RESEARCH ON THE STRUCTURE OF THE MATERIAL BASED ON NANO- AND MICRO-SIZED CUBIC BN SYNTHESIZED FROM MECHANICALLY ACTIVATED GRAPHITE-LIKE BN WITH THE ADDITION OF ALUMINUM UNDER HPHT CONDITIONS

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In the article the structure and phase composition of the material based on nano- and micro-sized cubic boron nitride (cBN) obtained under high pressure and high temperature conditions from mechanically activated graphite-like boron nitride (hBN) in the presence of aluminum (Al), which plays the role of an initiator for the phase transformation hBN → cBN, are investigated. It has been shown that the use of mechanical activation contributes to the formation of cBN nuclei in hBN, which makes it possible to increase the dispersion of the final product. The technological parameters of the cBN synthesis and the amount of Al have a significant effect on the structure of the material as well as the content of the cubic BN phase in it. The increase in the pressure for the hBN (MA) -10% Al system from 2.5 to 5.5 GPa and the temperature from 1550 °C to 1750 °C contributes to the increase of the content of the cBN phase from 10-15% to 90%. In this case, the size of cBN grains synthesized at pressures of 2.5 and 5.5 GPa is in the range of 200-500 nm and 40-120 nm, respectively. The increase in the amount of Al, temperature and duration for the cBN synthesis leads to the formation of large cBN grains with a size of about 10-50 μm.

Keywords: mechanical activation, phase transformation, nanostructured cubic boron nitride, high pressure and temperature, synthesis.

Introduction

At the present time cubic boron nitride (cBN) is used in the production of tools for highly efficient abrasive and blade machining of a wide class of machine-building materials [1]. Cubic BN is of a lower hardness to diamond, but has a higher thermal stability and chemical inertness, which makes it indispensable for processing alloy steels, cast irons, as well as nickel and titanium alloys, heat-resistant wear-resistant coatings, surfacing, etc. [2].

The industrial production of cBN is based on the phase transformation of graphite-like boron nitride (hBN) into cubic BN under high pressure and high temperature (HPHT) conditions in the presence of catalysts (initiators) [3]. As a rule, the spontaneous crystallization method used in industry makes it possible to synthesize cBN powders from units to several hundred micrometers efficiently. However, the synthesis of cBN nano- and submicro- and micro-powders is associated with a sharp rise in the cost of the production process and, accordingly, their cost on the market. At the same time, an increase in the level of physical, mechanical and operational characteristics of blade and abrasive tools is associated with the use of highly dispersed (nano- and submicron) cBN powders in their production. Therefore, the development of technological processes for the synthesis of both cBN powders and cBN containing materials is an urgent task today.

1. Effect of mechanical activation on structural and phase transformations in hBN

One of the most effective ways to increase the dispersion of the synthesized cBN is mechanical activation (MA) of the initial reaction mixture. It is known that the use of mechanically activated hBN as a starting material leads to an increase in the number of crystallization centers and a decrease in the size of cBN crystals during subsequent HPHT treatment [4, 5]. In a number of experimental studies [6-8], it has been shown a strong effect of MA on the structure of hBN as well as the dispersion and phase composition of the synthesized material.

For example, milling of hBN particles is observed after mechanical treatment of the hBN powder in a ball mill. At the same time there is a decrease in the size of the coherent scattering regions (CSR) hBN from 120 nm for the initial hBN powder to 100 nm for the processed one during 7.5 h and up to 63 nm for the processed one for 15 h. There is also a decrease in the lattice parameters and, as a consequence, a decrease in the volume of the unit cell in the first case by 0.059% and in the second case by 0.171%. With increasing duration of milling, the shift of hBN reflections towards larger angles and their broadening indicates the development of a defect structure of hBN. In this case, the phase composition of the powder does not change [9]. Intensive activation in a planetary ball mill (PBM) leads to the formation of BN particles with a crystallite size of 4-10 nm, while the specific surface area of BN powder activated in a PCM increases 3-6 times as compared with attritor treatment. After activation, BN powder is in an aggregated state and represents aggregates with a size of 0.5-2 μm, consisting of individual particles with a size of 50-200 nm. With an increase in the MA treatment duration, the transformation of the hBN substructure from crystalline to nanocrystalline and amorphous is observed [10].

It is shown in [11] that as a result of prolonged MA (180 h) of graphite-like BN in a PBM, a product is formed based on nanocrystalline and amorphous hBN with a turbostratic structure with a nanocrystal grain size less than 3 nm. In the resulting amorphous a-BN, along with sp^2-hybridized interatomic bonds, there is a-BN with sp^3-type bonds. In [12], the transformation of hBN into diamond-like high-pressure phases (wurtzitew BN and cBN) is established in the process of MA in a PBM. After 12-hourMA treatment, the yield of these phases is about 20% and does not change with an increase in duration. It indicates the reversible nature of the phase transformation. The reverse transition of the cBN phase into hBN with recrystallization of the latter during the MA of hBNis observed in [13]. Thus, the results of the above researches point out to the formation of high-pressure diamond-like phases during MA of hBN. They serve as crystallization centers, and this stimulates the formation of cBN crystals.

2. HPHT treatment of mechanically activated hBN

It is known that thermobaric HPHT treatment of mechanically activated hBN powder without activating additives under high pressures of 6.0-10.0 GPa and temperatures of the order of 2000 °C makes it possible to form a polycrystalline superhard material (PSHM) mainly based on the cBN phase with a grain size within 0.4-1.1 microns. In turn, cBN grains are characterized by a fragmented substructure with a subgrain size of 25-50 nm [10]. At lower pressures of 2.5-4.5 GPa, a nanostructured material is formed on the basis of mechanically activated hBN, its phase composition is predominantly represented by the hexagonal BN phase [14]. Additional stimulation of the cBN formation takes place due to the use of initiators (catalysts) for the transformation of graphite-like BN into the cubic BN phase [15]. Thus, in the presence of initiators, the degree of conversion hBN → cBN during the synthesis of coarse-grained (40-315 μm) cBN powders from mechanically activated hBN increases from 40 to 70 wt. % [16]. However, in this case, the addition of catalysts leads to an increase in the size of cBN grains as a result of their recrystallization [17, 18]. To exclude grain growth, it is necessary to increase the pressure of HPHT treatment, but this significantly increases the cost of the final product.

However, in practice, at present the task is to increase the content of nano- and micro-sized cBN grains in the synthesized product with economically justified parameters of cBN synthesis. The aim of this work is to study the possibility of synthesizing a material based on nano- and micro-sized cBN grains under relatively low pressures of HPHT treatment of mechanically activated hBN in the presence of an initiator of the hBN → cBN phase transformation and to study the structure and phase composition of the obtained material.

3. Initial materials and research methods

The hBN produced by PJSC "Zaporozhabraziv" (Ukraine) with a hexagonal phase content of 97–98% with a particle size of 5 to 100 μm is used as the initial powder. Mechanical activation of hBN powders is carried out in a PBM "Aktivator-2S" (Russia) at a drum rotation speed of 1820 rpm and a centrifugal acceleration of milling bodies of 600 m/s^2 for 10 min. The ratio of the masses of milling bodies to the mass of the processed powder = 10. The size of the hBN powder particles after MA is 0.05-0.2 μm, the specific surface area, measured by the BET method, is 27 m^2/g. Aluminum is used as the initiator of the transformation, which is effectively used to activate the phase transformation in BN in the synthesis of polycrystalline cBN [19].

HPHT treatment of mechanically activated hBN powders is carried out in a high-pressure apparatus "anvil with a hole" at pressures of 2.5 and 5.5 GPa and temperatures from 1400 to 1950 ^{o}C for 15-60 s. The morphology of surface and fracture of the sintered samples is investigated on an atomic force microscope (AFM) NT-206 (Micro Test Machines Co, Belarus) in the contact mode. The microstructure of the obtained materials is studied with a high-resolution scanning electron microscope (SEM) "Mira" ("Tescan", Czech Republic). X-ray studies of the powders are performed on a Bruker D8 ADVANCE diffractometer in Cu-Ka radiation in an automatic recording mode. Phase analysis of diffraction patterns is performed using the ICDD PDF2 X-ray standards database. The structural parameters are calculated by the least squares method with a full-profile analysis of diffractograms in TOPAS software using the Pawley iterative procedure. Semi-quantitative phase analysis (S-Q) is performed using the RIR (Reference Intensity Ratio).

The technology for obtaining material containing nano- and micro-sized cubic BN consists of the following operations. At the first stage of material preparation, hBN powder was mechanically activated in a planetary ball mill. Then, a phase transformation initiator aluminum (Al) was applied onto the powder by a chemical-thermal method. It has been previously shown that the formation of an Al film on the surface of the hBN powder (i.e., the modification of hBN with aluminum) leads to an increase in the content of dispersed cBN and a decrease in the technological parameters of the hBN → cBN phase transition [20]. In this paper, Al in the amount of 10 and 40 wt. % is applied directly to the mechanically activated hBN powder by the method of chemical thermal deposition [20].

Technology for applying aluminum to hBN powder is as follows. Al powder was added to a weighed portion to hBN powder in an amount of 10 or 40 wt. % and stirred. Then the mixture was annealed in a sealed container in the aluminum halides atmosphere at the temperature of 900°C for 1.5–3.0 h. As a result, a fine-grained (nanocrystalline) coating is formed on the hBN powder in the form of an "island-type" film.

After that the hBN powder was pressed with a force of 3–5 tons/cm^{2}, and pressed samples were obtained in the form of tablets with a diameter of 5–10 mm and a height of 6–8 mm. The tablets were sintered under conditions of high pressures and temperatures on a DO-138 press unit with a force of 6.3 MN (630 tons) in special high-pressure apparatuses. The samples were heated by direct current passing through a tubular graphite heater containing a sample inside. Duration of temperature increase to operating values was 10–15 s.

4. Experimental part. Discussion of the results

4.1 hBN$_{MA}$ - 10% Al system, pressure 2.5 GPa

X-ray diffraction analysis of the material samples obtained at a pressure of 2.5 GPa, in a temperature range of 1400–1550 °C for 15-30 s with the addition of 10% aluminum (Fig.1) shows the presence of boron nitride phases, graphite-like and cubic BN, in the material, as well as aluminum compounds – α-Al$_2$O$_3$, AlB$_2$and AlN.
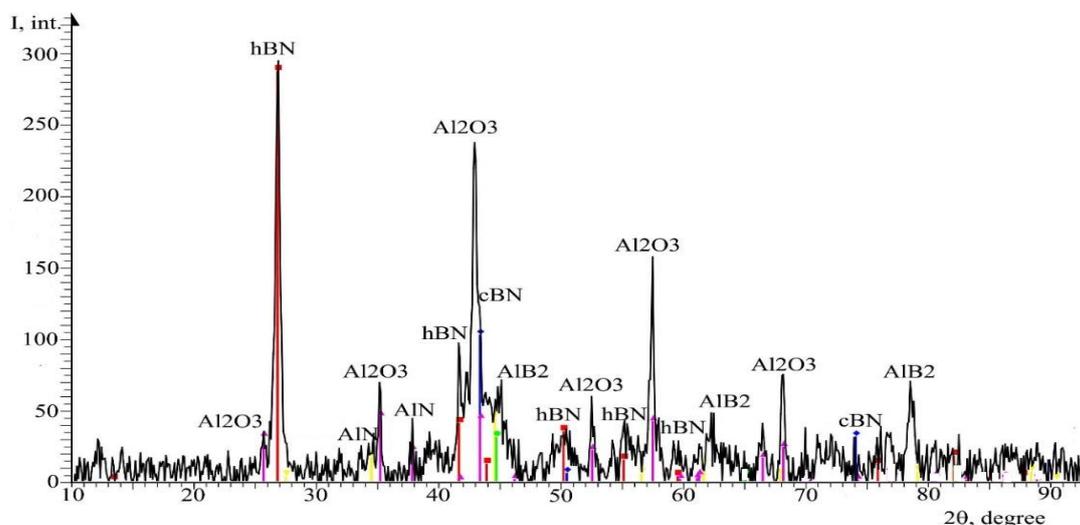
Fig. 1. X-ray diffraction pattern after HPHT treatment: at a pressure of 2.5 GPa, a temperature of 1550 °C, a holding time of 15 s. Additive - 10 wt% Al

The formation of corundum α-Al_2O_3 in the material can be associated with the presence of oxygen (oxygen-containing compounds) adsorbed on the surface of the initial hBN and aluminum powders. As a result of the research on the fine structure of the material, it is defined that the size of the CSR of the cBN phase is 20 nm, the lattice parameter is increased and equal to a = 0.3679 nm, it may be associated with the formation of solid solutions of Al in cBN [19]. The content of the cBN phase in the resulting material is about 10–15%. For the hBN phase, the CSR size is 30 nm, the lattice parameters are a = 0.2498 nm, b = 0.2504 nm, c = 0.6651 nm, and it practically coincides with the tabular values from the used base of X-ray diffraction standards ICDD PDF2. The CSR sizes of α-Al_2O_3 corundum and aluminum boride AlB_2 are 280 and 35 nm, respectively. At a higher synthesis temperature at a pressure of 2.5 GPa, graphite-like BN is predominantly formed, and its content increases with increasing holding time

4.2 hBN$_{MA}$ - 10% Al system, pressure 5.5 GPa

X-ray diffraction analysis of the samples with 10% aluminum obtained at a synthesis pressure of 5.5 GPa in a temperature range of 1550-1750 °C and holding for 15-30 s shows the presence of a cubic BN phase mostly and a relatively small (up to 10%) the amount of graphite-like BN in them (Fig. 2). Analysis of the fine structure shows that the size of the CSR in the cBN phase is about 40 nm, the lattice parameter is a = 0.361696 nm. The content of the cBN phase in the resulting material is estimated at 90%. For the hBN phase, the CSR size is about 50 nm.
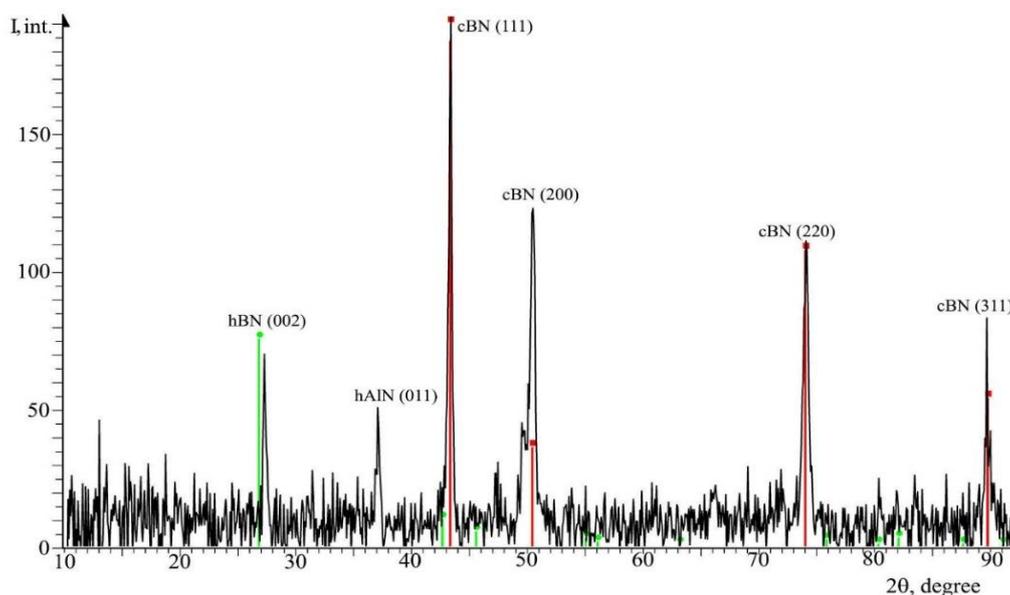
Fig. 2. X-ray diffraction pattern of the sample after HPHT treatment at a pressure of 5.5 GPa, temperature 1750 °C, synthesis time 15 s. Additive - 10 wt% Al

Fig. 3 shows the structure of the samples obtained with the addition of 10% Al at pressures of 2.5 and 5.5 GPa and temperatures of 1550 °C and 1750 °C, respectively. The grain size of cBN, estimated by scanning and atomic force microscopy, is within 200-500 nm and 40-120 nm for the samples synthesized at pressures of 2.5 and 5.5 GPa, respectively, and at the temperatures indicated above. Large (micron) hBN particles with a characteristic layered structure are not detected in the samples of the cBN-based material at the given HPHT parameters.

In this case, the preservation of the nano- and submicron-grained structure of cBN synthesized with the addition of 10% Al may be due to a number of structural and technological factors. First, in the process of the synthesis, the nanostructured refractory compounds α-Al_2O_3 and AlB_2 are formed, their presence along the grain boundaries of cBN prevents growth of cBN. Secondly, technological modes (high pressure and short synthesis time) also contribute to the stabilization of the cBN grain size.

a)

b)

c)
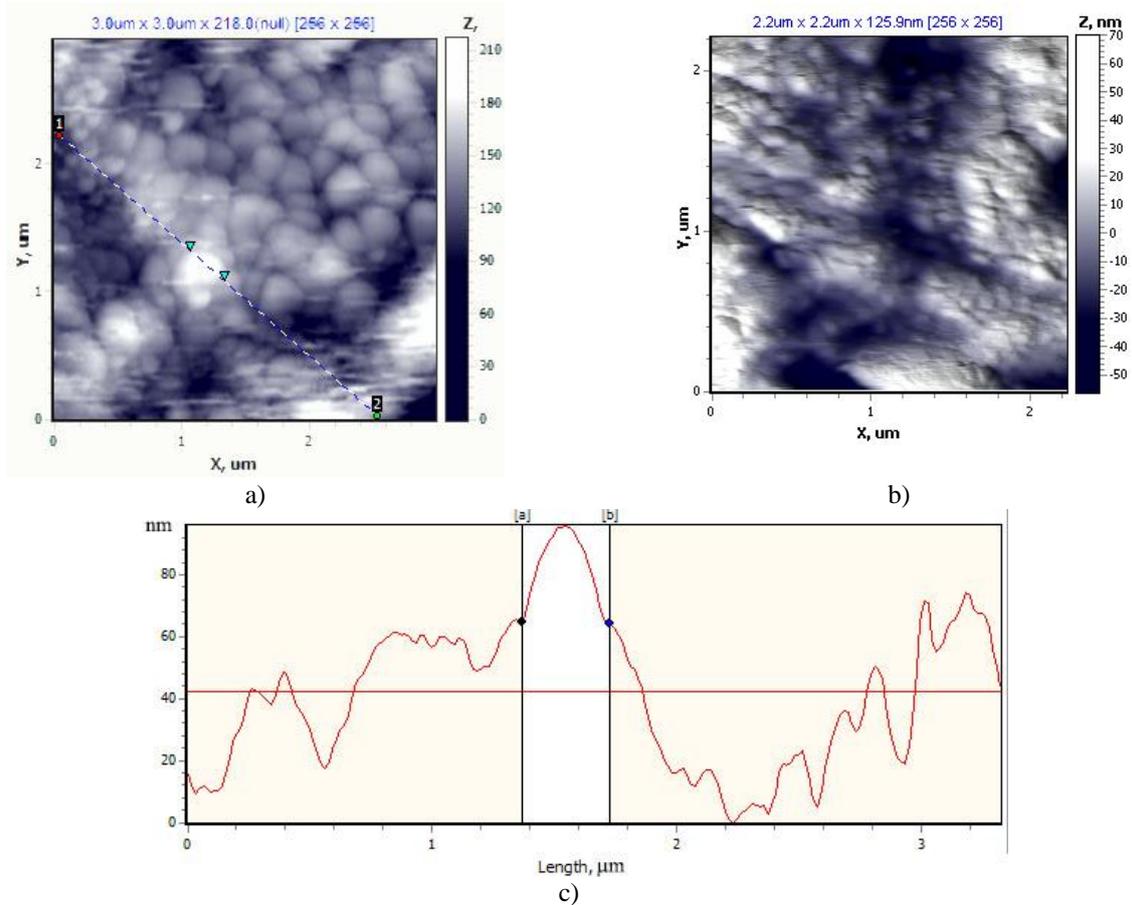
Fig. 3. The fracture of the samples obtained in the hBN MA - 10% Al system after synthesis for 30 s:
a - pressure 2.5 GPa, temperature 1550 °C; b - pressure 5.5 GPa, temperature 1750 °C;
c - surface roughness of the structure shown in Fig. 3a

4.3 hBN$_{MA}$ - 40% Al system, pressure 2.5 GPa

Fig. 4 shows the microstructure of the obtained samples (pressure 2.5 GPa, time 30 s, temperature 1550 °C, amount of Al 40 wt.%). In this case, technological additives of boron and silicon are also introduced into the reaction mixture in an amount of 1-2 wt. % to eliminate the negative effect of oxygen on the crystallization process and to improve the fluidity of the melt.

a)

b)
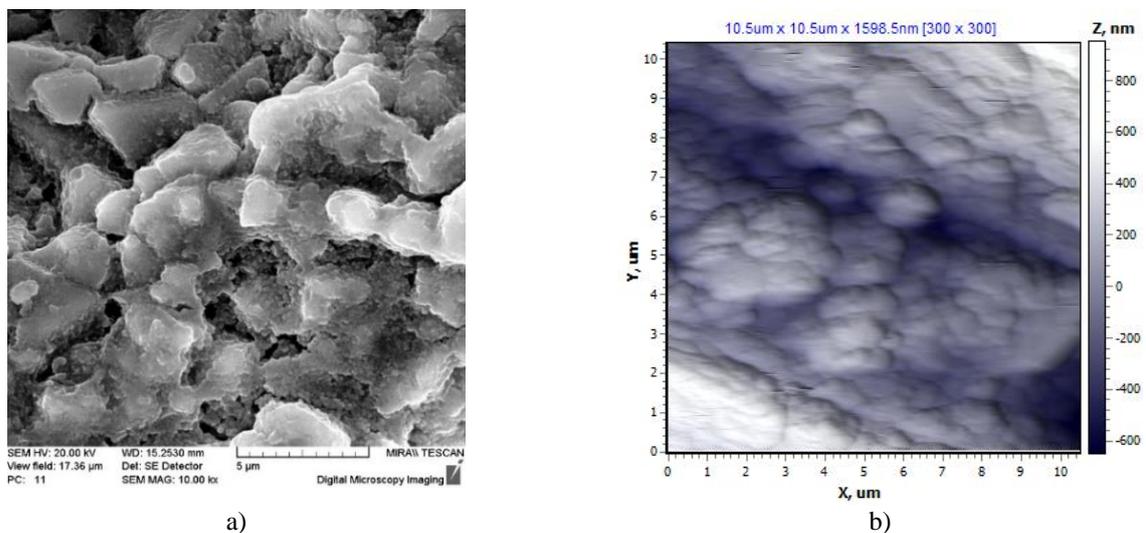
Fig. 4. The structure of the material after HPHT treatment at a pressure of 2.5 GPa, exposure time 30 s, temperature 1550 °C: a - general view of the fracture surface, SEM; b - aggregate structure, AFM

Thus, the material obtained at a pressure of 2.5 GPa for 30 s represents individual loose agglomerates up to 5 μm in size, consisting of submicron cBN particles, as well as individual cBN particles of the order of 500 nm. AFM analysis also confirms the presence of polyhedral cBN particles with a size of 200-800 nm, collected in porous agglomerates.

4.4 hBN$_{MA}$ - 40% Al system, pressure 5.5 GPa.

A different structure is observed in the samples obtained by HPHT treatment at a pressure of 5.5 GPa, temperatures of 1850-1950 °C for 30-60 s. The studies by the SEM method have shown that in this case the particles of two types are observed in the material (Fig. 5): the large polycrystalline particles of cBN with a size of 10-50 μm (Fig. 5, a, b) and smaller faceted cBN grains of cubic habit with a size of 1-4 μm (Fig. 5, c).

The large polycrystalline particles of cBN are formed as a result of sintering of smaller grains. AFM analysis shows that cBN grains in the indicated size range are both poly- and single crystals. In this case, micron cBN grains are surrounded by fine cBN grains 100-800 nm in size with a characteristic tetrahedral habit (Fig. 5, d-f).

a)   b)   c)

d   e   f
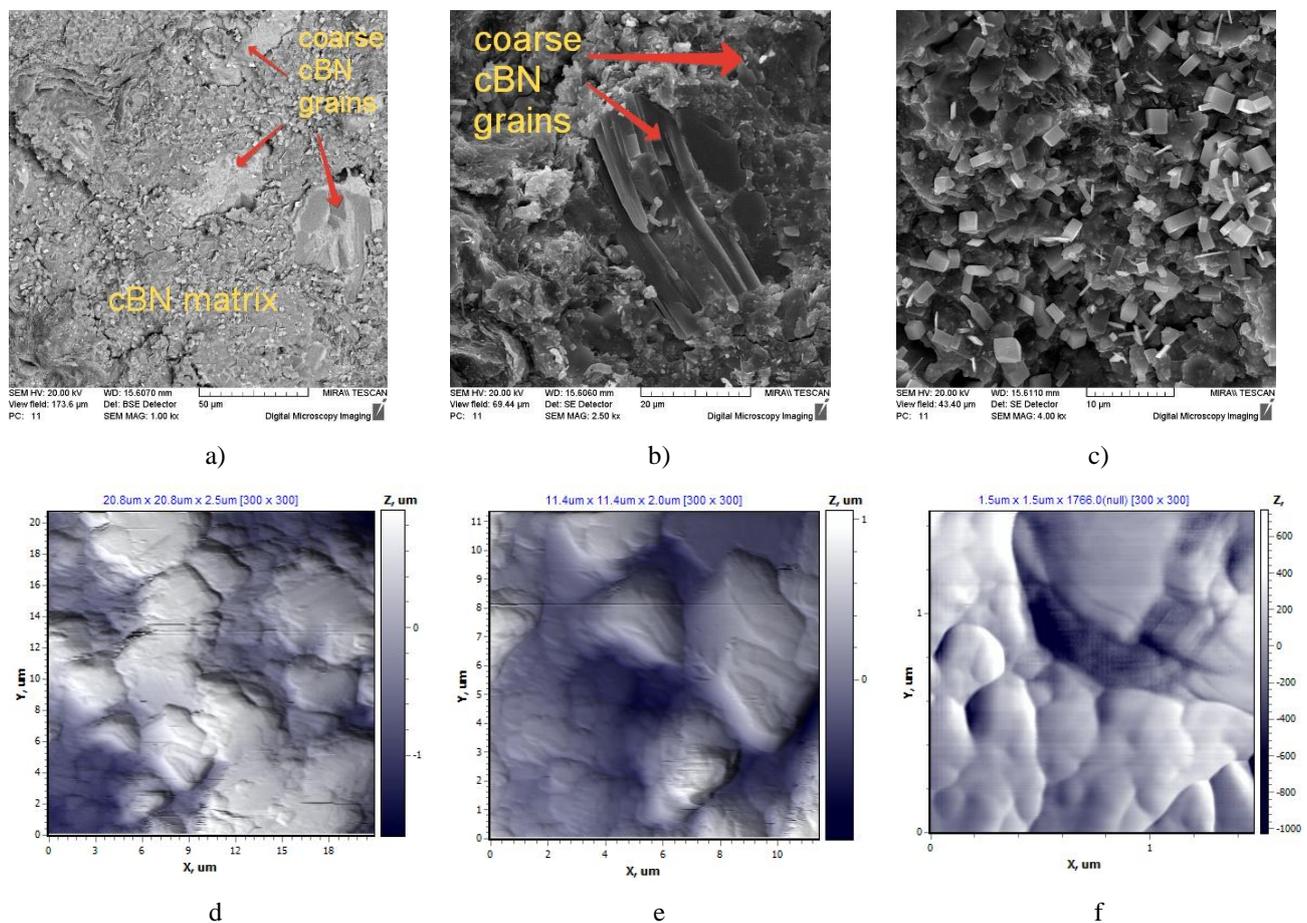
Fig. 5. The structure of the material after HPHT treatment at a pressure of 5.5 GPa,
a temperature of 1950 °C, synthesis time 60 s: a-c- general view of the fracture surface, SEM;
d-f - the structure of cBN crystals (polycrystals), AFM

According to the data of X-ray analysis (Fig. 6), the main phases in the synthesized material are cBN (up to 60%), corundum Al_2O_3 (up to 20%), residual (unreacted) aluminum Al and the boron nitride phase $B_{50}N_{1.87}$. In this case, an increase in the aluminum content to 40%, the synthesis temperature and a longer holding time lead to the growth of cBN grains and their sintering into polycrystals, despite the presence of refractory compounds that play the role of a stabilizer of the grain structure of cBN.

We can see a certain sequence for the morphological changes in the structure of the obtained material. At high pressures and temperatures in the stability region of cBN, the transition of graphite-like BN to the cubic modification of BN takes place. In this case, mechanical activation and the introduction of aluminum

stimulate additionally the phase transformation of the layered structure of graphite-like BN into a cBN modification with a close-packed lattice and a different grain morphology.
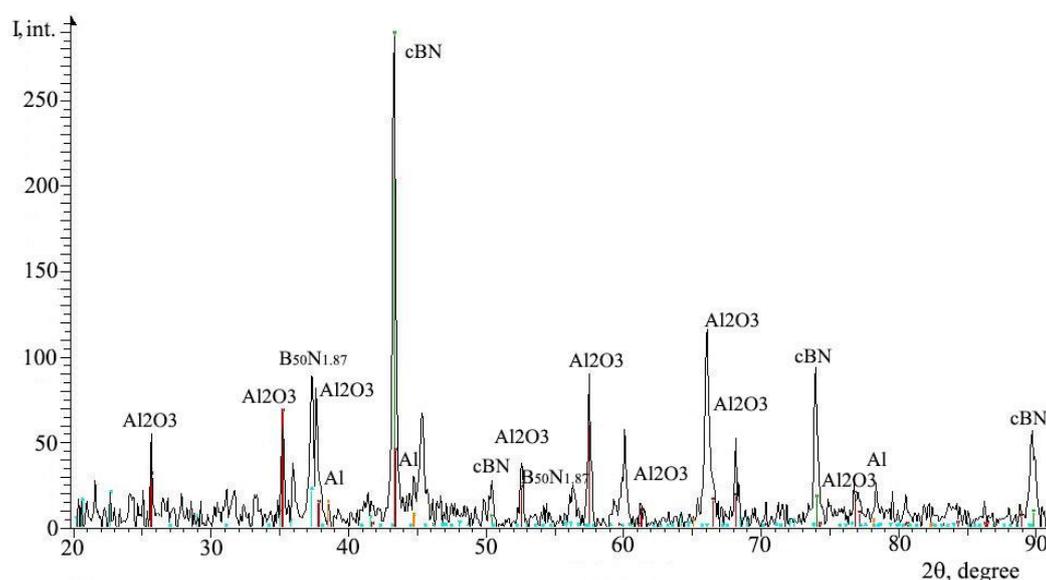
Fig. 6. X-ray diffraction pattern of the material after HPHT treatment at a pressure of 5.5 GPa, a temperature of 1950 °C, and a synthesis time of 60 s. Additive - 40 wt.% Al

Thus, the formation of cBN grains of tetrahedral or cubic habit takes place. At higher temperatures, a collective recrystallization in cBN and the formation of large polycrystalline grains based on smaller primary cBN grains are observed.

Conclusion

The use of MA of hBN leads to formation of cBN nuclei in hBN, and this makes it possible to increase the dispersion of the cBN grains and to reduce the parameters of the hBN $\rightarrow$ cBN phase transformation under HPHT conditions. Aluminum deposited as a coating on the surface of mechanically activated hBN as an initiator of the synthesis process contributes to the phase transformation of mechanically activated graphite-like BN into cBN in the pressure range of 2.5–5.5 GPa. With the use of Al additive in an amount of 10 wt. %, the material mainly consists of highly dispersed cBN (nano- and submicro-sized), and its amount increases from 10-15% to 90% with an increase in pressure from 2.5 to 5.5 GPa. An increase in the content of the initiator (Al) from 10 to 40 wt. % with an increase in the holding time from 15 to 60 s in the investigated range of pressures and temperatures stimulates the formation of large single cBN particles and their sintering into polycrystals.

REFERENCES

1   Novikov N.V., Klimenko S.A. *Tools made of superhard materials*. Moscow, 2014, 608 p. [in Russian]

2   Shulzhenko A.A., Bozhko S.A., Sokolov A.N., et al. *Synthesis, sintering and properties of cubic boron nitride*. Kiev, Naukovadumka Publ., 1993, 255 p. [in Russian]

3   Novikov. N.V. *Superhard materials. Obtaining and application*: In Vol. 1: *Synthesis of diamonds and similar materials*. Ed. A.A. Shulzhenko. Kiev: V. Bakul Institute for Superhard Materials, IPC "ALKON" of NAS of Ukraine, 2003, 320 p. [in Russian]

4   Sokolov A.N., Shulzhenko A.A., Tkach V.N., Budyak A.A. Investigation of the effect of mechanical activation of hexagonal boron nitride on the phase transformation into cubic modification. *Rock-cutting and metal-working tools – equipment, technology for its manufacture and use*. Kiev: V. Bakul Institute for Superhard Materials, 2005, No. 8, pp. 149-154. [in Russian]

.

5   Gameza L.M., Vityaz P. A., Antonovich Ya.V., Mosunov E.I., Senyut V.T., Uniarkha L.S. Synthesis of cubic boron nitride in the BN–NaN$_3$ system. *Powder metallurgy*. Minsk, 2015, No. 38. pp. 115–118. [in Russian]

6   Du Yong-hui, Zhang Bo-bo, Wang Shao-wei, Zhang Tie-chen. Synthesis of Cubic Boron Nitride Using Ball Milling Hexagonal Boron Nitride. *J. of Synthetic. Crystals.*, 2016, Vol. 45, No. 10, pp. 2441–2445. doi:10.16553/j.cnki.issn1000-985x.2016.10.016

7   Streletsky A.N., Permenov D. G., Streletsky K. A. Mechanochemistry of a hexagonal boron nitride. 1. Destruction and amorphization during mechanical treatment. *Colloid J.*, 2010, Vol. 72, No. 4, pp. 532–541 [in Russian]

8   Senyut V.T., Vityaz P.A., Kovaliova S.A., Grigorieva T.F. Effect of mechanical activation of powders BN – (TiN, AlN) on the structure of composite material obtained by ultrahigh pressure sintering. *Mater. Today: Proceedings*, 2019, No. 12, pp.102–105. https://doi.org/10.1016/j.matpr.2019.03.074

9   Vityaz P.A., Senyut V.T. Synthesis and application of nanostructural superhard materials of tool appointment. *Proceedings of the National Academy of Sciences of Belarus. Physical-technical series*, 2015, No. 3, pp. 60-76. [in Russian]

10   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. https://doi.org/10.15372 /KhUR20160208

11   Huang J.Y., Yasuda H., Mori H. HRTEM and EELS Studies on the Amorphization of Hexagonal Boron Nitride Induced by Ball Milling. *J. Am. Ceram. Soc.*, 2000, Vol. 83, No. 2, pp. 403–409. https://doi.org/10.1111/j.1151-2916.2000.tb01204.x

12   Batsanov S.S., Gavrilkin S.M., Bezduganov S.V., Romanov P.N. Reversible phase transformation in boron nitride upon pulsed mechanical action. *Inorganic materials*, 2008, Vol.44, No.11, pp.1332–1334. [in Russian]

13   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.

14   Senyut V.T., Kovaleva S.A., Valkovich I.V., et al. Effect of mechanical activation and high pressure high temperature treatment on the synthesis of the material based on nanostructured boron nitride. *Mechanicsof Machines, Mechanismsand Materials*, 2019, No. 3 (48), pp. 69–76.

15   Golubev A.S., Kurdyumov A.V., Pilyankevich A.N. *Boron nitride: structure, properties, production*. Kiev, Naukovadumka Publ., 1987, 200 p. [in Russian]

16   Shulzhenko A.A., Borimsky I.A., Borimsky A.I., et al. Effect of the intensity of mechanical activation on the structure of the hexagonal boron nitride. *Rock-cutting and metal-working tools – equipment, technology for its manufacture and use*. Kiev: V. Bakul Institute for Superhard Materials, 2011, No. 14. pp. 370-376. [in Russian]

17   Vityaz P.A., Senyut V.T., Kheifets M.L., Kolmakov A.G. Production of alumo-matrix composite material modified by nanostructured cubic boron nitride. *Proceedings of the National Academy of Sciences of Belarus. Physical-technical series,* 2018, Vol. 63, No.3, pp. 271–279. doi.org/10.29235/1561-8358-2018-63-3-271-279 [in Russian]

18   Senyut, V.T. Study of synergistic effect of mechanical activation and high pressure and high temperature sintering on the structure of the material based on boron nitride. *Eurasian Phys. Tech. J.* 2020, Vol, 17, No.1(33), pp. 19–25. doi: 10.31489/2020No1/19-25

19   Butylenko, A.K., Bartnitskaya, T.S., Lugovskaya, E.S., Timofeeva, I.I. Annealing of cubic boron nitride by aluminum. *Pis'ma Tekhn. Fiz.*, 1977, Vol. 3 (20), pp. 1094–1095. [in Russian]

20   Senyut V.T., Vityaz P.A., Kovaleva S.A., et al. Synthesis of polycrystalline cubic boron nitride from hexagonal boron nitride after mechanical activation and modification with aluminum. *Inorganic Materials: Applied Research*, 2016, Vol. 7, No.1, pp. 53–57. doi: 10.1134 / S2075113316010238.