Chemical Reactions in Hexagonal Boron Nitride System

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Chemical reactions of synthesis of hexagonal boron nitride and their mechanisms are discussed and classified. Based on their analyses, a ternary B–N–O diagram is suggested, in which virtual compositions of hexagonal boron nitride ceramic and preceding materials, starting with a mixture of raw materials, through oligomolecular semi-organic precursors and turbo-stratic boron nitride powder are specified. Beside the composition, processes of conversion between particular substances, such as synthesis, decomposition and crystallization of boron nitride powder, and sintering and hydrolysis of ceramic, are characterized by vectors—elements of the ternary diagram. The dynamic model is suggested to be generally applied to systems with prevailingly covalent character, where the polymerization is regarded as a controlling chemical process. © 1996 Academic Press, Inc.

I. INTRODUCTION

1.1. Review

Preparation of a binary compound of boron with nitrogen was first reported as early in 1842 (1). Since that time, there have been many routes invented to synthesize boron nitride, from direct synthesis of boron with nitrogen to get fine boron nitride (BN) powder (2, 3) to deposition self-consistent solid layers formed by pyrolyzing gaseous precursors typically consisting of boron halides and ammonia (4, 5). Wide-spread, commercialized methods to prepare BN in the range of tons, however, are based on simultaneous reducing and nitriding of boric oxide, boric acid, and its salts. The most obvious route to prepare boron nitride in mass quantity has been the carbo-reductive nitriding of boric oxide in nitrogen (6, 7). The amount of carbon must be controlled very precisely to prevent contamination of boron nitride with unreacted carbon, and the product of the process must be washed from unreacted boria (8).

In another group of preparation methods giving relatively pure products, hydrogen has been used as a reduction agent. Positive results were achieved when hydrogen was present in the initial stage in its radical form, especially directly bound to nitrogen as ammonia or in an amine or imine group. For example, replacing nitrogen by ammonia gas enabled one to reduce the reaction temperatures by 400–500 K (9). A disadvantage of this process consists in low melting points of boric compounds which lay substantially lower than the reaction temperature and the reaction surface is thus drastically reduced. This obstacle was overcome by applying inert fillers, such as calcium carbonate, retaining the large reaction surface. After finishing the nitriding, calcia and unreacted boria had to be leached out by diluted hydrochloric acid. The leaching could be skipped when boron nitride was used as a filler (10).

Applying cyanide salts or organic materials containing amino- or imino- groups to the starting boric compound brings another advantage, since the boric compound undergoes a chemical reaction with them before being converted to nitride and is stabilized against undesirable melting. An example, already cited by Balmain (1), is annealing a mixture of boric oxide with sodium cyanide to prepare yellowish powder called "aethogen" due to its luminescence properties. A variety of organic compounds bearing organically bound nitrogen and hydrogen were systematically tested by O'Connor (11), who mixed them with boric acid, then dehydrated them at around 200°C, and finally nitrided solid foams in ammonia around 1000°C. The highest yields of boron nitride were obtained when a super-stoichiometric amount of urea was mixed with boric acid. Products of this operation were well sinterable and easily crystalizable by an additional annealing in nitrogen. X-ray analysis showed that such a low-temperature form of boron nitride possessed structural faults resembling those which were found in some forms of graphite and named as turbostratic (12).

There have been many attempts to quantify the process of formation of boron nitride by chemical equations and several reaction mechanisms have had been proposed. For example, in a mechanism taking boric oxide and ammonia as starting substances, formation of a complex compound $(B_2O_3)_n \cdot NH_3$ at 200°C is suggested as the first step. At 350°C, additional molecules of ammonia react with the adduct, water is released, and boron nitride becomes a

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third component of the complex—$(BN)_x(B_2O_3)y \cdot NH_3$. Formation of pure boron nitride is completed at 1500°C by decomposition of the adduct (13).

The same starting materials were used by Vikulin *et al.* (14) but this proposal of the reaction mechanism is quite different. The author proposed a polymer with the formula $[-NH-BO(OH)-]_n$ as a starting point for the formation of hexagonal boron nitride. The next step is the formation of linear chains with the formula $[-HN-O-BH-]_n$, being then converted onto oxygen-free linear polymers $[-HN-BH-NH-]_n$. The polymerizing proceeds and the next intermediate linear polymer is composed from polycondenzed B_3N_3 hexagons. By their cross-linking, the boron nitride planar macromolecule is finally formed.

Another scheme has been proposed by Saito and Ushio (15). Starting from boric acid and ammonium rhodanide, a polymer with the formula $[NH-BO(OH)]_n$ is formed between 160 and 200°C. The substance is converted onto an oxygen-free polymer described by the formula $[NH=BH]_n$. Formation of boron nitride proceeds by gradual liberating of hydrogen at higher temperatures. Hydrogen-free product is finally obtained at 800°C.

Using tools of organic chemistry is the common feature of these mechanisms (13–15), however, characterization of a monomeric unit having transition character between the initial oxide and the resulting nitride is missing in all the proposals.

1.2. Works Preceding This Paper

Boric oxide and ammonia were applied as the initial substances for suggesting a chemical model of formation of boron nitride (16, 17). The presented model, which has been confirmed by the results of chemical analysis, is based on four consecutive steps:

(i) At first, molecules of ammonia occupy the surface of boric acid with their orientation in an agreement with the distribution of partial electronic charges in both substances.

(ii) In the next stage, the following chemical reaction takes a place, giving origin to a reactive bi-radical:

$$B_2O_3 + 2\,NH_3 = 2\,HNBOH + H_2O. \qquad [1]$$

(iii) This is immediately stabilized by a trimerization, already giving a fundamental unit with $3C_2$ symmetry, where a hexagon formed alternatively from boron and nitrogen atoms is a precursor of the boron nitride monolayer, and possessing $-OH$ leaving groups at boron and $H-$ radicals at nitrogen sites, respectively.

(iv) The growth of the planar boron nitride network, which is terminated by hydrogen and hydroxyl radicals,

then proceeds by a reaction of the trimeric hexagonal nucleus with other, surrounding monomers. For example, for an ideal case of the hexagonal the symmetry, the other nine monomers have to approach the trimer and react with its marginal radicals according to the following equation:

$$(NH)_3(BOH)_3 + 9\,HNBOH$$
$$= (NH)_6(BN)_6(BOH)_6 + 6\,H_2O. \qquad [2]$$
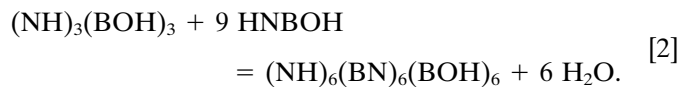
The rational formula of the reaction product tells that the core of the molecule is formed by six boron–nitrogen pairs having exclusively the character of boron nitride, and by the same number of peripheral groups (BOH and NH, respectively) being located at the periphery and giving a change to proceed the growth.

The growth of a planar boron nitride network could be progressed *ad libitum*. However, from a comparison of the size of the boron nitride monolayer with chemical composition of real products it can be derived that the so-called turbostratic form of boron nitride consisting of small-size crystallites can be described by the formula $(NH)(BN)_{26}(BOH)$ and that of the crystalline hexagonal boron nitride composed from substantially larger layers has a formula $(NH)(BN)_{188}(BOH)$ when keeping the hexagonal symmetry of the planar macromolecules.

In another paper (18) coexistence of boron nitride with boric oxide is discussed. It was found that the coexistence has a specific chemical character since an interaction between these two compounds has a chemical distinction. However, no evidence that these two compounds form a solid solution as other nitride–oxide systems, such as that of aluminum or silicon, has been found. Thus, despite the interaction, from the viewpoint of boron nitride formation, both boron nitride and boric oxide should be regarded as more or less independent chemical individuals.

A ternary B–N–O diagram was used to describe chemical composition of BN powders and ceramics (16, 17) and layered BCN substances (19). The goal of this paper is to enhance the applicability of ternary chemical diagrams even for description of chemical reactions occurring in synthesis of prevailingly covalent-bound compounds and their further processing. Hexagonal boron nitride has been used as a model system.

2. ANALYSIS OF THE PROBLEM

Fundamental techniques to synthesize boron nitride, discussed in previous sections, are comprehended in Fig. 1. With respect to mineralogical, hydrological, and atmospheric conditions of our planet, just oxide-based sources of boron can be expected in the nature. In general, for
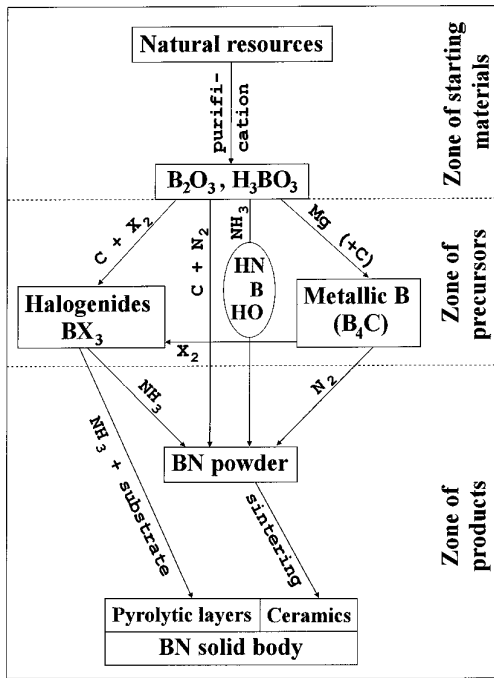
FIG. 1. Flow diagram of preparation of hexagonal boron nitride materials.

TABLE 1
Rectified Molar Concentrations of Boron, Nitrogen, and Oxygen in Amide-Based Systems

Chemical system	Boron content (mol %)	Nitrogen content (mol %)	Oxygen content (mol %)
$B_2O_3 + 2NH_3$	28.57	28.57	42.86
$B_2O_3 + CO(NH_2)_2$	25.00	25.00	50.00
$H_3BO_3 + NH_3$	20.00	20.00	60.00
$2H_3BO_3 + CO(NH_2)_2$	18.18	18.18	63.64
NHBOH	33.33	33.33	33.33

obtaining boron nitride, the reducing and nitriding of them are necessary after being purified. The scheme is divided into three sections:

—a zone of starting boron carriers obtained after the purification,

—a zone containing virtual precursors, such as elemental boron or volatile halogenides, and a precursor with a formula NHBOH suggested for the amide process (16, 17), and

—a zone of final products, consisting of powder and self-consistent solid bodies as ceramic and pyrolytic layers. Figure 1 further shows that an amide process represents reasonable method of synthesis to be modeled since the number of technological operations and number of elements in the system are limited.

In general, to illustrate the chemical composition of chemical objects consisting of n elements, an $(n - 1)$ dimensional diagram should be used. With respect to the starting materials (boric acid and urea), five elements have to be regarded—hydrogen, boron, carbon, nitrogen, and oxygen. In the system studied in this paper, therefore, a four-dimensional diagram should be applied. To simplify the system, hydrogen and carbon are disregarded, the concentration of other elements, boron, nitrogen, and oxygen, are recalculated to give together 100%, and compositions of studied subjects are plotted in a two-dimensional, B–N–O diagram.

3. CHEMICAL REACTIONS IN HEXAGONAL BORON NITRIDE SYSTEM

3.1. Reactions in Synthesis of Powder

Routes to prepare boron nitride, using boric oxide or boric acid and ammonia or urea as starting materials, will be analyzed. The simplest case, based on a reaction of boric oxide with ammonia Eq. [1], has already been applied for modeling TBN formation (16, 17). Remaining combinations are then shown in Eqs. [3]–[5]. Especially the last process, in which boric acid is used, has been technologically widely utilized. In all the three cases, formation of a monomer substance with a formula NHBOH beside gaseous exhausts (water and carbon dioxide) formed by combining leaving groups is suggested as the first step of boron nitride formation. Owing to the character of the starting substances and the oxygen-to-nitrogen molar ratio, the trimer with rational formula $(NH)_3(BOH)_3$ or $HO_3(BN)_3H_3$ can be understood as a substance bearing partially organic and inorganic character and at the same time it represents a transition point between boric oxide and boron nitride. The starting composition of the three chemical systems, when initial substances are present at ratios corresponding to those in Eqs. [1] and [3]–[5], was calculated so that the molar concentrations of the three elements of the interest were rectified to total 100%. The results of the calculation together with the rectified composition of the monomer are shown in Table 1.

$$B_2O_3 + CO(NH_2)_2 = 2\,HNBOH + CO_2 \qquad [3]$$

$$H_3BO_3 + NH_3 = 2\,HNBOH + H_2O \qquad [4]$$

$$2\,H_3BO_3 + CO(NH_2)_2 = 2\,HNBOH + CO_2 + 3\,H_2O \quad [5]$$

A ternary B–N–O diagram was constructed and within the diagram points describing the rectified chemical composition of starting materials, linear monomer, and final substances were plotted; see Fig. 2. Since the number of analyzed elements was reduced, the points corresponding to water, carbon dioxide, and ammonia are identical with
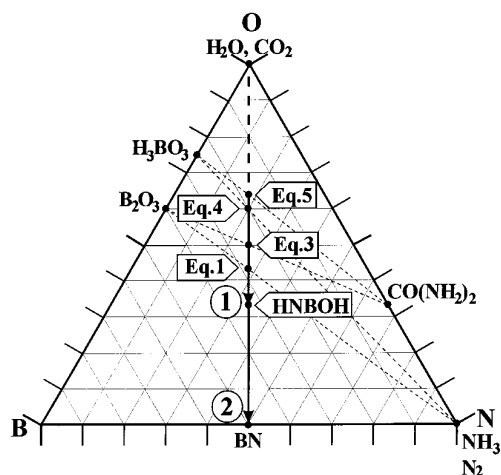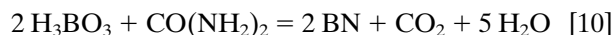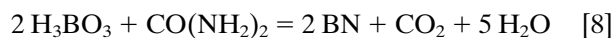
FIG. 2. B–N–O ternary diagram describing synthesis ① and crystallization ② of boron nitride powder in amide process.

those of elemental oxygen and nitrogen. Compounds containing two elements of the B–N–O trinity (boric oxide and acid, urea and boron nitride) are located at the sides of the triangle. A point belonging to a reaction product—monomer HNBOH—is plotted in the center of the triangle.

Another fact can be read out from the ternary diagram. When a pair of points describing the composition of starting materials in any single reaction is connected with a straight line, and the same operation is done with the reaction products, a crossing point represents stoichiometric ratios between the starting materials and reaction products, expressing thus the law of conservation of mass; compare the data in Table 1 and crossing points marked as Eqs. [1] and [3]–[5] in Fig. 2. When connecting the crossing points with the point assigned to the HNBOH monomer, a set of vectors describing chemical changes in solid phase is obtained. The longer the distance between the points in a particular pair, the bigger is the change in composition of the solid phase and the larger is the relative fraction of released exhausts. All the four vectors share the same line and differ from each other in the position of the initial point which is given by the initial composition of the starting substances, ①. For obtaining pure boron nitride, the following summary equation can be applied:

$$\text{HNBOH} = \text{BN} + \text{H}_2\text{O}. \qquad [6]$$
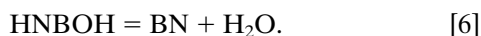
The above written equation expresses a secondary step in which the formation of theoretically pure boron nitride is completed, ②, and is identical for all the studied variations of the amide system. The following set of equations then represents summary quantification of complete processes starting from boric acid or its anhydride and ammonia or urea.

$$\text{B}_2\text{O}_3 + 2\,\text{NH}_3 = 2\,\text{BN} + 3\,\text{H}_2\text{O} \qquad [7]$$

$$2\,\text{H}_3\text{BO}_3 + \text{CO(NH}_2)_2 = 2\,\text{BN} + \text{CO}_2 + 5\,\text{H}_2\text{O} \qquad [8]$$

$$\text{B}_2\text{O}_3 + \text{CO(NH}_2)_2 = 2\,\text{BN} + \text{CO}_2 + 2\,\text{H}_2\text{O} \qquad [9]$$

$$2\,\text{H}_3\text{BO}_3 + \text{CO(NH}_2)_2 = 2\,\text{BN} + \text{CO}_2 + 5\,\text{H}_2\text{O} \qquad [10]$$

The monomer HNBOH is called the precursor of boron nitride. On the other hand, it has been declared that a layered substance containing exclusively boron and nitrogen, is an ideal case where BN layers are infinitely large. For real boron nitride materials the formula $\text{HO(BN)}_x\text{H}$ was suggested where the index x is proportional to the size (width) of a BN monolayer. It was shown by comparing chemical composition with the size of BN crystallites that turbostratic boron nitride prepared at 900°C has an approximate formula $\text{HO(BN)}_{27}\text{H}$ (16, 17). If we suppose hexagonal symmetry, the closest homolog can be described by the formula $\text{HO(BN)}_{26}\text{H}$. With respect to Eq. [2], the general stoichiometric equation for growth of boron nitride monolayers (and subsequently for entire crystallites) can be written as

$$\text{HO(BN)}_x\text{H} = x/y\,\text{HO(BN)}_y\text{H} + (1 - x/y)\,\text{H}_2\text{O}. \qquad [11]$$
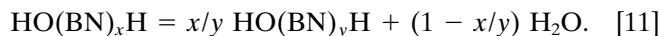
Composition of boron nitride-rich polymers with the general formula $\text{HO(BN)}_x\text{H}$ is then represented by points within a straight line having its ends in points assigned to the monomer HNBOH ($x = 1$) and pure boron nitride. The higher the fraction of boron nitride in the polymer, the bigger is the modulus of the vector and the closer is the point located to that of pure boron nitride. The process of elongation of the vector is then identical with the crystallization and purification of boron nitride. The full-length vector ② in the figure then corresponds to a formation of ideally crystallized hexagonal boron nitride with infinitesimally large macromolecules in its single crystal ($x \to \infty$).

For modeling HBN formation and growth of planar macromolecules, the boric acid–ammonia system has been chosen (Fig. 3). In the first step, a linear precursor NHBOH is formed (scheme A), which is then stabilized by trimerization in a form of a hexagonal nucleus (scheme B). The growth of two-dimensional objects then proceeds by reactions of the trimer with additional linear monomers and the primary hexagon (I) becomes surrounded by six secondary hexagons (II); see the scheme C.

Schmid and Piontek prepared BN films from organic precursors (20). Based on the results of chemical analysis, they characterized the composition of a BN precursor (f-BN) with an ideal hexagonal symmetry, synthesized at 270°C and showing a significant turbostraticity in the XRD patterns, by a formula which can be written in a simplified version as $\text{F(BN)}_5(\text{BF}_2)$. If we, with respect to the difference in chemical composition of the starting materials,
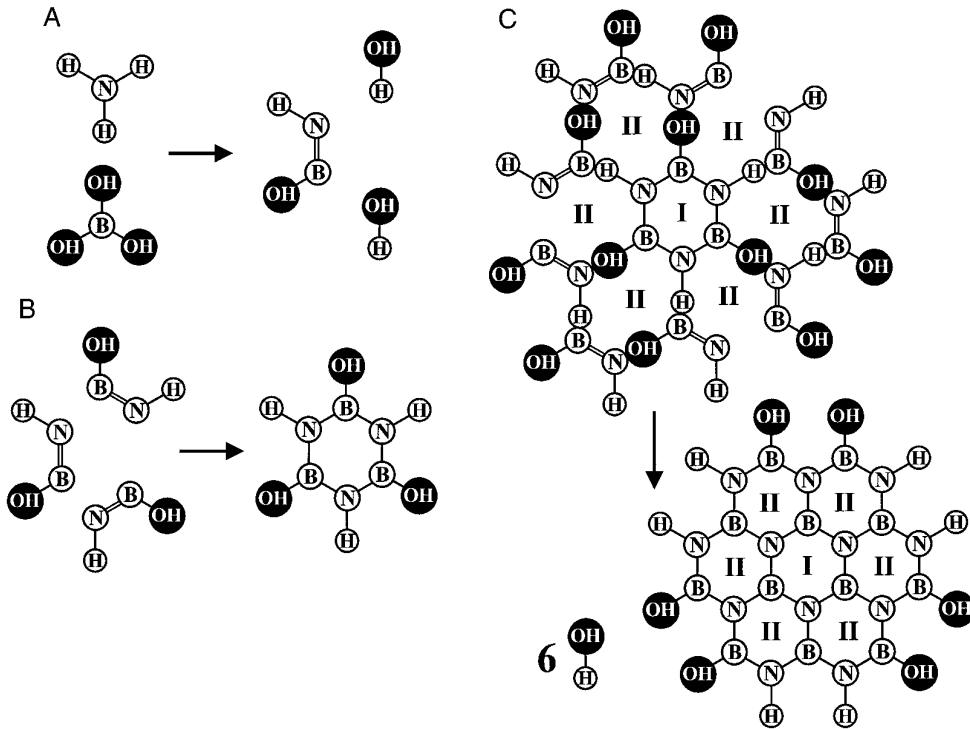
FIG. 3. Process of formation of hexagonal boron nitride.

substitute the hydroxyl group for fluorine and hydrogen for the $F(BN)_5(BF_2)$ group, a good agreement between the two models can be obtained. The structure of the f-BN then correspond to the fifth homolog with hexagonal symmetry if the development shown in Fig. 3c were continued farther. Further, they suggested an equation that described the formation of pure hexagonal BN by a complete releasing of BF_3 by recombining F and F_2B radicals from the peripheral nodes of the f-BN networks, which is in good agreement with Eqs. [6] and [11]. In contrast to our model, however, they do not regard the presence of any ligand atoms on the periphery of thermally stabilized hexagonal boron nitride.

It can be concluded now that the formation and growth of boron nitride crystalline nuclei to get a pure binary substance can be described by a vector lying in a line connecting water and boron nitride having the orientation toward the latter substance.

3.2. Reactions in Sintering of Ceramics

The sintering of boron nitride can be understood as a chemical process where small boron nitride crystallites in the starting turbostratic powder grow and the growth is accompanied with the formation of ceramic bonds between grains. Since the melting of boron nitride during the sintering is beyond expectation, the process can be explained by chemical means rather than by physical means. From

this point of view, powders with good sintering activity represent a system where formation of boron nitride crystals was intendedly interrupted for being completed as late as during the sintering. This means that a basic chemical reaction resembles that shown in Eqs. [2] and [11] (Fig. 4). However, here the growth does not proceed as an interaction of the crystal nuclei with HNBOH monomers since the starting materials are already consumed up. The growth
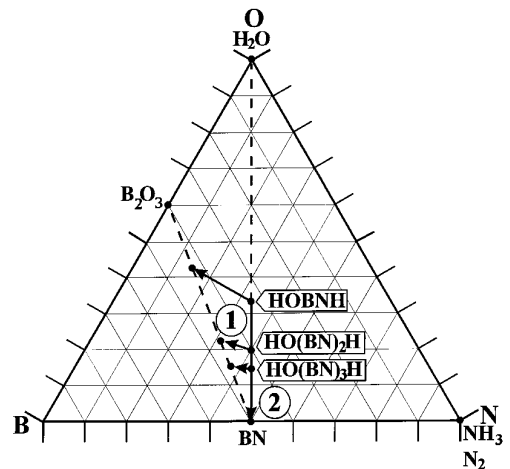

FIG. 4. B–N–O ternary diagram describing hot pressing ① and pressureless sintering ② of hexagonal boron nitride ceramics.

is ensured by the coalescence of tiny boron nitride crystallites with releasing water. For simplification of the following equation, model boron nitride powder is considered to be composed from crystallites of the same size and thus with identical x index:

$$n \, HO(BN)_x H = HO(BN)_{n*x}H + (n-1)H_2O. \quad [12]$$
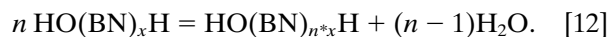
Since the sintering proceeds at temperatures far higher than 1000°C, a subsequent hydrolysis of boron nitride by the released water must be considered as a process following the coalescence. The smaller the BN macromolecules, the higher is the content of constitutionally bound water (H– and –OH groups) potentially causing the hydrolysis. From this viewpoint, the precursor $H(NB)_1OH$ is mainly endangered by the reconversion to boric oxide, but even in this case the hydrolysis cannot be completed up to total decomposition of boron nitride since in the solid products both the nitride and the oxide are contained at equimolar ratio (Eq. [13]). In the equations quantifying the hydrolysis process, the constitutional water was neglected in the formula for boron nitride on the side of the reaction products to keep the stoichiometric coefficients simple:

$$3 \, HO(BN)_1 H = BN + B_2O_3 + N_2 + 3 \, H_2. \quad [13]$$

The yield of boric oxide decreases with the growth of grain size in the starting BN powder. For the second and third homologs of the development of BN macromolecules, the following equations can be written:

$$3 \, HO(BN)_2 H = 4 \, BN + B_2O_3 + N_2 + 3 \, H_2 \quad [14]$$

$$3 \, HO(BN)_3 H = 7 \, BN + B_2O_3 + N_2 + 3 \, H_2. \quad [15]$$
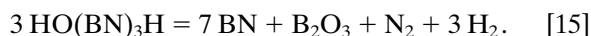
Equations [13]–[15] are described by corresponding vectors (①) in Fig. 4. Autogene hydrolytic process in turbostratic boron nitride, where the source of the hydrolyzing agent is hydroxylic radicals from the periphery of boron nitride macromolecules (Fig. 3), can be quantified by Eq. [16]. However, the oxygen concentration in this material (ca. 2.3 wt%) and the content of boric oxide in the product of hydrolysis (3.3 wt%) are too low for the corresponding vector to be visibly plotted in the diagram in Fig. 4.

$$3 \, HO(BN)_{27} H = 79 \, BN + B_2O_3 + N_2 + 3 \, H_2 \quad [16]$$
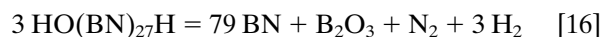
The actual yield of the hydrolysis is given by sintering conditions. For example, when being hot-pressed, the powder is enclosed in between rams and a graphite die, and its shrinkage is compensated by displacement of the rams. The released molecules of water are trapped to undergo the hydrolysis, especially in deeper layers of the pressed powder. It is seen that the fraction of gaseous by-products
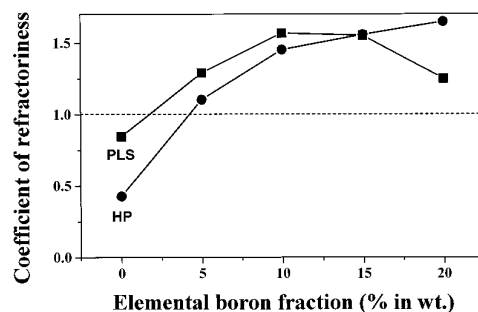

FIG. 5. Dependence of the coefficient of refractoriness in pressureless-sintered and hot-pressed BN ceramics on elemental boron nitride fraction in the starting powder (according to (21) and (22)).

of hydrolysis decreases with the enlarging of BN macromolecules and subsequently the crystals. This might be the reason why for hot isostatic pressing (HIP) crystalline BN powder rather than sinteractive turbostratic material is used. The pressure of gases released during HIP act against the environmental pressure of hot argon and therefore the densification cannot satisfactorily proceed.

In contrast, from pressureless-sintered powder, the water can escape rapidly and without a substantially harmful effect on boron nitride, especially when being sintered *in vacuo*. For this case, equations similar to Eq. [11] or Eq. [12] can be written and vector ② found.

The above presented considerations stand in good agreement with the results of measurement of flexural strength measured in both pressureless-sintered (21) and hot-pressed (22) ceramics at 1000°C and at room temperature, respectively. In both cases, elemental boron was added to BN powder to extract undesirable oxygen-bearing phases and to convert them onto inactive suboxides. If the refractoriness is defined as a ratio between flexural strength measured at these different temperatures, the materials prepared by different sintering techniques may be compared as shown in Fig. 5. By the extraction and conversion of the primary oxygen-bearing phases, the BN layers were allowed to get into closer contacts which helped to reveal the intrinsic refractoriness of polycrystalline boron nitride. When compared with the hot-pressed ceramics, the pressureless-sintered material required substantially lower portions of elemental boron to reveal the refractoriness, although due to the expansion caused by releasing of volatile substances, its density was substantially lower than that found in hot-pressed ceramics.

Moreover, the addition of elemental boron significantly hindered the growth of boron nitride grains especially when a microcrystalline BN powder was used (21, 22). This phenomenon was attributed to the direct interaction between hydroxyl radicals from the periphery of boron nitride networks as modeled elsewhere (23). In contrast to pressureless-sintered materials, the oxygen content in
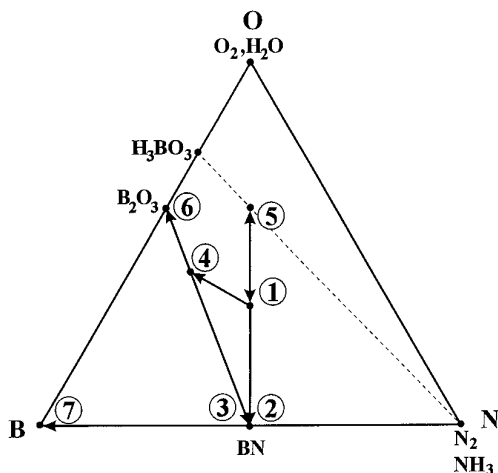
FIG. 6. B–N–O ternary diagram for describing chemical processes in hexagonal boron nitride. ①, powder synthesis (amide process); ②, crystallization and pressureless sintering; ③, powder synthesis (carbothermal process); ④, hot pressing; ⑤, hydrolysis; ⑥, oxidation; ⑦, peritectic decomposition.

the core of the hot-pressed ceramics was higher than that in starting BN powder (cf. Eq. [16]) and just in the sites adjacent to the walls of the press form a lower content was determined. Linear analysis of oxygen distribution in the hot-pressed ceramics showed that this element preferably occurred on the (hk0) planes of HBN crystals since the average distance between the maxima in the oxygen spectra was corresponding to the width of BN grains rather than to their thickness (22).

3.3. Summary of Reactions in Boron Nitride System

Up to the previous section, processes leading toward pure boron nitride have been discussed. These reactions, however, may run in opposite directions so that the hydrolysis ⑤ is a counterpart to the amide synthesis ① and crystallization ②, and water-free oxidation ⑥ is a process reverse to carbothermal synthesis ③ of boron nitride. If adding hot pressing ④ and peritectic decomposition of boron nitride treated at high temperature *in vacuo* ⑦, all the processes can be summarized by vectors marked with the same ciphers, as shown in Fig. 6.

Although the vectors describe the processes theoretically, in reality, the conversion of starting substances can never be completed and residing of them in the products must be regarded. To such a situation, a vector with the same orientation but a smaller modulus was already assigned. Moreover, kinetic factors must be considered, too. It is beyond expectation that the volatile oxygen-carrying substances are completely released from the pressureless-sintered bodies without a partial hydrolytic effect, or on another hand, they are completely converted onto boric oxide in the hot-pressed material. In real systems, both

the processes described by the vectors ② and ④ take part simultaneously and the significance of a particular contribution is controlled by the external pressure.

4. CONCLUSIONS

Chemical processes in the hexagonal boron nitride system were discussed. Since the substances in B–C–N–O–H have been shown to have more or less polymeric character and the reactions are mediated by radicals, the processes could be described by equations commonly used in organic chemisry. Beside stoichiometric equations, a two-dimensional ternary B–N–O diagram has been applied in which points representing chemical composition of particular substances were plotted. In the diagram, the chemical processes have been described by vectors having their origin in points assigned to chemical composition of starting substances and connecting points of composition of final products. The diagram hence represents a vector field containing linear subsets describing particular chemical processes—the vectors.

The subsets of the vector then express chemical composition of a process at a certain stage of conversion. The orientation of the vector is given by the corresponding stoichiometric equation and the modulus is defined by the degree of conversion. Additionally, the ternary diagram expresses the law of the conservation of the mass since the crossing point of a line connecting the points assigned to the substances undergoing the procedure (e.g., boric acid and ammonia) and that of the final products (boron nitride and water) correspond to the composition on the stoichiometric condition necessary for the quantitative course of the process.

This dynamic model is applicable to other solid-state systems with prevailingly covalent character of chemical bonds, where the chemical processes occur below the melting point of the constituents. The Si–C–N–O or Al–C–N–O systems might be attempted as other proper candidates.

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