

Interaction during Barothermal Processing of Wurtzite Boron Nitride with Diamonds Obtained under Different Synthesis Conditions

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We present the results of a study of the interaction at a pressure $p = 7.7$ GPa and a temperature $T = 1600$ °C and 1800 °C of wurtzite boron nitride, previously subjected to deformation processing by 4-fold rolling and having a particle size in the developed plane of $0.1...1.5$ microns, and diamond powders of various origin obtained under conditions of static synthesis in the presence of a metal solvent and shock-wave synthesis from carbon material. The diamond component had the following sizes: submicron powders of static synthesis of $0.1/0$ microns, dynamic synthesis diamonds $5...12$ nm. The initial charge before barothermal treatment consisted of 90 wt. % BNw and 10 wt. % diamonds. The duration of exposure to temperature under pressure was $\tau = 60$ s and $\tau = 120$ s. X-ray photography of the samples was carried out on a DRON-3 diffractometer in copper Cu-K α radiation with a graphite monochromator and digital recording of reflections in the automatic mode with a step movement of 0.1° and exposure duration at each point of 4° . It was found that in the contact interaction of BNw with diamonds, diamond dissolves in boron nitride with the formation of a BNC solid solution, which depends on p , T of the process parameters and the method for producing diamonds. At a temperature $T = 1600$ °C, there is no interaction of BNw with the diamond component. An increase in temperature to $T = 1800$ °C leads to the dissolution of diamonds in boron nitride, and their number depends on the time of exposure to temperature, and the interaction of dynamic synthesis diamonds occurs to a greater extent. Homogenization of the BNC solution is observed. To determine the mutual solubility of substances, Vegard's law was applied, and the quantitative content of dissolved diamond in sphalerite boron nitride was established, which is 2 times greater for dynamic synthesis diamonds than for static synthesis diamonds. The higher activity of dynamic synthesis diamonds is due to the feature of their crystalline structure – high dispersion and distortion. The dissolution of diamonds in BNw has a diffusion character.

Keywords: Wurtzite boron nitride, Diamond, Pressure, Temperature, Solubility.

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1. INTRODUCTION

Cubic boron nitride, a refractory compound that is an electronic and structural analogue of diamond, causes steady interest in obtaining a composite material formed in the diamond-BNw system with the formation of a BNC solid solution with a diamond-like lattice, which, having hardness approaching to diamond's, significantly exceeds its thermal and chemical resistance.

Many works are devoted to study of the possibility of the formation of a solid carbon solution in cubic boron nitride. One of the first [1] describes the interaction of carbon with turbostratic boron nitride at high pressures and temperatures near the triple point p - T of the boron nitride diagram and, as a consequence of this interaction, obtains a cubic modification of boron nitride with a carbon content of up to 6 %. Later, mainly the interaction of cubic boron nitride with diamond was studied under conditions of high pressures and temperatures [2-5].

As follows from the analysis of these works, a solid solution of composition B-N-C is formed on the basis of graphite-like boron carbonitrides C $_x$ -BN as a result of phase transitions accompanied by the formation of

dense modifications of carbon and boron nitride [6, 7].

The works of authors [5-8] have shown the possibility of obtaining thin oxide (ceramic) coatings on dielectric materials in microelectronics and optics by various methods. However, in these works there is no information about the microhardness of ceramic coatings deposited on the surfaces, as well as their impact on the accuracy and reliability of the products based on them.

We studied the interaction of diamond powders with wurtzite boron nitride (BNw). In [8], it was shown that in the BNw-diamond particle system at a pressure $p = 8$ GPa and a temperature of $1600-2000$ °C, a contact interaction of the components occurs with the formation of an interphase layer (Fig. 1). It was concluded that the main factor determining the formation of a BNC solid solution in BNw-diamond compositions is the metastability of the BNw phase and its deformation transformation into a sphalerite phase upon contact with diamond.

In the present work, the interaction in the BNw-diamond system is considered during the barothermal treatment of mixtures of such powders.

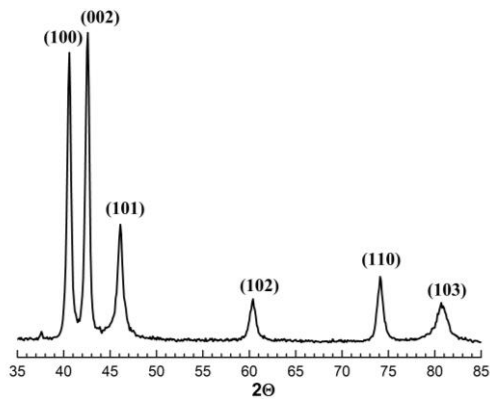


Fig. 1 – X-ray pattern of deformed BNw

2. INITIAL MATERIALS AND EXPERIMENTAL PROCEDURE

To study the interaction during sintering at high static pressures of BNw with diamond depending on the type of diamond powder obtained under static conditions in the presence of a solvent metal and under conditions of shock wave synthesis from a carbon material, a mixture consisting of 90 wt. % BNw and 10 wt. % diamonds was prepared.

To increase the activity and dispersion, BNw powder was subjected to deformation processing by 4-fold rolling, after which the bulk of particles of BNw had a size in the developed plane of 0.1...1.5 μm .

The diamond component was represented by two types – submicron static synthesis diamond powders with a size of 0.1/0 microns and dynamic synthesis diamonds with a particle size of 5...12 nm.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Fig. 2 shows the difference in the structural state of diamonds depending on the methods of their preparation. The broadening of all X-ray reflection lines of diamonds of dynamic synthesis (Fig. 2-2) indicates their increased dispersion and level of microstress in contrast to diamonds of static synthesis, the reflection lines of which are not broadened (Fig. 2-1).

An analysis of X-ray data showed (Fig. 3-1) that, as a result of processing at high pressures of a mixture of BNw with a diamond of static synthesis for $\tau = 60$ s at a temperature $T = 1600$ °C, there is a partial transformation of BNw into BNc, but the interaction of the components in the mixture is absent, and the reflection lines from the diamond phase are retained.

Barothermal treatment of a mixture of BNw with static synthesis diamond at a temperature $T = 1800$ °C and the same exposure time leads to almost complete conversion of BNw to BNc, and according to X-ray data (Fig. 3-2), the diamond component is retained. In the case of barothermal treatment at $T = 1800$ °C and sintering time $\tau = 120$ s (Fig. 3-3), judging by the decrease in the lattice period of BNc (Table 1), a slightly larger amount of diamond dissolves in it than when holding $\tau = 60$ s and temperatures $T = 1600$ and 1800 °C.

Under conditions of high pressures and temperatures, the interaction of BNw with a dynamic synthesis

diamond occurs to a greater extent than with a static synthesis diamond (Fig. 4).

An increase in temperature to $T = 1800$ °C promotes homogenization of the BNC solution, as evidenced by a decrease in the broadening of the X-ray reflection lines of BNc (Fig. 5).

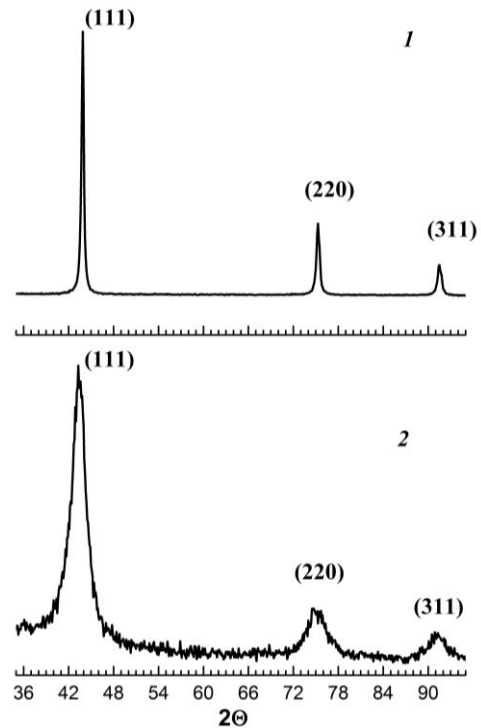


Fig. 2 – Radiographs of the source diamonds: 1 – diamond of static synthesis; 2 – dynamic synthesis diamond

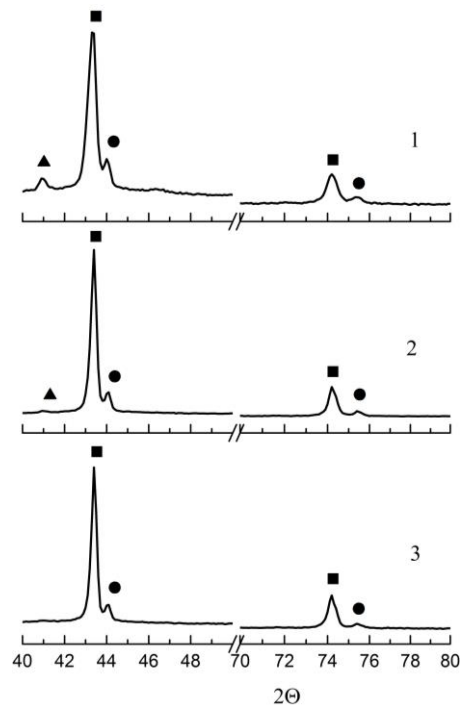


Fig. 3 – The result of the interaction of BNw with diamond of static synthesis: ● – diamond, ▲ – BNw, ■ – BNc. 1 – temperature $T = 1600$ °C, duration $\tau = 60$ s; 2 – $T = 1600$ °C, $\tau = 120$ s; and 3 – $T = 1800$ °C, $\tau = 120$ s

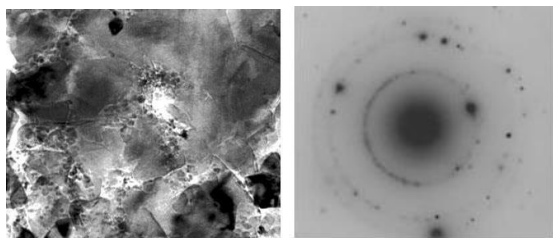


Fig. 4 – Fragment of the microstructure of the sample obtained at $T_{\text{ sint}} = 1800\text{ }^{\circ}\text{C}$ and $\tau = 120\text{ s}$ of the system BNw + diamond of dynamic synthesis

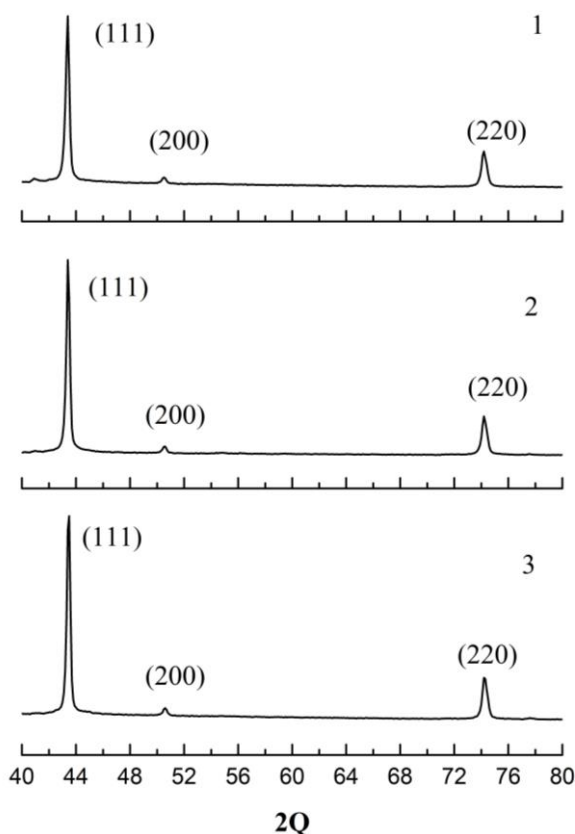


Fig. 5 – BNC resulting from the interaction of BNw with dynamic synthesis diamond: 1 – temperature $T = 1600\text{ }^{\circ}\text{C}$, duration $\tau = 60\text{ s}$; 2 – $T = 1600\text{ }^{\circ}\text{C}$, $\tau = 120\text{ s}$ and 3 – $T = 1800\text{ }^{\circ}\text{C}$, $\tau = 120\text{ s}$

Under all processing conditions, a complete transition of BNw to BNC is observed; a decrease in the lattice period of BNC indicates the dissolution of diamond in it, since the lattice period of sphalerite boron nitride is $a = 0.36198\text{ nm}$ and the diamond lattice period is $a = 0.35670\text{ nm}$.

Given the similarity of the structures of cubic boron nitride and diamond, as well as the proximity of their electronic structure – mainly covalent, it is possible to apply Vegard's law to BNC solid solutions, which allows one to approximately determine the mutual solubility of substances, in this case, to determine the solubility of diamond in cubic boron nitride (Fig. 6).

Using the calculated lattice periods of the processed mixtures and plotting their values on a straight line connecting the lattice periods of BNC (3.616 Å) and diamond (3.567 Å), we obtain the approximate value of the amount of dissolved diamond in sphalerite boron nitride, the values of which are given in Table 1.

Since positive and negative deviations from Vegard's law are possible, it is impossible to speak with accuracy about the quantitative content of dissolved diamond in sphalerite boron nitride. Nevertheless, Table 1 shows that the maximum amount of dissolved diamond in cubic boron nitride is observed as a result of the interaction of BNw with dynamic synthesis diamond under a pressure $p = 7.7\text{ GPa}$ and a temperature $T = 1800\text{ }^{\circ}\text{C}$ for $\tau = 120\text{ s}$. With a decrease in the exposure time under pressure to $\tau = 60\text{ s}$ at $T = 1600\text{ }^{\circ}\text{C}$ and at $T = 1800\text{ }^{\circ}\text{C}$, the solubility of diamond in boron nitride decreases.

The dependence of the solubility of diamond of dynamic synthesis in boron nitride on the time of their interaction under pressure indicates the diffusion nature of the solubility of diamond in boron nitride.

A decrease in the broadening of the X-ray reflection lines of the BNC solid solution with increasing temperature and holding the barothermal treatment indicates its ordering.

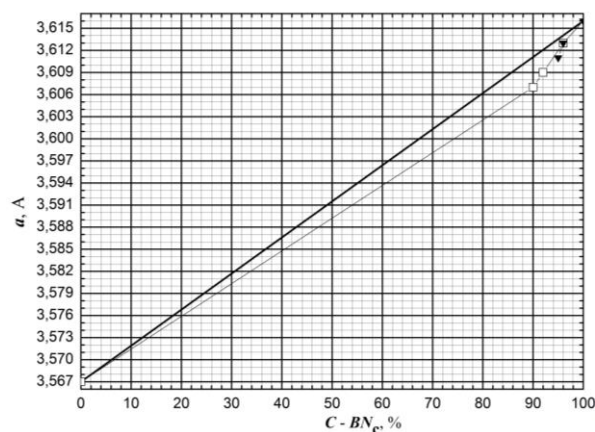


Fig. 6 – Lattice periods of BNC and diamond and their solid solutions in accordance with the Vegard law: ▲ – BNw, □ – BNC

Table 1 – Some characteristics of BNC solid solutions

Mixture processing modes		Static synthesis diamond		Dynamic synthesis diamond	
Temperature $T, ^{\circ}\text{C}$	Exposition time τ, s	BNC lattice period a, nm	The approximate carbon content in BNC, %	BNC lattice period a, nm	The approximate carbon content in BNC, %
1600	60	0.3616	0	0.3613	4
1800	60	0.3613	4	0.3609	8
1800	120	0.3611	5	0.3607	10

4. CONCLUSIONS

1. The difference between the interaction of diamonds of dynamic and static synthesis with BNw under conditions of high static pressures and temperatures has been established. Diamond dynamic synthesis, which has a high pressure and temperature, is due to the peculiarities of their crystalline structure – high dispersion and distortion.

2. The contact interaction of dynamic synthesis diamonds with BNw, accompanied by their dissolution and the formation of a cubic BNC phase, proceeds more intensively due to low CSR (coherent scattering region)

values in the presence of microdistortions of the crystal lattice.

3. Contact with diamond at high pressures and propagation conditions facilitates the restructuring of

the metastable structure of boron nitride into sphalerite boron nitride.

4. The diffusion nature of the solubility of diamond in BNw during their barothermal treatment was revealed.

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Взаємодія при баротермічній обробці вюртцитного нітриду бору з алмазами, отриманими при різних умовах синтезу

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Наведено результати дослідження взаємодії при тиску $p = 7,7$ ГПа і температурі $T = 1600$ і 1800 °С вюртцитного нітриду бору, попередньо підданого деформаційній обробці шляхом 4-х кратної прокатки і який має розмір часток в розвиненій площині 0,1...1,5 мкм, і алмазних порошків різного походження – отриманого в умовах статичного синтезу у присутності метала-розчинника і ударно-хвильовим синтезом з вуглецевого матеріалу. Алмазна складова мала такі розміри – субмікронні порошки статичного синтезу 0,1/0 мкм; алмази динамічного синтезу – 5...12 нм. Вихідна шихта перед баротермічною обробкою складалася з 90 мас. % BNв і 10 мас. % алмазів. Тривалість дії температури під тиском становила $\tau = 60$ с і $\tau = 120$ с. Рентгенівська зйомка зразків виконувалася на дифрактометрі ДРОН-3 в мідному Си-Ка випромінюванні з графітовим монохроматором і цифровою реєстрацією відображень в автоматичному режимі з кроковим переміщенням $0,1^\circ$ і тривалістю експозиції в кожній точці 4° . Встановлено, що при контактній взаємодії BNв з алмазами має місце розчинення алмазу в нітриді бору з утворенням твердого розчину BNC, залежне від p , T параметрів процесу і способу отримання алмазів. При температурі $T = 1600$ °С взаємодія BNв з алмазною складовою відсутня. Підвищення температури до $T = 1800$ °С призводить до розчинення алмазів в нітриді бору, і їх кількість залежить від часу впливу температури, причому взаємодія алмазів динамічного синтезу відбувається в більшій мірі. Спостерігається гомогенізація розчину BNC. Для визначення взаємної розчинності речовин застосований закон Вегарда, і встановлено кількісний вміст розчиненого алмазу в сфалеритному нітриді бору, який для алмазів динамічного синтезу у 2 рази більше, ніж для алмазів статичного синтезу. Більш висока активність алмазів динамічного синтезу обумовлена особливістю їх кристалічної будови – високою дисперсністю і дисторсією. Розчинення алмазів в BNв має дифузний характер.

Ключові слова: Вюртцитний нітрид бору, Алмаз, Тиск, Температура, Розчинність.