

A Contribution to the Crystallochemistry of Boron Nitride

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A reaction mechanism of formation and growth of hexagonal boron nitride planar macromolecules during reductive nitridation of oxidic boron compounds has been proposed. This model was verified by a comparison of computed values of oxygen contents with experimental results and a good agreement has been found. The growth of boron nitride crystallites is suggested to be of a condensation character and the termination of it is seen as a reaction of hydroxylic and hydrogen radicals in periphery areas of the macromolecules. By this approach an occurrence of a certain amount of oxygen in samples of hexagonal boron nitride treated even at high temperatures can be elucidated. © 1992 Academic Press, Inc.

1. Introduction

Hexagonal boron nitride is a layered substance. Its crystals are created by composition of planar macromolecules such that boron and nitrogen atoms alternate regularly in the direction of crystallographic axis c (1). The size of the planar boron nitride macromolecules, or their width which can be expressed by parameter L_a calculated from the diffraction line broadening, depends appreciably on the synthesis conditions, the temperature in particular (2). As compared to the low-temperature, so-called turbostratic, form of boron nitride, the width of the planar macromolecules in the crystals is more than tenfold greater (3). Growth of the macromolecules and thus also of the single-crystal zones of hexagonal boron nitride is usually accompanied by the liberation of oxygen "impurities" from the structure bonding, and these can be successively removed by conventional purification (4–6).

Three basic chemical models have been suggested for interpretation of the formation

and growth of macromolecules of hexagonal boron nitride by reductive nitridation of oxidic boron compounds with ammonia:

1. According to Saito and Ushio (7), a mixture of orthoboric acid ammonium rhodanide heated at 250°C gives a polymer $(\text{BNH})_n$; heated up, this polymer releases hydrogen, and pure boron nitride emerges at 800°C. To set up this pathway, the authors apparently proceeded from the analogous process occurring during the carbonization of fused aromatic hydrocarbons in the production of graphite.

2. Vikulin (4) differentiates two basic stages of the formation of planar boron nitride macromolecules. In the first, a linear polymer is crosslinked with the repeating motif $-\text{NH}-\text{O}-\text{BH}-$ being formed; in the second stage this polymer is crosslinked and the final structure emerges.

3. In the reaction of boric oxide with ammonia, their adduct $(\text{B}_2\text{O}_3)_n \cdot \text{NH}_3$ is first formed. Its boron nitride content increases gradually at the expense of the oxide, so that

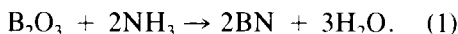
at temperatures higher than 1500°C, pure nitride is obtained (8).

These models fail to account for the presence of oxidic "impurities" in boron nitride, detectable even at temperatures in excess of 1800°C.

The aim of the present work is to suggest a reaction mechanism of formation of hexagonal boron nitride macromolecules and to verify it based on structure-chemical processes occurring in a system containing boron nitride prepared by reductive nitridation of oxidic boron compounds with ammonia.

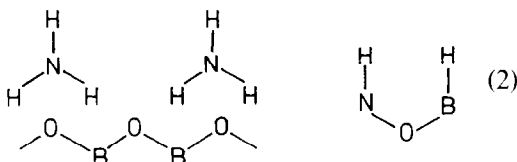
2. Analysis of the Problem

For all variants of description of the turbostratic form of hexagonal boron nitride by reductive nitridation of oxidic boron compounds, boric oxide and ammonia can be considered as the starting substances; these give boron nitride according to the overall equation

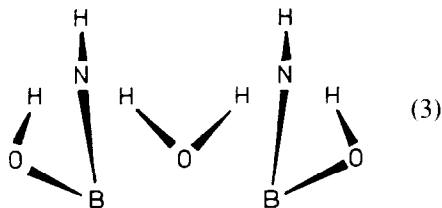


This process can be thought to comprise several stages as follows:

1. Occupation of the substrate boric oxide surface by ammonia in the molar ratio 1:2:



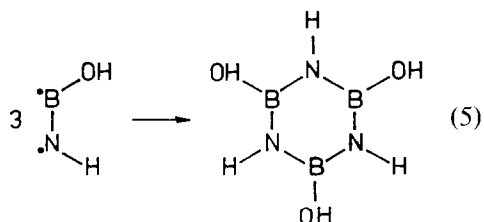
2. Electron density displacement in the $\text{B}_2\text{O}_3 \cdot 2\text{NH}_3$ adduct, homolytic splitting, and formation of new bonds:



This stage can be described by the equation

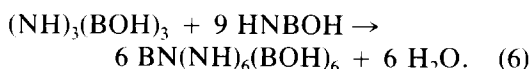


3. Stabilization of the starting monomer HNBOH by the Lewisian reaction of three monomers, corresponding with hybridized states both of boron and hydrogen atoms:

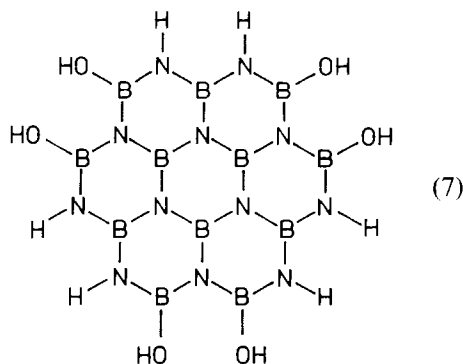


On the other hand, this trimer represents a transition from the starting oxide to boron nitride; on the other hand, it is the crystallization nucleus of the daughter phase—hexagonal boron nitride. This form owes its existence to the stabilizing effect of hydrogen bridges, by which the compound $(\text{NH})_3(\text{BOH})_3$ is bonded to the unreacted boron oxide.

4. The propagation of the process consists in the elementary nuclei of the hexagonal network being surrounded by additional monomers HNBOH while water is released. For instance, the nearest homologue of the elementary trimer with sixfold symmetry is formed in the reaction



The structure formula of the new formation is



5. The development of the macromolecular network can go on in this manner. The polymerization process can be interrupted by discontinuing ammonia feed, reducing temperature or depleting the mother substrate to such an extent that further development is impossible.

For the ideal case of sixfold symmetry of the polymerization products, which possess the lowest number of edge nodes with respect to the total number of atoms in the network, the following can be derived by mathematical induction:

(a) The formula of the products in the form $B_iN_iH_2O$, where i is the serial number of the planar formation homologue; for the starting trimer, $i = 1$; for the formation shown as (7), $i = 2$.

(b) Chemical composition and residual element contents in weight % (oxygen and hydrogen) in the i th homologue. The following relations hold true:

$$c_O^i = \frac{1599.9}{i \cdot 24.817 + 18.015} \quad (8)$$

$$c_H^i = \frac{201.6}{i \cdot 24.817 + 18.015} \quad (9)$$

(c) The size (width) of the i th homologue L_a^i ,

$$L_a^i = (2i - 1) \frac{\sqrt{3}}{2} \cdot L_a^0, \quad (10)$$

where $L_a^0 = 0.2504$ nm is the a_0 parameter of the hexagonal boron nitride lattice.

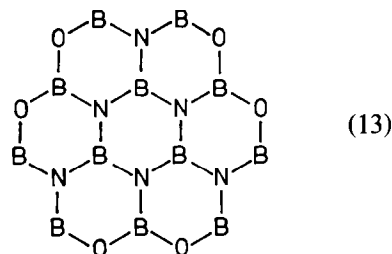
By combining relations (8)–(10), the dependence of the oxygen and nitrogen contents on the macromolecule width can be obtained as

$$c_O^i = \frac{27.9601}{L_a^i + 0.5317} \quad (11)$$

$$c_H^i = \frac{3.5232}{L_a^i + 0.5317} \quad (12)$$

Another way the growth of the planar hex-

agonal boron nitride macromolecules can be terminated consists in the occupation of the peripheral bivalent nodes by oxygen instead of by nitrogen. In this case, the formula $B_iN_{i-1}O$ follows for the i th homologue, which can be regarded as a copolymer $(BN)_{i-1} \cdot BO$ of boron nitride with peripherally bonded boron suboxide:



The size of the macromolecule thus constructed is given by the same relation as above (10); the hydrogen content, however, is invariably zero and the oxygen content obeys the equation

$$c_O^i = \frac{32.2855}{L_a^i + 0.2906} \quad (14)$$

3. Experimental Materials and Procedures

Turbostratic boron nitride samples were prepared by heating a dehydrated and thermally partly decomposed mixture of boric acid and urea (1 : 2) in ammonia at 850°C in a quartz glass retort.

Hexagonal boron nitride was synthesized so that the powder obtained by the above procedure was hot pressed in graphite die at a pressure of 10 MPa and temperature of 1800°C under nitrogen; a DSP 100-DAT apparatus (Dr. Fritsch KG, Germany) was employed.

Crystallographic changes in boron nitride were studied on samples annealed under nitrogen–hydrogen atmosphere (1 : 3, vol.).

Reductive chlorination (5, 6) was carried out in the equipment in which the primary turbostratic powder was also synthesized. Trichloromethane vapor was entrained into

the ammonia carrier from a bath at 20°C. Flow rates of all gaseous media in the above processes were at $1 \text{ cm} \cdot \text{s}^{-1}$.

Boron content was determined by potentiometric titration of the dissolved product of alkaline fusion of boron nitride (9); mannitol was added to increase the dissociation constant of orthoboric acid.

Nitrogen content was determined by acid–base titration of the sample decomposed by pressure mineralization in a PTFE autoclave (10).

Oxygen content was determined by fusion extraction on an RO 316 instrument (LECO, U.S.A.). This apparatus was also used to obtain evolvographs (so-called oxygen spectra), recording the course of oxygen detachment, in the form of carbon monoxide, from the boron nitride samples at increasing temperatures of analysis.

Hydrogen content was determined on a P40 C CHN-analyzer (Perkin–Elmer).

The boron nitride crystallite size (width, L_a parameter) was calculated from diffraction line broadening. The diffractographs were obtained on a DRON UM-1 instrument (U.S.S.R.); $\text{CuK}\alpha$ radiation, Ni filter.

Infrared spectra were measured on a Perkin–Elmer 325 spectrophotometer applying the KBr disc and Nujol mull techniques.

Photoelectron spectra were recorded on an ESCA 3 Mk II XPS spectrometer (VG Scientific) and accumulated on a Nicolet 1072 multichannel analyzer. An aluminum foil served as the X-ray source ($\text{AlK}\alpha = 1486.6 \text{ eV}$).

The specific surface area of the powder was measured by the BET method.

4. Experimental Results and Discussion

Assuming that the total boron, nitrogen, and oxygen contents in boron nitride preparations make up 100% (disregarding hydrogen), the composition of any preparation is uniquely determined by the corresponding point in the ternary B–N–O diagram (Fig.

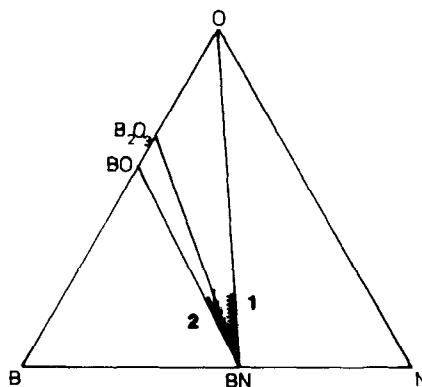


FIG. 1. The ternary B–N–O diagram: (1) the area of turbostratic boron nitride occurrence; (2) the area of hexagonal boron nitride occurrence.

1). For easier confrontation with the two variants of the hexagonal boron nitride macromolecule growth theory, three straight lines are indicated in the diagram, viz.:

—the line connecting B_2O_3 and BN, corresponding to mixtures of the two “pure” compounds with ranging proportions;

—the line connecting O and BN, representing the first, “hydroxylic” variant of growth of boron nitride macromolecules, in which hydroxyl groups and hydrogen atoms are assumed to be bonded to the peripheral boron or nitrogen atoms. (The homologue with serial number zero is water, here expressed as oxygen);

—the line connecting BO and BN, representing the second growth variant, in which oxygen atoms are considered in positions of peripheral bivalent nodes corresponding to nitrogen.

The figure demonstrates that the compositions of real boron nitride samples can be bounded by a triangular field whose vertices correspond to boron nitride, boric oxide, and water. The variant of the hexagonal boron nitride network growth involving the bonding of hydroxyl groups and hydrogen atoms in the peripheral part of the macro-

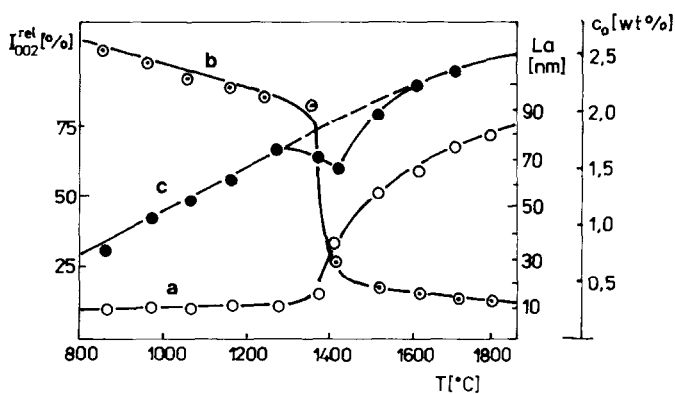


FIG. 2. Temperature dependence of crystallite width (○), peripherally bonded oxygen (○), and integral intensity of the (002) diffraction line (●).

molecules appears more likely than the other variant.

Furthermore, it is apparent that the low-temperature, turbostratic form of boron nitride, which consists of macromolecules smaller in size (as is demonstrated later), involves a relatively higher number of peripheral bivalent nodes with respect to the total number of atoms in the macromolecule, which is manifested by the occurrence of specimens of this form close to the BN–H₂O connecting line.

Macromolecular specimens possessing a crystal form which has an appreciably lower amount of peripherally bonded hydroxyl groups, and hence, of analytically determinable oxygen, thus occur preferentially near the BN–B₂O₃ connecting line.

Based on the results of analysis of 40 individually prepared homemade samples as well as samples of foreign origin, it can be concluded that real products referred to as boron nitride are actually two-component mixtures containing unreacted boric oxide in addition to B₇N₇H₂O.

For additional verification of this, the results of measurements of temperature changes in the crystallite size of boron nitride annealed in a nitrogen–hydrogen mixture were used (Fig. 2a).

If the above statement is true, then the peripherally bonded oxygen content can be determined based on the measured boron nitride crystallite size and the application of relation (11), Fig. 2b.

When measuring the intensity of radiation diffracted by the (002) plane it was observed that for samples exposed at 1300–1400°C, this intensity decreased; this fact can be explained in terms of scattering of the X-rays (Fig. 2c). Actually, the so-far isolated crystallites begin to approach each other spontaneously at these temperatures; the distance between them is so short that it is comparable to the wavelength of the characteristic X-rays emitted by the lamp employed (0.154 nm). Thus the isolated crystallites constitute an imperiodic lattice on which random scattering of the incident radiation takes place.

The oxygen content in the boron nitride preparations can be controlled basically by three procedures: washing the boric oxide with water; chemical refining by reductive halogenization (5, 6); or annealing the preparation in an inert medium in a mixture with carbon, as in the case of analysis by the fusion extraction method or when using graphite foam (11).

The advantages of elution with water or reductive chlorination include conservation

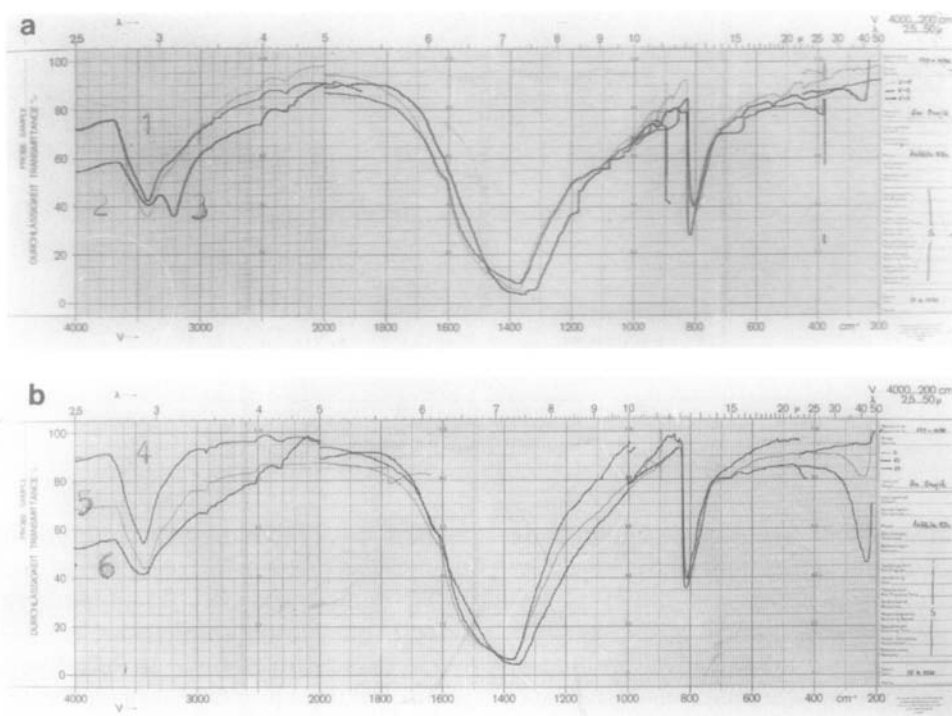


FIG. 3. Infrared spectra of boron nitride preparation No 1–6 (see Table I) before (a) and after (b) reductive chlorination.

of the crystallographic (and virtually also morphological) parameters of the material, the temperature of the refining procedures being not higher than the temperature of synthesis of the starting turbostratic boron nitride.

The preferential effect of reductive halogenization on the oxidically bonded oxygen is apparent from Fig. 3, showing infrared spectra of boron nitride preparations whose parameters are given in Table I.

The data in Table I indicate that the amount of oxygen that cannot be removed by reductive chlorination decreases with increasing crystallite size (width of planar macromolecules) of hexagonal boron nitride. The level of residual oxygen in the refined products corresponds to the calculated amount of oxygen bonded in peripheral hydroxyl groups. The lower residual

oxygen value than as corresponds to the theory for the turbostratic form of boron nitride (samples 4 and 5) can be explained in terms of formation of pyrolytic boron nitride from the gas phase (6); the mechanism of reductive nitridation of oxidic boron compounds is different from the mechanism of pyrolytic phase.

In the crystalline (hexagonal) samples, the elevated residual oxygen level as compared to the theory is apparently due to the existence of a diffusion barrier constituted by secondary boron nitride, which hinders the refining process.

The difference in oxygen bonding in boron nitride specimens with different crystallite size is apparent when comparing the IR spectra of samples 2 and 3. These samples contain oxygen in approximately equal amounts, their crystallite size, however, dif-

TABLE I
OXYGEN CONTENT, CRYSTALLITE WIDTH, INTERLAYER DISTANCE,
AND SPECIFIC SURFACE AREA OF BORON NITRIDE PREPARATIONS

Sample no.	Temperature of synthesis (°C)	c_0 (%)	L_a (nm)	d_{002} (nm)	Specific surf. area ($\text{m}^2 \text{g}^{-1}$)
1	850	7.71	11.2	0.353	106.7
2	1000	9.96	12.5	0.348	41.8
3	1800	9.64	79.0	0.336	11.1
4	850/1100 ^a	1.89	10.9	0.355	305.7
5	1000/1100 ^a	1.82	11.9	0.351	74.7
6	1800/1100 ^a	1.42	78.0	0.339	16.9

^a Temperature of reductive chlorination.

fers considerably. The presence of boric oxide as a chemical individual absorbing characteristic wavelengths 3,105 μm of infrared radiation was only evidenced for sample 3.

This difference can be interpreted in terms of the above-mentioned hydrogen bridges between the peripherally bonded hydroxyl groups and the hydrogen in boron nitride on the one hand, and boric oxide on the other hand. As the amount of peripherally situated active centers decreases due to growth of the crystallites, the amount of boric oxide so bonded decreases as well, while the total oxygen level remains unchanged, and so the released boric oxide becomes a separate phase.

The boron nitride refining process brought about removal of boric oxide, as follows from a comparison of samples 3 and 6 which are genetically related: the absorption band was absent from the spectrum of the latter sample at 3220 cm^{-1} .

Equilibrium between hydroxyl groups and boric oxide can be established in aqueous boron nitride suspension. Boron nitride samples with different crystallite size were eluted with water. After analysis of the dried samples, a relation was sought between the amounts of oxygen peripherally bonded in hydroxyl groups and the residual oxygen. Independent of the crystallite size, this con-

tent ratio was found equal to three with a high precision; see Fig. 4. In other words, in the equilibrium state (after elution with water), one formula unit ("molecule") of boric oxide corresponds to one hydroxyl group and one atom of hydrogen bonded on the periphery of the planar hexagonal boron nitride macromolecule.

An overall comparison of results of the deoxidation processes with the theoretical oxygen content in boron nitride is shown in Fig. 5.

The oxygen content in the refined products corresponds with the peripherally bonded oxygen content of turbostratic boron nitride. The oxygen content can be reduced

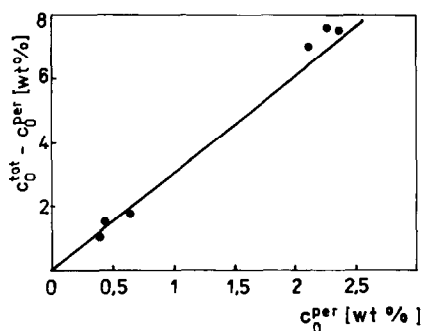


FIG. 4. Relation between residual content of oxygen and content of peripherally bonded oxygen.

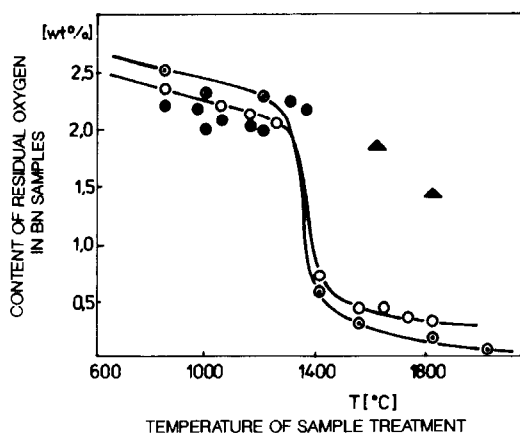


FIG. 5. A comparison of results of the deoxidation processes. Temperature of sample treatment vs. content of residual oxygen in BN samples (wt%): (○) calculated on the basis of measurement L_a ; (○) found after fusion extraction in the LECO instrument; (●) found after refinement by means of reductive chlorination; (▲) samples after washing by water.

appreciably by fusion extraction; this, however, is accompanied by a marked change in the crystallographic parameters and simultaneous formation of boron carbide at temperatures in excess of 1600°C.

The equilibrium state of the hot pressing product washed with water can be expressed by oxygen content roughly equal to triple c_0^{gr} .

The occurrence of different oxygen bonding types in hexagonal boron nitride, which are also indicated by ESCA measurements (see Table II) is confirmed by evolvo-

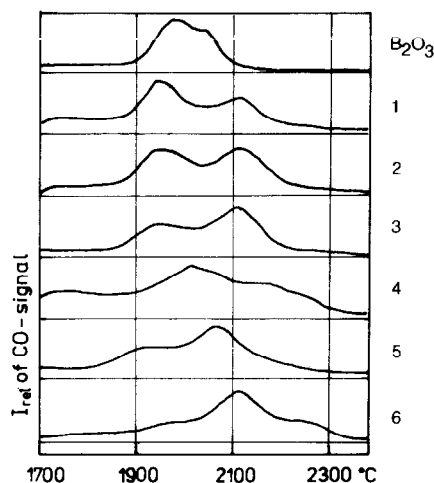


FIG. 6. Evolvo-graphs of boron nitride samples (for sample numbers, see Table I).

graphs of samples whose properties are given in Table I; see Fig. 6. By comparison with the evolvo-graphs of carbon monoxide obtained by reacting boric oxide with carbon, it was found that this substance liberates oxygen at temperatures higher than 1700°C. Reduction in the boric oxide content of boron nitride samples by reductive halogenization brought about relative increase in the fraction of nonoxidically bonded oxygen, which evolves at lower temperatures. The first region of oxygen liberation in the form of carbon monoxide lies within the 950–1250°C range.

The quantity of oxygen liberated in thi

TABLE II
Results of ESCA Analyses of Boron Nitride Preparation

Sample	C_{1s}	O_{1s}	N_{1s}	B_{1s}	Rel. intensity		
					N_{1s}/B_{1s}	O_{1s}/B_{1s}	
BN turbostratic no. 1	285.0	533.5	398.3	190.7	193.6	0.81	0.09
BN hexagonal no. 3	285.0	533.2	398.4	190.8	193.5	0.82	0.23

Note. Bonding energies of particular elements are related to the value $C_{1s} = 285.0$ eV.

temperature range corresponds with the specific surface area of the samples (Table I), the latter quantity mirroring the concentration of active centers and hence, the tendency of boron nitride to hydrolysis whose products are boric acids. The detachment of water thus bonded on the surface of real boron nitride samples (and its decomposition with carbon in the LECO analyzer was detected over the above temperature range.

The next region of oxygen liberation corresponds to the temperature range 1350–1800°C. The lower limit of this range is the temperature at which the rapid growth of boron nitride crystallites due to thermal exposure begins (see Fig. 2a). Coalescence of the crystallites begins about liberation of water according to the approximate equation



where $i = 27$ corresponds to the size of crystallites of turbostratic boron nitride synthesized at 850°C, whereas $i = 189$ corresponds to the crystalline material prepared by following heating at 1800°C.

The water released Eq. (15) is again decomposed by reaction with carbon and detected on the analyzer as carbon monoxide. Comparison of evolvographs of samples 4–6 demonstrates clearly how the growth of the boron nitride crystallites is accompanied by a decrease in the quantity of water that can be released by thermal exposure during the analysis, due to the decrease in the peripheral hydroxyl groups contents before and after the analysis. The additional maxima in the evolvographs at temperatures above approximately 1800°C corresponds to gaseous products of boric oxide carbidation (cf. evolvograph B_2O_3).

5. Conclusions

Macromolecules of hexagonal boron nitride can be regarded as planar objects in which boron and nitrogen atoms are triva-

lent and occupy alternate vertices of regular hexagons. The lateral boron and nitrogen atoms, which contribute two bonding electrons only, bind—via the remaining free electron—hydroxyl or hydrogen radicals stemming from the starting compounds or intermediates, in the nitridation of oxidic boron compounds with ammonia.

Oxygen occurs in hexagonal boron nitride in at least three different forms:

—In constitutionally bonded water, which is present in the peripheral region of the planar macromolecules and whose amount thus is dependent on the crystallite size;

—In hydrogen-bonded boric oxide, constituting an oxide packet on the periphery of the planar boron nitride macromolecules and thus losing its chemical identity. The amount of boric oxide so bonded is in equilibrium with that of peripherally bonded water, one stoichiometric unit of boric oxide corresponding to one “water” molecule. Thus, in the equilibrium state is one molecule of monohydrogenboric acid per one peripherally bonded boron and/or nitrogen atom;

—Free boric oxide, which is the only one of the three phases that is removable, by elution with water, reductive chlorination, or vacuum extraction, and is present particularly in crystalline boron nitride materials.

The growth of hexagonal boron nitride crystallites has a condensation character. Hence, rather than due to mass transport through the liquid phase, it is a consequence of mutual reorientation of the crystallites and subsequent coalescence during which the water, hitherto present in the form of hydroxyl and hydrogen radicals bonded in the peripheral region of the merging crystallites, is released. As the hexagonal boron nitride crystallites approach each other, scattering of X-rays takes place at a certain moment, whereupon the intensity of diffracted radiation decreases. This scattering is

due to the formation of active centers, viz., intercrystallite regions whose dimensions at a certain stage of mutual crystallite approaching become parable with the wavelength of the characteristic X-rays of the lamp used.

The temperature of hexagonal boron nitride synthesis and subsequent treating has a major effect on the crystallinity of the substance. The turbostratic form, whose crystallites are 10–12 nm broad, appears if the temperature of synthesis does not exceed 1350°C; it exhibits a high stability of the crystallite dimensions over a wide temperature region and a high constitutionally bonded water content (and hence oxygen content), viz., 2 to 2.5 wt%.

Boron nitride of mesographite type is formed at temperatures higher than 1350°C and exhibits a pronounced crystallite size lability at these temperatures; this is mirrored by the amount of peripherally bonded hydroxyl groups and hydrogen.

A perfectly crystalline material is an ideal case, which substances worked up at high temperatures approach. For practical purposes, boron nitride can be considered crys-

talline if its crystallites are larger in size than 50 nm and the layer spacing is lower than 0.335 nm; this state can be obtained if the workup temperature is not lower than 1500°C. The amount of oxygen in the peripheral hydroxyl groups then does not exceed 0.5 wt%.

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