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STUDY OF SYNERGISTIC EFFECT OF MECHANICAL ACTIVATION AND HIGH PRESSURE AND HIGH TEMPERATURE SINTERING ON THE STRUCTURE OF THE MATERIAL BASED ON BORON NITRIDE

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The paper considers the results of the research of the material based on boron nitride after mechanical activation and high pressure and high temperature sintering of hexagonal boron nitride. It is shown, that the structure and phase composition of the resulting material strongly depend on the technological route and the material synthesis conditions. The subsequent chemical purification of the BN powder after mechanical activation leads to a decrease in the content of the hexagonal boron nitride phase. High pressure in the sintering process promotes the formation of material based on cubic boron nitride with a crystallite size of about 50 nm. The additional modifying of boron nitride by aluminum in combination with the second mechanical activation decreases the sintering pressure from 7.7 to 5.5 GPa. At the same time, it leads to the cubic boron nitride grain growth due to the recrystallization process.

Keywords: nanocrystalline boron nitride, mechanical activation, chemical purification, modifying, high pressure and temperature, sintering.

Introduction

Synthesis of nanostructured ceramics based on dense modifications of boron nitride *(BN)* (wurtzite and cubic BN) is an important material science task, since the transition to the nanometer range of grain size for such materials implies an increase in their hardness and wear resistance and improves the performance of tools based on them [1]. Developed methods for producing of nanostructured super hard materials (SHM) based on cubic BN (cBN) by sintering of cBN nanopowders or by phase transformation of graphite-like (hexagonal) BN (hBN) or wurtzite BN (wBN) into cBN require an application of pressures over 8 GPa. That significantly limits the synthesis process of nanostructured STM based on cBN in practice [2].

It is known that preliminary mechanical activation (MA) of graphite-like BN leads to a decrease in the temperature of cBN synthesis under conditions of high pressures and temperatures in comparison to the inactivated hBN [3]. On the other hand, the use of mechanically activated hBN powders is accompanied by an increase in the dispersion of the synthesized cBN phase due to an increase in the number of crystallization centers in BN during MA [4]. The aim of this work is to study of the synergistic effect of MA and high pressure and high temperature (HPHT) sintering of hBN on the structure of composite material on its base.

1. Starting materials and research methods

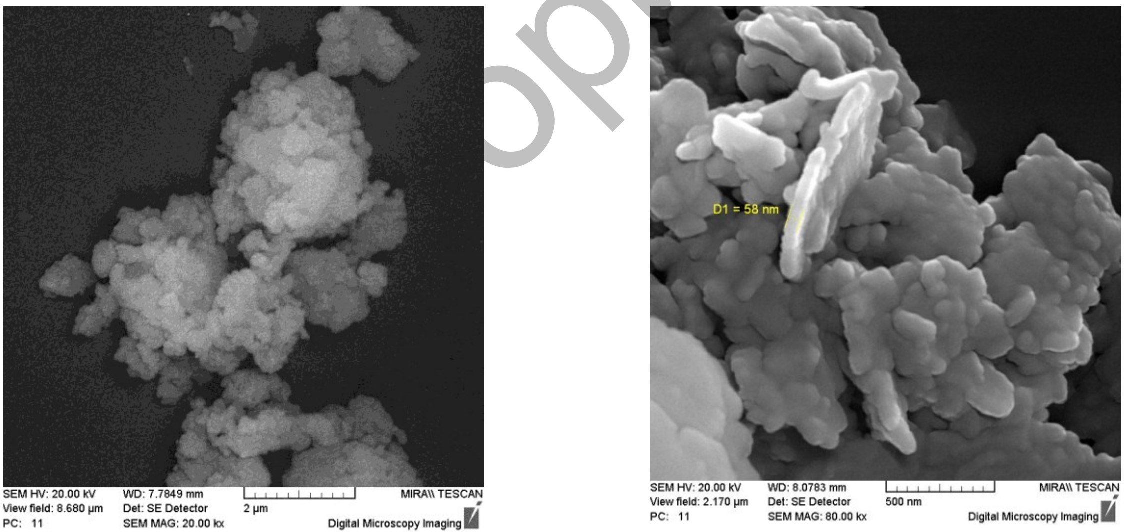
The hBN powder with the particle sizes within 5-100 μm is used as the initial material. Mechanical activation of the hBN powders is carried out in the planetary ball mill PBM AGO-2 (*Novic*, Russia) in an argon atmosphere at a drum rotation speed of 1000 rpm for 10 min. Steel balls of 5 mm diameter were used to achieve the ball-to-powder ratio of 20:1. Before the HPHT treatment, the BN powders after MA are purified from hBN by etching in a NaOH melt at 340°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 °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 Cu-K_α radiation. The study of specific surface is carried out with the BET methodusing analyzer SA 3100 (Beckman Coulter, USA). The Vickers microhardness of the samples is measured using a Buehler Micromet-II microhardness testing machine (Switzerland) at a load of 200 g.

2. Experimental part. Discussion of the results

2.1. Mechanical activation of the hBN powder

It is shown in [5] that during processing of hBN powder 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 [6]. Mechanical activation of the hBN powders in PBM leads to a partial decomposition of hBN and a decrease in boron and nitrogen content in it, and with increasing processing time the B_2O_3 content increases due to the oxidation of released boron. MA of the hBN powders in PBM promotes the formation of round-shaped agglomerates with a size in the range of 0.5–2 μm, consisting mainly of separate particles with a size in the range from 50 to 200 nm (Fig. 1). According to X-ray analysis data, the main phase of the powder after MA in PBM is hBN [7].



a b

Fig.1. SEM images of the hBN powder after MA in the PBM: x 20 000(a); x 80 000 (b)

X-ray diffraction analysis of the hBN powder after MA in PBM for 10 min shows the formation of high-pressure phases wBN and cBN (Fig. 2). A further increase in the MA duration does not lead to an increase in the intensity of reflexes of cBN. On the contrary, an increase in the intensity and MA time leads to the reverse process of the hBN formation [6, 8]. The subsequent chemical purification of the mechanically activated BN powders results in a decrease in the mass of powders to 5-20 wt. %.

Chemical purification allows to affect different phases of BN selectively: the hexagonal phase 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 the (002) hBN reflex on the X-ray pattern. At the same time, after chemical purification the intensity of the (111) cBN reflex practically does not decrease as compared to the powder before chemical purification. The specific surface of the powder after chemical purification increases up to values of 100-120 m^2/g [9].

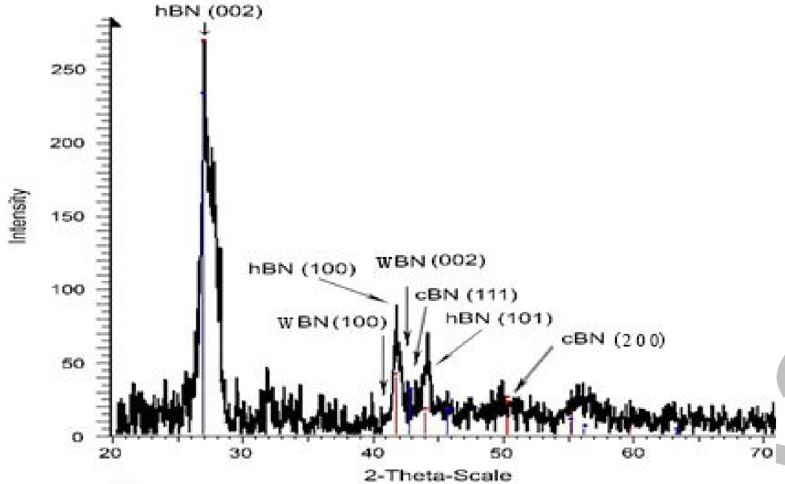
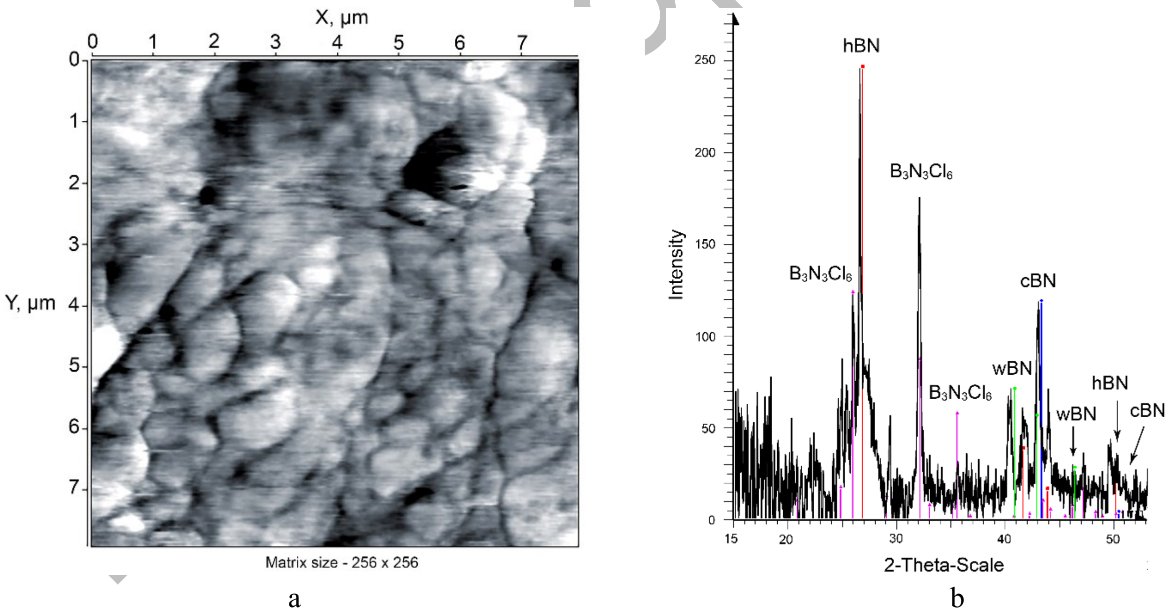


Fig. 2.X-ray diffraction patterns of the hBN powder after MA

2.2. HPHT sintering at the pressure of 2.5 GPa of the BN powder after MA and chemical purification

Sintering of the BN powder after MA at the pressures of 2.5 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 μm (Fig. 3 a).



a b

Fig.3. Structure of the compact material based on boron nitride after MA, chemical purification and sintering under pressure of 2.5 GPa and temperature of 1300°C: AFM image of the surface (a); X-ray diffraction pattern (b)

X-ray analysis of the material after the HPHT treatment shows the presence of the hBN, wBN and cBN phases, as well as the compound $B_3N_3Cl_6$ which is formed in the material as a result of interaction between BN phases and HCl (Fig. 3 b). An assessment of crystallite sizes (coherent

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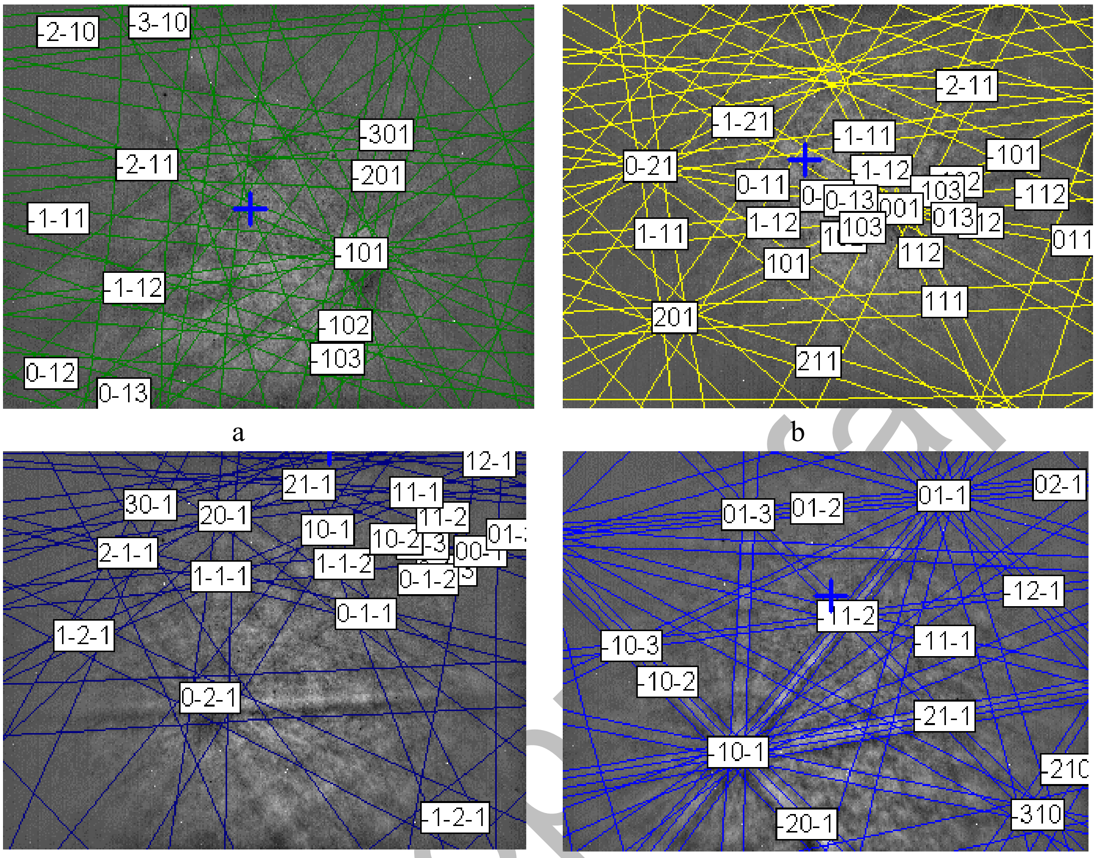
scattering regions, CSR) of the formed phases shows that CSR is 50 nm for the hBN and cBN phase, and 40 nm for $B_3N_3Cl_6$ phase.

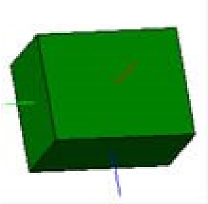
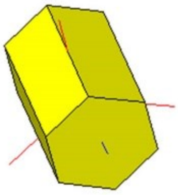
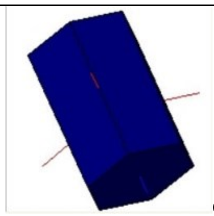
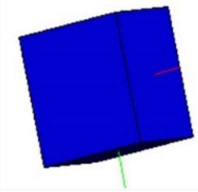


a b

c d

Fig.4. Crystallographic studies of the sintered samples based on hBN after MA, chemical purification and sintering at 2.5 GPa: orthorhombic BN phase (a); hexagonal BN phases (b, c); tetragonal BN phase (d)

Table 1. The parameters of the crystal structure of synthesized BN phases.

 a			 b			 c			 d		
Space group: 69			Space group: 164			Space group: 186			Space group: 134		
Laue group: 3.0mm			Laue group: 7.3m			Laue group: 9.6/mmm			Laue group: 5.4/mmm		
Ortorhombic 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	

The analysis of the sintered material by the EBSD method shows, that along with the BN phases indicated above, there are the BN phases of the orthorhombic, hexagonal and tetragonal syngonias (Fig. 4, table 1). 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. The Vickers microhardness of the obtained material is 7–10 GPa.

2.3. HPHT sintering of the BN powder after mechanical activation at the pressure of 7.7 GPa

According to X-ray analysis data, increasing the sintering pressure of mechanically activated BN powders up to 7.7 GPa and temperature up to 2000°C allows forming the material mainly based on the cBN phase. According to the AFM data, the obtained composite material has a grain microstructure with the grains of predominantly equilibrium shape and 0.4-0.6 μm in size (Fig. 5 a). Larger grains more than 1μm, formed as a result of the high-temperature recrystallization (Fig. 5b) are also found.

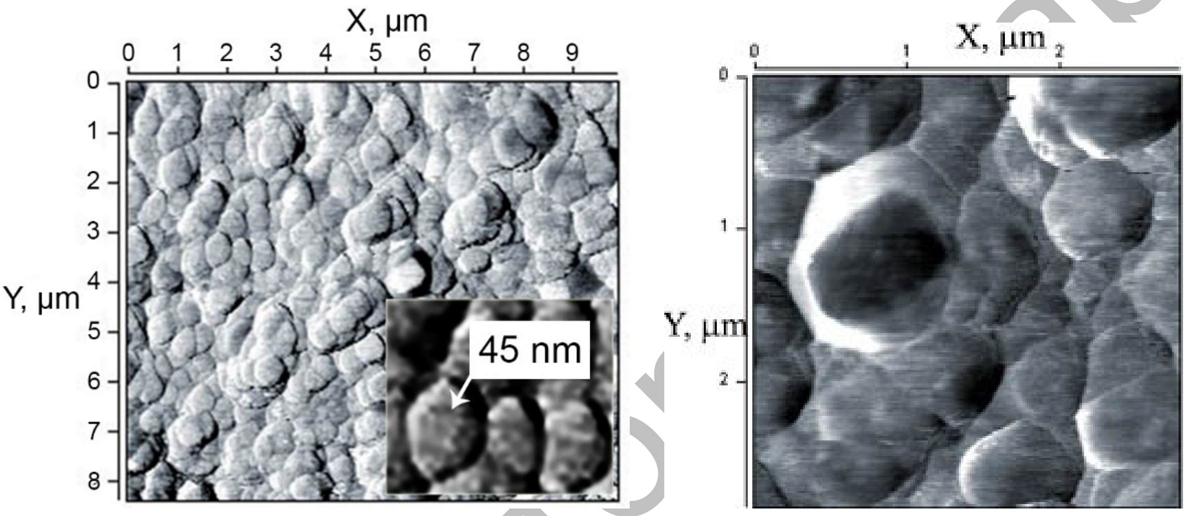


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Fig.5. The structure of the cBN-based nanostructured material obtained from hBN after MA and HPHT at the pressure of 7.7 GPa: a general view [9] (a); recrystallized cBN grains (b)

2.4. HPHT sintering of the mechanically activated Al-modified BN powder

The use of additives activating the sintering of the cBN powder 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 additives, and it is especially important in the case of the submicron- and nanopowders of cBN. Aluminum is often used as an activating additive for sintering the cBN powders under HPHT [10]. In addition, Al has catalytic properties and stimulates the phase transformation of hBN to cBN.

It is known [11] that the synthesis of cBN powders depends on the kinetics of dissolution of hBNin metal melts, i.e. on the degree of activity of its crystallite latter. For example, in [12] it is shown that electron beam processing of hBN+5% Al powder accelerates the phase transition of hBN into cBN and provides maximum values of compressive strength, microhardness and density of the cBN compacts. The activation of hBN+Al system is also possible with the "pumping" of mechanical energy into them. To improve the interaction between the hBN and Al during both MA and HPHT processes, it is suggested [13] to modify with Al mechanically activated hBN powder by the chemical-thermal method, and to apply the second MA again after modifying.

The chemical-thermal modifying of BN powder by Al after MAis high temperature processing at 900°C in adeoxidizing atmosphere in the presence of aluminum-containing compounds, was carried out at 900°C during 2 hours. After MA the chemical purification of BN powder was also performed as described earlier. After the chemical purification, modifying and re-activation in the PBM the BN powder is dense aggregates based on round and polyhedral particles with a size of 50-100 nm (Fig. 6). The specific surface area of the powder measured by the BET method is 103.2 m^2/g, that is within the range for the chemically purified BN powder after one-time MA [7, 9].

HPHT sintering of the mechanically activated Al-modified BN powder was performed at the pressure of 5.5 GPa and temperatures of 1650-2000 ^oC. As a result, it has been found that a material on the basis of polyhedral cBN grains larger than 1 μm are formed. In the material it can also be observed the cBN grains up to 5 μm in size, which are formed 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 1-3μm (Fig. 7). Some of cBN particles after recrystallization represent discs with the diameter of 3-5 μm and the thickness up to 1 μm.

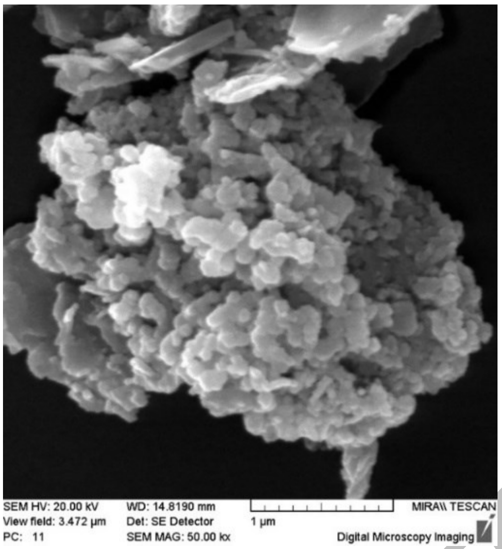

Fig. 6. SEM image of the morphology of the BN powder after MA, chemical-thermal modifying by Al and repeated MA in the PBM

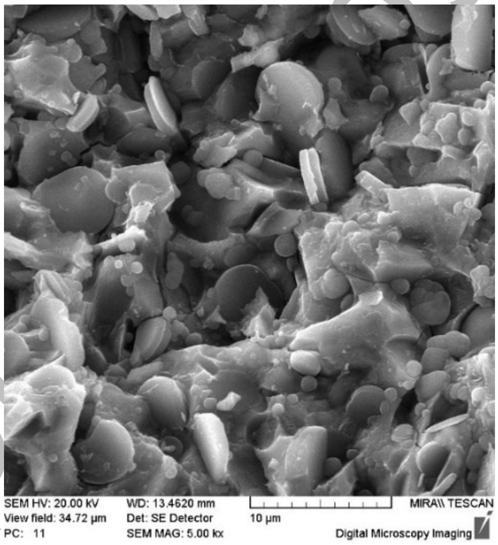

Fig. 7. Fracture of the polycrystalline material on the basis of cBN sintered at the pressure of 5.5 GPa and the temperature of 2000 ^oC

Along with cBN, in accordance with X-ray diffraction analysis in the sintered material there are the hBN phase, aluminum oxides Al_2O_3, AlO, aluminum oxynitride $Al_9O_3N_7$, aluminum boride AlB_2, and boron oxide B_2O_3 as well. The formation of oxides during the sintering can be explained by the oxygen adsorbed on the BN surface in the form of oxygen-containing compounds after chemical purification and washing the powder in water, as well as the diffusion of container material $CaCO_3$ from the container into the sintering region. The Vickers microhardness of the material sintered at the pressure of 5.5 GPa and the temperature of 2000 ^oC is 20 GPa. It can be concluded that both modifying by Al and the repeated MA activates cBN formation and its sintering, but at the same time there is the cBN recrystallization. In order to eliminate the cBN grain growth and preserve the nanostructured cBN it is necessary to increase the pressure while reducing the sintering temperature.

Conclusion

The synergistic effects of MA, chemical purification, chemical-thermal modifying by Al and HPHT sintering on the structure and phase composition of BN-based material were studied. The BN powder after chemical purification, modifying by Al and re-activation represent the dense aggregates based on nanoparticles with a size of 50-100 nm. The specific surface of the BN powder in this case is equal to 103.2 m^2/g.

In the material obtained at the pressure of 2.5 GPa and at the temperature range of 1000-1300°C there are the BN phases of orthorhombic and tetragonal crystallographic systems along with the hBN, wBN and cBN phases. Increasing the pressure of the HPHT sintering of the mechanically activated BN powders up to 7.7 GPa and the temperature up to 2000 °C allows to obtain the material mainly on the basis of the cBN phase with cBN crystallite size of about 50 nm. The chemical-thermal modifying by Al in combination with repeated MA makes it possible to activate HPHT sintering of BN powders at lower pressure of 5.5 GPa. In this case the size of the cBN grains increases up to 5 μm due to recrystallization of cBN.

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