold and reaches 70% – 80%.

It was thus confirmed [26] that the adsorption activity of UDD surface depends substantially on the method of chemical purification of nanodiamonds of detonation synthesis.

Studies of surface properties of UDD isolated from DB under the action of nitric acid and atmospheric oxygen [35] and modified by different reagents [36, 37] showed UDD to possess pronounced cation-exchange properties, which manifest themselves in the exposure of nanodiamonds to aqueous solutions. It was also found that UDD represent sorbents of high activity with respect to gases.[23]

As was mentioned above, chemical purification of UDD enriches the diamond surface with oxygen-containing groups that determine its cation-exchange properties as a sorbent. The surface of UDD oxidised by atmospheric oxygen bears a greater amount of oxygen-containing groups of the acid type (*i.e*., protogenic) compared with the diamonds of liquid-phase oxidation. As a result, the former nanodiamonds possess better ion-exchange properties. Hence, UDD can serve as promising sorbents for ions of a basic nature.

On the other hand, the method for cooling of the products of detonation synthesis plays a significant role in the formation of the nanodiamond surface. Comparison [38] of nanodiamonds obtained from the same explosive compositions and with charges of the same geometry (*i.e*., fused and pressed in the same moulds) but with different cooling procedures and isolated from the synthesis products by the same methods has shown that their surfaces differ in the composition and the number of admixed functional groups including those groups that affect the ion-exchange properties. Particularly, the use of ice as a cooling agent (*i.e*., as an armour for the charge) is beneficial for the maximum protection of UDD from the subsequent graphitisation. This refers primarily to its finest crystals, which have the highest specific surface area and, hence, high sorption activity.

The sorption capacity of UDD obtained in different conditions or purified by different methods was studied with respect to cesium ions.[38] It was found that the sorption capacity of nanodiamonds synthesised under identical conditions but purified using different oxidants and different treatment conditions varied from 0.01 to 0.50 mol kg^{-1}. This suggests that this depends on the nature of the oxidant and the conditions (duration, temperature) of UDD isolation from synthesis products. Samples obtained from DB by ozone purification exhibited the highest sorption

abilities (0.4–0.5 mol kg^{-1}). The value found exceeds substantially those of known natural sorbents[39] (0.01–0.15 mol kg^{-1} with respect to cesium) and is commensurable with the sorption capacity of KU-8-2 resin (0.8 mol kg^{-1}), which is a widely used ion-exchange resin.

An analysis of IR spectra showed that the UDD samples contain different polar functional groups: OH, NH, C–O, C=O, C–H, C–N, C=N, C–O–O in different concentrations. Nanodiamonds of higher sorption capacities are characterised by higher intensities of absorption bands of oxygen-containing (C=O, in the region of 1700 cm^{-1}) and peroxide (C–O–O, 1800–1900 cm^{-1}) groups compared with other samples. Apparently, it is the presence of these groups that is responsible for the enhanced cation-exchange ability of the samples under discussion.

An IR spectrum of UDD synthesised in a gaseous cooling medium shows a wide absorption band in the region of 1600–1900 cm^{-1}, which points to a higher concentration of oxygen-containing groups which determine the cation exchange.

It was proposed to use UDD as a potential sorbent for cesium radionuclides.[38] Compared with conventional ion-exchange resins, ion-exchange materials based on nanodiamonds possess basically better new characteristics: substantially higher thermal stability (400 °C in air compared with 120–150 °C for KU-8-2 resin), resistance against aggressive media, mechanical strength, the absence of swelling and high sorbent density (3.1–3.3 g cm^{-3} against 0.7–0.8 g cm^{-3} for KU-8-2).

In the context of the commercial application of UDD for deposition of composite electroplates, it is of interest to study the behaviour of UDD hydrosols in the presence of different ions under the action of an external electrical field and without it.

Electrochemical studies of an aqueous suspension of UDD were carried out in the pH range of 3–10, at an ionic strength varying from 10^{-4} to 10^{-1} in a temperature interval from 20 to 70 °C.[40] A combination of macroelectrophoresis and potentiometric and conductometric titrations were applied. The experimental data were analysed within the framework of a model that takes into account the complex nature of UDD aggregation with the formation of primary and secondary structures.[6,41]

The dependence of the exchange capacity (G) for UDD on the pH of KCl solutions with concentrations (c) of 0.1 and 0.01 mol $litre^{-1}$ was examined by potentiometric titration. The titration curves for UDD powders and sedimentation-unstable hydrosols virtually coincide, which points to the similarity of the structures (or specific surface areas) of coagulated precipitates and dried powders. A threshold of fast coagulation of the hydrosols and loss of sedimentation stability corresponds to pH 5.5 in KCl solution with $c = 0.01$ mol $litre^{-1}$. With an increase in pH, the exchange capacity of UDD increases from 0.05×10^3 μg-equiv. kg^{-1} (pH 3) to $(0.4–0.6) \times 10^3$ μg-equiv. kg^{-1} (pH 10). In the pH range of 9–10, the exchange capacity of the hydrosol substantially increases, in contrast to that of the UDD powder. This reflects different dispersion of nanodiamond particles.

On the basis of the specific surface value of 322 m^2 g^{-1} found by the BET method for powder particles,[40] the surface charge density was calculated, which made it possible to roughly assess the potential of the UDD surface for both powders and hydrosols. Figure 3 shows the dependences of the surface, diffusion and electrokinetic potentials on the solution pH.

The pH-dependences of the surface (curve *1*) and diffusion (curve *2*) potentials have similar shapes. The electrokinetic potential (curve *3*) was estimated from the results of macroelectrophoresis by using a formula valid for particles with unipolar conduction.[42]

From comparison of the potentials (see Fig. 3), it follows that a substantial volume ascribed to the immobile part of the electrical double layer can be attributed not only to the presence of water layers with different structures near the nanodiamond surface, but also to the immobilisation of the dispersion medium inside the UDD aggregates. Such a conclusion is confirmed by the different

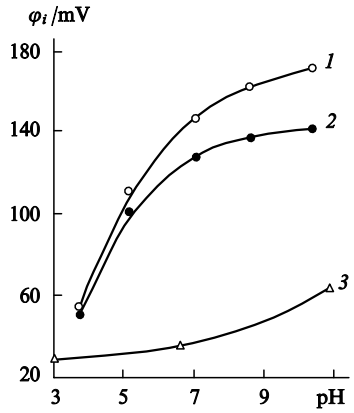


Figure 3. Dependences of (*1*) surface, (*2*) diffusion and (*3*) electrokinetic potentials (φ_i) on pH for UDD particles in a hydrosol in KCl solution ($c = 0.01$ mol $litre^{-1}$).[40]

shapes of the temperature dependences for electrokinetic and diffusion potentials.

At a low ionic strength (in a KCl solution with $c = 10^{-4}$ mol $litre^{-1}$), no apparent flocculation of primary aggregates occurs, and the destruction of the interfacial water layers, which proceeds at elevated temperatures, is accompanied by an increase in the electrophoretic mobility of UDD. In solutions of higher ionic strengths, the destruction of interfacial layers at elevated temperatures facilitates flocculation of primary aggregates. Water immobilised inside newly formed secondary aggregates does not necessarily take part in the motion; however, the exchanged ions retain their mobility. In this case, the electrophoretic mobility decreases and the diffusion potential remains unchanged. Indeed, the diffusion potential calculated for the isopolarisation mode from the data on the conductivity of UDD hydrosols, under an assumption of a constant size of hydrosol particles, does not decrease with an increase in the temperature (in contrast, a slight increase is observed).

Electrochemical studies of the surface allowed refinement of the structure of solid phase in UDD hysrosols. Using the values of the diffusion potentials found in potentiometric titration and the results of conductivity measurements at the isoconduction point (pH 6, KCl solution, $c = 0.01$ mol $litre^{-1}$), the sizes of non-conducting spherical UDD formations were determined and proved to coincide with the radii of primary aggregates (10–30 nm) estimated by electron microscopy.[6] This implies that primary aggregates are non-conducting, *i.e.*, have dense ion-impermeable structures.

Thus, UDD represent presumably a cation-exchange system with a variety of functional groups of different acidic strengths.[40] Hydrosols of UDD consist of dense primary aggregates which form ion-permeable secondary structures. Different shapes of the pH dependences for diffusion and electrokinetic potentials, as well as many other properties of UDD hydrosols as a function of pH, ionic strength and temperature are determined by the changes in their secondary structures.

VII. Chemical properties of ultradispersed diamonds

Studies of the chemical composition of DB and UDD were carried out by the methods of gas chromatography (CG), polarography, IR spectroscopy and X-ray photoelectron spectroscopy (XPS).[43] Table 8 shows the results of polarographic and GC studies of DB and UDD samples.

It follows from the data in Table 8 that the carbon of the UDD surface groups is oxidised to a higher degree and the hydrogen content is substantially lower compared with DB.

Table 8. Composition of desorbed gases and their activation energies.[43]

Sample	Composition of desorbed gases [a]		Activation energy of desorption [b] /kJ mol^{-1}
	gas	gas content /cm^3 g^{-1}	
DB [c]	CO_2	3.9	23.4
	N_2	0.7	22.5
	CH_4	4.03	47.6
	H_2	7.8	–
	CO	0.09	103.6
	NH_3	1.43	27.2
UDD [d]	CO_2	11.4	48.5
	N_2	0.83	23.0
	CH_4	1.7	28.4
	HCN	traces	–

Note. [a] Determination conditions: 673 K; desorption time, 2 h; pressure, 0.1 Pa. [b] At 573–773 K. [c] Elemental composition (%): C, 86.3; H, 0.4; N, 3.7; O, 9.6. [d] Elemental composition (%): C, 86.0; H, 0.1; N, 2.5; O, 11.4.

The IR spectroscopy data suggest the presence of the carbonyl, carboxy, hydroxy, methyl and nitrile groups on the surfaces of UDD and DB. Thermodesorpsion of large amounts of methane and hydrogen from a DB sample (Table 8) gives us grounds to assume that it has a different composition of surface groups. Apparently, this is associated with the following reactions involving carbon surface atoms with uncompensated bonds

$$\equiv R^1-Me + {}^{\bullet}CR^2R^3R^4 \longrightarrow R^1-CH_2-CR^2R^3R^4 + 0.5\,H_2\,, \quad (1)$$

$$\equiv R^1-Me + {}^{\bullet}CH_2R^2 \longrightarrow R^1=CHR^2 + CH_4\,. \quad (2)$$

If reactions (1) and (2) do occur, then the fraction of carbon atoms with uncompensated bonds (surface atoms) amounts to no less than 1.6 %. An estimation based on these data showed that the mean particle diameter is 45 nm (no more than 300 carbon atoms).

According to XPS results [21, 43], the C_{1s} band in the spectrum of DB represents a wide asymmetric peak (half-width, $\Delta E_{1/2}$ = 4.1 eV), which narrows after bombardment with argon ($\Delta E_{1/2}$ = 2.5 eV) and takes a shape typical of graphite and fine-grain coals. In this case, the surface charging is zero, which is typical of conducting substances. These results suggest that the bulk of the sample represents the graphite phase, whereas, in the surface layer (several tens of angstrom deep), the diamond carbon phase is located.

For UDD samples (see Table 8), a symmetrical C_{1s} peak ($\Delta E_{1/2}$ = 3.3 eV) is typical, and the surface charging is + 3.3 eV. After bombardment with argon, the shape of the carbon peak remains unchanged, and the surface charging reaches + 6.2 eV, $\Delta E_{1/2}$ = 2.9 eV. It was concluded that carbon in the surface layer (no less than 10-nm deep) of a sample is represented exclusively by the diamond phase.[43] The initial sample includes nitrogen and oxygen (O : C = 0.027, N : C = 0.020) as the admixtures. After bombardment with argon, the admixture content becomes lower than the threshold sensitivity of a spectrometer.

Thus, in DB particles the diamond-like carbon phase surrounds the graphite phase or, more precisely, a non-diamond carbon form. UDD particles consist entirely of a diamond-like carbon phase. Admixtures in the form of carbon compounds with oxygen and nitrogen are accumulated preferentially in the surface layer of a particle.

In accordance with a classification of functional derivatives of diamonds, UDD pertain to a group of 'colloidal diamonds' as regards the crystal sizes and the ratio of surface carbon atoms (C_s) to the total number of carbon atoms (C_{tot}) in a diamond crystal.[44]

For nanoparticles measuring 2–10 nm, the number of surface C atoms with respect to their total number in the core varies from 63% to 15%, *i.e.*, from 4 to 18 internal carbon layers are present. Hence, UDD properties should largely be determined by the chemical states of their surfaces, in contrast to coarse diamond crystals with $C_s/C_{tot} \to 0$. However, to date the chemical properties of UDD remain less understood as compared with diamonds of other types.

The functional 'coat' of UDD particles, the possibilities of their chemical modification in different gaseous media, and their behaviour at elevated temperatures have been studied.[27]

The UDD samples were produced at the Research Industrial Association (RIA) 'Altai' (Biisk) and purified by using oleum–nitric acid mixtures at 523 K. The isolated UDD were dark-grey powders with microcrystals of 3–8 nm, which, being placed in water, formed aggregates measuring up to 2×10^{-4} m. The elemental composition of these UDD (%) is given below.

C	H	O	N	Ash content
78.6–78.8	0.65–0.70	16.5–17.0	1.78–2.16	1.34–2.47

The high content of oxygen in UDD agrees with the C_s/C_{tot} ratio and the amount of possible functional oxygen-containing groups on the surfaces of diamond particles of such sizes.[44]

The first step of UDD modification included drying them in air and heating the fine fraction in a flow of nitrogen at 348 K in a flow-through system. In the second stage, UDD were heated at 673–973 K in a flow of a gas (N_2, CO_2, CH_4, H_2, air) passed at a rate of 5.6×10^{-7} m^3 s^{-1}.

The results obtained [27] allowed the authors to assess the effect of pretreatment of UDD on the temperature of oxidation initiation. After treatment with water oxidation starts at 673 K, whereas upon exposure to a $CH_4 + CO_2$ mixture, it begins at 773 K, *i.e.*, hydroxylated surfaces are oxidised more easily.

Studies on the behaviour of UDD in oxidising gas mixtures under isothermal heating showed that the oxidants may be arranged in the following series with respect to their activities: air $\gg CO_2 > H_2O$.

It was shown that all the temperature dependences of UDD oxidation rate clearly manifest two regions. In the low-temperature region (below 673 K), the change in the UDD mass depends little on the temperature, whereas in the high-temperature region oxidation sharply accelerates with an increase in temperature.

On the basis of the results obtained, the apparent activation energies of UDD oxidation were calculated (Table 9). This table also shows the temperatures of transition to high-temperature regions for different oxidation conditions.

As is seen from the data of Table 9, the activation energies in two regions differ by a factor of 3–6 for the same oxidant. Probably, this is associated with the fact that, in the low-temperature region, oxidation actively involves the 'coat' of functional groups present on the surface of UDD particles and their decom-

Table 9. Apparent activation energies (E_a) of UDD oxidation in low-temperature (I) and high-temperature (II) regions.

Oxidant	Temperature of I to II transition /K	E_a /kJ mol^{-1}	
		region I	region II
$O_2 + N_2$ (20% O_2)	673	24.7 ± 1.7	96.1 ± 4.2
$O_2 + N_2$ (10% O_2)	773	24.7 ± 1.7	96.1 ± 4.2
$O_2 + N_2$ (4% O_2)	773	25.5 ± 5.9	91.1 ± 13.0
CO_2	898	36.4 ± 7.1	120.4 ± 15.0
CO_2, K_2CO_3 (see [a])	838	18.8 ± 5.0	88.6 ± 5.0
H_2O	933	22.2 ± 13.4	152.2 ± 7.1
H_2O, K_2CO_3 (see [a])	703	20.5 ± 12.1	126.7 ± 10.0

Note. [a] Successive treatment.

position products, whereas in the high-temperature region only hydroxy groups take part in the reaction. In the presence of a catalyst (K_2CO_3), the activation energies of UDD oxidation are somewhat lower than that of the noncatalysed process. On the whole, the activation energies of UDD oxidation in the high temperature region are slightly lower compared with detonation diamonds synthesised from graphite and soot [45] and twice as low as those of kimberlite diamonds.[46]

The aforementioned results confirm the presence of a 'coat' of different functional groups on the surfaces of UDD particles and suggest that this 'coat' changes as a result of chemical modification and has a pronounced effect on physical and chemical properties of UDD, particularly, the resistance of the latter against oxidising gas mixtures, their compactibility (see Table 4), *etc*.

Furthermore, the results obtained allow us to conclude that UDD represent not simply diamond-like materials (*e.g*., see Ref. 4), but typical diamonds, the surface of which, as for the other diamond types, contains different functional groups that saturate free valences of carbon surface atoms. A unique specific feature of UDD is that, with respect to the C_s/C_{tot} ratio, they occupy an intermediate position in a series of functional derivatives of diamond cores, between low-molecular forms similar to adamantane functional derivatives and the polymeric forms representing diamond macro-crystals with specific functional 'coats'. It has been shown [44] that such a mesoregion corresponds to colloidal sizes of the particles. Therefore, bearing in mind that, due to the presence of a functional 'coat', an electrical double layer can surround UDD particles in solution, it is quite reasonable to call the latter particles colloidal diamonds.

VIII. Spectroscopy

Absorption spectra of UDD powders do not reveal any specific features in the optical range. A microscopic study have shown that UDD microparticles by themselves are colourless, so that the typical colour of the powder is, most probably, caused by diffuse scattering and reflection. The microparticles demonstrated no optical anisotropy.

The refractive index of UDD estimated by the immersion technique amounted to ~ 2.55 at the wavelength of 580 nm, which is substantially higher than that of natural diamonds and artificial diamonds of steady-state synthesis.

1. Infrared spectroscopy

The diamond lattice is known to possess over 50 defect centres active in the optical spectra. Most synthetic diamonds contain nitrogen as atomic dopant of substitution. With respect to shapes of the IR spectra, diamonds are divided into two types, *viz*., (I) with one-phonon absorption and (II) without absorption in the single-phonon spectrum range. The first group includes diamonds of the Ia type the one-phonon absorption of which is caused by three independent defective centres: A (1282, 1210, 1110, 480 cm^{-1}), B1 (1332, 1175, 1000, 775, 328 cm^{-1}) and B2 (1350–1380 cm^{-1}), and the diamonds of the Ib type the one-phonon absorption of which is caused by C centres. A well developed surface of UDD (up to 4.5×10^5 m^2 kg^{-1}) and high C_s/C_{tot} ratios that determine the high concentration of surface functional groups allow the method of IR spectroscopy to be used [27] with the aim of reliable identification of the nature of these functional groups.

For insufficiently purified UDD (produced by RIA 'Altai'), the spectra measured both before and after modification revealed absorption bands of carbonyl (1730–1790 cm^{-1}) and hydroxy groups (1640, 3400 cm^{-1}). A wide band with a maximum in the range of 1100–1140 cm^{-1} is probably related to the overall absorption of a number of admixed nitrogen centres of types A (two nitrogen atoms in neighbouring substitution cites), B1 (an accumulation of vacancies 'decorated' by nitrogen), B2 (laminar formations in the cube's plane) and C (isolated nitrogen atoms substituting carbon atoms in the lattice) and the vibrations of C–O–C fragments (NO_2 groups at primary and secondary carbon atoms, SO_2OH groups, OH groups in CO_2H and at ternary carbon atoms absorb in the same range, which complicates unambiguous interpretation).

Comparison of the spectra shows that the positions and intensities of the bands of the carbonyl-group absorption vary widely depending on the UDD modification conditions. Treatment in a nitrogen atmosphere at 937 K results in elimination of carbonyl and carboxy groups, which is indicated by reduced intensities of the corresponding bands. Independently of the modifying gas used, treatment at 673 K shifts the maximum at 1730 cm^{-1} to the region of 1780–1790 cm^{-1}, which indicates the formation of $-C(O)-O-C(O)-$ structures. Insignificant changes in the spectral patterns observed after treating UDD by different kinds of gases suggest that these gases affect insignificantly the composition of surface functional groups of these UDD samples under the conditions specified.

For UDD purified by the nitric-acid procedure (SDB 'Tekhnolog'), the IR spectrum slightly differs from previous spectra and contains characteristic bands at 3500 cm^{-1} (strong, wide), 1740 and 1640 cm^{-1} (both medium), 1260 and 1170 cm^{-1} (both strong and wide) and 610 cm^{-1} (wide, of medium intensity). These bands are well reproducible irrespective of the purification procedure used and, hence, can be assumed to be caused by UDD intrinsic absorption.

A band at 1260 cm^{-1} corresponds to one-phonon absorption of the diamond lattice. Presumably the width and intensity of this band are determined by distortion of the diamond lattice,[18] diamonds of the IIa type, which contain no admixtures, do not absorb in this region. The nature of the other bands in UDD IR spectrum is unclear. Evidently, they do not coincide with any known absorption centres in diamonds. It is possible that some of these bands are caused by adsorbed nitrogen and water.

Our results allowed also us to reveal additional bands dependent on the procedure used for the isolation of UDD. For instance, the spectrum of UDD treated by nitric acid shows bands at 2940, 1390, 1505, 650 cm^{-1}, which were absent in the spectrum of UDD treated by sulfuric acid (produced at RIA 'Altai'); in turn, the latter spectrum contained bands at 2800, 2205 and 670 cm^{-1}. Apparently, the latter bands are caused by the presence on UDD surfaces of conglomerates of functional groups either chemically bound or adsorbed in the course of treatment.

In contrast, due to a substantial amount of background impurities, IR spectra of non-purified DB appear to have a substantially uniform shape with prominent regions of enhanced absorption at 3300 and 1170 cm^{-1}. The presence and width of the latter correlate with the concentration of the diamond component in DB. The spectrum of diamond-free DB reveals none of these peculiarities. It cannot be ruled out that processing of a sufficient body of experimental data will allow development of a quantitative method for the estimation of the diamond concentration in DB.

On the whole, IR spectra of UDD and DB are a good source of information on their structures.

2. NMR and ESR spectra

^{13}C NMR spectra [21] of nanodiamonds involve four signals. A signal with δ 34.5 corresponds to the diamond carbon atoms; a broad signal in the region of δ 30 is due to the fact that carbon atoms are not structurally equivalent, first of all, due to the presence of defects and the Lonsdalite phase. Weakly pronounced peaks with δ 68 and 53 can be attributed either to the effect of partially oxidised structures or the presence of nitrogen atoms in the sample.

In the ^1H NMR spectrum,[21] three overlapping peaks were observed. A signal with δ 2.2 corresponds to the isolated C–OH groups, whereas a signal with δ 3.8 corresponds to bound C–OH groups. A signal with δ 6.7 most probably belongs to S–OH groups formed on the surface of a sample during its chemical

purification (in Ref. 21, oleum–nitric acid treatment of DB was applied).

In the ESR spectra, the UDD signal at 293 K is a singlet with a g-factor of 2.003 and a half-width $\Delta H_{1/2} = 6.3-8.3$ Œ.[21] The concentration of paramagnetic particles ranges from 2.7×10^{21} to 2.0×10^{22} kg^{-1}. The parameters of this signal are most close to the ESR signal of broken bonds on the diamond surface ($g = 2.0027$, $\Delta H_{1/2} = 5.5$ Œ).[47] A similar ESR spectrum was also observed for AV detonation diamonds.[48] It is of note that, despite a high concentration of nitrogen atoms in UDD ($\sim 1.6 \times 10^{24}$ kg^{-1}) no triplet signal associated with doped nitrogen atoms that substitute carbon in the diamond lattice was observed.

3. Raman spectra

Deconvoluted profiles reveal maxima at 1580 and 1620 cm^{-1}, which coincide well with the maxima of the density-of-states function of the sp^2-bound carbon atoms. This suggests that UDD involve an amorphous graphite phase.[20] A band with a maximum at 1530 cm^{-1} can be attributed to the sp^3-bound carbon atoms of that part of the structure which is susceptible to a severe distortion. Apparently, the appearance in the spectrum of a number of specific features of the phonon density of states for the sp^3-bound carbon atoms suggests that, in addition to an amorphous graphite phase, UDD involve an amorphous diamond carbon phase.

4. X-Ray diffraction spectra

X-Ray diffraction spectra [20] of UDD samples contain wide, symmetrical diffraction maxima at $2\theta = 43.9$, 75.3 and 91.5°, which can be adequately described by Lorentz profiles and correspond to the (111), (220) and (311) reflections of the diamond-like lattice with a parameter $a_0 = 0.3565 \pm 0.0005$ nm. The average size of UDD particles determined by using the Selyakov–Scherrer relationship from the half-widths of these lines for all diffraction maxima is equal to 4.5±0.5 nm.

In the region $2\theta = 17°$, an intense localised halo is detected; further, as θ decreases, an increase in the scattered radiation is observed. An intense scattering near the incident beam is typical of diffraction on disordered amorphous structures. Apparently, the observed halo cannot be caused by diffraction on macrostructures with a long-range order and should be associated with its scattering on structural units of a middle-range order. For UDD, not only spherical particles with sizes < 4 nm, but also ordered carbon chains and packages of planes can serve as such structural units. This makes it possible to explain the high intensity of the halo compared with the intensity of the basal (111) maximum. The size of these particles roughly estimated from the halo half-width (in accordance with the Selyakov–Scherrer formula, with assumption of a spherical shape) amounts to ~1.5 nm.

Apparently, it is these small (< 4 nm) ordered particles that represent the 'amorphous' diamond and graphite phases detected in the Raman spectra.

IX. Thermal analysis

Thermal analyses of UDD were carried out either in air or in an atmosphere of an inert gas.[21] On heating in air at a rate of 10 K min^{-1}, oxidation of UDD starts at 703 K,[49] whereas oxidation of diamonds of DSD (detonation synthetic diamond), DDG (detonation diamond with graphite nuclei) and SDB 1/0 (synthetic diamond micropowder) brands begins at 863, 843 and 923 K, respectively.[50] After heating in a neutral atmosphere below 1273 K, the mass loss is 3%–4%. Heating in a CO_2 atmosphere in the temperature range from 443 to 753 K increases the sample's mass by 5%, which can be attributed to CO_2 adsorption and displacement of lighter molecules. Heating in a hydrogen atmosphere is accompanied by HCN evolution.

A complex thermal analysis of UDD carried out in our studies showed that thermograms in air manifest three characteristic regions. At 373–383 K, the mass loss is 5%–7%. This process is endothermic and reversible. An analysis of gaseous products showed that 97%–98% of the gas evolved at this temperature represents nitrogen. Hence, it can be assumed that nitrogen captured from the atmosphere desorbs.

At 523 K, the decrease in the mass of a sample is accompanied by a positive thermal effect. At 753–773 K, an extesive mass loss occurs (up to 95%), which is accompanied by a substantial thermal effect up to 1023–1053 K. Thereafter, no changes take place, and the residual mass corresponds with a 10% accuracy to the ash content of the initial sample estimated according to a standard procedure. It can be assumed that in the interval from 773 to 1023 K carbon is intensively oxidised yielding an incombustible residue. It is noteworthy that oxidation is accompanied by an intense glow.

Wet UDD lose the main mass of water in the interval from 403 to 433 K. Thereafter, the parameters vary practically in the same way as for the predried samples.

Heating in an inert gas atmosphere (helium) at 383–393 K is also accompanied by desorption of nitrogen captured from the atmosphere. In the temperature range of 673–1173 K, a sample loses up to 10% of its mass and heat is liberated. Carbon dioxide and nitrogen are evolved (the molar ratio is 4:1) and the morphology of the material changes.

At 1153–1163 K, a slight positive thermal effect is observed; however, the mass of the sample remains unchanged. The process is accompanied by changes in the morphology and colour of the material. Note that according to the literature data [21] heating in an inert atmosphere entails a practically complete removal of surface groups (adsorbed and chemically bound) from diamond crystals.

X. Defects of the bulk structure

Bulk structural defects of UDD were studied [2] by the method of electron–positron annihilation for all the modes of diamond crystallisation discussed below.

Nanodiamonds were synthesised by detonation of trotyl–hexogen welded charges with 5 mass %–70 mass % of highly dispersed hexogen in water. To estimate the effect of the hexogen concentration and the type of bulk-structure defects and the degree of dispersion of UDD on the sintering process, not only the carbon/hydrogen ratio in the explosive mixture, but also the geometry of charges affecting the time of manifestation of high pressures and temperatures and quenching conditions were varied. After chemical purification, the crystalline structures of UDD were studied by the method of electron–positron annihilation of bulk structural defects. Moreover, a technique of low-temperature adsorption of nitrogen was used for estimating the specific surface area. For studying the sintering processes, UDD of the maximum density of bulk defects (the pycnometric density of 3.05–3.10 g cm^{-3}), the mean CSR size of 1.5–2.0 nm and the maximum degree of dispersion (the specific surface area of 420 m^2 g^{-1}) were chosen. UDD powders were sintered under a pressure of 4–12 GPa. Then, the microhardnesses of sinters and the crushing strengths of the polycrystalline grinding powders obtained were determined.

It was found that with an increase in the carbon temperature and its concentration in the detonation of carbon-containing explosives the distribution curve of vacancy clusters and pores passes through a maximum, after which their concentration begins to decrease. In the region of the maximum corresponding to 3900 K, both an increase in the concentration of vacancy clusters (*i.e.*, agglomerates of vacancies) and the highest concentration of micropores of radii of 1–2 nm in UDD are reached. The aggregates, which contain several vacancies and serve as nuclei for submicropores, represent the centres that capture positrons. The presence in UDD of positronium which has never been observed in diamonds suggests that it appears on the internal surfaces of submicropores formed from vacancy agglomerates.

The absence of submicropores and a low volume density of structural defects (pycnometric density of 3.3×10^3 kg m^{-3}) in

UDD crystallised from trotyl brings these diamonds closer to SDB 1/0 diamonds. This is indicated, for instance, by identical IR spectra of their powders.

XI. Electrophysical properties of ultradispersed diamonds

Diamonds are diamagnetics with a constant magnetic susceptibility ($\chi = -0.62 \times 10^{-8}$ m^3 kg^{-1}).[51] The magnetic susceptibility of UDD substantially differs from this value (see Table 3). The specific magnetic susceptibility of any powder material characterises quantitatively the magnetic properties of the powder as a whole, being the sum of specific magnetic susceptibilities (χ_i) of all components present in the powder with account of their compositions. Table 10 shows the values of magnetic susceptibilities for UDD admixtures.[52]

Table 10. Magnetic susceptibility of admixtures in UDD powder.[52]

Component	UDD	Micropowder of steady-state synthesis	$10^8\chi_i$ /m^3 kg^{-1} (see [a])
Diamond	+	+	−(0.1 – 0.5)
Metal	traces	+	$10^3 - 10^4$
Graphite	+	+	−(0.1 – 8.2)
Carbon materials	+	−	−(0.1 – 2.0)
Gelatine	−	+	−(0.5 – 0.9)

Note. [a] Tentative value.

According to the literature data,[21] the conductivities of UDD are minimal for samples heated at 573 K (resistivity of $\sim 10^{12}$ Ω m). Subsequent heating increases the conductivity (resistivity decreases to $6.0 \times 10^{10} - 2.0 \times 10^{11}$ Ω m). If the samples are heated in a carbon-dioxide atmosphere, then, at temperatures above 1173 K, the resistivity sharply decreases to 2.3×10^4 Ω m, which apparently manifests the beginning of graphitisation.

The permittivity (ε) of different UDD samples varies in a range from 1.7 to 2.7 (Ref. 21). The dissipation factor is $0.5 \times 10^{-3} - 1.0 \times 10^{-2}$.

Thus, UDD exhibit a number of properties that distinguish them from the known types of synthetic diamonds. Despite enhanced reactivity, the diamond-like carbon phase remains stable in neutral and reductive media up to 1273 K, as regards their physicochemical characteristics.

According to our results, at ~293 K the resistivity of a pressed UDD pellet is $10^6 - 10^7$ Ω m. After moistening the pellet, the resistivity sharply increases ($< 10^3$ Ω m for a sample with 5% of water). With further moistening, the resistivity remains unchanged and appears to be determined by the amount of absorbed water. It cannot be ruled out that these data can serve as a basis for the development of a method for determining the residual moisture in UDD.

Yet another important characteristic of the diamond surface is the electrokinetic potential (ζ potential). Taking into account the fact that its value depends substantially on the state of the nanodiamond surface, ζ potential values should be expected not to differ for different fractions of the same UDD and, more so, for UDD samples obtained by different methods of purification and surface modification.

Determination of ζ potential was carried out by electrophoresis based on an electrical current-induced directed transfer of particles of the dispersed medium with respect to the liquid phase.[53] The values of ζ potential were found for three fractions, *viz*., precipitated (I), intermediate (II) and suspended (III), which were obtained from UDD manufactured at RFNC-ARITP (Table 11).

Table 11. Basic physicochemical parameters of isolated UDD fractions.[53]

Parameter	Fraction I	Fraction II	Fraction III
Appearance	light-grey readily crumbling powder	grey powder	black thread-like quasi-crystal formations
Pycnometric density ($10^{-3}\rho$) /kg m^{-3}	3.3	3.2	3.1
[I.r] (mass %)	1.6	1.3	0.9
[C_{ox}] (mass %)	1.0	1.5	1.9
Viscosity [a] of UDD aqueous suspension /MPa s			
at [UDD] = 10 kg m^{-3}	1.04	1.07	1.12
at [UDD] = 60 kg m^{-3}	1.32	1.63	5.15
Electrokinetic potential /mV	+16	+32	+39

Note. Fractions are specified in the text. [a] At 293 K.

The value of ζ potential was also determined for UDD of UDD-TAH (produced at SDB 'Tekhnolog'). The samples were preliminarily purified by ion-exchange resins. For non-fractionated UDD (UDD-TAH), the value of the ζ potential of 32 – 34 mV was found (from three experiments) at 297 – 298 K (for a comparison, ζ potential of non-fractionated and non-dried UDD produced at RFNC-ARITP and similarly pretreated was ±25 – 26 mV).

For four isolated fractions of UDD (UDD-TAH), values of +55, +76, +25 and +33 mV, respectively, were obtained. The resistances (R) of the suspensions (not exceeding 2×10^{-5} Ω) differed only insignificantly after the measurements.

XII. Fractionation process and sedimentation stability

The fractionation process has been discussed in detail.[53] It was claimed that the traditional methods of fractionation of particles with respect to composition and size based on stirring of nanodiamonds in a chosen liquid and subsequent sedimentation under the action of gravity, cannot be applied to highly dispersed colloidal systems including UDD. In the best case, fine fractions are decanted and later form aggregates during drying. The use of organic liquids cannot be accepted due to the high sorption capacity of nanodiamonds (the author of the present work thinks differently).

UDD of different purity grades are shown to include a typical set of functional groups, which remain unchanged up to the destruction of the diamond structure. These are polar OH, NH, C=O, CH and C=N functional groups. It is these groups, especially, the carbonyl and hydroxy groups that determine the trend of UDD particles to form aggregates in aqueous solutions.

Centrifugation of a sedimentation-stable suspension for different periods allowed isolation of UDD fractions (see Table 11).[53] Analysis of IR spectra of the fractions isolated showed that practically the same functional groups were present in all the fractions; however, their concentration differed for different fractions.

UDD was considered as a complex composite material, which consists of individual fractions.[53] The latter differ from one another in the nature and composition of surface groups, as well as in the sizes of aggregates.

Ultrasonication of a dry UDD powder (UDD-STP, produced by Joint Stock Company 'Diamond Centre', St. Petersburg) in water allowed preparation of a stable suspension the dispersed composition of which remained unchanged for a month and

longer.[54] The average size of formed aggregates was 300 nm. An attempt to stabilise the suspension by using different surfactants failed. The UDD particles appear to be surrounded by surfactant molecules with hydrophobic tails directed towards the aqueous medium. Thus, additional hydrophobisation of UDD particles takes place, and the stability of the latter in water decreases.

It was found [55] that, with an increase in the ability of molecules of the medium to association (acetone < benzene < propan-2-ol < water), the degree of dispersion of UDD particles in suspensions also increases. Hence, the solvation of the accessible surface of diamond clusters is favoured not only by the polarity, but also by the tendency of substances to form π-complexes.

From the practical viewpoint, the most important goal is the preparation of stable UDD suspensions in non-polar organic solvents. Nanodiamond suspensions of such a kind will allow cluster compositions based on elastomers to be developed. A real way of solving this problem is to change the nature of the surface of UDD particles from hydrophilic to hydrophobic. For this purpose, a dry nanodiamond powder was added to a benzene solution of commercial co-polydimethyl siloxane and polyisoprene.[55] The adsorption of hydrophobic polymer chains on the surface of UDD clusters was assumed to be beneficial for stabilisation of the suspension. Indeed, the authors managed to enhance the degree of dispersion of UDD in an organic solvent. A method for modifying surfaces and optimising suspensions was developed;[54, 55] for this purpose, polyisoprene proved to be most suitable. Its use for the modification of the surfaces of UDD clusters gave a suspension in which particles measuring 300 nm predominated. This suspension retained its sedimentation stability for no less than 10 days.

XIII. The diamond – graphite structural phase transition

Systematic studies of the diamond – graphite structural phase transition were carried out for UDD clusters.[20] The phase transition occurs in the course of heating in an inert atmosphere in the temperature range of 720 – 1400 K. To detect the transition, the Raman spectroscopy and X-ray diffractometry were used.

The analysis of Raman spectra and X-ray diffraction patterns makes it possible to conclude that UDD represent a cluster material of a diamond crystalline structure with nanocrystals with a characteristic size of ~4.3 nm.

A narrow range of sizes of UDD nanoclusters, *viz*., 4 – 5 nm, was often reported.[17, 56, 57] Apparently, this is explained by the fact that for nanoclusters of small sizes diamond rather than graphite constitutes the thermodynamically stable form. This assumption is confirmed by the results of calculations.[58]

The fact that the lines in the Raman spectra of nanodiamonds coincide with the maxima of the function of phonon density of states in diamond and graphite suggests that UDD involve only small amounts of amorphous diamond and graphite. Inasmuch as nanodiamond clusters, like other ultra-dispersed materials, exist only in an aggregate form,[6] the amorphous phase apparently is located inside such aggregates on the surfaces of diamond cores. The presence of the amorphous phase was also confirmed by the results of X-ray diffractometry, which made it possible to assess the characteristic sizes of particles as ~1.5 nm.

The invariant position of a maximum at 1322 cm^{-1}, which is observed in the Raman spectra with an increase in the support temperature (T_{app}) up to 1000 K, points to the absence of any substantial changes in the structure of the diamond core at such annealing temperatures. This is confirmed by the data from X-ray diffractometry, which state that the graphite phase appears only at $T_{app} > 1200$ K.

The diamond – graphite structural phase transition in the annealing in an inert atmosphere starts from the cluster surfaces. As follows from the analysis of X-ray diffraction data, the graphite phase originates as a set of equidistant graphite nanoplates with a characteristic size < 4 nm and then at $T_{app} > 1200$ K the formation of this phase predominantly involves the diamond core.

The temperature of phase transition (T_{pt}) found correlates well with the results of electron microscopy,[59] according to which the core of a nanocrystalline diamond begins to decrease only as a temperature of 1300 K is reached. This process is accompanied by the transition of carbon into an onion-like structure. A peak at 1575 cm^{-1}, which appears in the Raman spectrum and is clearly pronounced at 1400 K, was interpreted [59] as the manifestation of the carbon onion-like structure. This fact confirms the correctness of the T_{pt} value determined.

It was noted [59] that the diamond – graphite phase transition starts in UDD at substantially lower temperatures compared with diamond single crystals for which $T_{pt} > 1900$ K (see Ref. 60). Such a decrease in a phase-transition temperature, *e.g*., a melting point, was observed earlier for metal clusters.[61]

In parallel with the formation of the graphite phase on the diamond core of a cluster, ordering of sp^2-bound carbon fragments present on original UDD occurs at $T_{app} > 720$ K. Such an sp^2-coordinated crystallisation, in the course of which a disordered (amorphous) phase of carbon located between diamond cores forms continuous graphite nets (patterns), takes place beyond the crystalline diamond core and reflects the changes in the amorphous sp^2-bound carbon. This crystallisation is indicated by an increase in the band intensity at 1350 and 1600 cm^{-1} in the Raman spectra and the appearance of a fine structure in the diffraction pattern in the region of low and medium angles at $T_{app} > 1300$ K.

XIV. A cluster model and the fractal nature of UDD aggregates

Being a structure of the classical type, a UDD particle consists of a relatively dense and ordered crystal-like core and a loose chemically labile shell. The diamond core determines the basic diamond-type properties of UDD, namely, their thermal and chemical stability, heat conduction and thermal diffusivity, low electrical conductivity, the X-ray diffraction pattern quasi-abrasiveness and quasi-hardness. The cluster shell is responsible for such properties of the substance as the sign and value of the UDD surface charge, the chemical composition of surface functional groups, absorption, adsorption, chemisorption and colloidal stability of UDD particles in liquid and other media. In contrast to 'classical' metal clusters the cores and ligand shells of which are built of chemically different elements, *viz.,* metal atoms and complexing ions, in UDD clusters both the cores and the stabilising shells are largely the carbon atoms. In this case, the diamond lattice of the core can gradate to a non-diamond periphery through a system of diamond-like polyhedral polycyclic structures and net patterns. The cluster boundary is stabilised by the products of interaction of periphery carbon atoms with the environment, *viz*., gaseous detonation products, oxidising mixtures and modifying reagents. Peripheral structures play a decisive role in aggregation of diamond clusters and their interaction with matrix substances of composite materials and coatings. The presence of two carbon components in UDD particles is confirmed by a number of experimental data (*e.g*., see Refs 62 and 63).

The structure of condensed detonation products is formed during both the main process, *viz*., in the chemical-reaction zone of the detonation wave, and in the discharge stage where the explosion products are scattered and undergo the action of reflected shock waves.[1, 4, 64] In the latter case, such secondary processes as graphitisation of diamonds and amorphisation of the crystal phase are highly probable. In addition to structural and phase transformations that affect the carbon core of the particles, chemical reactions of the condensed matter with gases take place in the detonation chamber. These interactions are highly diversified due to the wide temperature range and the impact loads that operate throughout the 'life-time' of the carbon condensate in the reactor.

Taking into account the fact that condensation of the diamond substance from detonation products proceeds in fractions of several tenths of a millisecond,[1,2,4] we assumed that, first of all, in the chemical-reaction zone, the primary products of explosive decomposition of the EM are not completely homogenised [64] and, secondly, segregation of condensed and molecular components of detonation products (DP) does not manage to proceed completely. Hence, condensed DP can retain certain 'chemical markers' of the diamond formation process, namely, molecular compounds and fragments of condensed structures, the composition and structure of which can indicate the mechanism of the EM free carbon condensation and reveal the intrinsic structure of a carbon particle.

The expected chemical markers can be divided into the following four groups:

— cage, bridged, alicyclic carbon compounds, which represent the fragments of diamond and diamond-like structures characterised by sp^3-hybridisation of the carbon atoms;

— derivatives of mono- and polycyclic aromatic compounds, which represent the fragments of graphite-like structures (sp^2-hybridisation of the carbon atoms);

— aliphatic (linear and branched) compounds, which represent the fragments of the maximally amorphous carbon-cluster periphery, as well as indications of the presence of carbyne structures;

— compounds that involve C – N and C – O bonds, representing the fragments of the surface layer of particles.

To detect and analyse these 'chemical markers', we experimentally studied the products of mild thermal and organolytic decomposition of UDD and DB.

Low-temperature (cold) extraction was carried out in a Soxhlet apparatus at a solid : liquid ratio of 1 : 10 and an extraction time of 10 – 12 h. Organolytic decomposition was accomplished under the conditions of the supercritical state of the solvent where the extractive power of the liquid is a minimum. This treatment was carried out in a steel autoclave of a volume of 0.4 litre at 573 – 673 K under a pressure > 5 MPa.

The extracts obtained were studied by the methods of low-temperature luminescence and IR spectroscopies, gas-liquid chromatography, chromato-mass spectrometry and ^{1}H NMR spectroscopy.

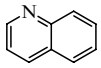
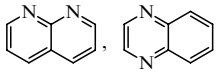
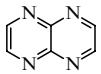
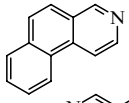
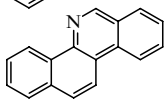
Different types of detonation charges including a sample which contained no diamonds (the so-called 'under-developed' charge) were subjected to cold extraction. Depending on the synthesis conditions, the DB contained variable amounts of extractable substances. These are largely bi- and polycyclic aromatic hydrocarbons with a single or several substituents in the rings. Thus compounds containing sp^2- and sp^3-hybridised carbon atoms were obtained among molecular products of low-temperature extraction of DB. However, it is evident that such compounds are formed most probably from ultradispersed graphite and turbostratic carbon rather than from diamond. Under cold extraction, the solid carbon matrix is not split, but its extractant-soluble molecular components are desorbed and washed out. Hence, it can be concluded that the compounds identified are the intermediates of a transition from primary products of EM detonation to a condensed carbon phase.

The following correlation is observed between the amount of extracted polyaromatic compounds, on the one hand, and the composition and perfectness of the diamond phase in the mixture (*i.e.*, the amount of various defects on the surface and in the bulk of diamond grains, the presence of lattice distortions dependent on both the detonation conditions and the configuration of the blasting chamber), on the other hand: the maximum yield of soluble substances ($\sim$ 5%) is reached for detonation carbon that contains no diamond.

A deeper extraction in combination with partial decomposition of the solid matter was carried out at 473 – 637 K and elevated pressure, *i.e.*, under conditions of supercritical states of organic solvents used. The supercritical liquefaction of carbon proceeds most completely in pyridine, which ranks among the most active solvents.

At present, we know the composition of simplest high-temperature (hot) extracts obtained by using the following relatively mild hydrocarbon solvents (Table 12): of normal structure (heptane and decane), aromatic (benzene and toluene) and alicyclic hydrocarbons (cyclohexane) and hydronaphthalenes (tetralin and decalin). These solvents are relatively stable under experimental conditions; their extraction ability increases in the following sequence: normal < aromatic < alicyclic hydrocarbons < hydronaphthalenes.

Table 12. Aromatic heterocyclic compounds in high-temperature extracts from UDD and DB isolated using different solvents.

Compound	DB, extraction by toluene	UDD, extraction by		
		benzene	cyclo-hexane	hydro-naphthalenes
	+	–	–	–
	+	–	–	+
	–	–	+	+
	+	+	+	+
	+	+	–	+
	–	–	+	+
	–	–	+	–
	+	–	–	–

Note. Sign '+' denotes the presence of a compound in the extract.

The extracts obtained differed in colour: from light yellow (normal hydrocarbons) to dark brown (hydronaphthalenes). Upon the treatment, the ratio of diamond to non-diamond phases changed, as well as the surface properties. Supercritical liquefaction allows solubilisation of up to 10 mass % of diamond-containing phase in 30 min. In this case, relatively weak and reactive chemical bonds are cleaved including elimination of the surface groups and most disordered near-surface carbon layers of clusters. Stable macroscopic structural units are retained as a solid carbon residue, microunits survive as individual molecules which pass into solution. Among the latter, polycyclic nitrogen-containing heretocycles (Table 12) with one and two nitrogen atoms in the ring and a number of rings up to four were detected.

Taking into account the laws of organic chemistry, the formation conditions of these compounds allow us to conclude that nitrogen is incorporated into the condensed carbon (including the diamond phase) as a result of primary reactions, most probably, due to polycondensation of nitrogen-containing monomers with carbon – nitrogen bonds. At first glance, this contradicts the ESR spectra for nanodiamonds [21] which demonstrated

no characteristic triplet signal related to admixed nitrogen atoms replacing carbon in the diamond lattice. However, this a comparison rather emphasises the difference between 'common' diffusional growth of a diamond crystal and the polycondensation mechanism of the formation of UDD during the detonation process. The former involves capture of admixed nitrogen atoms into the newly formed diamond lattice and distribution of such admixed atoms throughout the crystal bulk. In contrast, the formation of UDD first involves incorporation of nitrogen (more precisely, a nitrogen–carbon pair) into an aromatic ring (with a high binding energy in the ring, which is typical of aromatic structures), and then these rings are built into a compacting prototype structure of condensed carbon. In the latter case, the paramagnetic properties of nitrogen should differ from those of admixed nitrogen atoms.

The structure of the outer shell of a diamond cluster was also assessed on the basis of the results on thermodesorption. The studies were carried out on an LKB-2091 chromato-mass spectrometer (Sweden). Thermodesorption was carried out at 573 K in a flow of helium with collection of the products in a capillary cooled by liquid nitrogen. Then, thermodesorption products were vaporised and separated by chromatography on a capillary column with a weakly polar phase (SPB-5; column length, 60 m; diameter 3.2×10^{-4} m), at a helium flow (rate of 2.5×10^{-6} m^3 s^{-1}) in a mode of programmed temperature increase from 293 to 543 K (heating rate, 4 K min^{-1}).

The mass spectra were processed and the products were identified using a built-in computer RDR-2 using a mass spectra data base. Table 13 shows the composition of substances desorbed from the surface of the diamond-containing mixture and UDD.

Table 13. Products of thermodesorption (T = 253 K) from UDD and DB surfaces.

Compound	DB	UDD	UDD-H [a]
Acetonitrile	–	+ +	–
Nitromethane	–	+	–
Butanal	–	+	–
Butan-2-one	–	+	+
Tetrahydrofuran	–	+	–
Ethanol	–	–	+
Acetone	–	–	+
Ethyl acetate	–	+ +	+ + +
Benzene and its homologues	+ +	+ + +	+ +
Alkylbenzenes:			
C_9	+	+ + +	–
C_{10}	+ + +	+	–
Alkanes:			
C_7	–	+	+ + +
C_8	–	+	+
C_9	–	+	–
C_{10}	+ + +	+ + +	–
C_{11}	+	+	–
Alkenes:			
C_7	–	+	–
C_8	+	+	–
C_9	–	+	–
C_{10}	–	+ +	–
Terpene C_{10}	+	+ +	–
Alkylcyclopentanes	+	–	–
Naphthalene	+	+	–

Note. Three samples of each type were analysed. The signs '+', '+ +' and '+ + +' show that the compound was detected in thermodesorption products for one, two and three samples, correspondingly. [a] After hydrogen treatment.

Only hydrocarbons are desorbed from the DB surface: saturated C_8–C_{11}, unsaturated C_8–C_9, alicyclic and aromatic. The predominance of C_{10} alkanes and, probably, n-decane ($C_{10}H_{22}$) agrees with the result that detonation products contain carbyne, the structure of which is most thermodynamically favourable in the condensation of C_{10}–C_{12} carbon chains with the formation of cumulene bonds. The proportion of aromatic hydrocarbons including C_{10} alkylbenzenes among the substances desorbed from DB is comparatively small, although the presence of polycyclic aromatic nets in DB itself is unambiguously proved.[63] Hence, the degree of sp^2-type condensation of carbon is high enough; however, the polyaromatic nets have a very disordered, predominantly aliphatic coating, *viz*., a peculiar type of hydrocarbon 'fringe'. In the desoption products from the DB surface, hydrogen is present in an inactive C–H form, which agrees with the results of determination of active hydrogen on the surface of ultradispersed carbon.[31]

The composition of the desorption products from the UDD surface is more complex and diverse. In addition to hydrocarbons, oxygen- and nitrogen-containing compounds were identified, which are formed as a result of oxidation of the carbon surface. Benzene and C_7–C_{10} homologues are abundant and are second only to C_{10}-alkanes, n-decane prevailing among the latter. Of bridged alicyclic structures, camphene and terpene $C_{10}H_{16}$ are present. Such a composition of the desorption products suggests that the appearance of the diamond structures themselves at the interface is highly improbable. Stabilisation of the diamond structure in a UDD cluster occurs *via* various transition carbon structures. An exposure of UDD to a hydrogen flow at 673 K (UDD-H in Table 13) results in irreversible desorption of most of the C_8–C_{11} hydrocarbons; however, the decomposition of surface carbon structures with the formation of C_2–C_7 hydrocarbons goes on, *i.e*., the surface metastability is reproduced.

Below, certain characteristics of UDD cluster particles are summarised together with the methods of their estimation.

Characteristic	Method
Crystalline core with 4–6-nm diameter	X-ray diffractometry
The presence of peripheral condensed structures of the following types:	
— polyaromatic nets	selective oxidation, organolysis
— aromatic heterocycles	organolysis
Stabilising system of surface compounds:	organolysis, thermodesorption, hydrogenolysis
— aliphatic units	
— bridged structures	
— aromatic rings	
Surface functional groups:	IR spectroscopy,
— carboxyl	chemical analysis,
— carbonyl	potentiometry, polarography, thermodesorption, thermovacuum desorption
— ester	
— quinone	
— nitrile	

These so very diverse and different fragments are combined into a single particle and then into an ensemble of particles in accordance with the fractal rules by a non-continuous filling of a random volume by the mass of a substance.[65] Two- and three-dimensional classical models fail to describe these particles due to their very high C_s/C_{tot} ratio. The packing and arrangement of UDD crystals also cannot be described within the frameworks of the classical theory of filling. It is assumed[6] that the aggregates formed can have a fractal structure. The practical application of UDD requires these properties to be taken into account.

An original procedure has been developed for the direct determination of the fractal dimension of UDD aggregates in hydrosols.[41] The fractal dimension (D), which varied insignificantly in the range of 2.1–2.3, was studied as a function of the

pH, ionic strength and temperature. It was found that an increase in the temperature and ionic strength and a decrease in the pH favour flocculation accompanied by a decrease in the density and fractal dimension of UDD aggregates.

A two-stage mechanism for UDD aggregation was assumed. In the first stage, relatively compact primary aggregates are formed by a particle–cluster mechanism, which takes place in the oxidation of a non-diamond component of DB during its chemical purification. The second stage of cluster–cluster aggregation with the formation of a looser secondary structure is reversible and preferentially associated with the flocculation of primary aggregates.

It is by the structural heterogeneity of the interactions of clusters both with one another and with individual carbon-containing molecules (this is associated with the fact that different particles in powder systems are surrounded by different numbers of active 'neighbours'), as well as by highly irreversible conditions of UDD formation that the fact that the experimental values of UDD fractal dimension do not correspond to any definite type of aggregation (cluster–cluster, cluster–particles) can be explained.

XV. Comparison of properties of diamonds of different origins.

Table 14 (see Ref. 66) presents comparison of the properties of finely dispersed diamond powders of different origins synthesised by three different methods.

The chemical compositions of UDD synthesised by detonation of EM with a negative oxygen balance differ in the presence of substantial amounts of oxygen. Studies of electrophoretic properties of aqueous dispersions of UDD showed that the surface of particles acquires a considerable negative charge (−78.44 mV) caused apparently by ionogenic oxygen-containing groups.

Such a powder possesses high adsorption capacity. Being a characteristic of UDD, the adsorption potential exceeds that of SDB 1/0 powder by an order of magnitude, and the specific adsorption potential exceeds the corresponding value more than twice. On the other hand, with respect to magnetic and electrophysical characteristics UDD powders differ insignificantly from commercial diamond powders SDB 1/0 synthesised under steady-state conditions. Substantial differences are also observed in the values of the degree of surface hydrophilicity and electrophoretic charge: for UDD, they are two- and ten-fold higher, respectively.

Despite their fine degrees of dispersion, UDD have the same graphitisation threshold, although the initial temperature of oxidation in air is 50 K lower for UDD as compared with SDB 1/0 diamonds synthesised under steady-state conditions.

Diamonds obtained by a detonation impact on graphite and soot in an explosive mixture consist of two phases, cubic and hexagonal (Lonsdalite). UDD powders involve only a cubic modification.

XVI. Application fields of ultradispersed diamonds

1. Electrochemical and chemical co-deposition of ultradispersed diamonds with metals

Co-deposition of UDD with metals is applied in machine-building, ship-building, aircraft, electronic, radio-engineering, medical, and jewelry industries.[71–83]

Table 14. Characteristics of diamond powders of different nature.

Characteristic	SDB 1/0 [a]	Finely dispersed diamond [b]	UDD [c]
Phase composition	diamond of a cubic symmetry (a = 0.357 nm)	diamond of a cubic (a = 0.357 nm) and hexagonal (a = 0.252 nm) symmetry or a cubic symmetry [67]	diamond of a cubic symmetry (a = 0.357 nm)
Substructure:			
CSR size /nm	undetected [d]	10–12	4 [d]
microstresses of II kind ($\Delta\alpha/\alpha$)	–	1×10^{-3}–1.9×10^{-3}	absent [d]
dislocation density /m^{-2}	–	–	1.8×10^{17} (see [d])
ρ /g cm^{-3}	3.49	3.20–3.40 (see [67])	3.30
Particle size /nm	0–2000	41–82 (see [67]), 10–50 (from graphite) 20–800 (from soot) [68]	2–50 2–20 (see [69]) 4 (see [1])
S_{sp} /m^2 g^{-1}	13.5 (see [39])	20–42 (see [67]) 20–25 (from graphite) 35 (from soot) [68]	217 150–450 (results of the author)
Elemental composition (mass %)	C — 99.0; (Ni, Mn, Cr, Fe) [e] — 0.5; Si — 0.2; B — 0.2; (O, H) [e] — 0.1	–	C — 93.2–100; O — 0–6.8; Si – traces
[I.r.] (mass %)	< 0.1	0.1 (see [67])	< 2.0
T_{ox} /K (see [f])	723	–	673
T_g /K (see [g])	1373	> 1073 (see [69])	1373–1473
R /Ω m	1×10^{11} (see [70])	–	7.7×10^{9} (see [70])
Dissipation factor at a frequency of 10^3 Hz	0.0100	–	0.0145
$10^8\chi$ /m^2 kg^{-1}	0.5 (see [70])	–	< 1.0 (see [70])
Degree of hydrophilicity /J mol^{-1} kg^{-1}	−1480 (see [70])	–	−3100 (see [70])
Electrophoretic charge of the surface /mV	−6.53	–	−78.44
Adsorption potentials:			
A /J g^{-1}	14.2 (see [70])	–	384 (see [70])
A' /J m^{-2}	1.005	–	2.16

Note. Based largely on the results given in Ref. 66; the data of other studies are specified. [a] Synthesised by a steady-state method. [b] Synthesised by detonation-impact of graphite or soot in EM. [c] Synthesised by detonation of an EM with a negative oxygen balance. [d] The results by Yu I Sozin (Bakulev Institute of Superhard Metals, Kiev). [e] Total content. [f] Initial temperature of oxidation in air. [g] Initial temperature of graphitisation in vacuum.

Metal–diamond composition coatings are characterised by the following common features: superior wear-resistance and microhardness, substantial corrosion stability, low porosity, a sharply reduced friction coefficient, substantial adhesion and cohesion, high throwing power of electrolytes.

The advantages that may be achieved by using UDD in electroplating processes are listed below.

1. The quality and competitive characteristics of manufactured articles are improved. The articles are characterised by

— better resistance to wear and high microhardness;

Coating UDD + M, where M	Resistance to wear increases by a factor of n, where n	Microhardness, $(10^3 h)$/kg mm^{-3}
Cr	2–12	1.4
Ni	5–8	0.68
Cu	9–10	0.154
Au	1.8–5.5	0.25
Ag	4–12	0.18
Sn	3	–
Al	10–13	1.5

— enhanced adhesion and a reduced friction coefficient;

— reduced porosity (the porosity decreases six- to eightfold for UDD coatings with Zn, sevenfold with Sn, sixfold with Au, eightfold with Ag, and a pore-free coating is formed with Cu);

— high insulating ability of anodic alumina films (a relative weight gain of such a film is higher by a factor of 2.0–3.5);

— corrosion stability (for UDD co-deposits with Cu, no mass loss in standard tests was observed; for co-deposits with Zn, the corrosion resistance increased two- to fourfold);

— a sharp increase in the throwing power of electrolytes (threefold for UDD with Cu, 1.5–2.0-fold for co-deposits with Zn);

— enhanced elasticity (for UDD–Cu deposits, by a factor of 2–4);

2. The service life of articles increases two- to tenfold.

3. The economy in materials, energy and labour are achieved (the coating thickness is recommended to decrease two- to threefold);

4. The effectiveness of an electroplating unit increases by 20%–50% due to a decrease in the coating thickness and (in a number of cases) an acceleration of film formation.

5. The environmental parameters of the electroplating process improve.

Addition of UDD to the electrolyte for nickel plating results in a four- to ninefold increase in the wear-resistance of nickel plates.

The UDD content in metal films varies from 0.1 mass % to 1.5 mass % for all metals and from 0.5 mass % to 40 mass % for anodic oxide films.

For a 1×10^{-6}-m thick metal layer, UDD consumption is ~ 1 carat (2×10^{-4} kg) per 1 m^2.

2. Ultradispersed diamonds in polymer compositions

Modified polymers are applied in the manufacture of aircraft, cars, tractors and ships, in medicine, chemical and petrochemical industries, production of seals, cut-off devices of various kinds, in protective and anti-friction film coatings.[79, 83–91]

a. Film coatings based on fluoroelastomers and polysiloxanes

A technology of cold vulcanisation and filling of fluoroelastomers with UDD particles allows one to obtain coatings with a number of advantages.

1. The permeability with respect to hydrocarbons and polar solvents decreases by a factor of 50, *viz*., from 1.389×10^{-7} to 0.0278×10^{-7} kg m^{-2} s^{-1}. Co-polymers with ethylene and with perfluoroalkyl vinyl ethers (protective coatings) exhibit the highest chemical resistance to acidic and alkaline salt media.

2. The coefficient of dry friction with metal decreases to 0.01.

3. The elasticity and strength parameters improve: the stretch modulus at 100% elongation and the conditional rupture strength increase more than tenfold (from 8.5 to 92 MPa and from 15.7 to 173 MPa, respectively). In this case, the elongation increases by a factor of 1.6 (from 280% to 480%), and the residual elongation decreases by a factor of 1.2 (from 108% to 81%).

4. The strength of adhesion contacts increases

(a) for active surfaces (St.3 steel, zinc, aluminium), by 200%–500% (from 1.7 to 5.1 kN m^{-1} for St.3 and from 0.5 to 3.3 kN m^{-1} for aluminium);

(b) for inactive surfaces (lead, copper), the strength of adhesion contact is 2.8–3.1 kN m^{-1};

(c) the coating developed has the following dielectric characteristics:

— at 4000 MHz, the dissipation factor is 2.58–2.71 depending on the film thickness;

— at 5000 MHz, the transmission and reflection factors may reach 15.0 and 12.4, respectively, depending on the film thickness;

— at 11 000 MHz, the transmission and reflection factors may reach 14.3 and 12.4, respectively, depending on the film thickness.

The coating retains its physical and mechanical properties and operation efficiency under a load up to 2×10^6 kg m^{-2}.

Film coatings based on UDD-modified polysiloxanes possess enhanced elasticity and strength characteristics: the modulus at 100% elongation increases by a factor of 3 (from 19 to 53 MPa); the rupture strength also triples both at 100% (from 52 to 154 MPa) and absolute (from 730% to 1970%) elongation; the tear strength increases by a factor of 1.4.

Fluorine-containing elastomers modified with UDD possess improved elasticity and strength characteristics and are resistant to thermal ageing; the modulus at 100% elongation increases by a factor of 1.6 (from 7.9 to 12.5 MPa), the resistance to rupture is 1.1-times higher (from 15.4 to 16.5 MPa), the rupture elongation increases by a factor of 1.35 (from 210% to 285%).

The resistance of UDD-modified fluoroelastomers to abrasive wear increases by a factor of 1.5–2.0, *i.e*., with respect to this parameter, they are similar to polyisoprene rubbers.

b. Rubbers

Under thermal ageing at 573 K, UDD-containing rubbers either virtually retain their physical and mechanical characteristics at a level of analogous characteristics of standard compositions (non-subjected to heating) or exceed this level. The use of UDD is beneficial for cross-linking in non-destructive changes in the course of thermal ageing.

Polyisoprene rubbers modified by UDD demonstrate enhanced elasticity and strength characteristics. Thus, for the SKI-3 isoprene rubber, the modulus at 300% elongation increases by a factor of 1.6 (from 7.7 to 12.3 MPa), the conditional tensile strength increases by a factor of 1.4 (from 20.5 to 28.2 MPa), and the tear strength increases from 139 to 148 kN m^{-1}. The maximum swelling degree of rubbers in toluene decreases by 45%. These rubbers have a higher degree of vulcanisation and increased strength characteristics (approximately 30% higher than that of standard rubbers based on SKI-3) and higher wear endurance.

The increase in elongation with an increase in the modulus observed for these rubbers contradicts the commonly accepted notions. This points to the changes in the supramolecular structure of the rubber, evidenced by a substantial cohesion increase (by a factor of 1.6: from 1.7 to 2.7 MPa).

Modification of the SKI-5 isoprene rubber by UDD particles results in a 1.6–1.8-fold increase in the controlled strength parameters (modulus at 300% elongation, rupture and tear strengths) with retention of elastic properties.

Oil-containing rubbers modified by UDD possess higher degrees of vulcanisation compared with those without UDD (the modulus at 300% elongation increases from 5.8 to 7.4 MPa, relative elongation decreases from 700% to 610%). Moreover, rubbers that contain UDD together with technological carbon have a tear strength 25%–35% higher then the reference samples.

With introduction of UDD into a standard rubber mixture SKMS-30 ARK based on a butadiene–styrene co-polymer with 30% styrene units, the cohesion strength increases by a factor of 1.5–2.0 (from 1.6 to 3.1 MPa) compared with reference samples.

Rubbers modified by UDD are distinguished by high degrees of vulcanisation, their strength characteristics being practically equal to those of reference rubber, and twice surpass them in tear strength (which increases from 71 to 135 kN m^{-1}). The modulus at 300% elongation increases by a factor of 1.44 (from 7.9 to 11.4 MPa).

Butadiene–nitrile V-14 rubbers modified by UDD exhibit improved operating characteristics: the friction coefficient decreases by a factor of 1.5, wear resistance is enhanced by a factor of 1.3, the elasticity increases by a factor of 1.7, frost resistance also improves (the glass transition temperature decreases by 8%–10%).

For RSS natural rubber (Malaysia) modified by UDD, the modulus at 300% elongation increases threefold (from 1.8 to 5.4 MPa), which is accompanied by a certain improvement in operational characteristics.

Epoxy glues based on UDD exhibit good adhesion and cohesion properties.

Nanodiamonds are applied in technologies for polymerisation from solutions and melts, chemical solidification, and in the techniques for electron-beam, flame, and electrostatic sputtering. Standard equipment is used for fabrication of UDD-containing compositions.

Polymeric compositions containing UDD display substantial advantages.

1. The quality and commercial characteristics of the production improve: the articles exhibit superior strengths, wear resistance, resistance to ageing and action of abrasives. The friction coefficient is low for polyfluoroelastomers (such as co-polymers of polyvinylidene fluoride with perfluorinated co-monomers, *e.g.*, perfluoropropene) and high for polyisoprenes (SKI-3 and SKI-5). The materials and coatings can be adapted to particular technologies and articles.

2. Cheap polymeric starting materials can be substituted for expensive ones.

3. Expensive and deficient components and materials may be saved.

Nanodiamond consumption amounts to 1–5 kg per 1000 kg rubber (polymer) and 1–5 kg per 1000 m^2 of a polymeric coating or a film.

3. Ultradispersed diamonds in lubricants, greases, and lubricating–cooling liquids.

Modified lubricant compositions are used in machinery, metal working, engine-building, ship-building, the aircraft industry and transport.[79, 83, 92–100]

Addition of nanodiamonds to oils allows one to obtain high-quality sedimentation-resistant and environmentally safe systems with superhard particles that measure $< 5 \times 10^{-7}$ m.

The merits of UDD additives to oil compositions are as follows:

1. The quality and competitive characteristics of articles improve: the service life of vehicles and equipment increases; the economy of fuel and lubricants is achieved, these additives can serve as an alternative to expensive oils and special lubricants.

2. The friction torture is reduced by 20%–40%.

3. The wear of friction surfaces decreases by 30%–40%.

4. Fast run in of friction gears is observed.

The consumption of nanodiamonds is 0.01–0.2 kg per 1000 kg of oil.

4. Ultradispersed diamonds in abrasive tools

Tools fabricated from nanodiamonds are used in abrasive, mining and metal working industries, in machinery, electronics, medicine and jewelry production.[83, 101–103]

Below, the quality indices [microhardness (h), electrical resistivity (R), heat-conductivity (γ) and permittivity (ε)] are shown for clinkers obtained from diamond powders subjected to high pressures and temperatures, both for UDD themselves and diamond-oxide compositions with vitreous oxides (diamond ceramics).

	$10^{-3}h$ /kg mm^{-2}	R /Ω m	γ /W m^{-1} K^{-1}	ε
Individual UDD	3.0–3.5	10^9–10^{12}	100–150	7–9
Diamond ceramics (UDD + MgO)	3–4	10^{10}–10^{12}	120–160	8–10

For individual UDD, the density of defect-free fragments is $(3.35–3.50) \times 10^3$ kg m^{-3}.

These clinkers (the so-called diamond glasses) can easily be cut by ultrasound and laser, ground and polished. They can be used as abrasives in the working of materials of average hardness and in electronics.

Ultradispersed diamonds metallised by transition-metal clusters possess high microhardness [$h = (6–7) \times 10^3$ kg mm^{-2}] and represent excellent tool materials.

The use of UDD (0.5%–1.5%) for enhancing the strength properties of polymeric matrices of grinding and polishing tools results in a simultaneous increase in both strength (by a factor of 1.3–1.5) and elastic (by a factor of 1.8–2.0) properties of an abrasive tool.

5. Ultradispersed diamonds in microabrasive and polishing compositions.

Polishing systems (PS) that contain UDD are used in precision finishing of materials in radio engineering, electronics, optics, medicine and machinery.[79, 104–109]

The compositions allow one to obtain perfect mirror solid surfaces of required planeness, plane-parallelism, of any geometrical shape, containing no defects and dislocations, with the contour interval $R_z = 2–8$ nm (with an average deviation from a mean hypothetical surface $\sigma = 0.5–2.0$ nm).

The advantages of UDD-containing polishing systems are as follows.

1. The minute sizes of UDD ensure the minimum surface roughness and the colloidal stability of PS.

2. The chemical stability of UDD allows one to use chemically active additives to PS and to recover PS.

3. The amount of material removed from the surface being polished is small (the material losses decrease).

4. Owing to ion-exchange and sorption properties of UDD, the removed ionic and molecular products are immobilised on the UDD surface, which provides a clean surface.

5. The fractal structure of UDD aggregates ensures a controlled structurisation in PS suspensions and the absence of stressed and disrupted surface layers on a material being polished.

6. These systems are non-toxic.

7. Polishing systems with UDD allows one to enhance the quality and competitive characteristics of polished articles and to ensure the polishing of materials technologically difficult to work.

Nanodiamond consumption is 0.001–0.01 kg per 1 m^2 of the surface worked.

6. Ultradispersed diamonds in magnetic recording systems.

Nanodiamonds are used, first of all, as anti-friction additives and physical modifiers in ferromagnetic-varnish coatings of magnetic films and disks and, secondly, as the additives to electrochemical composition films destined to improve the magnetic recording device characteristics.[77, 79, 83]

1. The addition of UDD to a ferromagnetic layer sharply reduces its domain sizes (ferromagnetic grains), *i.e.*, the density of recording increases substantially.

When introduced into a varnish to form a special film destined for cleaning of recording heads, UDD provides polishing of the latter and enhances their resistance to wear.

Magnetically soft information carriers which contain UDD display the following advantages: abrasive wear of a magnetic-carrier layer decreases, optimum conditions are provided for operation of magnetic heads and reading devices, friction of the magnetic carrier decreases and stability of its motion is provided.

The consumption of nanodiamonds is 1% – 2% of the varnish mass.

2. As compared to individual CoP coatings, magnetically soft amorphous CoP – UDD films are shown to display the following advantages: a 1.3-fold increase in microhardness, a 4.5-fold increase in the resistance to wear, a 1.4-fold decrease in friction coefficient, a 2-fold increase in the service life of magnetic-head cores without any changes in their effectiveness.

For magnetically hard polycrystalline CoP – UDD coatings compared to individual CoP coatings both electrochemically and chemically deposited, the microhardness increases by a factor of 1.2, corrosion currents decrease by a factor of 1.6, the service life of the carriers of magnetic information increases.

Magnetic characteristics of both magnetically soft amorphous films and magnetically hard coatings remain unchanged with an addition of UDD.

Nanodiamond consumption is ~ 1 carat for a layer with 1×10^{-6} m thick.

7. Biological activity of ultra-dispersed diamonds

When UDD are used as potential medical drugs, their anomalously high adsorption capacities, high specific surface areas, abundance of free electrons on the surface (a multiple radical-donor), nanoscale sizes, a great amount of oxygen-containing functional groups on crystal surfaces, chemically inert grains and surface hydrophilicity are of great importance.[79, 110]

Nanodiamonds can be applied in oncology, gastroenterology, cardiology, dermatology, for curing vessel diseases, *etc*. They display no carcinogenic and mutagenic properties and are non-toxic.

Owing to their high adsorption capacities and other specific features, nanodiamonds exhibit extremely high activities with respect to pathogenic viruses, microbes and bacteria by absorbing them intensively. Nanodiamonds are selective sorbents and supports for biologically active substances, they can significantly enhance the action of drugs. The use of UDD normalises blood pressure. Moreover, UDD are effective drugs for different gastroenteric diseases, an excellent remedy for after-effects of burns, different skin diseases and intoxication.

The use of UDD in the form of aqueous and oil suspensions is beneficial for curing cancer patients; these tend to increase the effect of drugs, relieve pains, normalise peristalsis of the bowels, improve blood characteristics and activate the immune system, remove toxins from the organism and prolonge the patient's life.

The use of UDD in chemical and radio-therapy appears to be promising in the cure of malignant tumours for prevention of the mutagenic effect of drugs. At the same time, UDD do not reduce the therapeutic effect and are capable of preventing the appearance of mutations in normal cells or generation of secondary tumours under the action of anti-tumour drugs.

A therapeutic course requires $\sim 0.02 - 0.5$ g of UDD.

* * *

Thus, this survey demonstrates that UDD microcrystals with a narrow size distribution at about 430 nm manifest extremely varied and sometimes unusual properties. Undoubtedly, physico-chemical and chemical studies of UDD will be continued. It is possible that the main application fields of nanodiamonds are still to be found, although there are good grounds to believe that UDD can be applied virtually in any field, first of all, in high technologies.

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