

Synthesis of Superhard Materials Based on Sphalerite Boron Nitride Using Carbon Nanoparticles as a Phase Conversion Catalyst

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Abstract

Using modern ideas about the form of the phase diagram of boron nitride, the paper considers thermodynamic parameters and mechanisms of the synthesis of dense phases of boron nitride under equilibrium and nonequilibrium conditions. It has been verified that nanodiamonds, like fullerenes and carbon nanotubes, have catalytic properties and contribute to the solid-state conversion of graphite-like boron nitride to sphalerite modification at high pressures and temperatures.

We propose a mechanism for the interaction of nanodiamond under high pressures with the surface of graphite-like boron nitride, which leads to a change in the type of electronic bond in its lattice from sp^2 to sp^3 with the formation of boron nitride with a wurtzite structure and its subsequent transformation into sphalerite boron nitride by the shear mechanism.

The use of carbon-coated nanodiamonds resulted in an increase in the catalytically active centers of phase transformation in boron nitride in comparison with unmodified nanodiamonds, which was manifested in an increase in the content of sphalerite boron nitride in materials obtained under comparable technological synthesis conditions. Modified nanodiamonds also contribute to the intensification of the synthesis of superhard polycrystals as compared to uncoated nanodiamond additives, both due to the diffusion of carbon atoms along the grain boundaries of sphalerite boron nitride and due to the rearrangement of graphite microgroups into a diamond structure and sintering of the obtained diamond blocks with grains of sphalerite boron nitride.

The process parameters of obtaining superhard polycrystals based on sphalerite boron nitride with the addition of detonation nanodiamond powders after chemical cleaning and surface modification with non-diamond forms of carbon were found.

Keywords

Fullerenes; nanodiamonds; physicochemical analysis; state diagram of boron nitride; phase transformations; high pressures and temperatures.

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Introduction

The synthesis of sphalerite boron nitride (**cBN**) is caused by phase transformations of the original hexagonal boron nitride (**hBN**) under conditions of high pressures and temperatures. Process factors such as temperature, high pressure, strain rate, the presence of impurities, shear deformations significantly affect the occurrence of phase transformations in boron nitride and the formation of the microstructure of the material. One of the important conditions for the

formation of cBN is a decrease in the activation energy of phase transformation. In highly defective structures, the activation barrier of conversion decreases due to the high energy of elastic distortion of the crystal lattice near defects. An important role is also played by the structural perfection of the initial modification of boron nitride, solvent catalysts, and activating phase transitions of the additive, which can significantly reduce the temperature and pressure of nucleation of superhard phases [1].

Phase diagram of the state of boron nitride

The current understanding of the phase diagram of boron nitride is based on Ventorf's experimental results on the catalytic conversion of hBN to cBN at pressures above 4.0 GPa and on the melting process of hBN in the pressure range 3.0–7.0 GPa. Based on experimental data, as well as estimates of the position of the melting curve of cBN and the triple point of hBN–cBN–liquid, Bundy constructed a phase diagram of boron nitride, which is currently generally accepted [2].

In thermodynamic calculations of the hBN–cBN equilibrium curve, the values of the ΔH_{cBN} formation enthalpy (298.15 K) determined from the experimental equilibrium curve at high pressures and temperatures were used [3]. Due to the low accuracy of measuring p - and T -parameters in a thermobaric experiment, the error in determining the polymorphic transformation enthalpy used in the calculation can be quite large, therefore, the calculated position of the equilibrium line of boron nitride is also not very accurate.

In the chemical interaction in the B–N system at high pressures in a wide range of p , T -parameters, metastable crystallization of hBN takes place, which indicates the decisive role of kinetic factors in the formation of boron nitride. A significant influence on the polymorphic conversion of hBN–cBN can be exerted by trace amounts of oxygen (free and/or bound), leading to a decrease in the onset temperature of hBN conversion due to metastable crystallization of hBN in the B–N–O system. The foregoing makes us critically refer to attempts to construct the equilibrium curve of hBN–cBN, based on experimental data on the conversion of hBN–cBN. On the other hand, the thermochemistry of the interaction of cBN with elemental fluorine was studied by the method of fluorine calorimetry and the standard enthalpy of cBN formation was determined. Using this value, we calculated the temperature dependence of the Gibbs value change during the polymorphic transformation of a graphite-like modification of boron nitride into cubic and showed that at atmospheric pressure, the thermodynamically stable modification of boron nitride in the temperature range 0–1570 K is cBN, not hBN, as previously thought [4]. An alternative equilibrium phase p , T -diagram of boron nitride obtained by Solozhenko indicates the possibility of cBN synthesis at pressures and temperatures below the equilibrium line of the hexagonal and sphalerite phases on Corrigan – Bundy the p , T -diagram [5]. In practice, in most cases, cBN synthesis with the participation of catalysts is carried out at pressures and temperatures significantly exceeding the position of the equilibrium

line in the traditional phase diagram. This discrepancy can be explained by a significant amount of interfacial energy at the cBN–melt interface, higher than in diamond synthesis, critical cBN nucleation energy, high growth activation energy, lower diffusion coefficient of boron nitride in melts based on systems traditionally used for the synthesis of cBN. All this leads to a relatively low nucleation rate of cBN and makes it impossible to crystallize cBN below the threshold temperature even when a liquid phase appears in the system.

The state diagram of boron nitride as a function of pressure and temperature (Fig. 1) shows that there are a number of regions behind the liquid phase. In zone “h”, hexagonal boron nitride is stable, and boron nitride with a crystal structure of the wurtzite and sphalerite type is metastable in zones “w” and “sp”. In the “sp” zone, boron nitride is sphalerite stable, while boron nitride is hexagonal metastable [6].

The mechanism of formation of sphalerite boron nitride is more complex than the mechanisms of diamond formation. Ventorf proposed a model for the formation of cBN [7], according to which the metal reacts with boron nitride to form a MeN–BN-type complex in which BN dissolves, and cBN crystallizes in the melt under appropriate thermodynamic conditions. The phase transformation mechanism in which boron nitride of hexagonal modification is adsorbed by molten metal and then desorbed from it under certain p , T -conditions in the form of sphalerite boron nitride is described in [7, 8]. In [9, 10], a mechanism was proposed for the catalytic conversion of hexagonal boron nitride to sphalerite.

Currently, there is no generally accepted model for the phase transformation (in the presence of metals and their nitrides) of hexagonal boron nitride to sphalerite boron nitride. At the same time, experimental data show that the mechanism proposed by R.Kh. Ventorf is most often manifested [7].

Due to significant supersaturations at the initial stage and high growth rates, cBN crystals grow under cramped conditions; this determines the features of their morphology. Depending on the growth conditions, composition, and properties of the crystallization medium, the grown sphalerite boron nitride consists of aggregates, growth druses, recrystallization products, intergrowths, or single crystals of various degrees of crystalline perfection [10].

The topological model (Fig. 1b) of the state diagram of boron nitride (Fig. 1a) was built on the basis of studying the number of degrees of freedom during the formation of system bonds during the introduction of new components [10]. The analysis of the formation of the system bonds, covering the metastable state

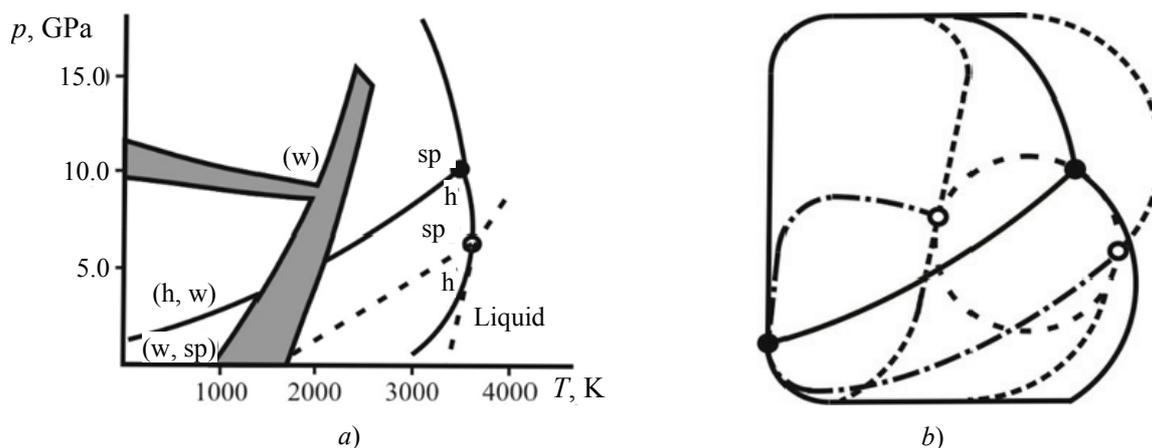


Fig. 1. Phase diagram of the state of boron nitride by F.R. Corrigan and F.P. Bundy (solid lines and shaded areas), V.L. Solozhenko (dashed lines) (a) and the topological model corresponding to the physicochemical system (b)

of the phases (Fig. 1a) and describing the various mechanisms of phase transformations of boron nitride (Fig. 1b), shows that only when considering new sites (not hatched points) from the standpoint of the formation of new chemical compounds, given the lines that distinguish their solutions (dashed lines in Fig. 1b), the stability of metastable states of a non-equilibrium system is ensured.

As shown in [11], the introduction of easily decomposed hydrogen and nitrogen-containing compounds into the batch for cBN synthesis leads to a decrease in the surface energy of the cBN melt interface and a lower work function for the formation of critical cBN nuclei. In addition, in the presence of fluid phases, the crystallization pressure of cBN in traditional growth systems decreases significantly. For example, in the hBN–MgB₂–NH₃ system, crystallization of boron nitride at temperatures of 1300–1500 K and a holding time of 1000 s was observed up to a pressure of 2.1–0.1 GPa [12]. The study of spontaneous crystallization of cBN in a supercritical fluid of the N–H system with a low viscosity showed that cBN is formed up to a pressure of 1.9 GPa, i.e. at significantly lower pressures under the conditions of thermodynamic stability of hBN according to the classical phase diagram of boron nitride [13].

Successful attempts to synthesize cBN at temperatures up to 500 °C and atmospheric pressure are also known, which is in full agreement with the proposed state diagram and indicates the decisive role of kinetic factors in the synthesis of cBN [1].

Carbon nanostructures as a catalyst for the phase transformation of hBN–cBN

Currently, along with traditional catalytically active substances, it is proposed to use nanoparticles of certain allotropic forms of carbon as a catalyst for the

synthesis of superhard materials. For example, in [14], C₆₀ fullerenes or mixtures of C₆₀ and C₇₀ fullerenes were used as a co-catalyst for the synthesis of diamond at high pressures and temperatures and were added as a small additive to 0.3 wt. % to graphite with a metal catalyst. The experiments showed that the conversion coefficient of graphite–diamond with fullerene co-catalyst increases by 1.8 times, *ceteris paribus*. In [15, 16], a model was proposed for the catalytic action of the fullerene molecule on the phase transition of graphite to diamond. Let us dwell on the consideration of this mechanism.

The possibility of modifying the carbon surface (graphite surface) with fullerenes and fullerene-like materials due to the high affinity between them [18] was shown in [17].

Due to the presence of C=C double bonds, the fullerene molecule is capable of a reversible cycloaddition reaction [19]. Polymerization of fullerenes (photochemical or under pressure) occurs by the mechanism of cyclic distribution [2 + 2].

By a similar mechanism, the reaction of the addition of fullerenes to aromatic hydrocarbons can be carried out. In Fig. 2a shows an example of the reaction of cycloaddition of fullerene with dehydrobenzene [20].

Since the initial unit cell of the graphite network is a benzene molecule devoid of hydrogen [21], the bond between the graphite (graphene) plane and the fullerene molecule can also be realized via the cycloaddition mechanism.

At the temperature and pressure of the synthesis of diamond from graphite, fullerene, located near the edge of the graphene plane, undergoes a cycloaddition reaction with it, forming structures similar to anhydrous adamantane (Fig. 2b).

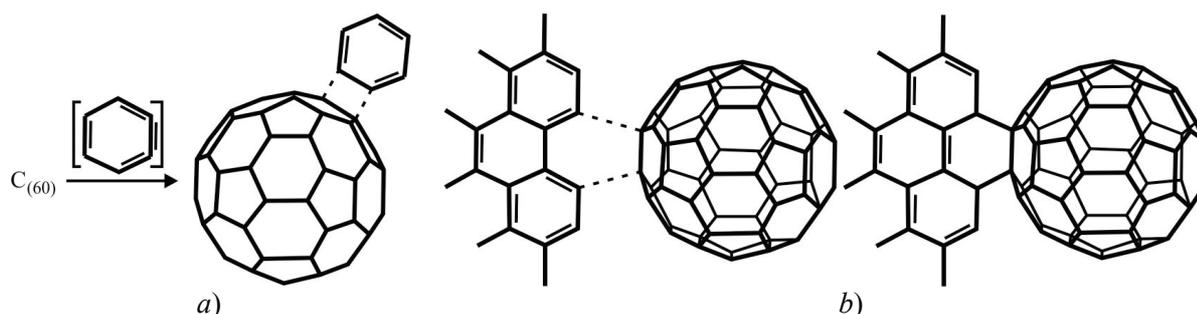


Fig. 2. Reaction scheme:

- a* – dimerization (cycloaddition [2 + 2]) of C_{60} fullerene molecule with dehydrobenzene [20];
b – cycloaddition of the C_{60} fullerene molecule to the edge of the graphene plane (using an example of a fragment of the graphene plane similar to the phenanthrene molecule) [15]

Adamantane-like structures are the nuclei of the diamond phase, which, in turn, as a result of the cycloaddition reaction, initiates a further transformation of the graphite lattice in the sp^2 state into a diamond lattice with the sp^3 state of carbon atoms. As a diamond crystal grows, the energy of a virtual double bond on its surface decreases and the process of diamond formation stops [16, 20].

This model allows us to qualitatively explain the increase in the degree of conversion of graphite-diamond when fullerenes are introduced into a mixture of a catalyst with graphite. It is important to note that due to the action of metal catalysts, additional deformation of the planar graphene structure can occur, which will contribute to the reaction of the graphite surface with fullerene [15, 20].

Crystalline boron nitride is the closest isoelectronic analog of carbon and, like it, exists in several polymorphic modifications. So, hBN, like graphite, has a layered structure and can be considered as a crystallographic analogue of graphite [10].

Just as the initial unit cell of a graphite network can be represented as a benzene molecule devoid of hydrogen, the initial unit cell of the hBN network can be represented by the dehydrogenated borazole molecule $B_3H_6N_3$. As a result of polycondensation of borazole or its polycyclic derivatives, hBN can form upon heating [21]. (For example, during the pyrolysis of borazole at a temperature of about 300 °C boron nitride is formed with a structure similar to that of graphite).

In [22], based on the theory of the density functional, taking into account the weak Van der Waals interaction, the possibility of the formation of covalent bonds of C_{20} fullerene with various two-dimensional structures was theoretically considered (Fig. 3). Based on the calculation results, it can be concluded that the C_{20} fullerene weakly interacts with the planar structures of graphene, BN, MoS_2 (Fig. 3*a-c*). In this case, the corrugation of 2D-crystals facilitates the redistribution of electron density in the interface region of the C_{20}

molecule and the surface of the monolayer with the formation of covalent bonds between the 2D-crystal and fullerene (Fig. 3*d-f*).

Fig. 3 presents the optimal configurations of the molecule of C- and 2D-crystals of various substances obtained on the basis of calculations [22].

Similarly to the above-considered model for the synthesis of diamond from graphite, the reaction of cycloaddition of fullerene (fullerene-like onion carbon) to the surface of hBN particles at high pressures and temperatures will also lead to the formation of a diamond-like (as in the case of diamond synthesis, an adamantane-like structure) and subsequent nucleation of boron nitride crystals with sphalerite structure. As in the fullerene-graphite system considered above, the development of the interaction process leads to a rearrangement of the entire graphite-like structure, initiated by local rearrangement of the hBN lattice with sp^2 type of hybridization into a lattice with sp^3 hybridization of atoms.

An example of the implementation of solid-phase synthesis of cBN from hBN without dissolving the initial graphite-like boron nitride using carbon nanoparticles was given in [23]. In this patent, carbon nanotubes (CNTs) were proposed to be used as a co-catalyst for phase transformation, the end surfaces of which are hemispheres – half of fullerene molecules, as well as nanofibers (NF). Due to their high catalytic activity, CNT and NF additives contribute to the complete conversion of hBN and graphite into dense phases at substantially lower synthesis temperatures and the formation of a fine-grained structure of the obtained superhard polycrystals.

A key factor in the process of conversion of hBN to cBN in the nanocarbon-hBN system is high pressure, which enhances the thermodynamic stimulus of phase transformation and stimulates the interaction of carbon nanoparticles with the surface of hBN particles, including, for example, due to deformation (corrugation) of the 002 hBN plane.

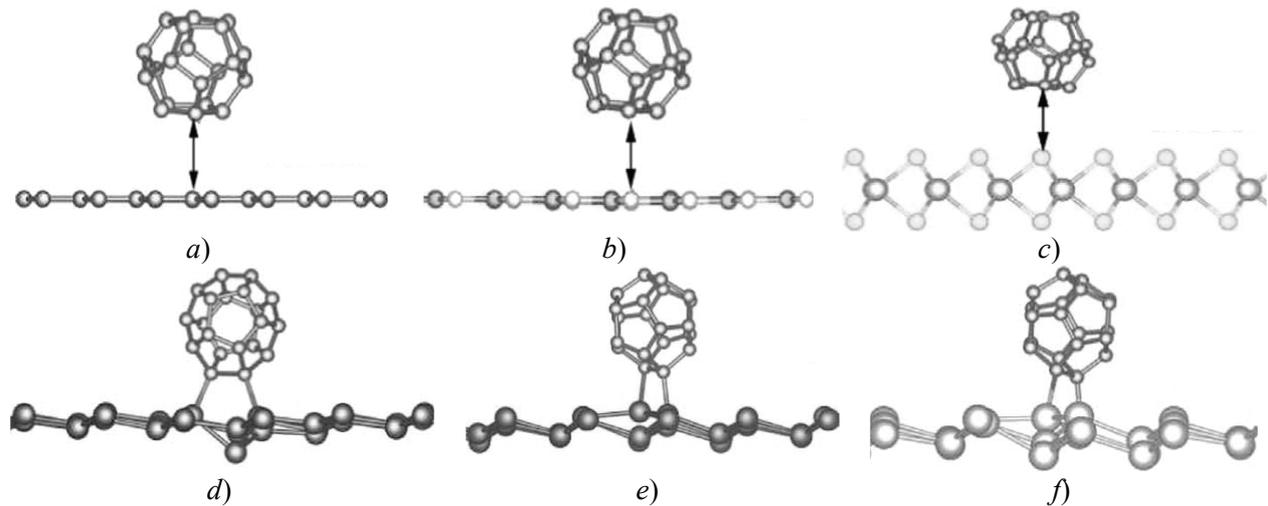


Fig. 3. The most stable atomic configurations of complexes:

a – C₂₀/graphene (2.93 Å); *b* – C₂₀/BN (2.88 Å); *c* – C₂₀/MoS₂ (3.0 Å);
d – C₂₀/Si (1.67 Å); *e* – C₂₀/Ge (1.74 Å); *f* – C₂₀/Sn (1.37 Å)

On the other hand, structural defects in hBN that occur when exposed to high pressures and temperatures in the presence of nanocarbon particles will also contribute to the nucleation of dense boron nitride phases.

Graphitization of nanodiamonds at high temperatures

Nanodiamonds are one of the most chemically active known forms of carbon with a highly active state of the surface, the value of which can reach 400 m²/g. Each crystallite has a large number of unpaired electrons – $(3-7) \cdot 10^{19}$ spin/cm³ and is a powerful multiple radical [24]. After chemical cleaning of impurities and non-diamond forms of carbon on the surface of nanodiamonds, a carbon shell with a thickness of 1–2 atomic layers is formed spontaneously in the sp² state, which is stable at room temperature and atmospheric pressure [25, 26]. Heat treatment under vacuum along with the removal of

adsorbed and chemisorbed impurities additionally contributes to the formation of graphite-like carbon on the surface of nanodiamond particles [27].

Vacuum annealing of nanodiamond particles at elevated temperatures (1000–2400 °C) leads to the formation on their basis of onion-like carbon (OLC) with a structure similar to fullerenes. With increasing annealing temperature, the number of graphite-like layers increases due to the diamond “core”, the size of which decreases [28]. Fig. 4 shows OLC samples obtained by high-temperature graphitization of nanodiamond particles in vacuum at various annealing temperatures. At temperatures of 1000–1500 °C, nanodiamond particles form, the core of which preserves the diamond structure, and the peripheral zone consists of sp² carbon layers (sp²–sp³ carbon nanocomposite). At annealing temperatures above 1500 °C (1800 K), the nanodiamond particles completely transform into onion-like carbon [29].

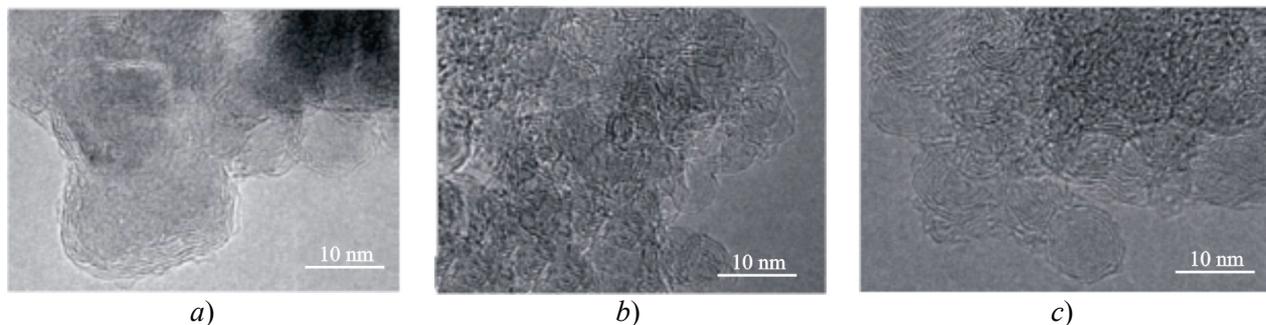


Fig.4. High resolution TEM OLC obtained by vacuum annealing nanodiamond particles at a value of vacuum of 10⁻⁶ Torr for 1 hour at 1400 K (a), 1650 K (b), 1850 K (c) [28]

It should be noted that with an increase in the annealing temperature, there is also an increase in the concentration of structural defects in the OLC formed on the basis of nanodiamond and an increase in the density of localized states of charge carriers associated with it at the Fermi level $N(E_F)$ [28]. 1000 °C is also observed during thermobaric treatment under conditions of high pressures and temperatures in the region of thermodynamic stability of graphite and diamond [30, 31].

The use of nanodiamonds as a catalyst for the phase transformation of hBN–cBN

For the synthesis of superhard material, we used technical hBN powder manufactured at PJSC “Zaporizhzhya Abrasive Plant” with particle sizes of 1–20 μm , a degree of three-dimensional ordering of 0.85, and a graphitization index of 1.45. As a phase transformation catalyst in boron nitride, a purified nanosized diamond powder produced by Sinta CJSC (Minsk, Belarus) with a content of non-combustible impurities of 1 wt. %. The powders were mixed in a ratio of 10 and 90 wt. %, 20 and 80 wt. % and 50 and 50 wt. % hBN and nanodiamond particles, respectively [32, 33]. Then, in a steel mold from mixtures, cylindrical billets with a diameter of 6 mm and a height of 5 mm were pressed.

Thermobaric treatment of the samples was carried out in an “anvil with a hole” high-pressure apparatus (HPA) at pressures of 4.2–7.0 GPa in the temperature range 300–2000 °C, and the processing time was 10–300 s (Fig. 5).

A container made of lithographic stone served as a pressure transmitting medium, inside of which was placed a tubular graphite heater with the studied material. Temperature control was carried out using chromel-alumel and platinum-platinum-rhodium thermocouples. Process parameters were controlled using a controller made on the basis of a PC-compatible industrial computer with a built-in graphical LCD-display and keyboard.

Under the action of high pressures, the grains of the hBN powder are crushed, while the level of intragranular defectiveness increases, as indicated by the broadening of diffraction lines. It is known [34] that during the pressing of initial billet from hBN, their strong texturing occurs. The grains of the powder are oriented hexagonal planes perpendicular to the direction of application of the pressing force.

The X-ray diffraction method showed that the formation of cBN from hBN with the addition of nanodiamond as a catalyst occurs at abnormally low temperatures. Thus, the presence of the cBN phase is

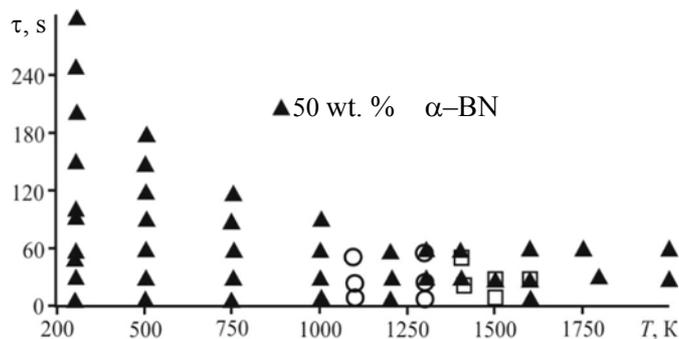


Fig. 5. The transformation region is hBN → cBN in temperature–time coordinates. Synthesis pressure 7 GPa

observed in samples obtained at a pressure of 7 GPa, temperatures of 250–300 °C, and exposure of 250–300 s [35]. An increase in the heating temperature at the same pressure leads to a further decrease in the cBN synthesis time. At a temperature of 600 °C, the presence of cBN is observed after isothermal exposure for 100–150 s (Fig. 6a), and at a temperature of 1000 °C after 60 s of synthesis. In this case, a feature of the solid-state transition hBN → cBN is the formation of a wurtzite phase wBN at the initial stage of transformation. For example, in the synthesis products obtained at a temperature of 1000 °C and isothermal exposure time of 10–15 s, the hBN and wBN phases are recorded without the presence of the cBN phase (Fig. 7a).

With a further increase in temperature, the cBN synthesis time decreases (Fig. 6b). Fig. 7b shows an electron microscopic (TEM) image of cBN particles synthesized at 1300 °C and isothermal exposure for 15 s.

An increase in the synthesis temperature leads to an increase in the intensity of cBN X-ray reflections, and an increase in isothermal exposure leads to a decrease in the intensity of hBN reflexes (Fig. 6c, d). At higher synthesis temperatures [35], a decrease in the intensity of lines corresponding to the nanodiamonds is noted. This may be due to partial graphitization of the nanodiamond occurring at high temperatures. To temperatures of 1900–2000 °C at a pressure of 7 GPa, partial graphitization of a nanodiamond does not lead to the development of the reverse transformation cBN → hBN.

Based on the data obtained, during thermobaric treatment of the mixture at the initial stage of conversion, wBNwBN is formed, and the synthesis temperature is accompanied by its transition to cBN at the second stage of the process. According to a number of signs (the absence of usually observed orientations between the initial and the resulting phases of boron

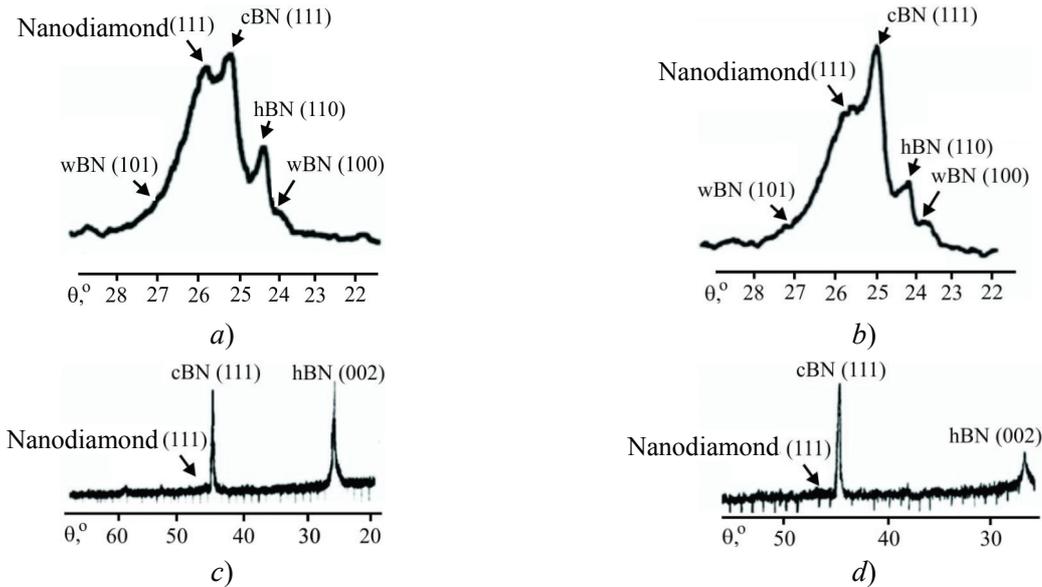


Fig. 6. Diffraction pattern (CoK α) of a cake from a nanodiamond mixture (50 wt. %) + hBN(50 wt. %) after thermobaric treatment at a pressure of 7 GPa:

a – temperature 600 °C, holding time 150 s; *b* – temperature 1300 °C, holding time 15 s; *c* – temperature 1600 °C, holding time 30 s; *d* – temperature 1600 °C, holding time 60 s

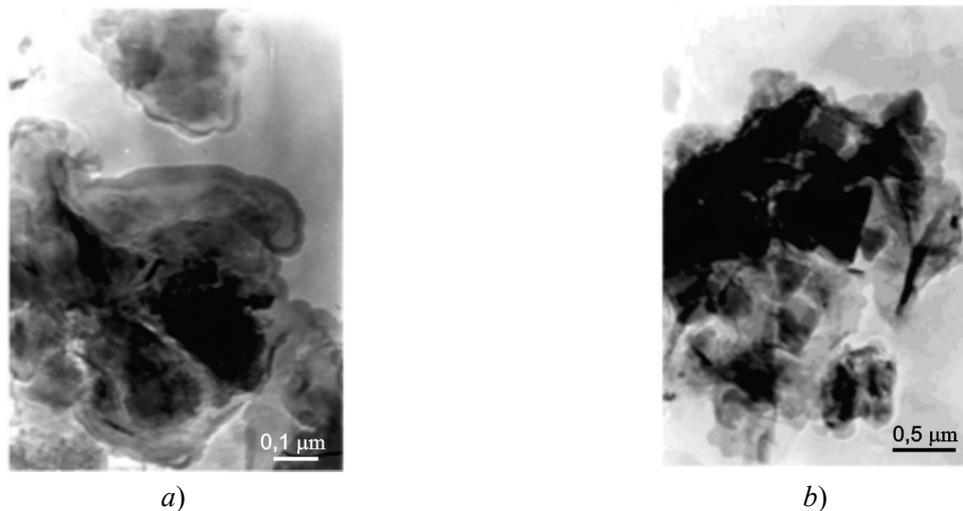


Fig. 7. Electron microscopic image:

a – portion of the cake containing hBN and wBN phases (dark areas) formed at the initial stage of solid-phase conversion of hBN particles to cBN (pressure 7 GPa, temperature 1000 °C, holding time 15 s); *b* – tetrahedral cBN particle after synthesis at a pressure of 7 GPa, a temperature of 1300 °C, and a holding time of 15 s

nitride [8], the use of activating additives, as well as the range of pressures and temperatures at which synthesis is carried out), we can speak of a catalytic transformation mechanism.

On the other hand, the observed sequence of hBN \rightarrow wBN \rightarrow cBN transitions is characteristic of direct phase transformations in boron nitride, combining the shear (hBN \rightarrow cBN transition and diffusion (wBN \rightarrow cBN transition) synthesis mechanisms [8, 10].

In contrast to the direct transition of hBN to cBN, which occurs at pressures of 7–10 GPa and

temperatures of 1700–2500 °C, also through the formation of an intermediate wurtzite phase, [34] the conversion of hBN into dense forms of boron nitride (wBN and cBN) at high pressures using nanodiamond particles was observed at significantly lower temperatures.

For the hBN-nanodiamond system, the following phase formation mechanism can be proposed. Under high pressure conditions, the nanodiamonds interact with the surface of hBN particles, which leads to deformation of the 002 hBN plane by the corrugation mechanism and a change in the type of electronic bond

in the lattice of boron nitride from sp^2 to sp^3 with the formation of wBN.

With an increase in temperature, the graphite-like structure of boron nitride is further rearranged through the wurtzite phase to the sphalerite modification. In this case, elongation of the Laue reflections of the cBN phase (in the diffraction pattern) is observed in microdiffraction patterns, which may indicate the appearance of strong internal stresses and the shear nature of the transition of wBN to cBN. The shear transformation mechanism is also confirmed by the presence of a deformation substructure of cBN crystals, including traces of plastic shifts in the (111) cBN plane.

At synthesis temperatures above 2000 °C in boron nitride, the thermal activation of the slip of partial dislocations and the transition of metastable wBN to cBN by the diffusion mechanism occur [8, 10].

At synthesis temperatures above 2300 °C and a pressure of 7 GPa, the process of reverse phase transformation of cBN to hBN begins. A decrease in the synthesis pressure leads to a decrease in the temperature of the reverse phase transformation in hBN.

Synthesis of a superhard material based on cBN from hBN with additives of nanodiamond particles modified with non-diamond carbon

Thermobaric treatment of hBN with the addition of nanodiamond particles was carried out in the field of catalytic synthesis at pressures of 4.2–6.0 GPa.

Detonation synthesis nanodiamond powder with a crystallite size of 4–10 nm, the particle surface of which was modified by carbon by gas-phase deposition [36] according to the Boudoir reaction $2CO = CO_2 + C$, was used as a phase-conversion catalyst.

For the synthesis of superhard material, a charge with a nanodiamond content of 2–10 wt. % was used. The hBN micropowder with a particle size of up to 20 μm was used as the basis of the charge. Fig. 8 shows the structure of samples of superhard cBN-based material on obtained at various synthesis parameters.

The experimental results allowed us to establish that the content of cBN in the material after synthesis increases with temperature from 1300 to 1750 °C and the exposure time from 15 to 45 s. By X-ray diffraction analysis, it was shown that under optimal synthesis conditions, the phase composition of the material samples is represented mainly with cBN. The size of the synthesized cBN particles in the material decreases with increasing pressure and increases with increasing temperature and the duration of isothermal exposure.

The use of carbon coated nanodiamond particles leads to an increase in the catalytically active centers of phase transformation in boron nitride as compared to unmodified particles, which is manifested in an increase in cBN content in materials with different types of additives (nanodiamond particles with and without carbon coating) obtained with comparable technological modes of synthesis.

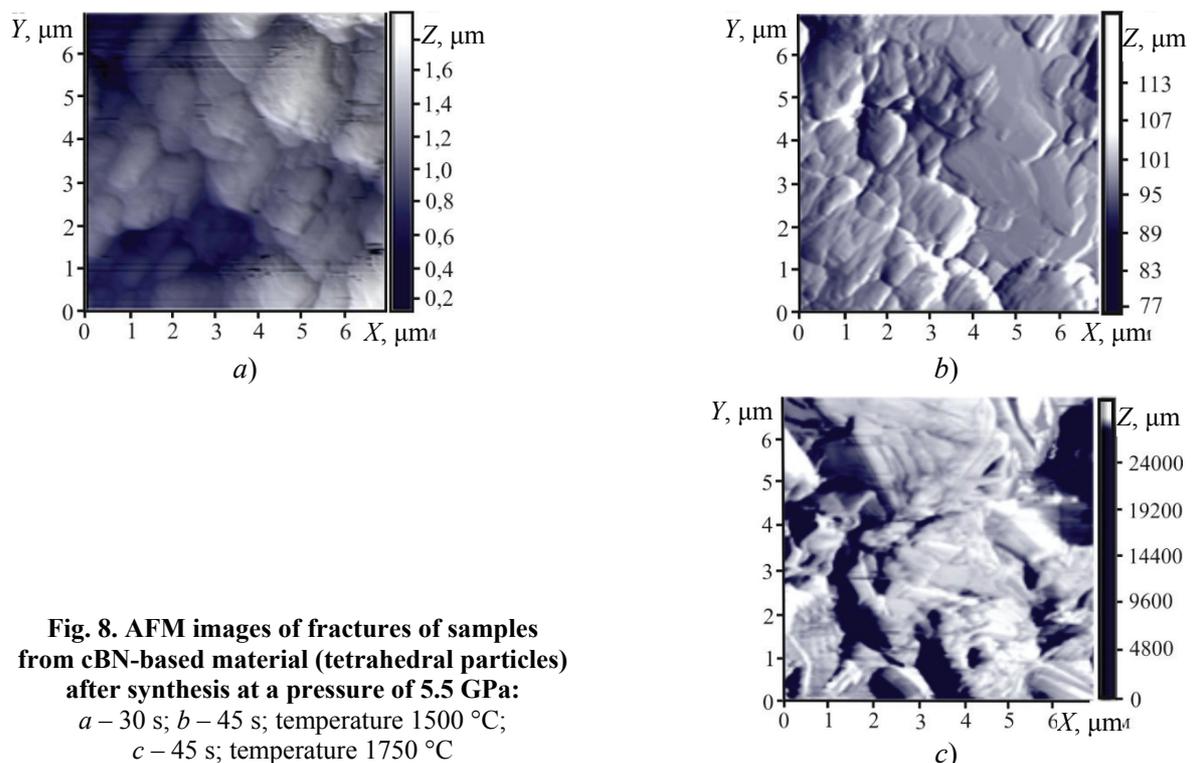


Fig. 8. AFM images of fractures of samples from cBN-based material (tetrahedral particles) after synthesis at a pressure of 5.5 GPa: *a* – 30 s; *b* – 45 s; temperature 1500 °C; *c* – 45 s; temperature 1750 °C

Modified nanodiamond particles also additionally contribute to the sintering (recrystallization) of cBN crystals compared to such uncoated particles (Fig. 8c) due to the diffusion of surface carbon atoms along the cBN grain boundaries and due to the rearrangement of graphite microgroups in the coating into a diamond structure and sintering of the obtained diamond layers and nanodiamond particles with cBN grains at high pressures and temperatures [37, 38].

At high temperatures, nanodiamond particles can also serve as nuclei for the growth of cBN crystals without the formation of an intermediate wBN by the diffusion mechanism.

It can be concluded that in the case of using nanodiamond particles modified with non-diamond carbon, the synthesis of superhard material based on cBN occurs in a manner similar to the catalytic one, including the interaction of nanodiamond particles and hBN, the formation of wBN, the transformation of which into cBN is then carried out by the diffusionless (martensitic) mechanism. An increase in the temperature and synthesis time leads to sintering of crystals (polycrystals) and to the growth of cBN particles formed as a result of recrystallization by the diffusion mechanism. Owing to metastability, wBN is not retained in the final product at given technological synthesis parameters.

Conclusion

The possibilities of using carbon nanostructures as catalysts for the phase transformation of layered modifications of carbon and boron nitride (graphite and hBN) into diamond and cBN under conditions of high pressures and temperatures are considered. It has been shown that nanodiamonds along with fullerenes and carbon nanotubes can activate the transition of hBN to cBN, due to the presence on their surface of thin layers of non-diamond carbon with an onion structure similar to that of fullerenes.

A mechanism has been proposed for the formation of cBN from hBN, which occurs at high pressures and temperatures in the presence of nanodiamond particles, which consists in the interaction of these particles with the hBN surface, corrugation of the 002 hBN plane, and the formation of cBN through a wurtzite modification in the region of its stability.

The use of nanodiamond particles, additionally modified with non-diamond carbon, leads to an increase in the catalytically active centers of cBN formation compared to unmodified nanodiamond particles and an increase in cBN content in the final product.

Modified nanodiamond particles contribute to the recrystallization and sintering of cBN crystals in the material, both due to the diffusion of carbon atoms and sintering of thin diamond layers and nanodiamond particles with cBN grains formed during the synthesis.

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