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CONSECUTIVE SOLID-PHASE hBN(1)→cBN→hBN(2) TRANSFORMATIONS AT 7 GPa UNDER EXTREMELY HIGH TEMPERATURE GRADIENTS

A new technical solution for the high-pressure cell (HPC) design has been developed applying to toroidal type apparatus (HPA-T30). The assembly of the cells enables to create a significant radially directed temperature gradient (∇T) of around 250 °C/mm within the reaction volume of the apparatus. The proposed procedure makes it possible to record temperature dependent structural changes and solid-state transformations of compounds within a single sample volume. The capabilities of the method was demonstrated by the example of the thermobaric behavior of graphite-like boron nitride (hBN) at a pressure of 7 GPa in a wide temperature range up to ~3000 °C. The evolution of the solid-phase transformations of primary hBN(1) followed the hBN(1)→cBN→hBN(2) sequence, i.e. included the reconversion stage of cubic cBN into secondary hBN(2) at temperatures above 2680 °C. The structural features of the final phase indicate the formation of a polycrystalline structure of hBN(2) at the stages of recrystallisation annealing (grain growth process) under high temperature thermobaric treatment.

Key words: *boron nitride, high pressure, temperature gradient, solid-phase transformations, reconversion, crystal structure*

Introduction

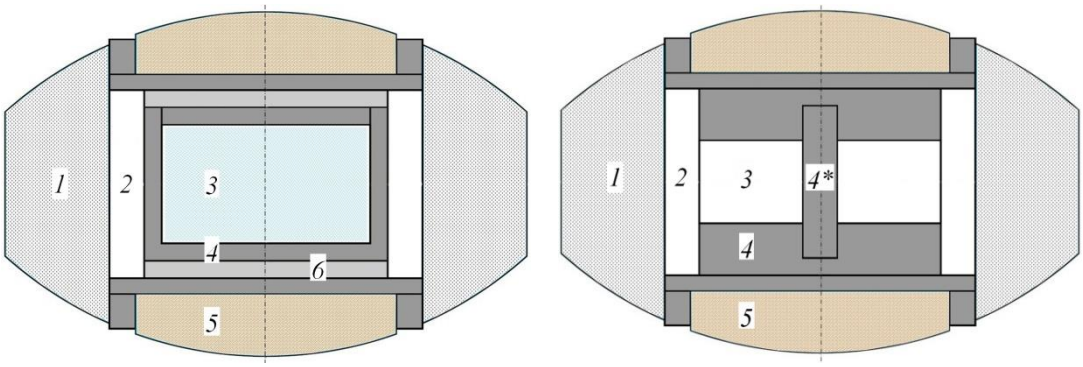
Temperature homogeneity within the reaction volumes of a high pressure cell (HPC) is usually a desirable factor in thermobaric experiments because the knowledge of thermodynamic conditions is critical to understanding the physic-chemical nature of the processes occurring under HPHT treatments. The optimized design of the HPC important both for performing fundamental physical research and for technological development [1–3]. A certain disadvantage of gradientless HPC is their restricted practical application in thermobaric experiments at extremely high temperatures above the level of 2200–2300 °C. High temperature exposure is particularly critical for the sealing gasket area as it can significantly increase the risk of depressurisation of the HPC volume [2].

Thermobaric steady-state conditions with the temperature gradient (∇T) in the reaction zone of the HPC are usually used purposefully in special cases, for example in technologies of diamond growing on the seed crystals [4]. Diffusion and convection fluxes that affect the rate of carbon transfer to the seed from the supersaturated metal melt solution are caused by the vertical ∇T in the growth volume of the cell. The seed crystals are placed in a relatively "cold" zone of the temperature field and temperature gradient is usually varied within 2–20 °C/mm.

In this work a radially directed ∇T in the reaction volume of the toroidal type apparatus (HPA-T30) was generated using not ordinary HPC assemble design. The possibility to reach much higher ∇T at least an order of magnitude was investigated. As for the new functional possibilities, the proposed method will allow to record structural changes and solid-phase transformations of compounds as a function of temperature in a volume of a single sample obtained in one experiment only.

Performing the experiment

The required thermobaric conditions were achieved in special high-pressure cells adapted to the HPA-T30 toroidal apparatus. The apparatus was used on the standard DO-044 press equipment. The experimental facilities and methods of the Łukasiewicz Research Network – Krakow Institute of Technology (Krakow, Poland) have been used. More detailed descriptions of a number of the aspects related to thermobaric experiments using HPA-T30 (and -T20) apparatus are available in our articles [2, 3]. The 7 GPa pressure in a cell with standard type of assembly is achieved at compression of the HPA-T30 by nominal force of 1750±20 ton (Fig. 1, *a*).



a *b*

Fig. 1. HPC assembly for p,T-experiments using the HPA-T30 in the standard version (a) and in the configuration with high T-gradient (b): 1 – container of cloudy marble ($CaCO_3$ mineral raw material, Turkey, Finike); 2 – sleeve made of hot-pressed hexagonal graphite-like boron nitride (hBN); 3 – sample; 4 – graphite heating system (isotropic fine-grained graphite of MG-1 grade or isostatically pressed graphite of SIGRAFINE® R8710 grade with bulk density d = 1.88 g/cm^3) ; 4 – axial rod-heater made of graphite; 5 – heat-insulating insert made of pyrophyllite (mineral rock from the deposits of the Slovechne-Ovruch ridge, Ukraine); 6 – pressed disk-heater made of low-ash natural graphite in a mixture with 40 vol. % ZrO_2*

In this work, extremely high temperatures were achieved in a relatively small volume of the sample, localized around an axial graphite rod-heater (*4**) (Fig. 1, *b)*. Previous experience on pressure calibration of the apparatus was used in the work. Above HPC assembly provides a substantially homogeneous temperature field in the sample volume. However, as already mentioned, the stability of such cell is usually limited to the temperature range of 2200–2300 °C.

The rod diameter was 2 mm with a length of 8.8 mm, which takes into account the depth of the contact zones. The outer diameter and thickness of the sample (*3)* were 14 and 4.8 mm,

respectively. A hole with a diameter of 2 mm was made along the sample axis for rod-heater (*4**) placing. The temperature field in the sample under stationary conditions of thermobaric action becomes significantly heterogeneous for such HPC assemble. In particular, in the central plane of the cell, the temperature gradient is most significant and is radially directed to its axis. It is worth noting that in this situation the critical area of sealing gasket is not exposed by high temperatures, which has a positive effect on the stability of HPA-T30 operation.

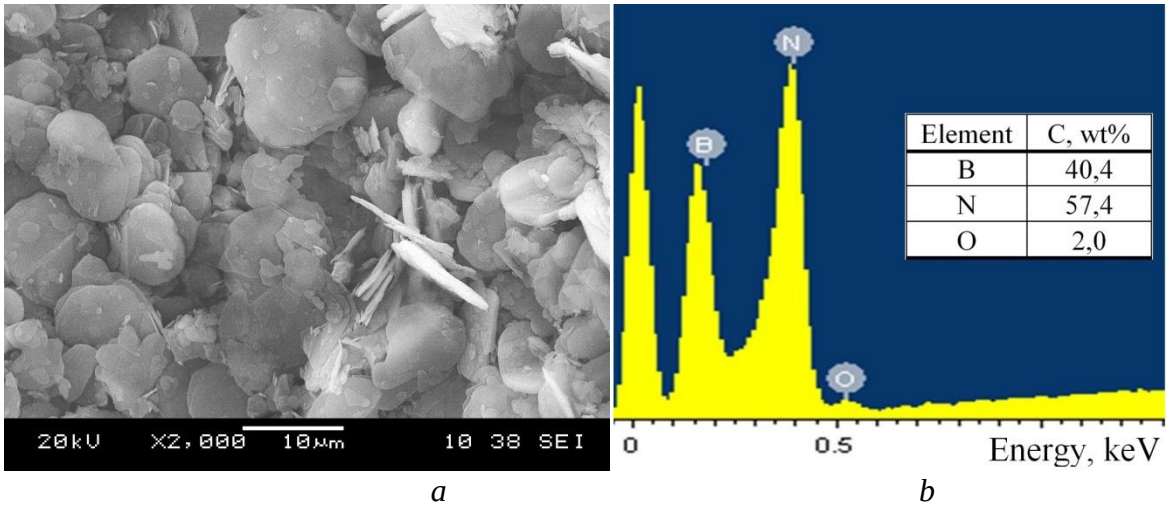
Undoubtedly, a certain evolution of the structural changes in the sample occurs already at the stage of temperature rise. Under quasi-stationary thermal conditions, with a relatively stable temperature distribution in the cell volume, structural changes and phase transformations in the sample are controlled by thermodynamic conditions and the kinetics of the corresponding processes. The space pattern of temperature-dependent evolutionary changes in any material can be recorded within a single sample after rapid quenching. In this work, to demonstrate this aspect of the proposed research method, a hexagonal modification of graphite-like boron nitride (hBN) was used as a initial material, whose behaviour under isothermal HPHT treatment (gradientless variant of the HPC) was studied in detail earlier, for example [5–9].

During the experiment, the sample was gradually heated by uniform magnification of the electric current power in the heater to 6 kW at a rate of 100 W/s. The exposure time at maximum electrical parameters was 30 s. After that, the current power was rapidly reduced to zero for 5 s (sample quenching stage).

The structural state of the obtained samples was studied by optical and electron microscopy (Zeiss Ultra Plus electron microscopy) combined with energy dispersive spectroscopy (EDS) and X-ray analysis (Panalytical diffractometer X′ PetrPRO X-ray diffraction system).

Results and discussion

Initial hBN. The external morphology of the initial (or primary hBN(1)) powder particles is characterised by a flake-round shape (thin plate habitus). Along the base plane the size of hBN(1) flakes reached 10 μm (Fig. 2, *a*).



a *b*

Fig. 2. Initial hBN(1) powder: a – external morphology and particles habit (SEM image); b - emission spectrum and chemical composition of the sample according to EDS data (inset)

According to the X-ray energy dispersive spectral analysis results, it was found that the powder contains oxygen impurities up to 2 wt % (Fig. 2*b*). The most likely explanation for the oxygen presence is the adsorbed molecular oxygen (O_2) on the powder surface. In addition, it is also possible that the initial powder contains a small amount of B_2O_3 too. The analysis of the profiles of 112 and 110 reflection lines on the X-ray diffraction pattern of hBN(1) was performed following the

approaches [9, 10]. The result obtained indicates a high level of 3D-ordering of the initial graphite-like structure with the turbostratic defects concentration in hexagons layers packing about $\gamma \approx 10$ %.

As mentioned above, the results of fundamental studies on the mechanisms of solid-phase hBN→cBN transformation have been discussed in various aspects in numerous publications, in particular [5–9]. At pressures of 7–10 GPa in the temperature region of weak diffusion, an alternative metastable behavior occurs during the phase transition. This process dominates in a 3D-ordered structure like hBN(1) one. As a result, an intermediate wurtzite boron nitride (wBN) is formed by cooperative shear deformation mechanisms. At increasing temperature, a metastable wBN progressively transforms into stable cBN due to layer-by-layer rearrangement of two-layer aa′bb′aa′bb′ wurtzite alternation into three-layer aa′bb′cc′aa′bb′cc′ sphalerite-like packing of the dense-packing hexagonal layers in boron and nitrogen sublattices.

At pressures of 7–8 GPa the rate of solid phase transformation of crystalline hBN into w-cBN becomes significant at temperatures starting from about 1500 °C. This transformation leads to the appearance of noticeable amounts of dense phases in the sample within a mere 30 to 40 seconds of thermobaric exposure [9, 11]. This temperature threshold is considered to be the low-temperature limit of the kinetic transformation region, which extends to the cBN↔hBN equilibrium temperature.

Behavior of hBN(1) in the ∇T field at a pressure of 7 GPa. Consecutive evolutionary structural changes and phase transformations in hBN(1) can be clearly seen in ∇T direction on longitudinal fracture surface of the sample (Fig. 3).

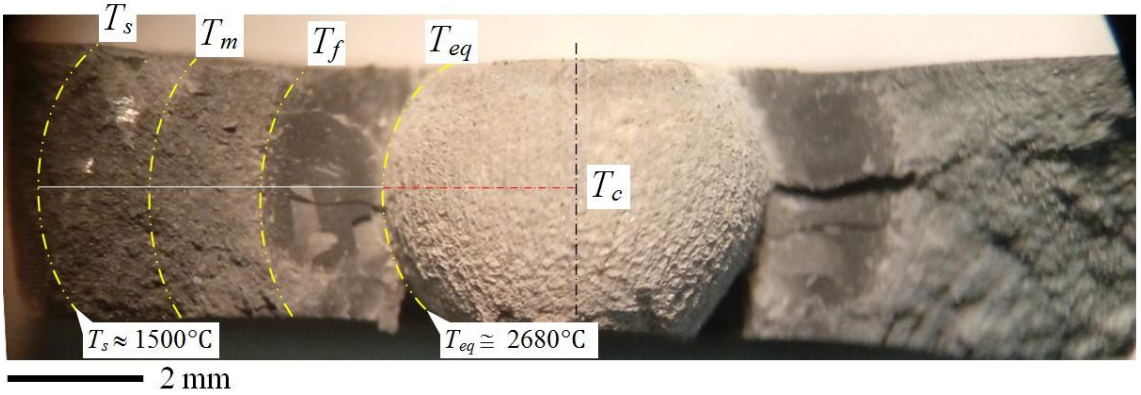


Fig. 3. The sequence of solid-phase transformations in the initial hBN(1) under high pressure ~7 GPa in the presence of a significant temperature gradient in the sample (axial longitudinal fracture of the sample): T_s – isotherm of starting conversion sintering resulting in stable cBN phase formation; T_m – the isotherm that conditionally corresponds to 50 % conversion of hBN(1)→cBN; T_f – the isotherm at which the conversion to cBN is finished; T_{eq} – the isotherm of cBN→hBN(2) reconversion which practically coincides with the temperature of cBN↔hBN equilibrium due to the impossibility of any overheating of the system at extremely high temperatures; T_c – the temperature in the center of the HPC (intersection point of the axis and radius)

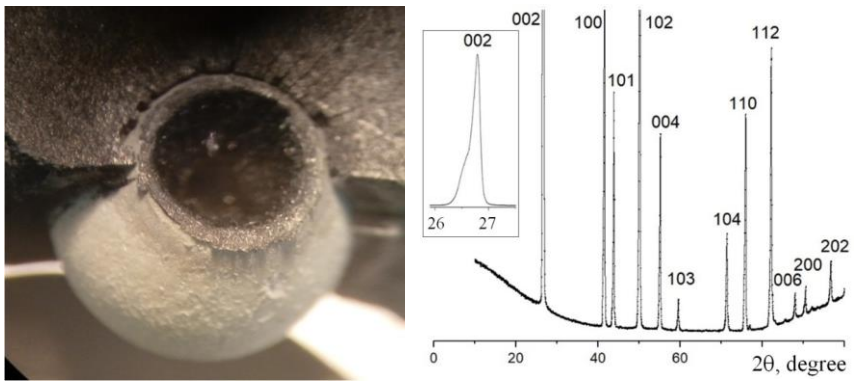
The T_s–T_f temperature interval. The evidence of the beginning of formation of dense BN phases is the presence of size effects. Their presence is associated with a significant difference in the molar volumes of the initial and final phases. The conversion from hBN to cBN results in a negative volume effect, with a relative value of 34.7%. As can be seen from Fig. 3, the T_s isotherm corresponds to the beginning of the sample profile narrowing in height. It is undoubtedly associated with volume effect of the BN(1)→w,cBN transformations. In general, this isotherm corresponds to the low-temperature kinetic limit of the conversion region at 7 GPa ($T_s \approx 1500$ °C [9, 11]). The region extends to the equilibrium temperature cBN↔hBN.

Stabilization of the profile occurs along the T_f isotherm where the conversion of the graphite-like structure BN to cubic one is fully completed. The intermediate isotherm T_m in Fig. 3 is conventionally shown as a profile with a 50 % degree of transformation. The evolutionary phase changes in the sample between the isotherms T_s and T_f can be represented by the sequence hBN(1)→h,w,cBN→cBN along the ∇T direction. The monophasic state of the polycrystalline cBN material is achieved at rather high temperatures near of 2200–2300 °C [12]. It should be noted that T_f is practically independent of pressure according to the results of *in situ* experiments performed up to 20 GPa [13].

The T_f–T_{eq} temperature interval. Unstable quasi-crystalline structure of the final phase and primary recrystallisation processes already occur at this stage of structural evolution. The formation of the quasi-crystalline structure is often thought to appear at incomplete hBN→cBN transformation [12]. The driving force of the process is determined by the joint action of external loading and phase slander. A more stable submicrocrystalline structure occurs after completion of transformation at $T \cong$ 2200–2300 °C. At increasing temperature, especially above 2400 °C, at first fine-grained and then coarse-grained cBN structures form due to normal grain growth process. The perfect boundaries of recrystallization origin and low dislocation density in the grains are a feature of substructure formed. The grain size in polycrystalline samples reaches tens of microns at finish stages of evolutionary structural changes [12].

At a pressure of 7 GPa the thermodynamic stability of cBN is bounded by a temperature of 2680 °C, which was found basing on a linear extrapolation of the known relationship p(GPa) = T(°C) / 400 + 0.3 for the cBN↔hBN equilibrium obtained by O. Fukunaga, S. Nakano, and T. Taniguchi in 2022 [14].

Taking into account the distance (ΔX) and the temperature difference between the isotherms T_s and T_{eq} , the temperature dependence along the radius towards the center of the HPC was found in the linear approximation as T(°C) = 1500 + 256.5· X(mm) (Fig. 3). Accordingly, we have ∇T ≅ 256 °C/mm and $T_f \cong$ 2270° C, the latter being consistent with [12]. Additionally, at the same approximation under quasi-stationary mode of thermobaric treatment the temperature at HPC center (the center of the heater rod) is $T_c \cong$ 3330° C.



a *b*

Fig. 4. Secondary hBN (white material) formed during the cBN→hBN(2) reconversion: a – a part of the sample separated along the T_{eq} isotherm (Fig. 3); b – the X-ray diffraction pattern of the white material corresponds to the spectrum exclusively of hBN with asymmetric 002 reflection profile (see inset)

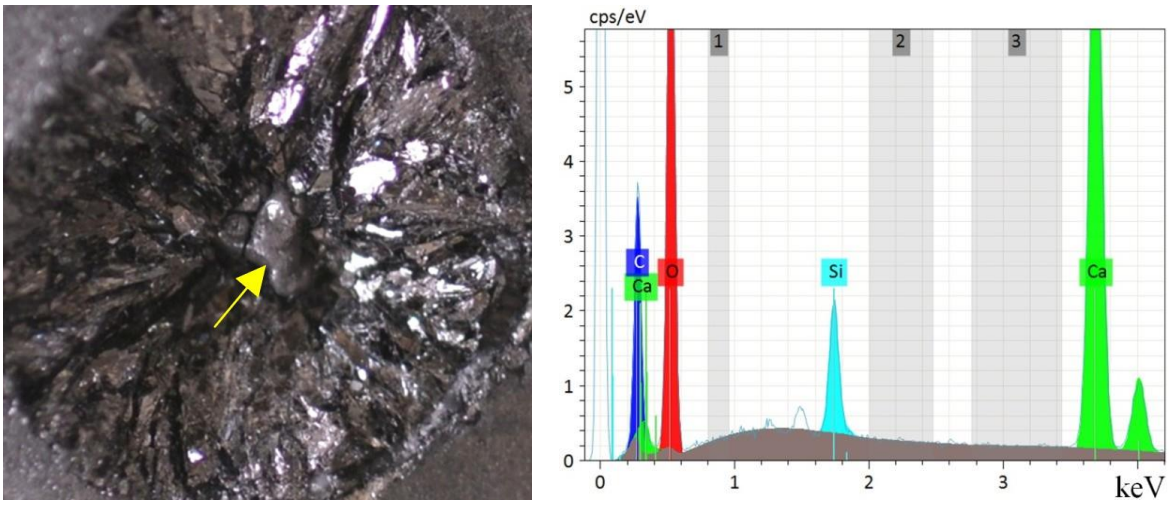
The temperature higher T_{eq}. The secondary hBN formation stage as a result of the cBN→hBN(2) reconversion begins at the moment of crossing the equilibrium temperature along the isotherm T_{eq} (Fig. 3, Fig. 4, *a)*. Overheating of any system is almost impossible due to the high diffusive mobility of atoms at extremely high temperatures ($T \geq$ 2680 °C). It is known that cBN→hBN(2) reconversion can also include an alternative metastable behavior with the rhombohedral graphite-like structure (rBN) formation (especially in the case of a perfect initial structure) [7]. However, under conditions of significant thermal activation, the system rapidly moves directly to the stable state bypassing any ways of metastable behavior. That is why the

cBN-hBN(2) interphase boundary is not spatially fuzzy and corresponds to the cBN↔hBN equilibrium temperature. The absence of metastable rBN in the obtained sample is confirmed by the results of X-ray examination (Fig. 4).

An important feature of the secondary hBN(2) obtained is the crystallinity of its structure formed under conditions of high-temperature collective recrystallization. A fracture surface of the sample looks coarse-grained with sparkling reflections from the individual grain surface. The grain size reaches 50–80 μm, according to optical microscope studies. Note that the particle size in the original hBN(1) is smaller an order of magnitude (Fig. 2, *a*).

A close examination of the X-ray diffraction pattern of hBN(2) reveals a "bump" in the reflection profile of plane 002 from the side of small 2θ angles (Fig. 4, *b*, inset). Obviously, the asymmetry arises due to the presence of areas of graphite-like structure with increased interlayer distance. Turbostratic defects are unlikely to be responsible for profile broadening since they are expected to disappear due to high-temperature annealing. The version of intercalation of impurities into the layered structure of hBN due to contamination of the HPC reaction volume seems more realistic. The ability of graphite to form intercalation compounds with increased interlayer distance is well known, for example [15]. This may indicate that graphite-like hBN has similar properties.

Further evidence that sample contamination may be real is the presence of impurities in the axial heater in the form of rounded inclusions of crystallized melt, sometimes quite large (Fig. 5, *a)*.



a *b*

Fig. 5. Internal structure and impurity composition of the axial rod-heater (4, Fig. 1, b): a – rounded re-melted inclusion in the central zone (indicated by an arrow); b - EDS emission spectrum from the material of inclusion*

Chemical composition of the inclusions in an axial graphite rod-heater according to EDS data

Element	Atomic number	Element composition, %		Definition error (1σ), %	
		Weight	Atomic	Absolute	Relative
Silicon	4	2.17	1.49	0.13	5.81
Carbon	6	13.85	22.29	2.08	15.02
Oxygen	8	52.68	63.64	6.76	12.83
Calcium	20	26.09	12.58	0.82	3.14

The mineral composition of inclusions has been not determined. According to the EDS data, they contain such elements as Si, C, O and Ca included probably with carbides, oxides, and carbooxides (Fig. 5, *b*, Table).

The graphite in the heater has a large-block radial-columnar recrystallized structure. Most likely, the inclusion is formed during the crystallization of a complex carbon-saturated melt, as evidenced by the smooth rounded surface and the absence of any signs of graphite wetting. Obviously, under the high-temperature barothermic treatment conditions the infiltration of the liquid phase (melted inclusion) into the sample structure is possible. Indeed, in the contact zone of the white hBN(2) sample with the heater a rather wide area of contaminated material was observed, which differed from the white part by its black color.

By various estimates, melting of boron nitride at high pressures (7–9 GPa) occurs at temperatures of approximately 3400 °C [16, 17]. Self-diffusion activity in deformed polycrystalline structures is most pronounced at about ~2400 °C [12]. According to our observations and evaluations at a pressure of 7 GPa, recrystallisation annealing occurs in stable phases: cBN – in the range T = 2400–2680 °C, and hBN – at T>2680 °C after cBN→hBN(2) reconversion.

Conclusions

Using of proposed HPC design to generate extremely high temperature gradients in reaction zone of HPA-T30 apparatus we can expedite the obtaining of primary data about thermobaric behaviour of various materials chemically inert to graphite. This is particularly important for high temperature compounds. Cells of this type can be used for fixing of structural changes (including solid-state transformations) up to ~3000 °C temperatures. The proposed methodology does not claim to be highly accurate in the data obtained. However, its use allows us to minimise the number of labour-intensive experiments carried out under HPHT treatments. In addition, it contributes to a more qualified strategic planning of scientific investigations concerning the study of the behavior of solid compounds under isothermal conditions at high pressures. Certain improvements in the design of the HPC are needed in the future, mainly to prevent contamination of the reaction zone under ultrahigh temperatures. The results of this work indicate the need to use special high-purity graphite materials in HPC heater structural elements.

The possibilities of the above "T-gradient method" in HPHT treatment have been demonstrated by investigation of hexagonal graphite-like BN behavior. In particular, at temperatures above ~2700 °C, even under short-term p,T-action, the structure of secondary hBN undergoes noticeable recrystallization after the stage of cBN→hBN(2) reconversion. It is assumed that accelerating hBN(2) grain growth through collective recrystallization will allow for the formation of large-sized hBN crystal aggregates. Obtaining large, defect-free crystals is essential for their application in microelectronic devices. Obviously, the main factors for further research are the optimization of the p,T-conditions and the adaptive increase in the duration of the grain growth process in polycrystalline hBN structure.

Acknowledgments

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ПОСЛІДОВНІ ТВЕРДОФАЗНІ ПЕРЕТВОРЕННЯ hBN(1)→cBN→hBN(2) ПРИ 7 ГПа В УМОВАХ ЕКСТРЕМАЛЬНО ВИСОКИХ ТЕМПЕРАТУРНИХ ГРАДІЄНТІВ

З використанням нових дизайнерських рішень при складанні комірок високого тиску апаратів тороїдального типу (АВТТ-30) досліджена можливість створення значного радіально спрямованого градієнта ∇T до ~ 250 °С/мм в реакційному об'ємі комірки. З точки зору методології термобаричного експерименту даний підхід дозволяє фіксувати структурні зміни та твердофазні перетворення сполук в залежності від температури в межах об'єму лише одного зразка. Можливості методики продемонстровані на прикладі термобаричної поведінки графітоподібного нітриду бору при тиску 7 ГПа в широкому діапазоні температур, що сягають рівня ~3000 °С. Еволюція твердофазних перетворень первинного hBN(1) відбувалась за послідовністю hBN(1)→cBN→hBN(2), тобто включала етап реконверсії кубічного cBN у вторинний hBN(2) при температурах вище 2680 °С. Структурні особливості кінцевої фази свідчать про формування полікристалічної структурі hBN(2) на етапах рекристалізаційного відпалу в умовах високотемпературної термобаричної дії.

Ключові слова: *нітрид бору, високий тиск, градієнт температури, твердофазні перетворення, реконверсія, кристалічна структура*

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РОЗРАХУНКИ ТЕМПЕРАТУРНИХ ПОЛІВ У ОСЕРЕДКУ РОБОЧОЇ КОМІРКИ АПАРАТІВ ВИСОКОГО ТИСКУ ТИПУ «ТОРОЇД» ТА «КЗ» ПРИ ОДЕРЖАННІ ОДНОШАРОВИХ НАДТВЕРДИХ КОМПОЗИТІВ СИСТЕМИ cBN–Al–TiC (TiN)

Висвітлено результати розрахунків температурних полів в робочій комірці апарату високого тиску методом комп'ютерного моделювання. Показано, як змінюється температурне поле, потоки тепла та температурні градієнти в залежності від умов спікання та складу шихти.

Ключові слова: *апарат високого тиску, комірка високого тиску, температурне поле, температурні градієнти, кубічний нітрид бору, алюміній, нітрид титану, карбід титану.*

Вступ

Полікристалічні надтверді матеріали на основі сфалеритного нітриду бору (PCBN матеріали) широко відомі як інструментальні матеріали для обробки деталей різанням [1]. Виготовлення таких матеріалів зазвичай відбувається із залученням техніки високого тиску (АВТ – апарати високого тиску) [2].

Додавання електропровідних фаз TiC та TiN у структуру полікристалів дозволяє отримувати електропровідні різальні PCBN матеріали, які можна обробляти методом електроіскрової обробки (ЕІО). Це зменшує економічні витрати порівняно з обробкою алмазним інструментом [3].

У роботі [4] для досягнення необхідних фізико-механічних властивостей в багатофакторному експерименті було досліджено вплив складу шихти системи cBN–Al–TiC (TiN) і дисперсності компонентів шихти на твердість і електропровідність PCBN композитів, спечених за високого тиску в сталевих АВТ типу «ковадло з заглибленням». Було виявлено, що геометрія робочого об'єму АВТ та схема зборки незначно впливають на електроопір композитів. Однак якість пластин значною мірою залежить від однорідності температурних полів у робочому об'ємі комірки високого тиску (КВТ) під час спікання. Однорідність температурних полів у робочому об'ємі досягається за допомогою корегування матеріалу і геометрії деталей комірок високого тиску, параметрів нагріву, властивостей робочої шихти. Важливо забезпечити в осередку робочого простору умови низькоградієнтного теплового поля для одержання однорідності структури та властивостей PCBN композитів.