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Structural and Phase Transformations in Boron Nitride Due to Attritor Treatment

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Abstract

The features of phase and structural transformations in the powder of graphite-like boron nitride occurring as the result of the treatment in an attritor are considered. It has been established that the attritor treatment causes an increase in the specific surface area of boron nitride particles by more than an order of magnitude. With increasing the time of the mechanical activation of the powder causes the transformation of BN substructure from the crystalline to nanocrystalline and amorphous one. It has been demonstrated that the phase transformations proceed in boron nitride with the formation of rhombohedral BN and high-pressure phases such as wurtzite and cubic BN with the particle size of submicron range. When the optimal intensity and duration of treatment are exceeded, a reverse transfer of cubic boron nitride is observed to give graphite-like (hexagonal) boron nitride with recrystallizing the latter.

Key words: graphite-like (hexagonal) boron nitride, mechanical activation, boron nitride, attritor, cubic boron nitride, phase transformations, amorphization

INTRODUCTION

The process of ultra-hard material synthesis (such as diamond and cubic boron nitride, CBN) is based on consecutive or simultaneous phase transformation and plastic deformation of the container of a high pressure zone as well as phase transformation within graphite or hexagonal (graphite-like) boron nitride (GBN) under the conditions of high pressure and temperature. Various factors, such as temperature, high pressure, deformation rate, the presence of impurities, large-scale plastic deformations exert a considerable effect on the course of phase transformations occurring and on the formation of the microstructure required for a material with preset physicomechanical properties.

According data presented in [1], shear deformations exert a considerable effect on phase transformations. This fact is exhibited, in particular, in a considerable reduction of the pressure and temperature of phase transitions and in the possibility of obtaining new phases those could not be synthesized under the given conditions without imposing shear deformations.

The authors of [1] proposed have also a method for CBN synthesis carried out with the help of a high pressure shear apparatus with diamond anvils. In this case the process of CBN formation from rhombohedral boron nitride occurs at a room temperature under shear deformation imposed. The pressure value required for imposing with respect to a sample in order to realize irreversible transition, amounts to less than 7 GPa, however the sample synthesized represents a small plate 300 μm in diameter and 50 μm thick.

The use of attritors, planetary and vibration mills allows researchers to increase the efficiency and productivity of processing the materials to a considerable extent. The initial raw material placed into a reaction chamber of such apparatus, is permanently under the influence of high pressure and shear deformation, which results in changing the structure and phase composition of the substances under activation.

One could distinguish the following prominent features of mechanical activation (MA):

1) realizing shear deformations under high pressure conditions; 2) the occurrence of a continuous flow of vacancies; 3) the improvement of the interaction with phase transformation activators. The authors of [2] theoretically demonstrated that the contact pressure falling on a particle under the influence of actuating bodied could amount up to 11.5 GPa. A significant amount of mechanical energy in this case is dissipated in the bulk of a particle to turn into heat, which results in an abrupt rise in the temperature within a local volume. As a result, a particle of the initial material is permanently in the excited state. The relaxation of such state proceeds *via* the emission of the flows of defects.

One of the most important conditions required for solid-phase transformations consists in the reduction of the activation energy of phase transformation. In defect-rich structures, the activation barrier of transformation is reduced owing to high energy of the elastic distortion of crystal lattice near to defects.

So, under the attritor processing of GBN powder, with increasing the time of processing van der Waals chemical bonds are breaking, distortions appear in the crystal lattice, structure imperfectness grows, the dislocation density increases. In the milling process under the action of shock loads, distortion of crystal lattice is observed to occur; atoms are shifted from crystal lattice points to occupy an intermediate position [3, 4].

Hence, at rather low temperature values, as the result of MA one could expect the formation of superhard phases' nuclei.

The analysis of the literature data demonstrates that the MA of GBN results in improving the technological parameters for phase transformation of initial hexagonal (graphite-like) BN modification into cubic BN with the subsequent BN processing under the conditions with high pressure and temperature values.

So, with the use of a reaction mixture based on GBN treated in a vibration-type mill then subjected to compression in a high pressure pressing apparatus (up to 7.7 GPa), one could gain a 200 °C decrease of the synthesis temperature for the cubic modification of BN, all other things being equal in comparison with raw mixture [5]. In this connection the studies concerning the MA influence upon the structure and phase composition of GBN powder and the possibility of obtaining new phases including superhard ones under attritor processing conditions is of a considerable theoretical and practical interest.

MATERIALS AND METHODS

As a research object we used graphite-like boron nitride taken from the Zaporozhye Abrasive Industrial Complex (Technical specification TU 2-036-1045–88), with the size of particles within the range of 5–50 μm. The powders were subjected to the processing in a vertical attritor with a conic case. The apparatus differs from traditional ones in the fact that the impeller and the case rotate in opposite directions, whereas the conic shape provides the rising and intense stirring of milling elements together with the material under processing. Similar design is characterized by extremely high activation rate. The frequency of shaft rotation in the experiments amounted to 400 and 980 min^{-1}. The processing of GBN powder was carried out with the addition of aqueous ammonia solution. The ratio between the mass of balls and the mass of powder amounted to 30 : 1.

The studies on the transformation of the structure and properties were carried out with the use physicochemical and metallophysical approaches. The specific surface area was measured using BET technique with the help of Aqusorb 2100 apparatus (Micromeritics, USA).

The size distribution of particles after different processing duration was determined by the method of scanning electron microscopy employing CamScan electron microscope (England) with the subsequent stereologic analysis of diffraction images obtained with the use of Magiscan image analyzer (Joyce Loebl, England).

The transmission electron microscopy was employed using EM-125 electron microscope with the accelerating voltage within the range of 20–150 kV.

The XRD structural analysis of powders was carried out using a general purpose DRON-3.0 X-ray diffractometer with monochromatized CuK_α radiation and secondary monochromatization performed by pyrolitic graphite; the slits af-

ter the tube being of 2°30′, 1, 6, those in front of the Soller counter being of 2°30′, 0.25. The rotation of a sample was performed in its own plane; the diffractometer control, the gathering and processing of the information were carried out employing X-ray software (2.0 and 2.1 versions) for automation of XRD structural analysis.

RESULTS AND DISCUSSION

The data we have obtained concerning the grinding kinetics indicate that during a short time, a considerable increase in the specific surface area of BN powder particles occurs. So, when the specific surface area for the particles of initial GBN amounts to 2.4 m^2/g, after grinding for 30 s (the frequency of impeller rotation being of 980 min^{-1}) this value reaches 5.7, after 2.5 min it is 11.4 m^2/g, after 5.0 min the value amounts to 79.9 m^2/g. The maximal specific surface area for BN after the processing longer than 10 min at the frequency of impeller rotation equal to 980 min^{-1} amounts to 85.2 m^2/g.

The fractographic analysis of the powder (Fig. 1) demonstrates that in the initial state the particles are flake-shaped with smoothed surface. The average size of GBN particles before the attritor processing amounts to 6.1 μm. Under the processing in attritor with the increase in the treatment time, the size of particles decreases, the shape changing insignificantly, however the particles have well-developed surface. So, when the initial average size of GBN particles is equal to 6.1 μm, after the MA (the frequency of impeller rotation being of 980 min^{-1}) for 0.5 min this value has decreased down to 3.8 μm. After the processing during 2.5 min the value has increased up to 4.7 μm, after 5 min of MA treatment the average size has increased up to 4.8 μm, whereas after 10 min of the mechanical treatment this value has amounted to less than 1 μm.

At the same time, as it has been demonstrated by the stereo analysis of fractograms, the average size of particles after the processing during 5 min even increases, which could be connected with their agglomeration. The

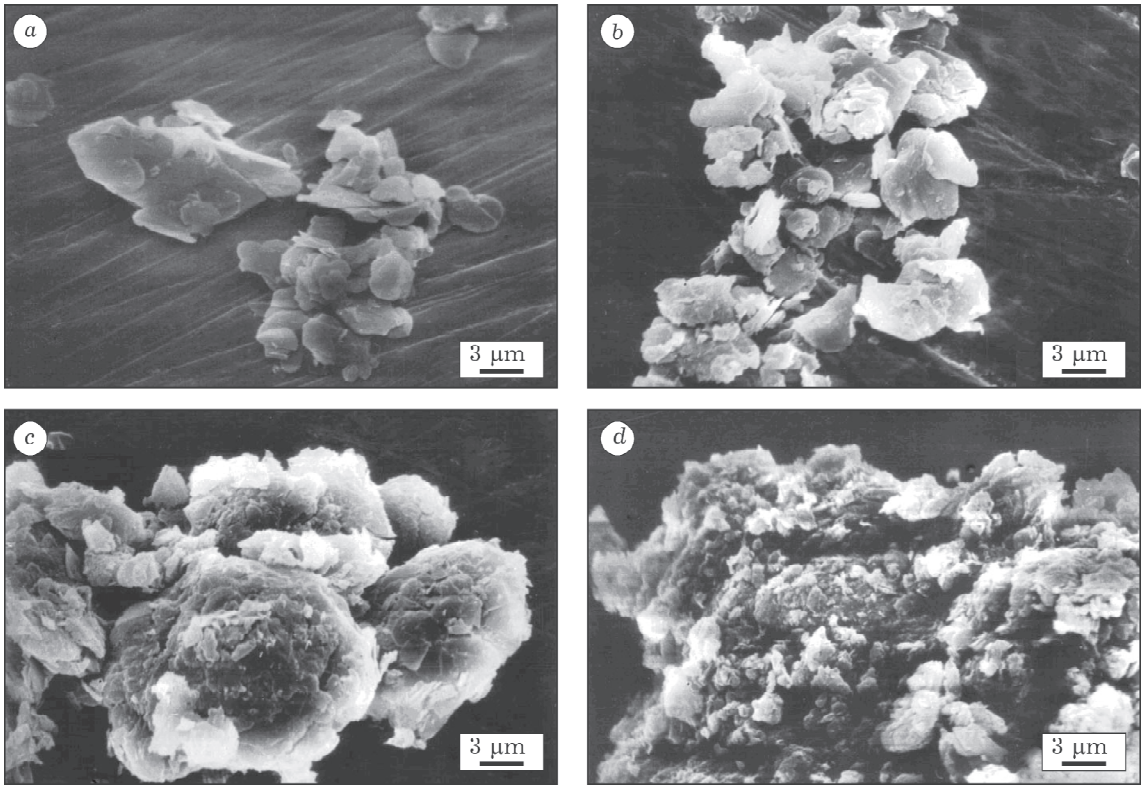

Fig. 1. Fractographic images obtained for the samples of hexagonal BN powder: *a* – initial, *b*–*d* – after attritor processing during 0.5, 2.5 and 5 min, respectively.

TABLE 1

Changing in the crystal parameters for the samples of hexagonal BN in the dispersion process within the attritor

Samples	Dispersion procedure duration, min	Crystal peak intensity (I_{002}), pulses	Interlayer distance (d_{002}), Å,		L_c, Å			L_a, Å		Lattice parameters a, b, c, Å
			crystal phase	"halo" phase	L_{002} (cr.)	L_{002} (halo)	L_{004} (cr.)	L_{100}	L_{110}	
ASTM card [34-421]	0	0	3.33	–	–	–	–	–	–	2.5041 6.6564
Initial	0	13 591	3.3439	–	400±11.207	±	248±6.081	294±6.44	373±15.226	2.5037 6.6570
Dispersed	0.5	9002	3.3421	3.3740	186±10.773	164±10.728	175±8.298	376±6.443	267±15.2333	2.4983 6.6688
Dispersed	5	2447	3.3500	3.3995	130±6.054	56±6.148	130±7.817	228±7.418	272±14.528	2.5048 6.6603

Fig. 2. Intensity of crystal peak (002) for hexagonal BN: *1* – initial, *2* – after 10 min of attritor processing (the frequency of impeller rotation amounting to 980 min^{-1}).

studies demonstrate that the particles are grinded due to the shear of planes with respect to each other and owing to breaking the particles of the powder. Just this is the fact resulting in the increase in the specific surface area of GBN powder.

Data concerning the X-ray analysis of the powder under investigation are presented in Fig. 2 and Table 1. It is seen that the attritor processing results in reducing the intensity of (002) GBN crystal peak. With increasing the time of the powder MA, the transformation of BN substructure is observed to occur from crystalline modification to nanocrystallline and amorphous one.

The results obtained allow us to assume that at different values of impeller rotation frequency during 0.5 min of the dispersion process, one could observe the destruction of crystals in basic planes to occur, with that the size of particles decreases; at the same time a great amount of disordered GBN, as well as separate layers of amorphous phase could be observed top appear. All this results in an increase in the specific surface area of powder and in a decrease of GBN interlayer distance d (002).

In the powder of GBN, the processes of the reduction of crystallite height L_c occur during all the time of dispersion procedure, i.e. their "sewing together" during the mechanical activation does not occur. With the increase in the dispersion procedure duration, a considerable internal stress is observed to appear (an increase in the interlayer distance d (002) occurs), which results in an abrupt increase in the specific surface area of GBN and in the further decreasing the L_c value (see Table 1).

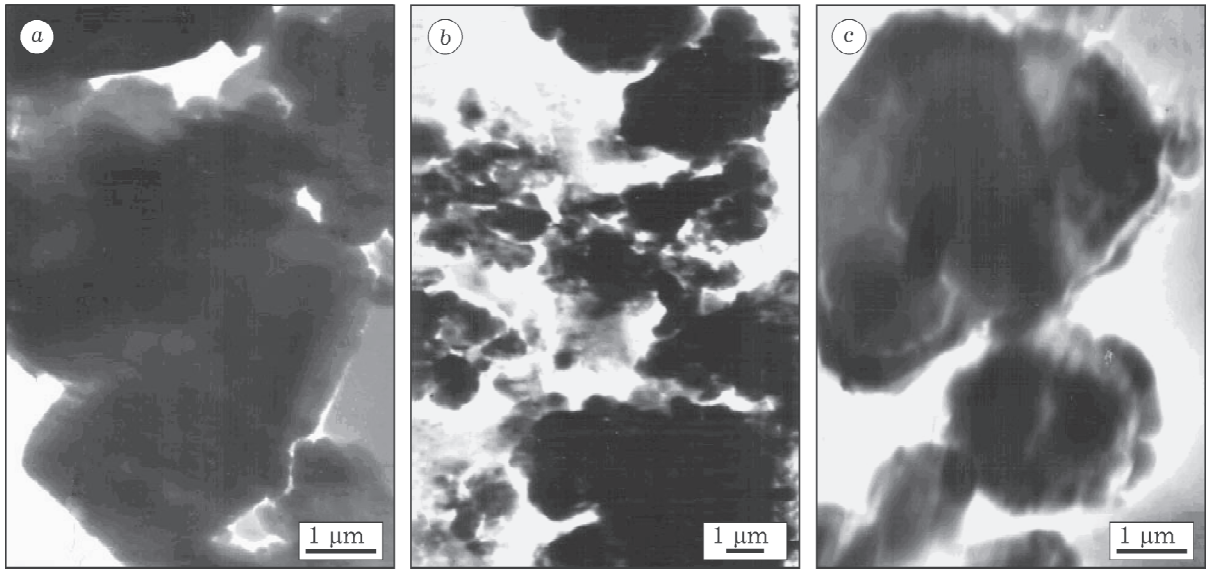

Fig. 3. Electron microscopy images of structural transformations in BN after mechanical activation during 5 (*a*), 10 (*b*) and 12.5 min (*c*). Frequency of impeller rotation amounting to 980 min^{-1}.

Figure 3 demonstrates the transformation of BN structural state depending on the MA duration.

According to atomic force microscopy data, the further grinding of GBN powder during 4 h at the impeller rotation frequency of 400 min^{-1} has allowed us to obtain BN particles with the size ranging within 35–300 nm.

The XRD structural analysis of the powders processed in the attritor during 1–4 h has allowed us to establish that when the time of processing increased one can observe the reflexes of cubic and wurtzite BN high pressure phases as well as of rhombohedral BN to appear (Fig. 4). With exceeding the optimum intensity and duration of MA, a reverse CBN transition into GBN with the recrystallization of the latter (see Fig. 3, *c*) is observed.

Thus, a principal possibility has been demonstrated concerning the obtaining of superhard BN modifications with cubic and wurtzite structure under the attritor processing of GBN with the size of particles ranging within submicronic and nanometre scale. The particles obtained can be also characterized by high values of specific surface area, which alongside with the small size allows one to use them efficiently for obtaining polycrystalline superhard materials, as well as to employ the particles modifying additives for various kinds of composites and coatings.

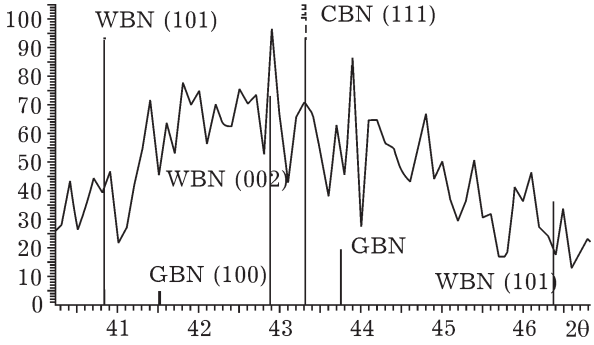

Fig. 4. Part of X-ray diffraction pattern for BN powder after the mechanical activation during 1–4 h. Alongside with the graphite-like boron nitride (GBN), the presence cubic (CBN) and wurtzite (WBN) modifications of BN is noted.

CONCLUSION

1. Dispersion process kinetics has been studied for powders. It has been established that after intense grinding for 10 min at the frequency of impeller rotation amounting to 980 min^{-1}, the specific surface area of BN powder increases more than by an order of magnitude (from 2.4 to 85.5 m^2/g).

2. The results of XRD structural analysis and electron microscopic investigation indicate that the attritor processing results in decreasing the intensity of GBN crystal peak (002). With the

increase in powder mechanical activation time, BN substructure transformation occurs from crystalline to nanocrystalline and amorphous modifications. Prolonged grinding of GBN powder at the frequency of impeller rotation amounting to 400 min^{-1} during 4 h has allowed us to obtain BN particles with the size of 35–300 nm.

3. According to the character of changing the parameters of fine structure and the specific surface area one could distinguish two stages of the dispersion process. At the first stage, as the result of intensive dispersion action, destructing the hexagonal BN crystals and decreasing the size of particles occurs; this results in an increase in the specific surface area of the powder. At the second stage, a considerable internal stress is observed to appear (an increase in the interlayer distance d (002) occurs) therefore the specific surface area of GBN particles abruptly increases.

4. A principal possibility has been demonstrated concerning the obtaining of superhard BN modifications with cubic and wurtzite structure under the attritor processing of GBN with the size of particles ranging within submicron and nanometre scale. The particles obtained can be also characterized by high values of specific surface, which alongside with the small size allows one to use them efficiently for obtaining polycrystalline superhard materials, as well as to employ the particles in modifying additives for various kinds of composites and coatings.

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