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## EFFECT OF MECHANICAL ACTIVATION AND HIGH PRESSURE HIGH TEMPERATURE TREATMENT ON SYNTHESIS OF MATERIAL BASED ON NANOSTRUCTURED BORON NITRIDE

*In the paper, the study of the influence of mechanical activation (MA) and subsequent high pressure high temperature (HPHT) treatment of the powder of hexagonal boron nitride (hBN) on its structure and phase composition is given. X-ray diffraction and electron microscope studies show that MA leads to the transformation of the BN substructure from crystalline to nanocrystalline and amorphous. At the same time, along with the formation of amorphous nanocrystalline cubic boron nitride (cBN) in BN powders after MA, another high-pressure phase — wurtzite boron nitride wBN is formed. As a result of sintering of the hBN powders after MA under pressure of 2.5 GPa and under temperature in the range of 1000–1300 °C, in addition to the hBN, wBN and cBN phases, the BN phases of rhombic, hexagonal and tetragonal crystallographic systems are formed in the resulting material. The HPHT treatment of the hBN powders after MA under pressure of 7 GPa allows to obtain a material containing a cBN phase with cBN crystallites about 50 nm in size. The addition of aluminum decreases the sintering pressure, but at the same time, due to recrystallization, the grain size of cBN in the obtained material increases by an order of magnitude compared with the original powder.*

**Keywords:** nanocrystalline BN, mechanical activation, chemical purification, high pressure high temperature

**Introduction.** At the present time the important task of scientific and technological progress is the improvement and development of existing and new

technologies for the synthesis of superhard materials (SHM) — diamond and cubic boron nitride (cBN). The current understanding about the phase diagram of

BN is based on the experimental data of Wentorf on the study of the catalytic transformation of hexagonal BN (hBN) to cBN under pressure above 4.0 GPa and the study of the melting process of hBN in the pressure range of 3.0–7.0 GPa. In the work of Bundy and Wentorf [1] on the basis of experimental data, as well as estimates of the position of the melting curve of the cBN and the triple point of the hBN-cBN-liquid, the phase diagram of BN is constructed, and at present it is generally accepted.

Diamonds and cBN are produced in special devices under pressure above 4 GPa and under temperature above 1400 K. Graphite is used as a source for the synthesis of diamonds, and hBN is used for the synthesis of cBN. Different metals and alloys are used to decrease the  $P$ ,  $T$ -parameters of the cBN synthesis. Thus, while synthesizing cBN, for example, magnesium-zinc alloy, as well as alkali and alkaline earth metals and their nitrides, borides, fluorides and hydrides, aluminum, magnesium and their nitrides are used [2].

It is known [3] that the synthesis of diamond and cBN powders depends on the kinetics of dissolution in metal melts of graphite or hBN, i. e. on the degree of activity of the latter. For example, in [4] it is shown that electron beam processing of hBN + 5 % aluminum powder accelerates the phase transition of hBN into cBN and provides maximum values of compressive strength, microhardness and density of cBN. The activation of these materials is also possible with the “pumping” of mechanical energy into them.

**State of the problem.** Experimental data by different authors show a strong effect of shear deformations on phase transformations. In particular, it is indicated a significant decrease in pressure and temperature of phase transitions and the possibility of obtaining new phases which cannot be synthesized under these conditions without shear deformations [5]. So, the following basic schemes of plastic deformation with a shear are known [6]:

- high pressure torsion;
- equal channel angular pressing;
- comprehensive forging;
- multi-axis deformation;
- accumulated rolling;
- screw pressing.

Figure 1 shows the basic methods of severe plastic deformation.

It is known that shear deformations affect phase transformations in BN. For example, in [5] a method for the cBN synthesis with the help of high-pressure shear apparatus with diamond anvils is proposed. Using the method, the formation of cBN from rhombohedral BN takes place at room temperature when shearing deformation is applied. In this case, the pressure, to be necessary for the sample to apply for an irreversible transition, is less than 7 GPa. However, the synthesized sample is a small plate with a diameter of 300  $\mu\text{m}$  and a thickness of 50  $\mu\text{m}$ .

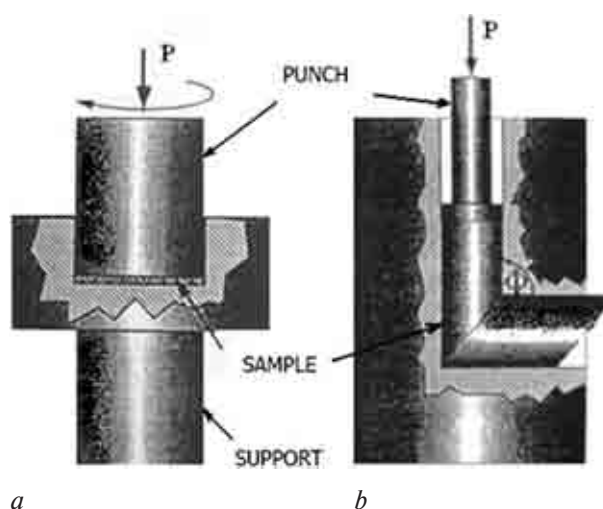


Figure 1 — Basic methods of severe plastic deformation [7]:  
a — high pressure torsion; b — equal channel angular pressing

The use of attritors, planetary and vibration mills can significantly improve the efficiency and productivity of material processing. The starting material placed in the reaction chamber of the devices is constantly under high pressure and shear deformations, and it results in a change in the structure and phase composition of activated substances.

Characteristic features of mechanical activation (MA) are the following: 1) effect of shear deformations under high pressure; 2) continuous vacancy flow; 3) improving of interaction between components. In [8], it is theoretically shown that the contact pressure on a particle between grinding bodies can reach 11.5 GPa. It corresponds to the stability region of cBN as shown in [1].

When processing the hBN powder in the attritor, van der Waals chemical bonds break with increasing processing time, and in the crystal lattice distortions appear, the structure becomes more defective, and the dislocation density increases. When milling under the shock loads, the crystal lattice is distorted, the atoms are displaced from the lattice sites and occupy intermediate positions [9]. Therefore, at relatively low temperatures, as a result of MA, nucleation of superhard BN phases can be expected.

It is known, that as a result of MA of hBN there is a decrease in the technological parameters of the phase transition of hBN into cBN under high pressure high temperature (HPHT) treatment. For example, using of hBN treated in vibrating mill and then sintered in a high-pressure apparatus (HPA) at a pressure of 7.7 GPa, the temperature of the cBN synthesis decreases by 200  $^{\circ}\text{C}$  in comparison with the unactivated hBN [10]. It is shown in [11] that during processing hBN in the attritor the BN substructure transforms from crystalline to nanocrystalline and amorphous occurs. During MA of hBN for 4 hours, the BN powder with sizes of 30–300 nm is synthesized, however the long MA duration results in the contamination of the BN powder [12].

The aim of this work is to study the effect of MA in the attritor and planetary ball mill (PBM), chemical purification and followed by high pressure and temperature treatment of the hBN powder on the structure of the synthesized material on its base.

**Starting materials and research methods.** The hBN powder with the particle sizes within 5–100  $\mu\text{m}$  is used as the initial material. Mechanical activation of the hBN powders is carried out in an attritor at an impeller rotation speed of 800 r/min for 25 min and in PBM AGO-2 (Novic, Russia) in an argon atmosphere at the drums rotation speed around general axis of  $\sim 1000$  r/min for 2.5–15 min. Steel balls of 5 mm diameter were used to achieve the ball-to-powder ratio of 30:1 and of 20:1 for attritor and PBM MA, respectively.

Before the HPHT treatment, the BN powders after MA are purified from hBN by etching in a NaOH melt at 340  $^{\circ}\text{C}$ , with adding 10 % aqueous HCl solution, and subsequent washing in distilled water and drying.

The HPHT treatment of powder mixtures after MA is carried out in a HPA of the “anvil with a hollow” type in the pressure range of 2.5–7.7 GPa and in the temperature range of 1000–2000  $^{\circ}\text{C}$ .

The study of the powder after MA is carried out with a high-resolution scanning electron microscope (SEM) Mira equipped with an electron backscatter diffraction (EBSD) detector (Tescan Co, Czech Republic). The morphology of the surface fracture of the obtained samples is studied with the atomic force microscope (AFM) NT-206 (MicroTestMachines Co, Belarus) in contact mode. Crystallographic studies of the samples are carried out with the EBSD method. X-ray powder researches are performed with a Bruker D8 ADVANCE diffractometer (Germany) in  $\text{Cu-K}\alpha$  radiation. The study of specific surface is carried out with the BET method using analyzer SA 3100 (Beckman Coulter, USA). The Vickers hardness of the samples is measured using a Buehler Micromet-II microhardness testing machine (Switzerland). The microhardness is measured at a load of 200 g.

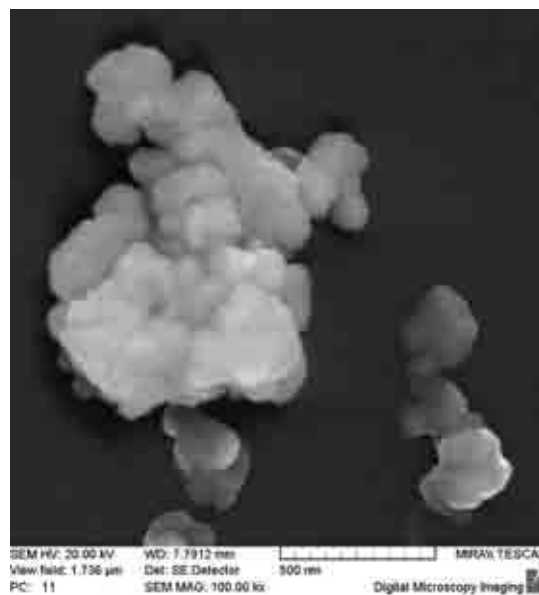
#### Experimental part and discussion of the results.

Mechanical activation of the hBN powders leads to a partial decomposition of hBN and a decrease in boron and nitrogen content in it, and with increasing processing time the  $\text{B}_2\text{O}_3$  content increases due to the oxidation of released boron [12]. MA of the hBN powders both in an attritor and in PBM promotes the formation of round-shaped agglomerates with a size in the range of 0.5–2  $\mu\text{m}$ , consisting mainly of separate particles with a size in the range of from 50 to 200 nm. It can be noted that MA in PBM leads to the formation of more dense agglomerates predominantly (Figure 2 *a*), than MA in an attritor (see Figure 2 *b*).

As the intensity of MA increases, the specific surface area of the powders increases. Thus, during MA the specific surface of the powders increases from 18.9  $\text{m}^2/\text{g}$  to 29.8  $\text{m}^2/\text{g}$  with an increase in the rotation speed of the impeller from 700 to 800 r/min for 25 min. Accordingly, the specific surface of the powder increases



*a*

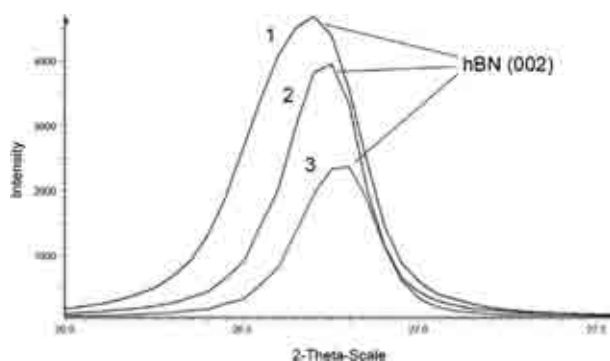


*b*

Figure 2 — SEM images of morphology of BN powder after MA: *a* — in PBM during 10 min; *b* — in attritor during 30 min

from 2.1 to 80  $\text{m}^2/\text{g}$  after MA in PBM within 10 min. According to X-ray analysis data, the main phase of the powder after MA in both the attritor and PBM is hBN. At the same time, processing in PBM leads to a significant decrease in the intensity of the reflex from the plane (002) of hBN, as well as to its displacement and broadening, and it can be caused by both a decrease in crystallite sizes, formation of a defective structure, and disordering processes in hBN [13].

With increasing MA duration, we can observe a decrease in the intensity of the reflex (002) of the hBN and its broadening caused by the destruction of the initial hBN particles and an increase in their defectiveness because of the hBN amorphization (Figure 3).



**Figure 3** — Change in intensity of reflex (002) of hBN depending on intensity of MA: 1 — initial hBN powder; 2 — hBN powder after MA in attritor; 3 — hBN powder after MA in PBM

Thus, the MA in an attritor within 25 min leads to a decrease in the hBN crystallite sizes  $\langle L \rangle$  from 120 nm to 40–50 nm. The MA in PBM results in an even greater decrease in  $\langle L \rangle$ : after treatment for 5 min  $\langle L \rangle = 9.2$  nm, after 10 min  $\langle L \rangle = 7.1$  nm and after 15 min  $\langle L \rangle = 4.5$  nm.

X-ray diffraction analysis performed with the powders after MA in PBM for 10 min shows that in this case on the X-ray patterns at the angular position  $43^\circ 21'$  corresponding to the main line (111) cBN, from the side of small angles, a characteristic halo is formed, and it indicates the formation of amorphous nanocrystalline cBN, as well as another high-pressure phase — wurtzite boron nitride (wBN).

A further increase in the MA duration does not lead to an increase in the intensity of reflexes of cBN. An increase in the intensity and MA time leads to the reverse process of the hBN formation. The subsequent chemical purification of the mechanically activated BN powders results in a decrease in the mass of powders to 5–20 wt. %

After MA of the hBN powders in PBM and subsequent chemical etching, there is powder with light yellowish color, characteristic of cBN, left, and it has an abrasive ability. After MA in an attritor and chemical etching the powder has a light gray color with a yellowish tint and a less pronounced abrasive ability. As a result of etching, the specific surface area of the BN powders increases sharply to 100–120 m<sup>2</sup>/g and does not depend on the intensity of MA. After MA in PBM and chemical purification, the BN powders morphologically are dense conglomerates of round-shaped particles about 100 nm in size, assembled in fragile loose plate-shaped aggregates 0.5–2 mm in size.

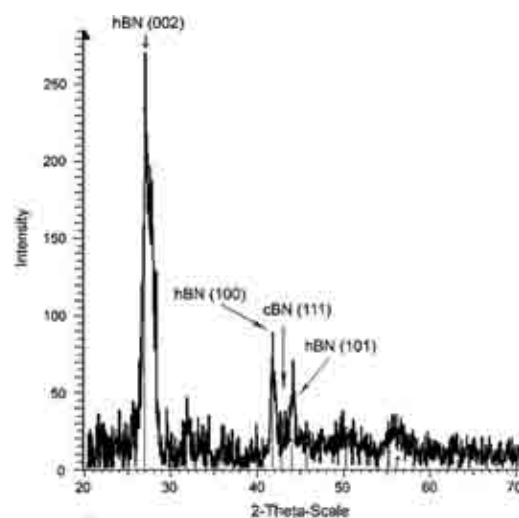
Chemical purification allows to affect different phases of BN selectively: the hexagonal phase of BN is less resistant to the aggressive action of NaOH and HCl under high temperature, therefore it is more strongly etched compared to cBN, and it is manifested in a sharp decrease in the intensity of (002) the hBN line on the X-ray pattern (Figure 4). At the same time, after chemical purification the intensity of (111) the cBN powder line practically does not decrease as compared to the powder before chemical purification.

**Sintering of the BN powders after MA under high pressure and temperature.** The purified BN powders after MA are used for sintering under high pressure and temperature in HPA with “anvil with a hole” according to the method described in [14]. The HPHT treatment is performed in the pressure range from 2.5 to 7.7 GPa and temperatures from 1000 to 2000 °C.

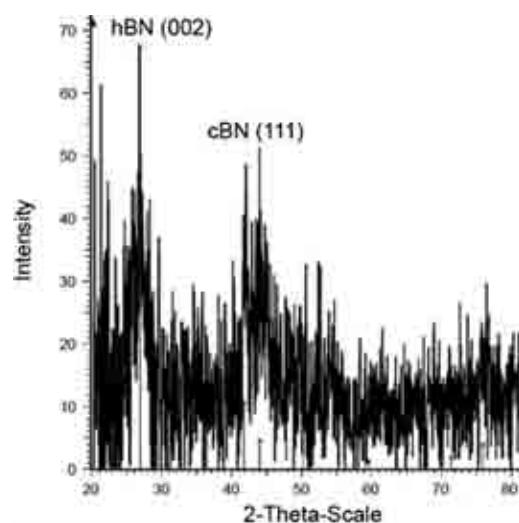
**Sintering of the BN powders after MA at pressure less than 3 GPa.** Sintering of the BN powders after MA at pressures less than 3 GPa in the temperature range of 1000–1300 °C leads to the formation of compact material based on plate polyhedral crystallites of BN with a size of ~ 0.1–0.5 mm (Figure 5 a).

X-ray analysis of the material after the HPHT treatment shows the presence of the hBN, wBN and cBN phases, as well as compounds B<sub>3</sub>N<sub>3</sub>Cl<sub>6</sub> in the material (see Figure 5 b).

An assessment of crystallite sizes (coherent scattering regions, CSR) of the formed phases shows that CSR is 50 nm for the hBN and cBN phase, and



a



b

**Figure 4** — X-ray diffraction patterns of powder samples after MA: a — before chemical purification; b — after chemical purification [12]

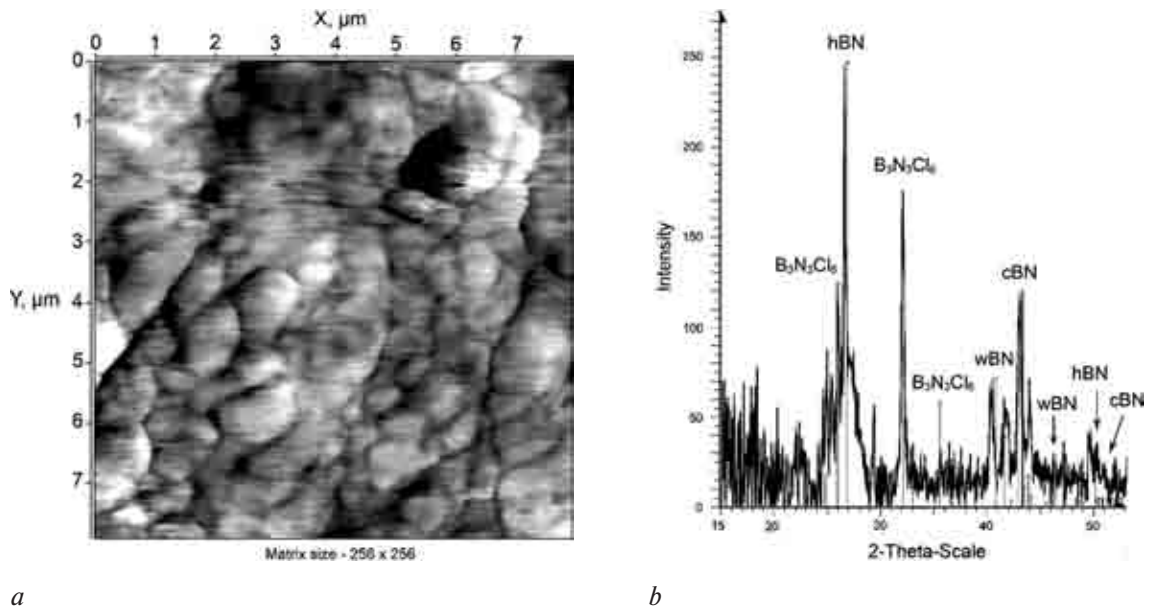


Figure 5 — Structure of compact material based on boron nitride after MA, chemical purification and sintering under pressure of 2.5 GPa and temperature of 1300 °C: a — AFM image of surface; b — X-ray pattern

40 nm for  $B_3N_2Cl_6$  phase. The analysis of the sintered material by the EBSD method shows, along with the BN phases indicated above, there are BN phases of the orthorhombic, hexagonal and tetragonal syngony (Table).

An increase in the temperature of the HPHT treatment above 1500 °C at pressure of 2.5 GPa leads to the formation of the hBN phase in the material. The Vickers microhardness of the obtained material is 7–10 GPa.

**Sintering of the BN powder after MA at pressure of 7 GPa.** According to X-ray analysis data, increasing the sintering pressure of mechanically activated BN powders up to 7 GPa and temperature up to 2000 °C

allows forming the material mainly based on the cBN phase, regardless of the intensity of MA. According to the AFM data, the obtained composite material has a grain microstructure with grains of predominantly equilibrium shape and 0.4–0.6 μm in size. Larger grains up to 1.1 mm, formed as a result of high-temperature recrystallization (Figure 6 a) are also found.

**Sintering of the mechanically activated BN with aluminum activating additives.** The use of additives activating the sintering of the cBN powders is of practical interest, because it leads to a decrease in the parameters (first of all, pressure) of the material sintering as compared to the sintering process without

Table — The parameters of the crystal structure of the different BN phases: a, b, c — stoichiometric composition; d — non-stoichiometric composition

a			b			c			d		
Spase group: 69			Spase group: 164			Spase group: 186			Spase group: 134		
Laue group:3, mmm			Laue group:7, 3m			Laue group:9, 6/mmm			Laue group:5, 4/mmm		
Rhombic syngony			Hexagonal syngony			Hexagonal syngony			Tetragonal syngony		
Unit cell length, Å			Unit cell length, Å			Unit cell length, Å			Unit cell length, Å		
a	b	c	a	b	c	a	b	c	a	b	c
2.50	4.34	3.35	2.51	2.51	6.69	2.52	2.52	6.70	8.63	8.63	5.13
Unit cell angles, grad			Unit cell angles, grad			Unit cell angles, grad			Unit cell angles, grad		
90°	90°	90°	90°	90°	120°	90°	90°	120°	90°	90°	90°
Composition, atom %			Composition, atom %			Composition, atom %			Composition, atom %		
B 50	N 50		B 50	N 50		B 50	N 50		B 96,5	N 3,5	

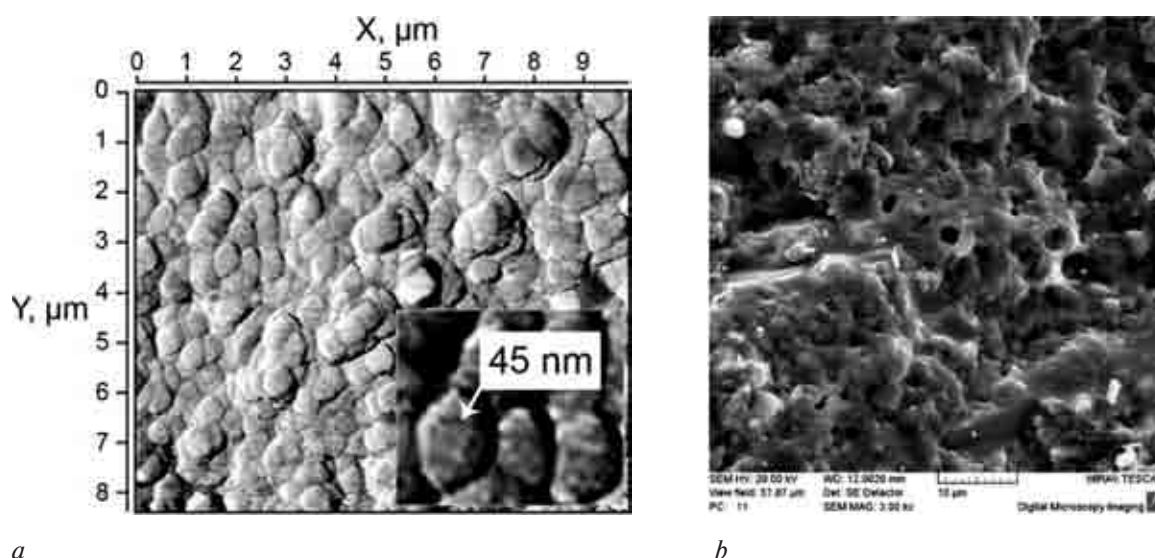


Figure 6 — Images of material based on cBN sintered at different pressures:  
*a* — AFM image; sintering pressure 7.0 GPa; *b* — SEM image; sintering pressure 5.5 GPa

additives, and it is especially important in the case of submicro and nano powders of SHM. Aluminum powder (25 wt.%) with a particle thickness of 0.2–0.5  $\mu\text{m}$  is used as an activating additive for sintering the cBN micropowders under HPHT. In addition, aluminum has catalytic properties and stimulates the phase transformation of the hexagonal modification of BN to cBN.

As a result, it has been found that the sintering material based on the cBN powder after MA is possible at pressures less than 7 GPa, and at the same time a material on the basis of polyhedral cBN grains larger than 1  $\mu\text{m}$  is formed, and it is 5–10 times larger than the size of the initial powder particles. We can also observe the cBN grains up to 10  $\mu\text{m}$  in size, which form as a result of collective recrystallization. The structure of the material is characterized by the presence of nanopores, there are separate micropores with a size of 1–3  $\mu\text{m}$  (see Figure 6 *b*). Along with cBN, in the material there are the hBN phase, aluminum oxides  $\text{Al}_2\text{O}_3$ , AlO, aluminum oxynitride  $\text{Al}_9\text{O}_3\text{N}_7$ , aluminum boride  $\text{AlB}_2$ , and boron oxide  $\text{B}_2\text{O}_3$  as well. The formation of oxides in the sintering treatment can be explained by the presence of oxygen on the BN powder in the form of oxygen-containing compounds after chemical purification and washing in water, as well as the diffusion of container material  $\text{CaCO}_3$  from the container into the sintering zone. The Vickers microhardness of the obtained material, measured under a load of 200 g, is 20 GPa. It can be concluded that the addition of aluminum activates sintering, but at the same time the cBN recrystallization is observed. In order to eliminate the cBN grain growth and preserve the nanostructured state of the material it is necessary to continue searching for optimal sintering conditions under high pressure.

**Conclusion.** The study of the influence of MA of varying intensity in the attritor and PBM on the structural characteristics and phase composition of the

BN powders has shown that when the hBN powder is mechanically activated, the hBN stoichiometry changes with its partial decomposition and release of boron and nitrogen.

The X-ray analysis have revealed that MA leads to a decrease in the intensity of the hBN crystalline peak (002). With an increase in the duration of MA, the BN substructure is transformed from crystalline to nanocrystalline and amorphous. The BN powder after MA represents aggregates up to 0.5–2  $\mu\text{m}$  in size, they consist of separate particles of polyhedral shape with sizes in the range of 50–200 nm.

The specific surface area of the BN powders increases from 18.9–29.8  $\text{m}^2/\text{g}$  (after attritor MA) and from 80  $\text{m}^2/\text{g}$  (after PBM MA) up to values of 100–120  $\text{m}^2/\text{g}$  after MA and chemical purification.

The phase composition of the material from the mechanically activated BN powders depends on the conditions of the HPHT treatment. Thus, in the material obtained at pressure of 2.5 GPa in the temperature range of 1000–1300  $^\circ\text{C}$ , along with the hBN, wBN and cBN phases, there are the BN phases of orthorhombic, hexagonal and tetragonal syngony (crystallographic systems). An increase in the sintering temperature of the mechanically activated BN powders above 1500  $^\circ\text{C}$  at that pressure leads to the formation of only the hBN phase in the material.

Increasing the pressure of the HPHT treatment of the mechanically activated BN powders up to 7 GPa and temperature up to 2000  $^\circ\text{C}$  allows to receive the material mainly on the basis of the cBN phase, regardless of the intensity of the MA. The material has a grain microstructure with a grain size of 0.4–0.6  $\mu\text{m}$  and a cBN crystallite size of about 50 nm.

The addition of aluminum makes it possible to activate sintering of the mechanically modified BN powders at lower pressures, however because of recrystallization, the size of the cBN grains increases by 5–10 times as compared to the initial powder.

## References

1. Bundy F.P., Wentorf R.H. Direct transformation of hexagonal boron nitride in denser forms. *Journal of Chemical Physics*, 1963, vol. 38, no. 5, pp. 1144–1149.
2. Aleshin V.G., et al. *Sinteticheskie sverkhтвердые материалы: в 3-х томах. Том 1. Синтез сверхтвердых материалов* [Synthetic superhard materials: in 3 volumes. Volume 1. Synthesis of superhard materials]. Kiev, Naukova dumka Publ., 1986. 175 p.
3. Fedoseev D.V., Deryagin B.V., Varshavskaya I.G., Semenova-Tyan-Shanskaya A.S. *Krystallizatsiya almaza* [Diamond Crystallization]. Moscow, Nauka Publ., 1984. 134 p.
4. Vasilevsky I.N., Pobol I.L., Leusenko A.A. Issledovanie vliyaniya elektronno-luchevogo nagreva na kinetiku fazovykh prevrashcheniy i svoystva nitrída bora [Study of the effect of electron beam heating on the kinetics of phase transformations and properties of boron nitride]. *Novyye materialy i tekhnologii* [New materials and technologies], 1994, pp. 60–61.
5. Novikov N.V., Shvedov L.K., Levitas V.I., Petrusha I.A., Polotnyak S.B. Eksperimentalnoe issledovanie vliyaniya sdvigovoy deformatsii na fazovye prevrashcheniya v razlichnykh materialakh [Experimental study of the effect of shear strain on phase transformations in various materials]. *Sintez, spekanie, i svoystva sverkhтвердых материалов* [Synthesis, sintering and properties of superhard materials], 2000, pp. 131–144.
6. Faraji G., Kim H.S., Kashi H.T. *Severe plastic deformation. 1-st edition. Methods, processing and properties*. Elsevier, 2018. 324 p.
7. Matrenin S.V., Ovechkin B.B. *Nanostrukturnye materialy v mashinostroyeni* [Nanostructured materials in engineering]. Tomsk, Tomskiy politekhnicheskii universitet Publ., 2009. 186 p.
8. Zhdanovich G.M., Lupareva V.M. Matematicheskiy metod opredeleniya kontaktnogo davleniya pri soudarenii sharov i chastits v izmelchayushchem ustroystve — attritore [Mathematical method for determining the contact pressure in the collision of balls and particles in a grinding device — attritor]. *Poroshkovaya metallurgiya* [Powder metallurgy], 2006, no. 29, pp. 93–97.
9. Vityaz P.A., Senyut V.T., Gameza L.M., Stefanovich A.A., Mosunov E.I., Kovaleva S. Issledovanie vozdeystviya attritornoy i termobaricheskoy obrabotki na strukturu i svoystva materiala na osnove nitrída bora [Investigation of attritor and thermobaric treatment on the structure and properties of a material based on boron nitride]. *Materialy III Mezhdunarodnogo seminara "Nanostrukturnye materialy — 2004: Belarus — Rossiya"* [Proc. 3rd International Workshop «Nanostructured Materials — 2004: Belarus — Russia»]. Minsk, 2004, pp. 154–155.
10. Horiuchi S., Huang J.Y., He L.L., Mao J.F., Taniguchi T. Facilitated synthesis of cubic boron nitride by a mechanochemical effect. *Philosophical Magazine A*, 1998, vol. 78, no. 5, pp. 1065–1072.
11. Senyut V.T., Kovaleva S.A., Mosunov E.I., Stefanovich A.A. Structural and phase transformations in boron nitride during attritor treatment. *Chemistry for sustainable development*, 2009, vol. 17, no. 6, pp. 647–652.
12. Senyut V.T., Kovaleva S.A., Gamzeleva T.V., Grigorieva T.F. Investigation of the structural features of boron nitride after mechanical activation in attritor and planetary mill followed by agglomeration at high pressure and temperature. *Chemistry for sustainable development*, 2016, vol. 24, no. 2, pp. 169–175.
13. Vityaz P.A., Senyut V.T. Sintez i primeneniye nanostrukturnykh sverkhтвердых материалов instrumentalnogo naznacheniya [Synthesis and application of nanostructural superhard materials of tool appointment]. *Izvestiya Natsionalnoy akademii nauk Belarusi. Seriya fiziko-tekhnicheskikh nauk* [Proceedings of the National Academy of Sciences of Belarus. Physical-technical series], 2015, no. 3, pp. 60–76.
14. Vityaz P.A., Gritsuk V.D., Senyut V.T. *Sintez i primeneniye sverkhтвердых материалов* [Synthesis and application of superhard materials]. Minsk, Belorusskaya nauka Publ., 2005. 359 p.

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## ВЛИЯНИЕ МЕХАНИЧЕСКОЙ АКТИВАЦИИ И ОБРАБОТКИ ПРИ ВЫСОКОМ ДАВЛЕНИИ И ТЕМПЕРАТУРЕ НА ПРОЦЕСС СИНТЕЗА МАТЕРИАЛА НА ОСНОВЕ НАНОСТРУКТУРНОГО НИТРИДА БОРА

*В статье представлены исследования влияния механической активации (МА) и последующей обработки под высоким давлением и температурой (ВДВТ) порошка гексагонального нитрида бора ( $hBN$ ) на его структуру и фазовый состав. Проведенные рентгеноструктурные и электронно-микроскопические исследования показывают, что МА приводит к превращению субструктуры  $BN$  из кристаллической в нанокристаллическую и аморфную. Одновременно с образованием аморфно-нанокристаллического кубического нитрида бора ( $cBN$ ) в порошках  $BN$  после МА образуется еще одна фаза высокого давления — вюрцитный нитрид бора  $wBN$ . В результате спекания порошков  $hBN$  после МА под давлением 2,5 ГПа в интервале температур 1000–1300 °С, помимо фаз  $hBN$ ,  $wBN$  и  $cBN$ , в полученном материале формируются фазы  $BN$  ромбической, гексагональной и тетрагональной кристаллографических систем. Термобарическая обработка порошков  $hBN$  после МА под давлением 7 ГПа позволяет получить материал, содержащий фазу  $cBN$  с размером кристаллитов около 50 нм. Добавки алюминия снижают давление спекания, но в то же время вследствие рекристаллизации размер зерна  $cBN$  в полученном материале увеличивается на порядок по сравнению с исходным порошком.*

**Ключевые слова:** нанокристаллический  $BN$ , механическая активация, химическая очистка, высокое давление и температура

### Список литературы

1. Bundy, F.P. Direct transformation of hexagonal boron nitride in denser forms / F.P. Bundy, R.H. Wentorf // J. Chem. Phys. — 1963. — Vol. 38, No 5. — Pp. 1144–1149.
2. Синтетические сверхтвердые материалы: в 3-х т. Т. 1. Синтез сверхтвердых материалов / Редкол.: Н.В. Новиков (отв. ред.) [и др.]. — Киев: Наук. думка, 1986. — С. 175.
3. Кристаллизация алмаза / Д.В. Федосеев [и др.]. — М.: Наука, 1984.
4. Исследование влияния электронно-лучевого нагрева на кинетику фазовых превращений и свойства нитрида бора / И.Н. Василевский [и др.] // Новые материалы и технологии: тез. докл. — Минск, 1994. — С. 60–61.
5. Экспериментальное исследование влияния сдвиговой деформации на фазовые превращения в различных материалах / Н.В. Новиков [и др.] // Синтез, спекание и свойства сверхтвердых материалов: сб. науч. тр.; Ин-т сверхтвердых материалов им. В.Н. Бакуля НАН Украины. — Киев, 2000. — С. 131–144.
6. Faraji, Ghader Severe Plastic Deformation. 1st Edition. Methods, Processing and Properties / Ghader Faraji, H.S. Kim, Hessam Torabzadeh Kashi. — Elsevier, 2018. — 324 p.
7. Матренин, С.В. Наноструктурные материалы в машиностроении: учебное пособие / С.В. Матренин, Б.Б. Овечкин; Томский политехнический университет. — Томск: Изд-во Томского политехнического университета, 2009. — 186 с.
8. Жданович, Г.М. Математический метод определения контактного давления при соударении шаров и частиц в измельчающем устройстве — атриторе / Г.М. Жданович, В.М. Лупарева // Порошковая металлургия: республ. межведом. сб. научн. тр. / Гл. ред. О.В. Роман. — Минск: Тонпик, 2006. — Вып. 29. — С. 93–97.
9. Исследование воздействия атриторной и термобарической обработки на структуру и свойства материала на основе нитрида бора / П.А. Витязь [и др.] // Сб. тр. III междунар. семинара «Наноструктурные материалы — 2004: Беларусь–Россия», Минск, Беларусь. — 2004. — С. 154–155.
10. Facilitated synthesis of cubic boron nitride by a mechanochemical effect / S. Horiuchi [et al.] // Phil. Mag. A. — 1998. — Vol. 78, No. 5. — Pp. 1065–1072.
11. Структурные и фазовые превращения в нитриде бора при атриторной обработке / В.Т. Сенюць [и др.] // Химия в интересах устойчивого развития. 2009. — Т. 17, № 6. — С. 647–652.
12. Сенюць, В.Т. Исследование структурных особенностей нитрида бора после механоактивации в атриторе и планетарной мельнице с последующим спеканием в условиях высоких давлений и температур / В.Т. Сенюць [и др.] // Химия в интересах устойчивого развития. — 2016. — Т. 24, № 2. — С. 169–175.
13. Витязь, П.А. Синтез и применение наноструктурных сверхтвердых материалов инструментального назначения / П.А. Витязь, В.Т. Сенюць // Известия НАН Беларуси. Сер. физ.-техн. наук. — 2015. — № 3. — С. 60–76.
14. Витязь, П.А. Синтез и применение сверхтвердых материалов / П.А. Витязь [и др.]. — Минск: Беларус. навука, 2005. — 359 с.