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HYDROLYSIS AND THERMOBARIC BEHAVIOUR OF AMORPHOUS BN: STRUCTURAL CHANGES AND CUBIC BN FORMATION

The aim of this work was to study the thermobaric behaviour of the X-ray amorphous a-BN in the supply condition with elucidation of pressure-temperature conditions of cubic BN forming without traditional solvent catalysts facilitating phase conversion. The source powders were obtained using a modified urea process in combination with thermomechanical treatment of the furnace charge. The technology allows reducing the synthesis temperature almost 2 times, while significantly increasing of BN product yield (> 96%). The very small sizes of the structural cluster elements of final a-BN (< 2 nm) cause the heightened activity of this precursor. The powders thermobaric treatment was performed in toroidal type high-pressure apparatus at pressures 6.5 and 8 GPa and temperature ranges of 1350–2200 °C. XRD methods (Ultima IV, Rigaku, diffractometer, Japan) and scanning electronic microscopy (FEI Verios 400L XHR SEM, USA) were employed for structural studies. It was found, that initial a-BN is characterized by higher chemical activity, which results in a partial hydrolysis of the compound when moisture is absorbed from the open atmosphere. The fusible reaction products, including orthoboric acid H_3BO_3*, ammonium pentaborate* $NH_4B_5O_8{\cdot}4H_2O$ *and ammonia nitrate* NH_4NO_3*, play a key role in the of structural transformation and a-BN→cBN recrystallization processes. It was found that at pressure of 6.5 GPa full conversion with the formation of spacious segregation of cBN nanoparticles (crystals) takes place even at 1400 °C within 45 s of p,T-action which is ascribed to catalytic effect of the fluid phases. From the standpoint of research-applied potential of results obtained, they can be viewed as a definite basis for development of technology for nanodispersed cBN powders synthesis with their further use for sintering superhard materials, in particular, tool-making materials.*

Key words*: boron nitride, amorphous structure, hydrolysis, high pressure, phase transformation*

Introduction

Mass crystallization processes from multicomponent systems with solvents-catalysts facilitating the conversion of graphite-like boron nitride (*gr*-BN) to cubic (cBN) are currently most widely used worldwide in production technologies of dispersed cBN materials. The millions carats of powders are annually synthesized by leading industrial companies for production of superhard cutting materials and abrasive tools. The sintering technologies at manufactoring of polycrystals and composite materials based on BN cubic phase have undoubted exceptional advantages over the processes of direct *gr*-BN solid-phase transformation into cBN. Among them the relatively low parameters of p,T-action are important, which allows to produce large-size sintered blanks, but the most significant is the possibility of flexible adaptation of composites and their performance to specific conditions of use in metalworking. Purposeful changes of the structure, composition and content of components of cutting material based on cBN (composites of BL and BH groups) allow to diversify this adaptive function [1, 2].

Meanwhile, the interest to making of polycrystalline cBN by *gr*-BN direct solid-phase transformations, as usual at more high pressures and temperatures, has not subsided since the publication of F. R. Corrigan and F. P. Bundy [3]. Material science researches in this area have recently received a new motivation and impulse due to development of new technologies of BN powdered materials which define the genesis and peculiarities of its structural state. In particular, special attention is drawn to the reports about the "extra-hardness" of the cBN polycrystals obtained (HV ~ 60–110 GPa), which is 2–3 times exceeds the single crystals hardness [4–10]. Of course, the structural factor is decisive in this case. In the course of solid-phase transformation the p,T-conditions and features of grain grows processes (recrystallization) should be taken into account if it is necessary to fix the submicron or nanocrystalline structural state of cBN polycrystals. The effects of structure strain hardening, in particular due to grain nanotwinning, are also relevant when reaching extra level of mechanical properties of the final product. Extreme thermobaric conditions are typically required for such processes implementation: pressures $p = 9–20$ GPa (mainly $p > 15$ GPa), temperatures $T = 1500–2300$ °C, duration of action is 20–30 minutes. In many cases the exploratory researches in this area had a fundamental trend as a rule. The sizes of the samples obtained are rather small and consist of 1.5–2 mm, which is in general sufficient to studding of their structure peculiarities. On the other hand, the possibilities of testing of physical and mechanical properties, in particular from the standpoint of instrumental material science, are significantly limited.

In the processes of direct solid-phase transformation of powdered *gr*-BN initial materials (direct conversion sintering method – DCS by [11]) a dispersity of the system causes facilitated diffusion activity and promotes the *gr*-BN→cBN conversion.

At using of high-purity hBN crystalline powders, which were previously deoxidized to the level of oxygen concentrations of 0.06–0.07 mass %, a limit density of cBN polycrystals was reported to have achieved (porosity was less of 0.5 %) and as a result a translucency of the samples in the visible spectral region has arisen [9, 12, 13]. In the known technical solutions baric conditions needed to high-strength cBN structure formation were significantly "softened". The required pressures were typically around 7.7–10.5 GPa and it gave rise to technical possibilities to make the large-sized cBN polycrystals using appropriate high pressure apparatuses (HPA) with enlarged reaction volume. Under these thermobaric conditions the blanks with a diameter of 6–12 mm and a thickness of 5–15 mm were produced depending on type of HPA. As for temperature conditions, the hBN→cBN conversion was turned out to reach only at temperatures $T > 2200$ °C.

The similar high temperatures are required in case of high-purity bulk pyrolytic materials based on *gr*-BN if it is necessary to form an essentially homogeneous (monophase) state of final cBN product [9, 14]. From the standpoint of instrumental application of cBN polycrystals it is important to consider a possible high temperature grain growth process which threatens to the structural weakening of the cutting insert material [9]. In addition, in pure materials a high mobility of intergranular boundaries is known to accelerate undesired collective recrystallization. Taking into account known data concerning peculiarities of the conditions-structure-properties triad the obvious conclusion follows that at additional mechanical or mechanochemical activations of initial powders the thermobaric parameters of the *gr*-BN→cBN conversion are certainly reduced.

Methods of high-energy mechanical activation of hBN powders are often used to clarify to what extent a structural instability affects not only the processes of cubic BN spontaneous crystallization but also DCS features, for example [15, 16]. At the same time, note that the negative consequence of activated state concludes in increasing of powder sorption capacity – adsorption and retaining of gases and moisture. Thus, finding out the effects of influence requires considering of more complex mechanisms that are essentially related to the mechanochemical nature of activated state of the initial hBN powders.

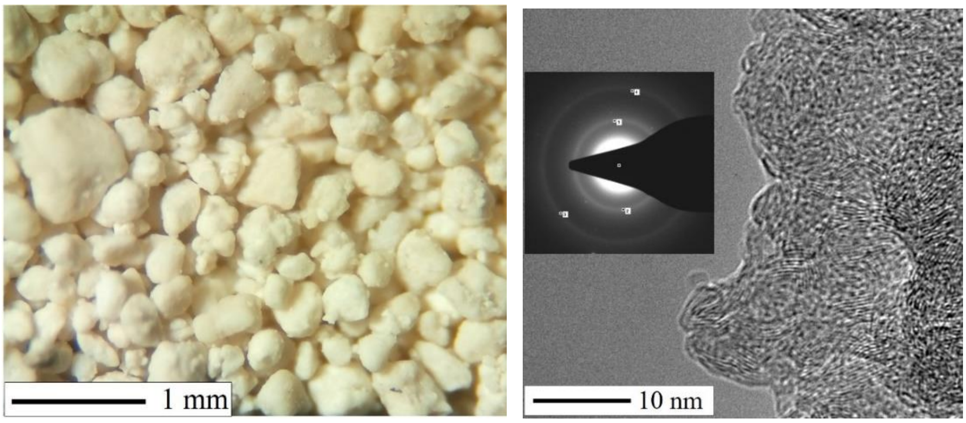
In this work we studied the thermobaric behavior of X-ray amorphous boron nitride (*a*-BN) obtained by modified urea process in combination with thermomechanical processing of the furnace charge. This technology allows reducing the synthesis temperature of *a*-BN almost 2 times, while significantly increasing of BN product yield (> 96%). Very small sizes of the structural cluster elements of final *a*-BN (< 2 nm) cause the heightened activity of this precursor.

Experimental studies and results obtained

The needed conditions of thermobaric action were created using a toroidal type of HPA [17, 18]. The available varieties of toroidal HPA-20 (reaction volume V $\approx$ 0.5 cm^3) and toroidal HPA-30 (V $\approx$ 1 cm^3) were used in both experiments. The pressure in toroidal HPA-20 using for previous probe-based experiments was set according to the calibration of the apparatus at room temperature. The temperature in the sample center was estimated by thermocouple calibration with parabolic extrapolation of data to 2200 °C. The method of assembling high pressure cells and other technique devices corresponded to those described in [19]. In case of HPA-30 a special p,T-parameters correction was performed taking into account a pressure dependences of the melting temperatures of Ag and Pt as well as eutectic melting in the Mo-C system. The point of intersection of the melting curve Pt with the line of thermodynamic equilibrium of graphite-diamond (p = 7.15 GPa; T = 2083 °C) was assumed as reference p,T-point [20, 21]. Thermobaric loads in the work corresponded to pressures of 6.5 and 8 GPa with an error of ± 0.3 GPa and temperatures in the range of 1350–2200 °C with an error of ±50 °C. The duration of p,T-action did not exceed 60 s.

The XRD studies were fulfilled in focusable Bragg-Brentano reflection geometry in monochromatic CuKα radiation using Ultima IV diffractometer (Rigaku, Japan). A curved graphite single crystal installed on a diffracted beam was used as a monochromator. Diffractograms were taken using step-by-step scanning in the range of angles 2θ from 20 to 100 degrees. Based on the lines extension analysis (*hkl*) with $l \neq 0$, the degree of three-dimensional ordering of *gr*-BN (P_3) structures was estimated by O.V.Kurdyumov's method [22]. Electron microscopic studies were performed using a FEI Verios 400L XHR SEM microscope (USA).

In the supply state the *a*-BN is a dispersed product prone to agglomeration (fig. 1, *a*).



a *b*

Fig. 1. Initial a-BN: a –an appearance of the agglomerated product (supply state); b – HRTEM image of disordered BN and SAD from the structure fragment

Agglomerates (granules) have a predominantly round shape and the internal organization of their structure consisting probably of different levels is responsible for the rather high strength of the granules. It may also indicate a high level of structural instability of a lower level self-connected structural elements. A significant disorders of *gr*-BN lattice were found by high-resolution transmission electron microscopy (HRTEM) a (fig. 1, *b*). Selected area (electron) diffraction (SAD) from structure fragment shows strong diffuse ring reflections corresponding to the 002 and 100 indices of *gr*-BN planes.

Heat treatment of the initial *a*-BN in the agglomerated state at 100 °C for 5 h leads to some weight loss Δm ≈1.6 wt. % of the sample due to thermal desorption of gases and moisture (fig. 2). Note that at drying the *a*-BN powder was placed in the oven in a natural manner and distributed in even layer with a thickness of 5 mm on a titanium deck.

Being in the open air with a relative humidity of φ ≈ 60 % (room temperature 20–25 °C) after drying powder was observed to slow saturate with gases and moisture results in a significant change in mass (step 2, fig. 2). Subsequent re-annealing at 100 °C after a certain thermodesorption stabilizes the sample mass at a level which was above the starting one. It may indicate the partial hydrolysis of *a*-BN (step 3). After that, the sample again starts to saturate with gases and humidity in the open air (step 4). Experimental data on the kinetics processes at all steps are well approximated by exponential functions (fig. 2, table 1).

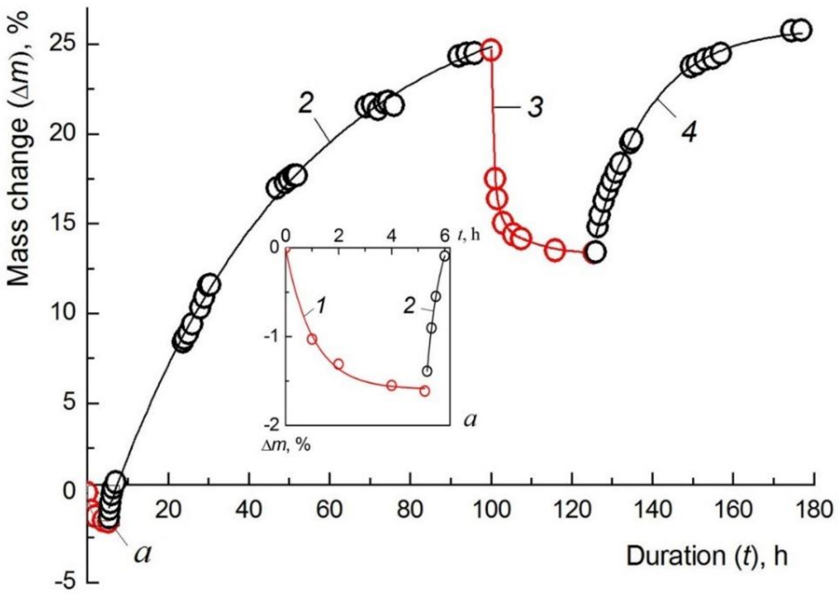


Fig. 2. Thermodesorption of gases and moisture from a-BN agglomerated powder at 100 °C (1, 3), as well as the reverse saturation process in the open air (2, 4). The Δm (wt. %) corresponds to the ratio to the starting sample mass of a-BN in the supply state; a – initial stages of drying (enlarged image)

Table 1. **General characteristics of gassing and gas saturation processes for agglomerated *a*-BN during heat treatment (fig. 2)**

Stage (fig. 2)	Process characteristics	Duration, h	Asymptotic limit, %	Standard error, %
1	Thermal desorption of gases and moisture at $T = 100$ °C in drying oven	5	-1.59	± 0.04
2	Adsorption of gases and moisture in the open air at T 20–25 °C	95	28.89	± 0.37
3	Thermal desorption of gases and hydrolysis at $T = 100$ °C in drying oven	25	13.38	± 0.47
4	Adsorption of gases and moisture in the open air at $T = 20–25$ °C	50	25.91	± 0.27

The obtained results show extremely high chemical activity of *a*-BN which is not typical for highly crystalline dispersed hBN products absolutely. The *a*-BN hydrolysis depending on the amount of moisture and treatment conditions is possible with the formation of boric acid under the reaction [23]

$$BN + 3H_2O = H_3BO_3 + NH_3\uparrow$$

or ammonium pentaborate according to reaction [23, 24]

$$5BN + 12H_2O = NH_4B_5O_8{\cdot}4H_2O + 4NH_3\uparrow.$$

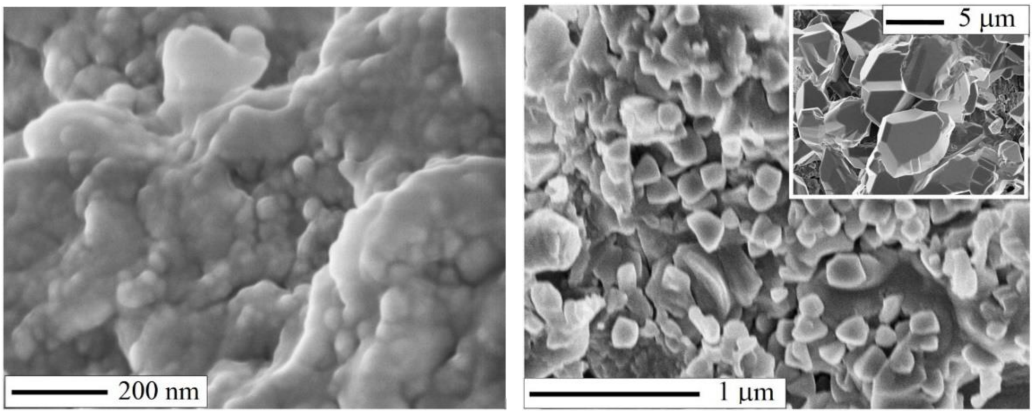
Based on the results of studies by infrared spectroscopy [25] amorphized by mechanical activation (h$\to$*a*)BN powder at the initial stages of hydrolysis forms X-ray amorphous $NH_4B_5O_6(OH)_4 \cdot 4H_2O$ according to the reaction

$$5BN + 14H_2O \to NH_4B_5O_6(OH)_4{\cdot}4H_2O + 4NH_3\uparrow.$$

When the hydrolysis product is heated, a new phase appears, which can be interpreted as ammonium pentaborate $NH_4B_5O_8{\cdot}4H_2O$. As a result of thermal dissociation $NH_4B_5O_6(OH)_4$ at T < 300 °C $NH_4B_5O_8$ is formed, which is registered by X-ray diffraction methods [25, 26]. Hydrolysis (h$\to$*a*)BN takes place even at room temperature under the action of atmospheric moisture, in which case, the smell of ammonia is felt.

In our experiment in the process of heat treatment at third stage at 100 °C (fig. 2) also stated the fact of ammonia release by organoleptic sensation. If we follow the version that the stabilization of the sample mass ends with the formation of $NH_4B_5O_6(OH)_4 \cdot 4H_2O$, then based on the mass balance of the initial and final reaction products, the calculation of the proportion of hydrolyzed *a*-BN at 100 °C shows that this proportion is δ =10.2 mass % (from the dry product starting mass). If we assume that the hydrolysis product completely decomposed within of 95 hours of thermal treatment, having formed $NH_4B_5O_8$, then a similar calculation results in δ = 24.4 mass %. Thus, there is some uncertainty in the value δ due to the lack of specific data on the composition of *a*-BN hydrolysis products.

Returning to the initial *a*-BN, the pronounced flowability and compaction ability at usual compression in steel molds were found to be inherent for the powder in state as supplied. As a result, it is possible to obtain solidity samples of the required size for outfitting in the high pressure cells of the HPA. A density of self-bound *a*-BN compact samples meanwhile is relatively small and does not exceed 1.45 g/cm^3 at a maximum compression pressure p = 0.6 GPa (fig. 3, *a*). Note that some varieties of highly crystalline hBN powders are compacted by pressing to a density of ~ 2.14 g/cm^3 which corresponds to a porosity of 6.6% only.



a *b*

Fig. 3. Microtopography of the samples structure (SEM images): a – initial a-BN compacted by pressure of 0.6 GPa; b – microstructure after thermobaric action (p = 8 GPa, T = 1350 °C, t = 60 s) and crystals aggregation of impurity phase (insert)

In the bulk sample made by compaction of *a*-BN powder using steel mold the nanoscale structure is quite clearly revealed – the structure elements with a size of 30–50 nm in a shape close to spherical one (nanosized balls). Undoubtedly, the real structure of the balls is such, as shown in fig.1, *b*. In the first preliminary thermobaric experiments with the initial *a*-BN (state of supply) at p = 8 GPa and T = 1350 °C (t = 60 s) the structure of the material was found to evolve rapidly. Flat face polyhedral forms appear on the crystals the sizes of which are mainly in the range of 100–200 nm (fig. 3, *b*). The aggregations of much larger crystals were also observed (insert in fig. 3, *b*). The habits of these crystals do not correspond to hBN hexagonal symmetry and therefore, most likely, they belong to the impurity phases. X-ray studies indicated that *a*-BN has been almost completely recrystallized into hBN with $P_3 \approx 97\%$ (fig. 4).

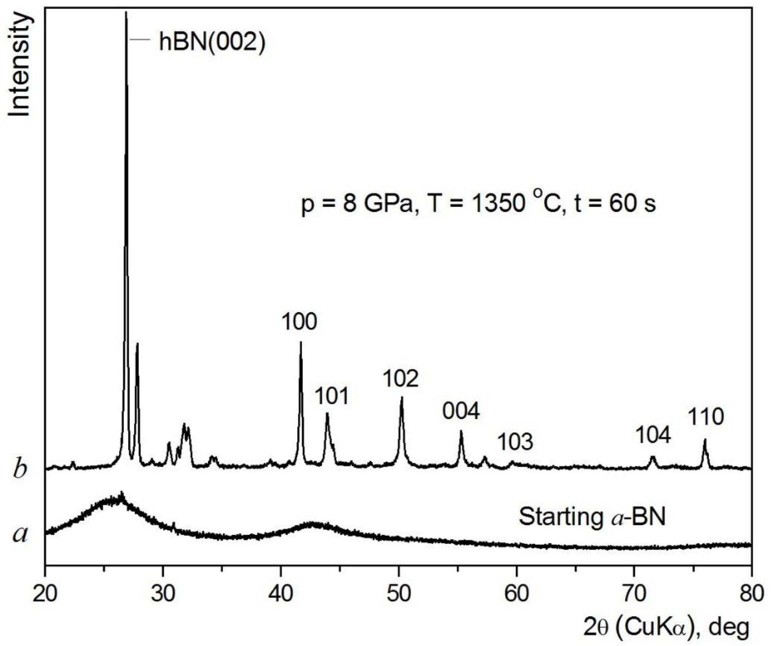


Fig. 4. XRD profiles of the samples: a – an initial a-BN; b – HP-HT treated products obtained from a-BN as the starting material at p = 8 GPa; T = 1350 °C and t = 60 s

All hBN reflections are present on the corresponding X-ray profile (fig. 4, *b*). The texture of the phase is weak, cBN peaks are not observed. From hBN profile analysis it was determined that there is a deviation from stoichiometry with the presence of vacancies in the boron sublattice. An unusual change in the lattice periods is also recorded – decreased *c* = 0.66459 nm instead of 0.66612 nm, and increased *a* = 0.25051 nm instead of 0.2504 nm. The group of peaks between the position of hBN (002) and 35 deg of 2θ can be associated with the impurity phase, most likely with boric acid H_3BO_3. The presence of ammonium nitrate NH_4NO_3 and urea $(NH_2)_2CO$ is also not excluded, but for these phases there is a coincidence of only 2–3 weak lines.

The formation of structurally perfect hBN at relatively low temperature can be explained by solution-melts mechanism of recrystallization controlled by the presence of impurity phases in the liquid state. The process takes place in cBN thermodynamic stability region and corresponds to the alternative behaviour according to the Ostwald's rule of stages and metastable transitions [27]. A more stable state with cBN formation is not achieved due to insufficiently high kinetic activity in a multicomponent system at 1350 °C.

In subsequent experiments, we used preliminarily homogenized *a*-BN powder. For this an initial agglomerated *a*-BN powder (20 g) has been subjected to ultrasonic disintegration in ethyl alcohol (150 ml) for 1 h (three times of 20 min duration with alcohol restitution after the sedimentation of dispersed product). An alcohol was evaporated from the precipitate in the open air at 40 °C for 12 h and after that the adsorbed gases were additionally removed by thermal desorption at 150 °C for 1 h using a drying oven. The density of the samples after mold compaction of the disintegrated *a*-BN powder was d ≅ 1.3 g/cm^3. The toroidal HPA-30 was used in this series of p,T-loads.

The main features of the thermobaric *a*-BN behaviour at temperatures in the range of 1400–2200 °C were the formation of cBN and the absence of even a trace amount of residual graphite-like phase since the most intense reflection of hBN (002) was not observed on X-ray profiles of the samples (fig. 5, insert). The group of peaks between 22 deg. of 2θ and position of cBN (111) belongs undoubtedly to the impurity phases mainly ammonium pentaborate $NH_4B_5O_8{\cdot}4H_2O$ and ammonium nitrates NH_4NO_3 the relative content of which varies depending on p,T,t-conditions (fig. 5, table 2). The sample obtained at highest parameters of thermobaric action (p = GPa, T = 2200 °C, t = 60 s) consists of cBN and ammonium pentaborate $NH_4B_5O_8{\cdot}4H_2O$ only.

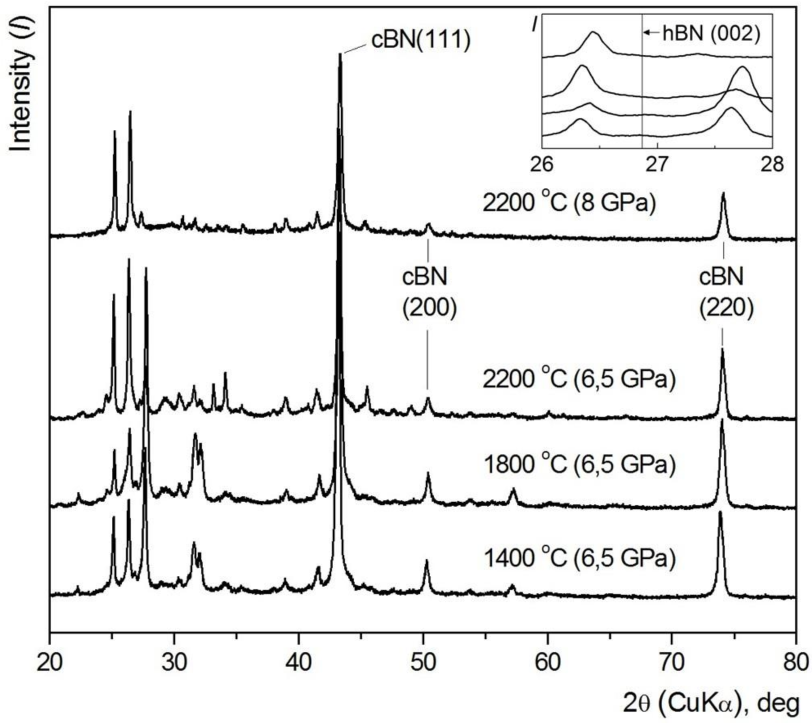


Fig. 5. XRD profiles of the samples obtained from a-BN as the starting material at different p,T,t-parameters of thermobaric action: the insert shows no hBN (002) reflection (the most intense hBN peak); the reflections of impurity phases are localized in the range of 22–43 deg of 2θ (Table 2)

Table 2. **Phase and impurity composition of samples according to PDF database and relative intensity of main reflections of each of components**

Thermobaric action parameters			BN phases and impurities with space groups of symmetry and relative intensity of main reflections, %					
p, GPa	T, °C	t, s	hBN *$P6_3/mmc$*	cBN *$F\bar{4}3m$*	H_3BO_3 $P\bar{1}$, $(NH_2)_2CO$? NH_4NO_3 ?	$NH_4B_5O_8{\cdot}4H_2O$ *Pmmm* 31-0043 Bba2	NH_4NO_3 *Pmmn* 73-1518 Pbnm	NH_4NO_3 *Pmmn* 70-1443 Pmnm
8	1350	60	79	–	21	–	–	–
6.5	1400	45	–	69	–	12	19	–
6.5	1800	45	–	62	–	7	31	–
6.5	2200	45	–	61	–	25	8	6
8	2200	60	–	73	–	27	–	–

SEM studies have shown that at pressure of 6.5 GPa and temperatures from the range of 1400–2200 °C the *a*-BN into cBN transformation is completed by the formation of specific nanodisperse structures with extended segregations of mostly rounded particles (crystals). The particles size varies from

20–40 nm to 100 nm depending on temperature of thermobaric action (fig. 6, *a*–*c*).

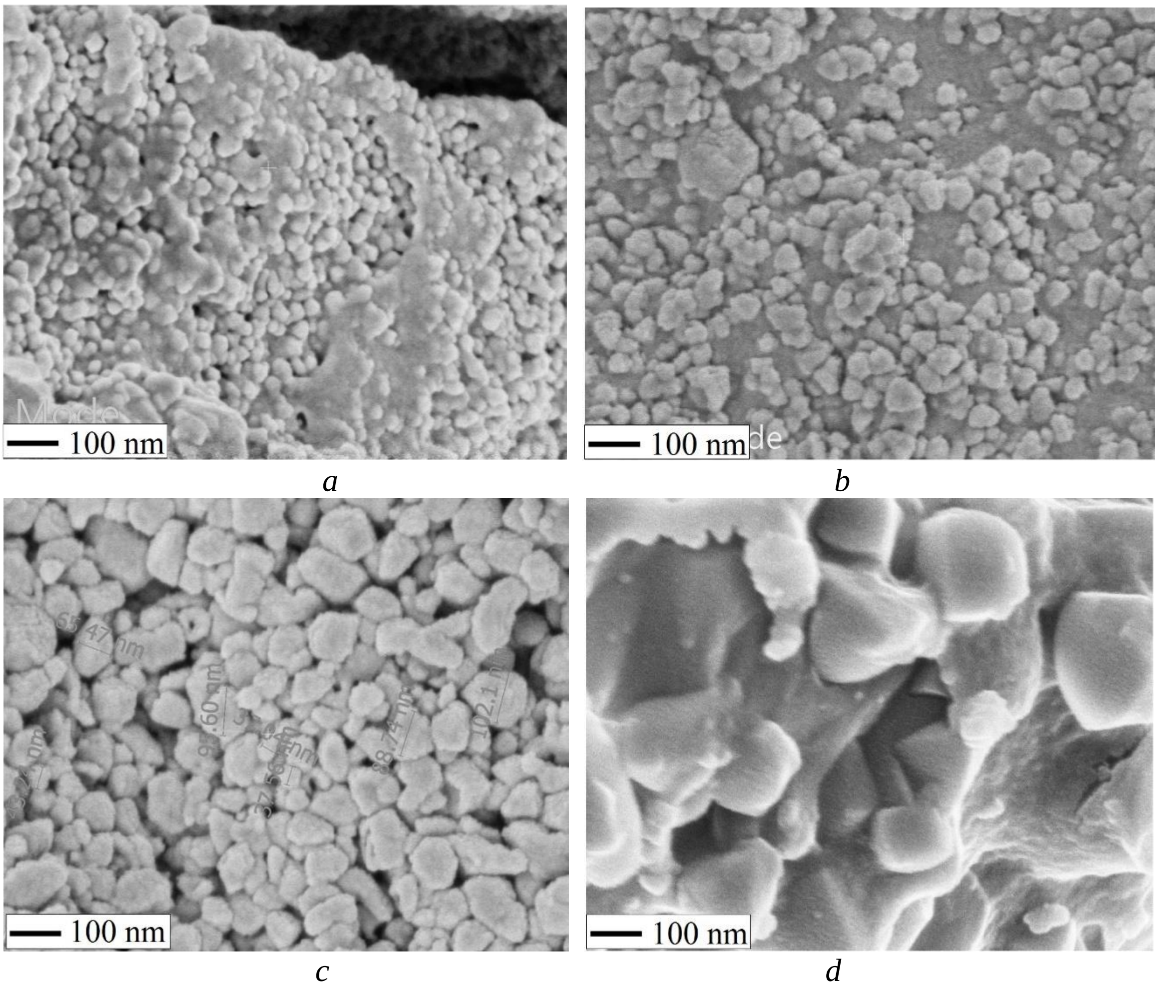


Fig. 6. Microstructures of samples obtained from a-BN as the starting material depending on temperature: a, b, c –1400, 1800, 2200 °C respectively (HPA-30, p = 6.5 GPa, t = 45 s); d – 2200 °C (HPA-20, p = 8 GPa, t = 60 s)

Note that at normal pressure the melting points of impurity phases, including ammonium pentaborate (table 2), do not exceed 200 °C which is virtually an order of magnitude lower than the temperatures of thermobaric treatment of *a*-BN in our experiments. Thus, it is likely that in such p,T-conditions the impurity phases pass to the supercritical region, i.e. form supercritical fluids (SCF). The conversion of *a*-BN→cBN is essentially a metamorphic process in presence of fluids. Therefore phase transformation may be substantially accelerated and facilitated due to the participation of the movable SCF component. In this regard, note that the most known feature of various SCFs is their high efficiency as solvents for organic and inorganic compounds, for example [28]. In addition, recall that as early as 1975 T. Kobayashi et al. put forward and experimentally confirmed the hypothesis according to which $NH_4B_5O_8$ melt, formed due chemical interaction between hBN and H_2O, acts as a solvent through which at high pressures and temperatures the hBN into cBN transformation was realized [29]. In developing the hypothesis the authors also foresaw new solvent catalysts for cBN obtaining such as urea $(NH_2)_2CO$, ammonium nitrate NH_4NO_3 and others.

At pressure of 6.5 GPa the cBN particles size increased by 4–5 times up to 100 nm with changing of p,T-action temperature from 1400 to 2200 °C. Certainly the particle growing is thermodynamically stimulated. This spontaneous process is facilitated and intensified with rising of diffusion activity in a system containing SCF. Based on formal signs the process has common features with the recondensation of particles with the participation of a liquid solvent medium (Ostwald ripening). Under the conditions of high pressure compression of the sample other evolutional mechanisms are also probable, especially at increasing temperatures, which are similar to the dynamic coalescence of contacting particles (Smolukhovsky ripening model).

In addition to a growing of cBN particles the strong changes in the sample microstructure appear with pressure increasing to 8 GPa (HPA-20; T = 2200 °C, t = 60 s). There are signs of morphological evolution of the segregate state of cBN phase. The changes were characterized by transition to the stage of cBN particles consolidation (sintering) with the formation of extensional frame structures which in general still remained rather disintegrated (fig. 6, *d*).The main reason for the material discontinuity is undoubtedly the inclusions of impurity phases, in this case of ammonium pentaborate (fig. 5, table 2). Note that from the point of view of petrogenesis a pressure solution creep mechanism with SCF participation may dominate in the processes of formation of such consolidated structures [30]. The pressure solution is largely governed by chemical potential differences between dissimilar crystals faces as well as the inhomogeneous stress state of the sample structure. The evolutional sequence of the process consists of dissolving, diffusion-controlled transfer and following precipitation of a substance on low-potential free surfaces. An increasing of material density is the consequence of macroscopic structural changes caused by the action of the described mechanism.

Concluding remarks and perspectives

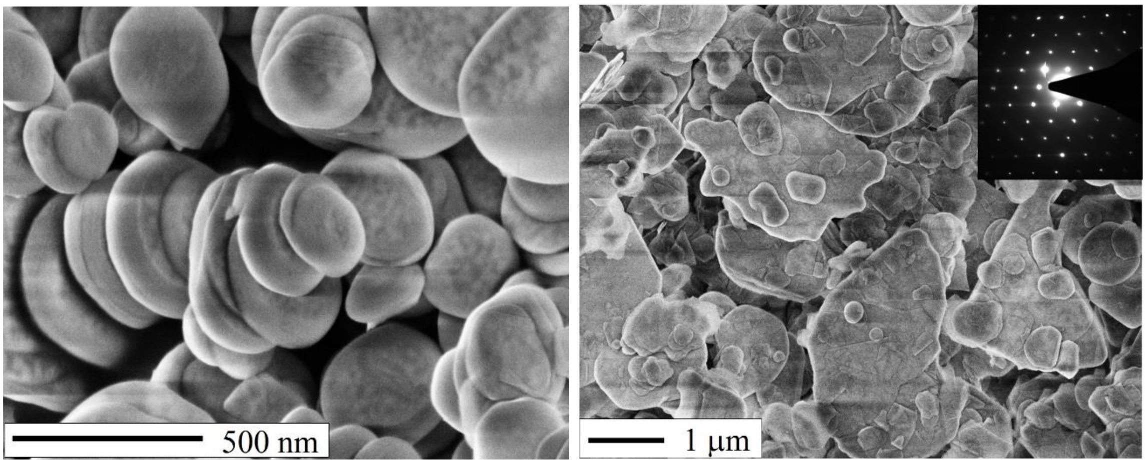
The aim of this work was to study the thermobaric behaviour of the X-ray amorphous *a*-BN (delivery state) with elucidation of *p*,*T*-conditions of cBN formation no using the traditional solvent-catalysts. In the course of studies, it was found that *a*-BN is characterized by heightened chemical activity – the powder being in the open air rather noticeably adsorbs gases including atmospheric humidity resulting in the partial hydrolysis of the samples with temperature increasing.

Low-melting products of chemical reactions such as H_3BO_3, $NH_4B_5O_8{\cdot}4H_2O$ and NH_4NO_3 facilitate the processes of structural transformations and *a*-BN→cBN recrystallization. At pressure of 6.5 GPa a conversion of *gr*-BN goes with formation of extended segregation of cBN nanoparticles (crystals). Complete *a*-BN→cBN transformation occurs even at 1400 °C of p,T-action during of 45 s, which may be attributed to the catalytic effect of fluid phases. Most likely SCF phases emerge on based of above products of hydrolysis. Note, in terms of the quasi-equilibrium approach, that regardless of the thermodynamics of the initial and final phases the presence of melt-solvents leads to increasing of entropy of the activation state (ΔS_a) of the conversion process. Therefore, free activation energy of *a*-BN→cBN transformation (ΔG_a) should reduced since $\Delta G_a = \Delta H_a - T\Delta S_a$, where ΔH_a is the enthalpy of activation. Thus, it can be concluded that SCF-phases acting as BN solvents form an active medium for cBN spontaneous mass crystallization.

From the standpoint of scientific and applied potential of the results obtained they may be hypothetically considered as a certain basis for the development of technology for synthesis of nanodispersed cBN powders. This fine-grained cBN product is interesting for use as a starting one for producing sintered superhard bodies in particular with a finer structure for special instrumental use. We emphasize that the methods of recovering, enrichment and purification should be adapted to particularities of synthesized product, in particular, taking into account the nanodispersed state of cBN. In this regard, it’s necessary to focus on the results obtained by T. Taniguchi, et al. [16], where similar study has been performed. The authors went through the entire technological sequence from synthesis to sintering of cBN powders and demonstrated some mechanical and optical properties of the sintered polycrystalline fine-grained body. The Vickers hardness was about 40 GPa at indentation load of 4.8 N and sample exhibited high translucency testified to a high level of its purity.

Taking into account the results of thermobaric experiments using HPA-30, the evolutionary processes of structural and phase transformations of the *a*-BN (supply state) were found to not correspond to the features of DCS and are actually a process of catalytic synthesis of cBN. The high density cBN polycrystalline structures with perfect grain boundaries of recrystallization origin were not formed at any parameters of *p,T*-treatment. The obvious reason for such behaviour consists in the significant amount of impurity phases that emerge due to *a*-BN partial hydrolysis and further remain in the final product with cBN. On the other hand, it should be noted, that special methods of purity maintaining of mechanically activated *a*-BN do not provide the desired results [16]. The *a*-BN→cBN phase conversion of activated powders without contamination was found quite difficult to achieve even compared to the known results for DCS of crystalline hBN powders.

The last circumstance increases the interest to use the *gr*-BN with high level of three-dimensional structural ordering as the starting high-purity dispersed materials. Product line of Dan Yardeni associates Ltd., Innovative Materials and Technologies, contains a number of *gr*-BN powders produced by thermal treatment (recrystallization annealing) of the initial *a*-BN: turbostratic and quasi-turbostratic BN; quasicrystalline (*t*, h)BN in synthetic combination with turbostratic component; crystalline hBN and other (fig. 7).



a *b*

Fig. 7. Changing of gr-BN particles morphology depending on temperature of recrystallization annealing of the a-BN powder in a pure nitrogen atmosphere (SEM image): a – quasicrystalline (t, h) BN with turbostratic component (1500 °C); b – crystalline hBN (1600 °C)

The detailed study of the above *gr*-BN powders transformation behavior during thermobaric action, further clarification of DCS conditions of a full *gr*-BN→cBN conversion combined with researches of physical and mechanical properties produced cBN polycrystalline structures are important for further work including from the standpoint of instrumental materials science.

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ГІДРОЛІЗ ТА ТЕРМОБАРИЧНА ПОВЕДІНКА АМОРФНОГО BN: СТРУКТУРНІ ЗМІНИ І УТВОРЕННЯ КУБІЧНОГО BN

Мета роботи полягала в вивченні термобаричної поведінки рентгеноаморфного a-BN в стані постачання з з'ясуванням p,T-умов одержання кубічного BN без використання будь-яких традиційних каталізаторів розчинників, що полегшують фазове перетворення. Вихідні порошки отримували за модифікованим карбамідним процесом в поєднанні з термомеханічною обробкою шихти. Термобаричну обробку порошків виконували в апаратах тороїдального типу при тисках 6,5 і 8 ГПа та температурах з діапазону 1350–2200 °С. Для структурних досліджень були залучені рентгенівські методи (дифрактометр Ultima IV, Rigaku, Японія) та скануюча електронна мікроскопія (FEI Verios 400L XHR SEM, США). Встановлено, що для вихідного a-BN притаманна підвищена хімічна активність, внаслідок чого при поглинанні вологи з відкритої атмосфери відбувається частковий гідроліз сполуки. Легкоплавкі продукти реакцій, в тому числі ортоборна кислота H_3BO_3, пентаборат амонію $NH_4B_5O_8{\cdot}4H_2O$ і нітрати амонію NH_4NO_3, відіграють ключову роль в процесах структурних змін та перекристалізації a-BN→cBN. При тиску 6,5 ГПа повне перетворення з формуванням просторих сегрегацій наночастинок (кристалів) cBN відбувається навіть при 1400 °С за 45 с p,T-дії, що пов'язується з каталітичним ефектом флюїдних фаз. З точки зору науково-прикладного потенціалу отриманих результатів їх можна розглядати як певну основу для розробки технології синтезу нанодисперсних порошків cBN з послідуючим використанням їх для спікання надтвердих матеріалів, зокрема інструментального призначення.

Ключові слова*: нітрид бору, аморфна структура, гідроліз, високий тиск, фазове перетворення*

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ГИДРОЛИЗ И ТЕРМОБАРИЧЕСКОЕ ПОВЕДЕНИЕ АМОРФНОГО BN: СТРУКТУРНЫЕ ИЗМЕНЕНИЯ И ОБРАЗОВАНИЕ КУБИЧЕСКОГО BN

Цель работы заключалась в изучении особенностей термобарического поведения рентгеноаморфного a-BN в состоянии поставки с выяснением p,T-условий получения кубического BN без использования каких-либо традиционных катализаторов-растворителей, облегчающих фазовое превращение. Исходные порошки получены модифицированным карбамидным методом в сочетании с термомеханической обработкой шихты. Термобарическую обработку порошков выполняли в аппаратах тороидального типа при давлениях 6,5 и 8 ГПа и температурах из диапазона 1350–2200 °С. Для структурных исследований были привлечены рентгеновские методы (дифрактометр Ultima IV, Rigaku, Япония) и сканирующая электронная микроскопия (FEI Verios 400L XHR SEM, США). Установлено, что для a-BN присуща повышенная химическая активность, в результате чего при поглощении влаги из открытой атмосферы происходит частичный гидролиз соединения. Легкоплавкие продукты реакций, в том числе ортоборная кислота H_3BO_3, пентаборат аммония $NH_4B_5O_8{\cdot}4H_2O$ и нитраты аммония NH_4NO_3, играют ключевую роль в процессах структурных *изменений и перекристаллизации a-BN→cBN. При давлении 6,5 ГПа полное превращение с формированием обширных сегрегаций наночастиц (кристаллов) cBN происходит даже при 1400 °С за 45 с р,Т-действия, что связывается с каталитическим эффектом флюидных фаз. С точки зрения научно-прикладного потенциала полученных результатов их можно рассматривать как определенную основу для разработки технологии синтеза нанодисперсных порошков cBN с последующим использованием их для спекания сверхтвердых материалов, в частности инструментального назначения.*

***Ключевые слова**: нитрид бора, аморфная структура, гидролиз, высокое давление, фазовое превращение*

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ТЕПЛОПРОВІДНІСТЬ МОНО- І ПОЛІКРИСТАЛІЧНОГО АЛМАЗУ ТА КОМПОЗИТІВ НА ЙОГО ОСНОВІ (ОГЛЯД)

Проведено аналіз накопиченого теоретичного і експериментального доробку з вивчення теплопровідності моно- і полікристалічного алмазу та композитів на його основі.

Як випливає з наведеного огляду, моно- і полікристалічний алмаз різного генезису та композити на їх основі завдяки унікальним теплофізичним властивостям є фактично безконкурентними при використанні як тепловідводи в електронних пристроях великої потужності. Створення спеціальних технологій виготовлення монокристалів алмазу (вирощування методом Т-градієнту в HPHT умовах або з використанням CVD-методу вирощування) дозволили одержувати монокристали з теплопровідністю, яка не поступається природним монокристалам алмазу типу IIa. Сучасні прогресивні алмазні полікристалічні і композиційні матеріали мають величезний потенціал для вирішення великої кількості проблем у різних високотехнологічних галузях, в тому числі і при використанні їх як теплопровідного інструментального або конструкційного матеріалу, або при застосуванні в теплообмінних пристроях, що працюють за екстремальних теплових навантажень. Створення нових технологій одержання алмазних композиційних матеріалів з високою теплопровідністю (до 1000 Вт·м$^{-1}$·К$^{-1}$) дозволить їм конкурувати з природним алмазом при розробці якісно нових приладів наступного покоління.

***Ключові слова**: алмаз, полікристалічний і композиційний матеріал, домішки, ізотопний склад*

Алмаз є представником найбільш простих гомеополярних кристалів[1], який має ряд унікальних властивостей: найбільш високу серед відомих матеріалів твердість, міцність під час стиску, виключну хімічну стійкість і інертність до агресивних середовищ. У алмаза дуже значна ширина забороненої зони (найбільша серед елементів IV групи періодичної системи елементів), внаслідок чого бездомішковий алмаз є одним з найкращих ізоляторів і прозорий практично для любих довжин хвиль видимої області [1].

Теплопровідність є однією з найважливіших властивостей алмазу, що визначає його функціональне призначення та галузі застосування, а у випадку використання алмазу як тепловідводу в електронних приладах ця характеристика є визначальною, оскільки надзвичайно висока теплопровідність алмазу (до 2500 Вт/(м×К) [2, 3] в поєднанні з його низькою діелектричною проникністю (ε = 5,7) [4] забезпечують ідеальну комбінацію властивостей для тепловідводів в пристроях великої потужності. До недавнього часу не

[1]Гомеополярной зв'язок - хімічний зв'язок між двома атомами, що здійснюється одночасним володінням пари електронів обома атомами