

## Obtaining nanocrystalline superhard materials from surface-modified nanodiamond powder

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**Abstract:** During sintering of a nanodiamond powder with a coating based on non-diamond forms of carbon with a thickness of about 10 Å at relatively low pressures and temperatures, a nanostructured diamond material is formed by the transition of graphite-like carbon to diamond. It has been shown that nanodiamond powder modified with non-diamond forms of carbon is an “active” base on which a nanometer layer of graphite-like carbon transforms into diamond during thermobaric sintering. The influence of preliminary annealing of nanodiamonds in a dis ammonia atmosphere and in oxidizing and hydrocarbon-containing atmospheres on the structure and microhardness of nanodiamond polycrystals has been shown. It has been established that the atmosphere in which modifying annealing is carried out affects the content of the diamond phase and the size of nanodiamond crystallites in a polycrystalline material. The preliminary modification (functionalization) of the nanodiamond surface with carbon-containing compounds stimulates the process of diamond formation. In this case, the most significant increase in the microhardness of diamond polycrystals is observed after the modification of nanodiamonds in oxidizing and hydrocarbon atmospheres. It has also been established that the modifying treatment of nanodiamonds with hydrocarbons stimulates the processes of diamond synthesis, and an increase in pressure suppresses the graphitization of diamond and activates the transformation of graphite-like carbon into diamond, which contributes to sintering of diamond grains.

**Keywords:** nanoparticles; superhard materials; diamond synthesis; surface modification.

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## Получение нанокристаллических сверхтвёрдых материалов из поверхностно-модифицированного порошка наноалмаза

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**Аннотация:** В процессе спекания при относительно низких давлениях и температурах наноалмазного порошка с покрытием на основе неалмазных форм углерода толщиной порядка 10 Å происходит формирование наноструктурного алмазного материала путем перехода графитоподобного углерода в алмаз. Показано, что наноалмазный порошок, модифицированный неалмазными формами углерода, представляет собой «активную»

основу, на которой в процессе термобарического спекания происходит переход нанометрового слоя графитоподобного углерода в алмаз. Показано влияние предварительного отжига наноалмазов в атмосфере диссаммиака, в окислительной и углеводородсодержащей атмосферах на структуру и микротвердость наноалмазных поликристаллов. Установлено, что атмосфера, в которой осуществляется модифицирующий отжиг, влияет на содержание алмазной фазы и размер кристаллитов наноалмазов в поликристаллическом материале. Показано, что предварительное модифицирование (функционализация) поверхности наноалмазов углеродсодержащими соединениями стимулирует процесс алмазообразования. При этом наиболее существенный рост микротвердости алмазных поликристаллов наблюдается после модифицирования наноалмазов в окислительной и углеводородной атмосферах. Установлено, что модифицирующая обработка наноалмазов углеводородами стимулирует процессы синтеза алмаза, а рост давления подавляет процесс графитизации алмаза и активирует трансформацию графитоподобного углерода в алмаз, что способствует спеканию алмазных зерен.

**Ключевые слова:** наночастицы; сверхтвердые материалы; синтез алмаза; поверхностное модифицирование.

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## 1. Introduction

The development of new polycrystalline superhard materials (PSHM) based on diamond is associated with the need to improve their physical and mechanical characteristics in accordance with the requirements for modern machining tools [1]. It is possible to achieve a high level of characteristics due to the formation of nanostructures in the synthesized material, which follows from the Hall-Petch relation connecting the mechanical properties of the material to the size of its structural components [2]. Due to nanostructuring in a diamond polycrystal, it is possible to realize a unique set of mechanical characteristics, for example, a combination of high hardness and crack resistance, which are unattainable for diamond PSHMs based on coarse-grained diamond powders.

At the same time, the use of existing industrial technologies for the production of diamond PSHMs does not allow creating superhard materials based on nanodiamonds with a high level of physicochemical characteristics, which is due to the specifics of the structure of nanodiamonds, the phase and chemical state of the surface of nanodiamond powders [3, 4].

Unsatisfactory compressibility and high porosity of compacts from nanodiamond powders, active recrystallization and graphitization of nanodiamond during thermobaric treatment necessitate the development of technologies that make it possible to form a dense polycrystalline material in which the nanostructure of the initial powder is preserved. Technological solutions used to obtain diamond ceramics based on coarse-grained diamond powders at high pressures  $P$  and temperatures  $T$  turned out to be ineffective for obtaining nanostructured polycrystalline diamond materials [3, 4].

The use of activating additives, metal catalysts used to reduce the parameters of the phase

transformation of graphite into diamond, provokes the reverse transition of nanodiamonds into graphite, thereby reducing physicochemical characteristics of diamond nanostructured PSHMs even at ultrahigh  $P$  and  $T$  sintering parameters.

Therefore, the aim of the work is to develop scientific and technological foundations for obtaining nanocrystalline diamond materials based on nanodiamonds by complex physicochemical modification of nanodiamonds, which consists in the formation of a functional coating based on nanostructured non-diamond carbon and additional modification of the nanodiamond surface with carbon-containing compounds.

For nuclei (particles of graphite and diamond of small sizes), the equilibrium line on the phase diagram of carbon can be located significantly lower than for the corresponding "bulk" phases, because in this case, the surface energy makes a significant contribution to their total thermodynamic potential [5, 6]:

$$\mu = \mu_0 + \frac{2\sigma V}{R},$$

where  $\mu_0$  is the chemical potential of the bulk phase;  $V$  is the atomic volume;  $R$  is the radius of the particle.

According to Tchaikovsky and Rosenberg (1984) [7], the diamond-graphite transition curve shifts to lower pressures for particles smaller than 100 nm.

According to the results of theoretical studies [8–11], for particle sizes in the nanorange, diamond is a more stable form of carbon compared to graphite. According to [12], the boundaries of the stability regions for diamond and graphite are 10.2 nm at room temperature, 6.1 nm at 525 °C, 4.8 nm at 800 °C, and 4.3 nm at 1100 °C.

The theoretical results obtained were confirmed in experimental studies of diamond formation

processes by heating nanographite (onion-like carbon or OLC) without applying pressure [13–16] or in  $P$ ,  $T$  modes corresponding to the parameters of thermodynamic stability of “bulk” graphite. For example, in the process of thermobaric treatment of a fullerene-containing mixture at a pressure of 2 GPa and a temperature above 1300 K in the presence of catalyst metals, diamond crystals were synthesized in the size range of 100–800  $\mu\text{m}$  [17].

One of the ways to obtain a diamond nanostructured material by converting graphite into diamond is the phase transition of graphite crystallites (nanostructured graphite, graphite-like onion carbon) into diamond at high pressures and temperatures, excluding both diamond recrystallization and graphitization.

As a starting material for these purposes, detonation synthesis nanodiamond with a particle size of 4–10 nm can be used [18].

In [19, 20], the transformation of the detonation nanodiamond structure during its vacuum heat treatment was studied. As a result, it has been found that vacuum annealing of nanodiamond at temperatures of 1000–2400  $^{\circ}\text{C}$  leads to the formation of an onion-like OLC structure similar to fullerenes on its basis. With an increase in the annealing temperature, the number of graphite-like layers on the diamond surface increases due to the diamond “core”, the size of which decreases in this case [21]. At temperatures of 1000–1500  $^{\circ}\text{C}$ , nanodiamond particles are formed, the core of which retains the diamond  $\text{sp}^3$  structure, and the peripheral zone consists of layers of  $\text{sp}^2$  carbon ( $\text{sp}^2$ - $\text{sp}^3$  carbon nanocomposite). At annealing temperatures above 1500  $^{\circ}\text{C}$  (1800 K), nanodiamond particles are completely transformed into carbon of an onion structure with its further transformation into graphite [22].

In turn, the use of onion carbon obtained from nanodiamonds by vacuum annealing as a starting material makes it possible to synthesize nanopolycrystalline diamond material with a diamond phase content of  $\sim 80\%$  and a hardness of up to 42 GPa without activating additives at moderate  $P$ ,  $T$ -parameters ( $P = 4\text{--}6$  GPa,  $T = 1000\text{--}1400$   $^{\circ}\text{C}$ ,  $t = 10\text{--}30$  min) [23].

In [3, 24], it was proposed to use detonation nanodiamonds with a graphitized surface and a diamond “core” as a feedstock for the synthesis of nanostructured diamond materials.

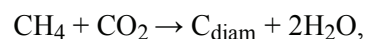
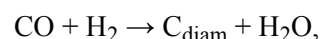
The use of “nanodiamond–nanographite” composite powders makes it possible to maximize the area of direct contact between the diamond surface and graphite, which will increase the probability of diamond nucleation due to autoepitaxy and reduce the

likelihood of contamination of synthesis products with impurities [25–30].

This approach makes it possible to obtain nanostructured diamond composites due to the “graphite–diamond” phase transition below the equilibrium line of “bulk” graphite and diamond in the carbon phase diagram [31].

There is an alternative approach according to which diamond is formed not only at high  $P$  and  $T$  parameters due to phase transformation in carbon, but also at low pressures as a result of polycondensation of simple carbon-containing molecules [32]. The proposed polygenetic approach [33] takes into account not only physical, but also chemical factors, such as the polycondensation of light carbon-containing compounds without the use of high pressures, as well as transformation of graphite into diamond at high pressures, which takes into account chemical factors.

In accordance with the polycondensation model, the synthesis of diamond (as the ultimate product of polycondensation) can proceed at low pressures by reactions of the type



Synthesis of diamond can also take place taking into account the intermediate gasification of non-diamond forms of carbon according to the following scheme:



At low temperatures of the gas phase, diamond is formed as a result of polycondensation of the initial molecules according to the molecular mechanism. At high temperatures, both undissociated initial molecules and intermediate compounds formed during the decomposition of the initial molecules, as well as ions and radical particles participate in the polycondensation [33]. Regardless of the initial composition of the precursors, the key role in the gas-phase synthesis of diamond can belong to the following radicals:  $\text{CH}_3^*$ ,  $\text{C}_2\text{H}^*$  [34, 35].

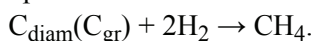
The process of gas-phase deposition of diamond is heterogeneous-catalytic: it is carried out at the substrate temperature with the participation of the substrate and the diamond film growing on it. The catalysts can be the substrate and the growing diamond, as well as the components of the gas phase. In this case, for the diamond formation, it is necessary that the rate of the diamond formation phase be higher than the rate of graphite formation,

and the rate of graphite oxidation should be higher than the rate of diamond oxidation [33, 36].

The region of diamond formation [37] on the H–C–O diagram (Fig. 1) is located between regions with a high reduction potential (the region of hydrocarbons, during the polycondensation of which predominantly graphite and forms of diamond carbon are obtained) and a high oxidizing potential (the region of  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{O}_2$ , in which neither diamond nor graphite can form and remain, because their complete conversion will occur according to the reaction:



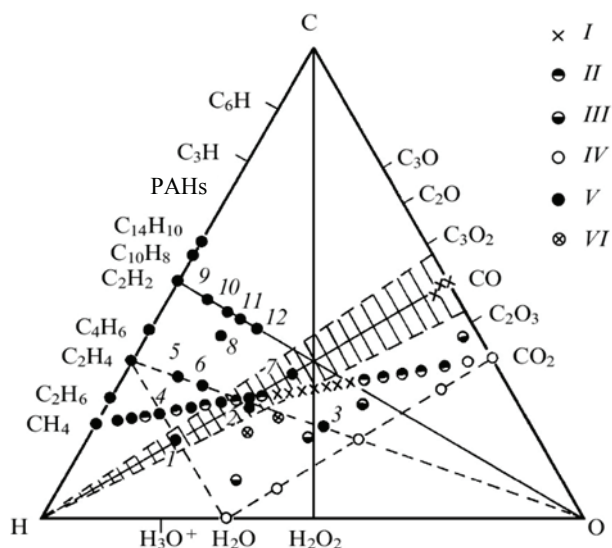
This region should be limited by mixtures rich in hydrogen, in which the hydrogenolysis of diamond and graphite is possible:



The diamond formation is affected by the composition of the gas mixture from which it is formed. It is shown that the synthesis of diamond, obtained by the methods of chemical vapor deposition (CVD), comes from mixtures of a certain composition, which form a kind of “corridor” on the O–H–C diagram, expanding from the H vertex to the CO composition. The possibility of the formation of nanodiamonds from a gas at low temperatures and pressures without a substrate due to the addition of oxygen to the H–C system (and thus its transfer to the O–H–C system) was substantiated in [33–37]. In this system, it is possible to select oxygen pressures at which the diamond core will be more stable than the graphite core ( $P_{ig} > P_{id}$ ). These conditions are possible in the range of oxygen fugacity close to the upper limit of carbon stability in this system with respect to oxygen, where the equilibrium pressure of methane drops sharply. Calculations performed for the O–H–C system under  $P$ – $T$  conditions corresponding to the parameters of diamond synthesis by CVD methods showed that the oxygen pressure in these cases should correspond to the hydrogen and carbon dioxide compositions of gas mixtures [38].

The functional cover of a certain composition on the surface of carbon particles (diamond, graphite) also plays an important role in the deposition of diamond and graphite in gas-phase processes. It can be created by a special modifying chemical treatment of diamond crystals and powders based on non-diamond forms of carbon under the conditions of their high-temperature treatment (annealing) in an appropriate atmosphere [33, 39, 40].

According to [41], an important factor for the simultaneous formation of graphite and diamond at low pressure is the ratio of the critical radii of



**Fig. 1.** Diagram reflecting the stoichiometric conditions of the processes of diamond and graphite polycondensation and the conversion of diamond and graphite substances by oxidizers, with points obtained experimentally by the authors [33]:

*I* – formation of a diamond substance on a diamond substrate by growing a diamond lattice; *II* – graphitization of the diamond substrate under the conditions of the experiment with mixtures  $\text{CH}_4 + \text{CO}_2$ ; *III* – selective oxidation of graphite and retention of diamond in the reaction ( $\text{C}_{\text{diam}}(\text{C}_{\text{gr}}) + \text{H}_2\text{O} (\text{CO}_2, \text{O}_2) \rightarrow \text{CO} + \text{H}_2$ ); *IV* – complete oxidation of graphite and diamond; *V* – formation of compaction products of the graphite series from individual organic substances; *VI* – formation of a diamond film outside the diamond region; *I* – methanol; 2 – formaldehyde, acetic acid; 3 – formic acid; 4 – ethanol; 5 – acetone; 6 – acetaldehyde; 7 – pyruvic acid; 8 – acrolein; 9 – phenol; 10 – furan; 11 – dioxybenzenes; 12 – phloroglucinol

graphite ( $R_g$ ) and diamond ( $R_d$ ), which depend on the ratio of chemical potentials:

$$R_g / R_d = \Delta\mu_d / \Delta\mu_g.$$

The chemical potentials of graphite  $\Delta\mu_g$  and diamond  $\Delta\mu_d$  can be expressed as follows:

$$\Delta\mu_g = RT \ln(P_i / P_{ig});$$

$$\Delta\mu_d = RT \ln(P_i / P_{id}),$$

where  $P_i$  and  $P_{id}$  are current (true) and equilibrium pressures of carbon-containing gases;  $R$  is the universal gas constant;  $T$  is temperature.

In the region of graphite stability,  $P_{ig} > P_{id}$  which corresponds to the predominant formation of graphite from the fluid or gas phase ( $R_g < R_d$ ). The conditions for the predominant (most probable) formation of diamond correspond to the condition



$P_{ig} > P_{id}$  ( $R_g > R_d$ ). The difference between  $\Delta\mu_g$  and  $\Delta\mu_d$  depends on the difference between  $P_i/P_{ig}$  and  $P_i/P_{id}$ .

At low pressures, this difference tends to zero; therefore,  $R_g \approx R_d$  which corresponds to the optimal conditions for the formation of diamond from fluids (gases) in the region of graphite stability.

Thus, in order to increase the probability of diamond formation by chemical deposition methods, along with an atmosphere of a certain composition and favorable kinetic conditions, it is necessary to have critical diamond growth nuclei, which can be both epitaxial diamond films and some non-diamond forms of carbon.

Thus, in [42], a unique nucleation method of diamond films on a silicon substrate is considered using carbon clusters  $C_{60}$  and  $C_{70}$  fullerenes as nuclei. The use of  $C_{60}$  fullerene molecules makes it possible to increase the growth rate of the diamond film by a factor of  $10^4$ , and the use of  $C_{70}$  molecules by a factor of  $10^{10}$ . In the case of the  $C_{70}$  molecule, an additional increase in the growth rate of the diamond film is due to a favorable crystal structure correspondence between the structural elements of fullerene and diamond, as well as to deformations of the pyrene and triphenylene elements of the fullerene structure [33].

From this standpoint, the use of surface-graphitized nanodiamonds with closed graphene layers on the surface (structures of the “onion carbon – diamond core” type) is of great scientific and practical interest for the synthesis of nanopolycrystalline diamond films and bulk materials.

The formation processes of diamond nanostructured composites at high pressures and temperatures were studied in [43] depending on the surface state of diamond nanopowders. Depending on the surface state of initial nanosized diamond particles, the formation process of a polycrystalline material based on it is realized both due to the diffusion growth of diamond crystallites (in the case of purified nanodiamond powder) and by combining the diffusion and martensitic mechanisms of diamond formation (for nanodiamonds with non-diamond (graphite-like) surface carbon). Adaptation of the structure of diamond nanostructured materials based on purified diamond powders manifests itself at high temperatures and relatively low pressures accompanying the onset of the diamond graphitization process.

For polycrystals from diamond powders with non-diamond forms of carbon on the surface, the

adaptation of the structure is associated with the phase transformation of non-diamond forms of carbon into diamond and is most noticeable in the low-temperature region at high pressures. At the same time, the issue of synthesizing a nanocrystalline material based on diamond at lower parameters of thermobaric treatment is of theoretical and practical interest.

According to the studies [20, 44], the phase composition of nanodiamond powders and composite materials based on them is largely determined by the atmosphere of preliminary annealing of nanodiamonds. In particular, if heat treatment of nanodiamonds in an inert atmosphere leads to the appearance of graphite in them, then annealing in a hydrogen atmosphere in nanodiamond powder increases the fraction of  $sp^3$  carbon [20, 44]. Modification of nanodiamonds (a detonation diamond-containing mixture) in a protective (reducing) atmosphere of various compositions also has an overwhelming effect on the structural-phase composition of the resulting diamond materials at the nano-, meso-, and microstructural levels [45, 46].

As a result of annealing of nanodiamonds in a hydrogen atmosphere, oxygen and oxygen-containing functional groups are removed from the surface of nanodiamonds, which leads to an increase in the temperature of the diamond–graphite reverse phase transformation and enhances the properties of diamond polycrystals sintered under conditions of high pressures and temperatures [47, 48].

Treatment of nanodiamonds with pressures of 6–8 GPa at temperatures above 1000 °C in a hydrogen-containing atmosphere (fluid) based on naphthalene decomposition products (mixtures of  $CH_4$ ,  $H_2$  and other hydrocarbons) promotes the reduction (destruction) of oxygen-containing groups, thereby protecting the nanodiamond core from graphitization and ensures diffusion carbon to the surface of nanodiamonds. During the thermal decomposition of naphthalene in the diamond stability region, in addition to the formation of various hydrocarbons, carbon nanoparticles, which participate in the process of nanodiamond growth to submicron and micron sizes, are additionally formed [49]. Preliminary treatment of nanodiamonds with saturated acyclic hydrocarbons (hexane, paraffin, mono- and dibasic alcohols) before sintering in the region of diamond stability (5–8 GPa, 1300–1800 °C) leads to the growth of diamond particles due to the so-called oriented attachment mechanism. The addition of organic carbon-containing compounds stimulates the implementation of this mechanism of nanodiamond growth in the  $P$ ,  $T$ -region of diamond stability [50].

Based on numerous studies, it can be argued that the functional coating on the surface of both diamond nanoparticles and non-diamond forms of carbon (graphite, graphite-like onion carbon, fullerenes) plays an important role in the processes of diamond polycondensation.

In this regard, the complex modification of nanodiamonds with a thin layer of non-diamond carbon, followed by treatment (functionalization) of the nanodiamond surface in various gaseous media (reductive, oxidizing, hydrocarbon) will contribute to the preservation of the original diamond and the formation of a diamond phase both due to the decomposition of carbon-containing molecules and diffusion of carbon to the nanodiamond surface and due to the transition of non-diamond carbon to diamond at lower pressures and temperatures corresponding to the stability region of “bulk” graphite in the phase diagram of carbon.

## 2. Materials and Methods

### 2.1. Materials

The initial material for obtaining nanostructured PSHMs is nanodiamond powder produced by NP CJSC Sinta (Minsk), purified from impurities and non-diamond forms of carbon. The formation of a carbon coating on purified nanodiamonds was carried out by vacuum annealing at a temperature of 950 °C.

### 2.2. Determination of the structure and properties of powders

The appearance of the powders was examined using a Micro-200 optical microscope (Planar Production Association, Belarus). Transmission electron microscopy (TEM) was performed using an EM-125 electron microscope with an accelerating voltage in the range of 20–150 kV. The morphology of the surface and fracture of the sintered samples was studied using an atomic force microscope (AFM) NT-206 (ODO MicroTestMashiny, Belarus) in the contact mode. The microstructure of the obtained diamond materials was studied on a certified high-resolution scanning electron microscope (SEM) Mira by Tescan (Czech Republic) with a resolution of 1.7 nm (at 30 kV) and 2.0 nm (at 20 kV).

X-ray studies of the powders were performed on a Bruker D8 ADVANCE diffractometer in Cu-K $\alpha$  radiation in automatic shooting mode.

The microhardness of the nanostructured composites was determined on a Micromet-II microhardness tester (Buehler, Switzerland) with a diamond indenter according to the Vickers scale

with an indenter load of 100 g. The compact density was measured by weighing in carbon tetrachloride.

Grinding of sintering products was carried out in an NK 40 desktop laboratory vibrating mill (Russia) for 5 min.

### 2.3. Surface modification of nanodiamond surface by vacuum annealing

Surface modification of purified nanodiamond powder with non-diamond (graphite-like) carbon was carried out by vacuum annealing of nanodiamonds under the following conditions: the residual pressure in the vacuum chamber was  $10^{-3}$  mm Hg. Art., annealing temperature was 900 °C.

After vacuum annealing, a thin  $sp^2$ -carbon layer up to 1 nm thick was formed on the surface of nanodiamonds [20]. The weight reduction of nanodiamond powder after heat treatment was 10 wt. % due to the desorption of surface functional groups and compounds of carbon with oxygen and nitrogen, as well as adsorbed water [51]. Annealed nanodiamond powder forms aggregated with a grain size of 0.1–1  $\mu$ m based on diamond crystallites about 10 nm in size [52].

Next, by briquetting the nanodiamond powder at a pressing pressure of 400–600 MPa, porous preforms were obtained (Fig. 2) with a porosity of about 55–60 % and a pore size in the range of 10–100 nm, which were then mechanically ground into granules. The structure of preforms based on nanodiamonds with a pyrocarbon coating is described in [53].

Gas-phase modification of the obtained granules was carried out in various gaseous media. On the one hand, the annealing of nanodiamonds in granules makes it possible to ensure the purity of the powder from impurities (the absence of penetration of foreign inclusions and impurities), on the other hand, during annealing in a carbon-containing gas environment, under appropriately selected conditions, grains of finely dispersed diamond powders can coalesce [54].

### 2.4. Chemical surface modification of powders and thermobaric treatment

Modification of granulated powders was carried out by annealing them, respectively, in reducing, oxidizing and hydrocarbon atmospheres in a sealed container under a fusible seal [3] at a temperature of 900 °C.

Thermobaric treatment of nanodiamonds after modification was carried out under conditions of high



**Fig. 2.** Pressing surface from nanodiamonds modified with  $sp^2$ -carbon:  $a - \times 100$ ;  $b - \times 400$

static pressures in an “anvil with a hole” high-pressure apparatus in the pressure range of 1.0–4.0 GPa at temperatures from 1100 to 1450 °C for 15–30 s.

### 3. Results and Discussion

Fig. 2 shows an image of the surface structure of a porous sample made of nanodiamonds modified with  $sp^2$ -carbon.

#### 3.1. Investigation of the material structure after annealing in a protective disammonia atmosphere and thermobaric treatment

The study determined the effect of preliminary annealing in a disammonia atmosphere and parameters of thermobaric sintering on the structure of a material based on nanodiamonds with graphite-like carbon on the surface.

As an atmosphere for modification, dissammonium composition was used, %:  $H_2 - 75$ ;  $O_2 \leq 0,002$ ;  $NH_3 - 0,005-0,01$ ;  $N_2$  was the rest (dew point temperature was 30 °C).

Based on the data of X-ray diffraction analysis, it has been found that annealing in a disammonia reducing atmosphere and thermobaric treatment in the pressure range of 1.0–2.5 GPa at a temperature of 1400 °C and a time of more than 15 s leads to the appearance of graphite, the content of which increases with increasing time of thermobaric treatment. This agrees with the previously obtained data on thermobaric treatment in the indicated  $P$ ,  $T$  range of dissammonium-modified purified nanodiamonds and diamond detonation charge containing non-diamond forms of carbon (NFC) in an amount of up to 50 wt. % [3, 28, 55].

The size assessment of the coherent scattering regions (CSR) of the diamond phase showed that the size of diamond crystallites slightly increased compared to the initial one and is in the range of

**Table 1.** Sizes of graphite and diamond crystallites after modification of nanodiamonds with NFC in dissammonium and thermobaric sintering

Processing options		Crystallite size $D_{\text{effect}}$ , Å	
$P$ , GPa	$t$ , s	Graphite phase	Diamond phase
1.0	15	$65 \pm 1.1$	$55 \pm 1.1$
1.0	30	$85 \pm 1.1$	$57 \pm 1.1$
1.5	45	$107 \pm 1.1$	$88 \pm 1.1$
2.5	30	$105 \pm 1.1$	$74 \pm 1.1$
2.5	60	$109 \pm 4.0$	$96 \pm 4.0$

5–10 nm after sintering for 15–60 s. Similar values were also obtained by analyzing the resulting nanomaterial with a scanning electron microscope. The size of coherent scattering regions (CSR) of graphite increases from 5.5 nm to 10–11 nm after 15 and 30–60 s of thermobaric treatment, respectively (Table 1).

#### 3.2. Study of the material structure after annealing in an oxidizing atmosphere of carbon monoxide and thermobaric treatment

Modification of nanodiamonds with a graphitized surface in an oxidizing atmosphere based on carbon monoxide  $CO_2$  does not prevent graphitization of nanodiamonds during their thermobaric treatment under the same conditions, but leads to a more significant growth of diamond nanocrystallites (20–40 nm) compared to treatment in a disammonia reducing atmosphere.



**Table 2.** Sizes of graphite and diamond crystallites after annealing of nanodiamonds with NFC in an oxidizing CO<sub>2</sub> atmosphere and thermobaric sintering

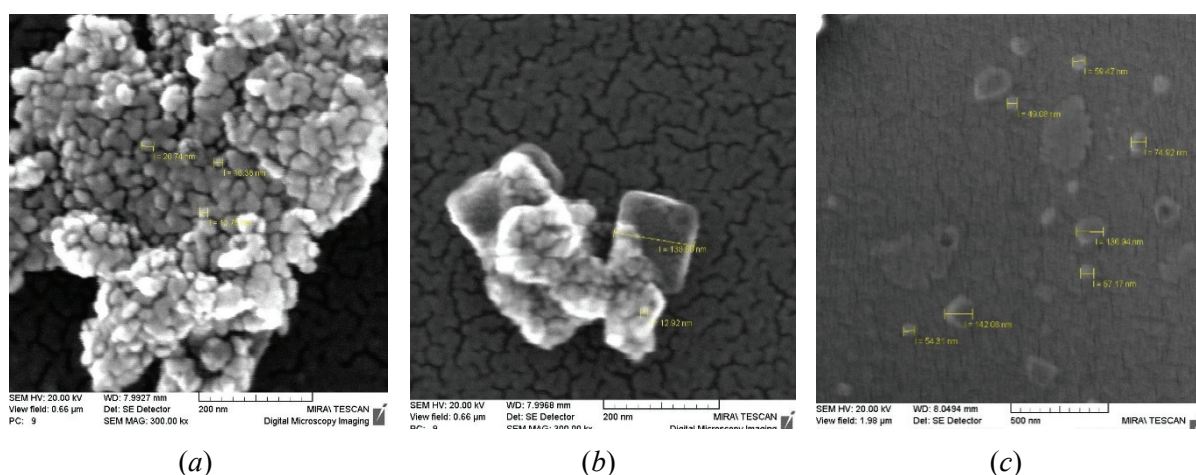
Processing options		Crystallite size $D_{\text{effect}}, \text{\AA}$	
$P, \text{GPa}$	$t, \text{s}$	Graphite phase	Diamond phase
1.5	15	$60 \pm 1.1$	$54 \pm 1.1$
1.5	30	$90 \pm 1.1$	$85 \pm 1.1$
1.5	60	$95 \pm 1.1$	$98 \pm 1.1$
2.5	30	$55 \pm 4.0$	$90 \pm 4.0$
2.5	60	$60 \pm 4.0$	$107 \pm 4.0$

In this case, the growth of diamond crystallites can be represented in accordance with the reactions according to the scheme:



In parallel with an increase in the time of thermobaric treatment, the growth of graphite crystallites is observed (see Table 2), however, with an increase in pressure, the growth of graphite crystallites slows down.

The sizes of crystallites of the diamond and graphite phases after annealing of nanodiamonds in an oxidizing atmosphere and subsequent thermobaric treatment are given in Table 2, and the appearance and structure of the resulting material are shown in Fig. 3a, b.



(a)

(b)

(c)

**Fig. 3.** Structure of as intered material based on nanodiamonds after annealing in an oxidizing atmosphere of CO<sub>2</sub> and thermobaric treatment at a pressure of 2.5 GPa: a – thermobaric treatment time 30 s; b, c – 60 s; a, b – sintered diamond polycrystalline particles; c – individual diamond crystallites

### 3.3. Study of the material structure after modification with hydrocarbon-containing compounds and thermobaric treatment

Previously [3, 47, 48], it has been demonstrated that the preliminary modification of purified nanodiamonds with hydrogen and hydrocarbons (methane) prevents graphitization of nanodiamonds during sintering under high pressure (6–8 GPa) due to the purification of the nanodiamond surface from oxygen and oxygen-containing groups and promotes sintering of the material, which manifests itself in an increase in its mechanical properties (microhardness).

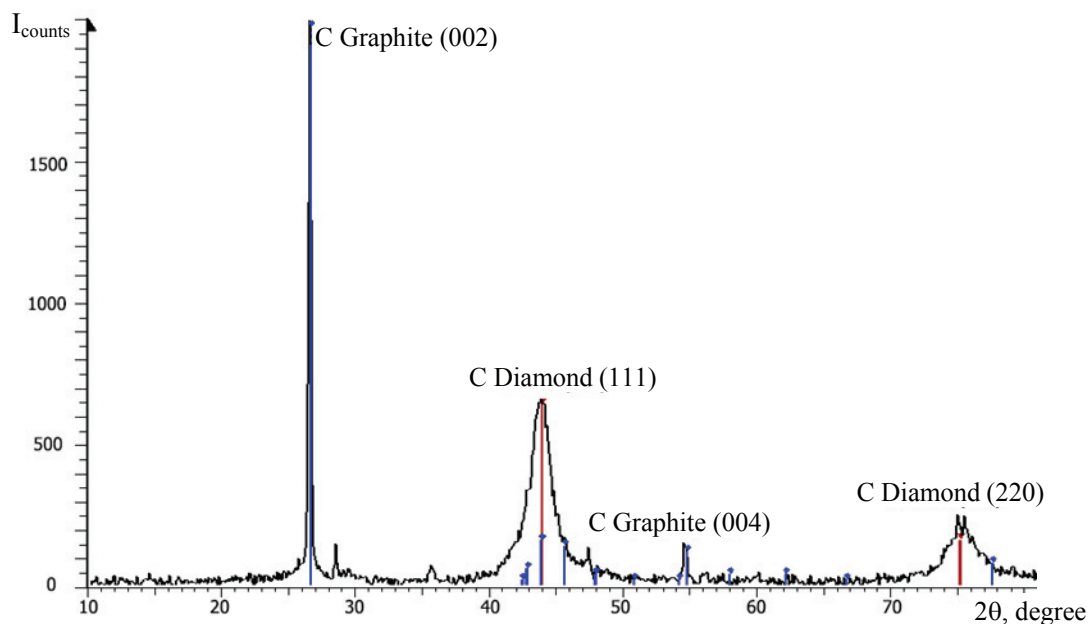
The influence of modification of nanodiamonds coated with non-diamond carbon with hydrocarbon-containing compounds on the synthesis of diamond nanopolycrystalline material at a lower pressure level of 1–4 GPa was studied.

Modification of nanodiamonds with hydrocarbon-containing compounds was carried out by two methods: heat treatment (annealing) of nanodiamonds in a hydrocarbon (methane) atmosphere, as well as by adding ethyl alcohol C<sub>2</sub>H<sub>5</sub>OH followed by annealing (drying) of nanodiamonds at a temperature of 90 °C.

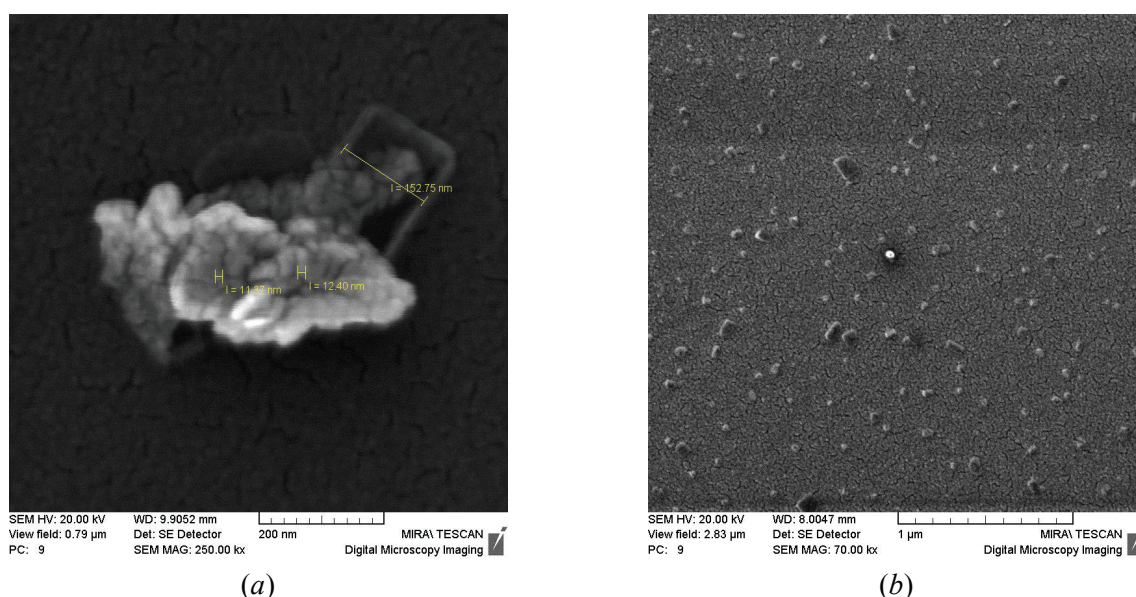
*Study of the material structure after modification with methane.* As in the previous cases,  $P$ ,  $T$ -treatment of nanodiamonds after modification with methane at pressures of 1.5–2.5 GPa, temperatures above 1400 °C and time over 15 s is accompanied by the processes of graphitization and recrystallization of nanodiamonds (Fig. 4).

It should be noted that as a result of mechanical dispersion (grinding) of compacts in a planetary mill for 5 min, a large number of nanopolycrystalline





**Fig. 4.** X-ray pattern of the material based on nanodiamonds after modification with methane ( $\text{CH}_4$ ) and  $P$ ,  $T$ -treatment at  $P - 1.5 \text{ GPa}$ ,  $T - 1450 \text{ }^\circ\text{C}$ ,  $t - 30 \text{ s}$



**Fig. 5.** Polycrystalline particles based on nanodiamonds after modifying annealing in a methane atmosphere and sintering at a pressure of 2.5 GPa:  
*a* – individual polycrystalline particles; *b* – particles of submicron size with faceting

(and possibly single-crystalline) diamond particles of submicron and micron sizes are formed on their basis, which indicates the active occurrence of diamond crystallization and recrystallization processes and the formation of sufficiently strong bonds between diamond crystallites in a polycrystal.

Fig. 5 shows the structure of the nanodiamond material after annealing in a hydrocarbon atmosphere of methane and sintering at a pressure of 2.5 GPa. Fig. 5*a* shows submicron particles based on nanodiamond crystallites with sizes of about

10–15 nm, as well as a larger (about 150 nm) faceted particle formed as a result of recrystallization. Fig. 5*b* shows faceted particles (the sizes of the obtained particles are mainly 50–200 nm).

*Study of the material structure after modification with alcohol.* Under conditions of high pressures and temperatures, ethanol dehydrates to form ethylene  $\text{C}_2\text{H}_4$ , water, and products of its thermal decomposition ( $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{C}_4\text{H}_6$ ,  $\text{C}_6\text{H}_6$ ) [56] which form a fluid based on them. These compounds, on the one hand, contribute to the destruction of oxygen-

containing groups on the surface of nanodiamonds, protecting the diamond core of nanodiamonds from graphitization, and, on the other hand, ensure the growth of the diamond phase on the surface of initial nanodiamond grains [49]. The resulting water also has a catalytic effect on the process of diamond formation.

Thermobaric treatment of nanodiamonds after their modification with ethyl alcohol was carried out at pressures of 2.5 and 4.0 GPa and a temperature of 1450 °C with isothermal exposure for 15–30 s. The structure of the obtained material is shown in Fig. 6.

The analysis of the microstructure of the obtained nanodiamond materials shows that an increase in the duration of the thermobaric treatment from 15 to 30 s leads to an increase in the average size of diamond crystallites from 5–12 to 10–20 nm. At the same time, an increase in the pressure of thermobaric treatment to 4.0 GPa at the same temperature and duration of thermobaric treatment contributes to the suppression of the graphitization process and the formation of nanostructured polycrystalline diamond particles up to 2 µm in size.

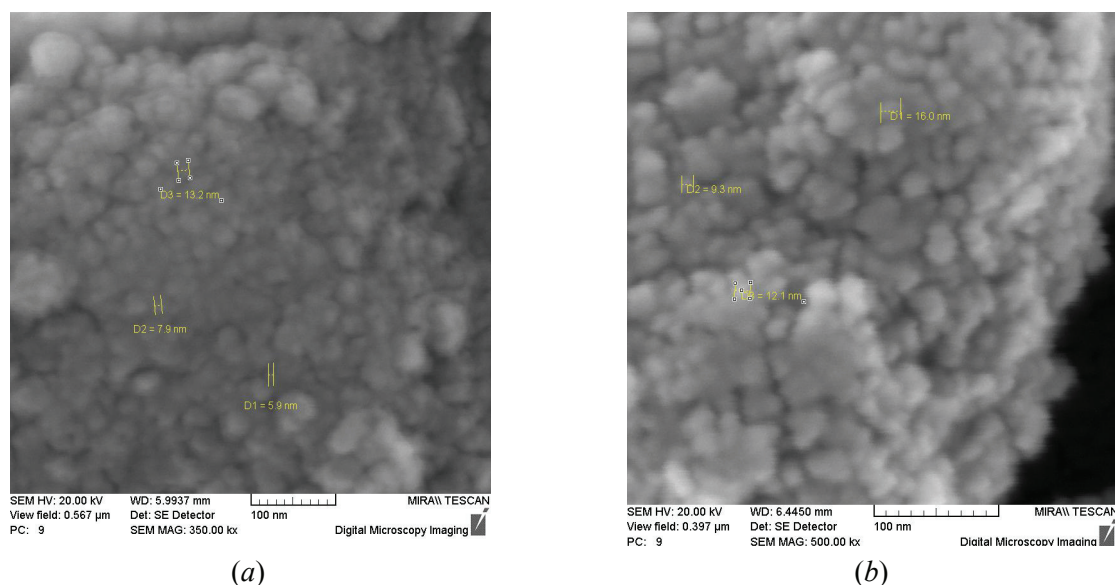
The data given in the table demonstrates that an increase in the pressure of thermobaric treatment for this system promotes the growth of diamond crystallites and suppresses the growth of graphite crystallites.

It can be noted that, in general, modification with hydrocarbon-containing compounds promotes the synthesis and growth of diamond crystallites and their sintering into polycrystals (Fig. 7).

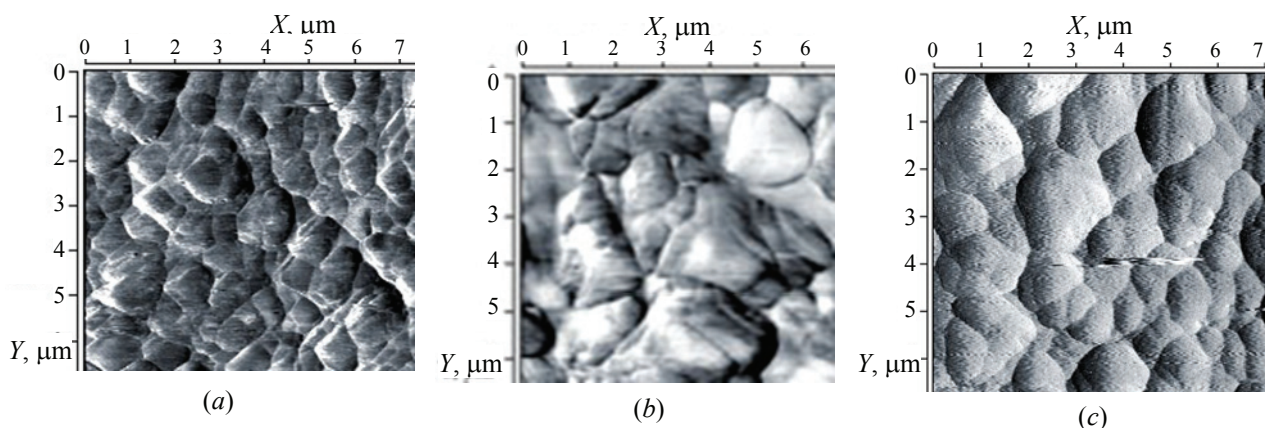
**Table 3.** Sizes of graphite and diamond crystallites in the products of nanodiamond sintering with non-diamond carbon after their modification in a methane atmosphere depending on pressure

Processing options	Phase	Crystallite size $D_{\text{effect}}, \text{\AA}$
$P = 2.5 \text{ GPa},$ $t = 15 \text{ s}$	Graphite	$89 \pm 6.941$
	Diamond	$25 \pm 5.803$
$P = 4.0 \text{ GPa},$ $t = 15 \text{ s}$	Graphite	$72 \pm 11.766$
	Diamond	$30 \pm 5.803$

Thus, the modifying treatment of nanodiamonds before their thermobaric sintering leads to an increase in the microhardness of diamond polycrystals. The microhardness of a material based on nanodiamonds that have not undergone preliminary processing and sintered in the pressure range of 2.5–4.0 GPa does not exceed 6–8 GPa [3, 52]. Annealing in dissammonium and thermobaric treatment in the same pressure range leads to an increase in the microhardness of sintered polycrystals to 8–10 GPa, treatment in an oxidizing atmosphere to 12–15 GPa, and modification with hydrocarbon-containing compounds (methane, alcohol) to 20–25 GPa. The scatter in the microhardness values of the samples may be due to the highly nonequilibrium conditions of diamond synthesis under high-speed sintering conditions.



**Fig. 6.** Structure of the sintered material based on nanodiamonds after modification in alcohol and thermobaric treatment at pressures of 2.5 GPa:  
a – time of thermobaric treatment 15 s; b – 30 s



**Fig. 7.** Comparison of the material structures based on nanodiamonds after modification and thermobaric treatment: *a* – modification in a reducing atmosphere (dissammonium); *b* – in a  $\text{CH}_4$  hydrocarbon atmosphere; *c* – modification in alcohol  $\text{C}_2\text{H}_5\text{OH}$  (Thermobaric treatment pressure was 2.5 GPa, time was 30 s)

The data presented allows concluding that the greatest increase in the material microhardness takes place after modifying treatment, which stimulates the processes of diamond synthesis from hydrocarbon-containing compounds.

At the same time, an increase in the pressure of thermobaric treatment additionally increases the thermodynamic stimulus for the transformation of thin carbon layers into diamond and stimulates the growth and sintering of diamond grains.

#### 4. Conclusion

1. It has been shown that the production of nanopolycrystalline diamond materials based on detonation nanodiamonds can be carried out at relatively low pressures of thermobaric sintering, corresponding to the stability region of “bulk” graphite.

Detonation synthesis nanodiamond with a particle size of 4–10 nm with a thin coating based on graphite-like carbon (non-diamond forms of carbon) additionally modified with carbon-containing compounds in the C–O–H system can serve as a starting material for these purposes.

It has been demonstrated that the functionalization (modification) of the nanodiamond surface with carbon-containing compounds ( $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_5\text{OH}$ ) coated with graphite-like carbon plays a decisive role in the processes of diamond polycondensation during the synthesis of nanopolycrystalline diamond material.

2. It has been established that as a result of modifying the nanodiamond surface with dissammonium, the size of nanodiamond crystallites after sintering at pressures of 1.0–2.5 GPa practically does not increase compared to the initial one and is in

the range of 5–10 nm. The size of graphite crystallites increases from 5.5 nm after sintering for 15 s to 10–11 nm after 30–60 s of thermobaric treatment.

The regularities of changes in the phase composition and sizes of diamond and graphite crystallites in nanocomposites based on nanodiamond with a graphitized surface after annealing in a reducing atmosphere of dissammonium and sintering in the stability region of “bulk” graphite do not change compared to composites based on a diamond detonation charge and nanodiamonds with a non-diamond surface carbon forms.

3. Modification of nanodiamond with non-diamond forms of carbon (NFC) in an oxidizing atmosphere based on carbon monoxide  $\text{CO}_2$  does not prevent nanodiamond graphitization during their thermobaric treatment under the same conditions, but leads to a more significant growth of diamond nanocrystallites (20–40 nm) compared to treatment of dissammonia in a reducing atmosphere due to reactions according to the scheme:  $\text{C}_{\text{gr}} + \text{CO}_2 \rightarrow [2\text{CO}] \rightarrow \text{C}_{\text{diam}} + \text{CO}_2$ .

Modification of nanodiamonds with  $\text{CH}_4$  methane and subsequent sintering at pressures of 1.5–2.5 GPa at temperatures above 1400 °C and sintering time of more than 15 s is also accompanied by the processes of graphitization and recrystallization of nanodiamonds. In this case, the formation of polycrystalline (single-crystalline) diamond particles of submicron and micron sizes indicates the active occurrence of diamond crystallization and recrystallization processes and the formation of strong bonds between diamond crystallites in a polycrystal.

Modification of nanodiamond with non-diamond forms of carbon (NFC) with ethyl alcohol and



thermobaric treatment at pressures of 2.5 and 4.0 GPa and a temperature of 1450 °C with isothermal exposure for 15–30 s leads to an increase in the average size of diamond crystallites from 5–12 to 10–20 nm. At the same time, an increase in the pressure of thermobaric treatment to 4.0 GPa at the same temperature and duration of thermobaric treatment contributes to the suppression of the graphitization process and the formation of nanostructured polycrystalline diamond particles up to 2 µm in size.

4. Modifying treatment of nanodiamonds before their thermobaric sintering leads to an increase in the microhardness of diamond polycrystals. The microhardness of the material based on nanodiamond particles that have not undergone pretreatment and sintered in the pressure range of 2.5–4.0 GPa does not exceed 6–8 GPa. Annealing in dissimiac and thermobaric treatment in the same pressure range leads to an increase in the microhardness of sintered polycrystals to 8–10 GPa, treatment in an oxidizing atmosphere to 12–15 GPa, modification with hydrocarbon-containing compounds (methane, alcohol) – up to 20–25 GPa.

As a result, it can be concluded that the greatest increase in the microhardness of the material occurs after the modifying treatment with hydrocarbons, which stimulates the processes of diamond synthesis from the gas phase. Increasing the pressure of thermobaric treatment from 1.5 to 4 GPa suppresses the diamond graphitization process and increases the thermodynamic stimulus for the transformation of graphite-like carbon into diamond, activating recrystallization and sintering of diamond grains.

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## 6. Conflict of interests

The authors declare no conflict of interest.

## References

1. Bogatyreva GP, Burykin VV, Gargin VV, Gurvich RA, Devin LN, Dub SN et al. Novikov NV, Klimenko SA (eds.) *Superhard material tools*. Moscow: Mashinostroyeniye Publ.; 2014. 608 p. (In Russ.)
2. Andrievsky RA, Glezer AM. Size effects in nanocrystalline materials: II. Mechanical and physical properties. *Fizika metallov i metallovedeniye = The Physics of Metals and Metallography*. 2000;(89)1:91-112 (In Russ.)
3. Vityaz PA, Zhornik VI, Il'yushchenko AF, Senyut VT, Komarov AI, Korzhenevsky AP, Ivakhnik AV. *Nanodiamonds of detonation synthesis: preparation and application*. Vityaz PA (ed.). Minsk: Belorusskaya Nauka; 2013. 381 p. (In Russ.)
4. Vityaz PA, Gritsuk VD, Senyut VT. *Synthesis and applications of superhard materials*. Minsk: Belorusskaya Nauka; 2005. 359 p. (In Russ.)
5. Fedoseev DV, Deryagin BV, Varshavskaya IG, Semenova-Tyan-Shanskaya AS. Chuzhko RK (ed.) *Diamond nucleation at high pressures*. Moscow: Nauka; 1984. 27 p. (In Russ.)
6. Fedoseev DV, Deryagin BV, Varshavskaya IG, Semenova-Tyan-Shanskaya AS. *Diamond crystallization*. Moscow: Nauka; 1984. 136 p. (In Russ.)
7. Tchaikovsky EF, Rosenberg GK. Phase diagram of carbon and the possibility of obtaining diamond at low pressures. *Doklady Akademii nauk SSSR*. 1984;279(6): 1372-1375 (In Russ.)
8. Yolshina LA, Muradymov RV, Vovkotrub EG, Smirnov SV. Diamond synthesis in aluminum matrix in molten alkali-halide at ambient pressure. *Diamond and Related Materials*. 2015;55:1-11. DOI:10.1016/j.diamond.2015.02.005
9. Badziag P, Verwoerd WS, Ellis WP, Greimer NR. Nanometer-sized diamonds are more stable than graphite. *Nature*. 1990;343:244-245. DOI:10.1038/343244a0
10. Gamarnik MY. Energetical preference of diamond nanoparticles. *Physical review B*. 1996;54(3): 2150-2156. DOI:10.1103/physrevb.54.2150
11. Manuella FC. Can nanodiamonds grow in serpentinite-hosted hydrothermal systems? A theoretical modelling study. *Mineralogical Magazine*. 2013;77(8): 3163-3174. DOI:10.1180/minmag.2013.077.8.10
12. Jiang Q, Li JC, Wilde G. The size dependence of the diamond-graphite transition. *Journal of Physics Condensed Matter*. 2000;12:5623-5627. DOI:10.1088/0953-8984/12/26/309
13. Tomita S, Fujii M, Hayashi S, Yamamoto K. Transformations of carbon onions to diamond by low-temperature heat treatment in air. *Diamond and Related Materials*. 2000;9(3-6):856-860. DOI:10.1016/S0925-9635(99)00217-4
14. Zaiser M, Banhart F. Radiation-induced transformation of graphite to diamond. *Physical Review Letters*. 1997;9:3680-3683. DOI:10.1103/PhysRevLett.79.3680
15. Banhart F, Ajayan PM. Self-compression and diamond formation in carbon onions. *Advanced Materials*. 1997;9(3):261-263. DOI:10.1002/adma.19970090319
16. Xiao J, Ouyang G, Liu P, Wang CX, Yang GW. Reversible nanodiamond-carbon onion phase transformations. *Nano Letters*. 2014;14(6):3645-3652. DOI:10.1021/nl5014234
17. Shipilo VB, Zvonarev EV, Kuzey AM, Zaitsev VA, Gorlach AG. *Obtaining, properties and application of powders of diamond and cubic boron nitride*. Vityaz PA (Ed.). Minsk: Belaruskaya Nauka; 2003. 335 p. (In Russ.)
18. Dolmatov VYu. *Detonation of nanodiamonds. Preparation, properties, application*. St. Petersburg: NPO "Professional"; 2011. 536 p. (In Russ.)
19. Okotrub AV, Bulusheva LG, Gusel'nikov AV, Kuznetsov VL, Butenko YuV. Field emission from products

of nanodiamond annealing. *Carbon*. 2004;42(5-6):1099-1102. DOI:10.1016/j.carbon.2003.12.007

20. Vul AYa. Characterization and physical properties of UNCD particles. In: Shenderova O, Gruen D (eds.) *Ultrananocrystalline diamond: synthesis, properties and applications*. N-Y: William Andrew Publ.; 2006. p. 379-404.

21. Romanenko AI, Anikeeva OB, Kuznetsov VL, Buryakov TI, Tkachev EN, Moseenkov SI, Arzhannikov AV. Influence of gamma irradiation on electrophysical properties of onion-like carbon. *Journal of Optoelectronics and Advanced Materials*. 2008;10(7):1745-1748.

22. Shenderova O, Jones C, Borjanovic V, Hens S, Cunningham G, Moseenkov S. Detonation nanodiamond and onion-like carbon: applications in composites. *Physica Status Solidi (A) Applications and Materials Science*. 2008;205(9):2245-2251. DOI:10.1002/pssa.200879706

23. Wang Z, Li Y, Zou Q, Dai L, Yu Q, Luo Y, Luo W, Yin Y. Effect of sintering parameters on microstructure and properties of nanopolycrystalline diamond bulks synthesized from onion-like carbon. *Diamond and Related Materials*. 2021;111:108233. DOI:10.1016/j.diamond.2020.108233

24. Vityaz PA, Senyut VT, Kheifets ML, Kolmakov AG, Klimenko SA. Synthesis of diamond nanostructured materials based on nanodiamonds. *Doklady NAN Belarusi*. 2012;56(6):87-91. (In Russ.)

25. Senyut VT, Markova LV, Gamzeleva TV, Kovaleva SA, Valkovich IV. Study of the structure of carbon composites based on nanodiamonds and diamond-containing detonation synthesis charge. *Collected papers: Nanostructures in condensed media*. Vityaz PA (ed.). Minsk: BSU Publ.; 2011. p. 99-105. (In Russ.)

26. Vityaz PA, Senyut VT, Kheifets ML, Kolmakov AG. Synthesis of polycrystalline diamond materials based on detonation nanodiamonds. *Izvestiya vysshikh uchebnykh zavedeniy. Seriya: khimiya i khimicheskaya tekhnologiya = ChemChemTech*. 2013;56(7):105-108. (In Russ.)

27. Senyut VT. Influence of modification of nanodiamonds on the structural characteristics of superhard composites sintered on their basis under conditions of high pressures and temperatures. *Vestnik Polotskogo gosudarstvennogo universiteta. Seriya V. Promyshlennost'. Prikladnye nauki*. 2014;3:43-52. (In Russ.)

28. Senyut VT, Markova LV, Gamzeleva TV. Carbon nanocomposites based on pressure-sintered modified nanodiamonds. *Poroshkovaya metallurgiya = Powder Metallurgy and Metal Ceramics*. 2015;38:132-141. (In Russ.)

29. Vityaz PA, Senyut VT, Markova LV, Gamzeleva TV, Heyfets ML. Structure peculiarities of carbon nanocomposites on basis of sintered modified nanodiamonds. *Izvestiya vysshikh uchebnykh zavedeniy. Seriya: Khimiya i khimicheskaya tekhnologiya = ChemChemTech*. 2015;58(7):40-44. (In Russ.)

30. Vityaz PA, Zhornik VI, Senyut VT. Superhard composite materials on the base of nanodiamonds. *Nanoscience and Technology*. 2019;10(4):385-402. DOI:10.1615/NanoSciTechnolIntJ.2020031692

31. Kheifets ML, Kolmakov AG, Vityaz PA, Senyut VT. Improvement of manufacture technology of nanostructured diamond materials with the use of

physicochemical nonequilibrium analysis. *Inorganic Materials: Applied Research*. 2016;7(1):137-142. DOI:10.1134/S2075113316010081

32. Digonskiy SV. *Gas-phase processes of synthesis and sintering of refractory substances (silicon carbide, pyrographite, diamond, cubic boron nitride)*. Moscow: GEOS; 2013. 464 p. (In Russ.)

33. Dolmatov VYu, Ozerin AN, Kulakova II, Bochechka OO, Lapchuk NM, Myllymaki V, Vehanen A. Detonation nanodiamonds: new aspects in the theory and practice of synthesis, properties and applications. *Russian Chemical Reviews*. 2020;9(12):1428-1462. DOI:10.1070/RCR4924

34. Novikov VP, Dymont VP. Synthesis of diamondlike films by an electrochemical method at atmospheric pressure and low temperature. *Applied Physics Letters*. 1997;70(2):200-202. DOI:10.1063/1.118355

35. Aublanc P, Novikov VP, Kuznetsova LV, Mermoux M. Diamond synthesis by electrolysis of acetates. *Diamond and Related Materials*. 2001;10:942-946. DOI:10.1016/S0925-9635(00)00548-3

36. Linnik SA, Zenkmn SP, Gaidaichuk AV. Heteroepitaxial growth of diamond from the gas phase: problems and prospects (review). *Pribory i tekhnika eksperimenta = Instruments and Experimental Techniques*. 2021;2:5-18. DOI:10.31857/S0032816221010328 (In Russ.)

37. Bachman PK, Leers D, Lydtin H. Towards a general concept of diamond chemical vapour deposition. *Diamond and Related Materials*. 1991;1(1):1-12. DOI:10.1016/0925-9635(91)90005-U

38. Vorobyov AE, Vorobyov KA. *Nanodiamonds*. Moscow: Mir Nauki; 2018. 161 p. (In Russ.)

39. Gubarevich TM, Kostyukova NM, Sataev RR, Fomina LV. Investigation of the microimpurity composition of ultradispersed diamond. *Sverkhтвердые материалы = Journal of Superhard Materials*. 1991;5:30-34. (In Russ.)

40. Gubarevich TM, Turitsyna OF, Poleva LI, Tyshetskaya AV. Active hydrogen on the surface of ultradispersed carbon. *Zhurnal prikladnoy khimii = Russian Journal of Applied Chemistry*. 1992;65:1269-1273. (In Russ.)

41. Simakov SK. Nano- and micron-sized diamond genesis in nature: An overview. *Geoscience Frontiers*. 2018;9:1849-1858. DOI:10.1016/j.gsf.2017.10.006

42. Meilunas RJ, Chang RPH, Liu S, Kappes MM. Nucleation of diamond films on surfaces using carbon clusters. *Applied Physics Letters*. 1991;59(26):3461-3463. DOI:10.1063/1.105678

43. Vityaz PA, Kheifets ML, Senyut VT, Kolmakov AG, Klimenko SA. Methods of physicochemical analysis and multifractal parametrization in the process of diamond nanostructured composites formation at high pressures and temperatures. *Advanced Materials and Technologies*. 2019;3:26-40. DOI:10.17277/amt.2019.03.pp.026-040

44. Dolmatov VYu. *Ultradispersed Diamonds of Detonation Synthesis. Production, Properties, and Applications*. St. Petersburg: St. Petersburg State University; 2003. 344 p. (In Russ.)

45. Vityaz PA, Senyut VT, Il'yushchenko AF, Heyfez ML, Solntsev KA, Barinov SM, Kolmakov AG. Influence of thermobaric treatment on structure and

mechanical and physical properties of schungite carbon. *Inorganic Materials: Applied Research*. 2013;4(1):60-65. DOI:10.1134/S2075113313010127

46. Senyut VT, Kovaleva SA, Rzhetsky VA, Markova LV, Gamzeleva TV, Kheifets ML. *Analysis of the structure of superhard nanocomposites based on nanodiamonds and dense forms of boron nitride*. Migun NP (ed.). Minsk: Institute of Applied Physics of the NAS of Belarus; 2013. p. 328-334 (In Russ.)

47. Bochechka AA. Features of nanodispersed diamond powders and their consolidation under exposure to high pressure and temperature (Review). *Sverkhtverdyye materialy = Journal of Superhard Materials*. 2003;5:3-10. (In Russ.)

48. Danilenko VV. *Synthesis and sintering of diamonds by explosion*. Moscow: Energoatomizdat; 2003. 272 p. (In Russ.)

49. Varfolomeeva TD, Lyapin AG, Popova SV, Borovikov NF, Zibrov IP, Brazhkin VV. Behavior of detonation nanodiamond at high pressures and temperatures in the presence of hydrogen-containing fluid. *Inorganic Materials*. 2016;52:351-356. DOI:10.1134/S0020168516040142

50. Dideikin AT, Eidelman ED, Kidalov SV, Kirilenko DA, Meilakhs AP, Shakhov FM, Shvidchenko AV, Sokolov VV, Babunz RA, Vul AY. Oriented-attachment growth of diamond single crystal from detonation nanodiamonds. *Diamond and Related Materials*. 2015;75:85-90. DOI:10.1016/j.diamond.2017.02.009

51. Bogatyreva GP, Voloshin MN, Marinich MA et al. Surface and electrophysical properties of detonation synthesis nanodiamond. *Sverkhtverdyye materialy = Journal of Superhard Materials*. 1999;6:42-46. (In Russ.)

52. Vityaz PA, Zhornik VI, Kukareko VA, Komarov AI, Senyut VT. *Modification of materials and coatings by nanosized diamond-containing additives*. Minsk: Belaruskaya nauka Publ.; 2011. 522 p. (In Russ.)

53. Gordeev SK. Nanoporous and nanofragmental carbon composite materials. In: Benedek G, Milani P, Ralchenko VG (eds.). *Nanostructured Carbon for Advanced Applications*. NATO Science Series, vol. 24. Dordrecht: Springer; 2001. p. 71-88. DOI:10.1007/978-94-010-0858-7\_4

54. Bogatyreva GP, Nikitin YuV, Poltoratsky VG. Obtaining superhard composite materials at low pressures. *Sverkhtverdyye materialy = Journal of Superhard Materials*. 1996;1:30-36. (In Russ.)

55. Vityaz PA, Senyut VT, Kheifets ML. Synthesis of polycrystalline superhard materials from modified nanodiamonds. *Izvestiya natsional'noy akademii nauk Belarusi. Seriya fiziko-tehnicheskikh nauk*. 2016;3:5-10. (In Russ.)

56. Brodsky AM, Kalinenko RA, Lavrovsky KP, Shevelkova LV, Yampolsky YuP. On the patterns of transformations of ethylene and acetylene during high-temperature decomposition of hydrocarbons. *Doklady Akademii nauk SSSR*. 1965;163(4):920-923. (In Russ.)

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