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A Coexistence of Boron Nitride and Boric Oxide

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Crystallization of turbostratic boron nitride, prepared from a mixture with varying ratios of boric acid and urea, was studied by heating from 220 to 1100°C. Formation of boron nitride layers was observed at temperatures as low as 220°C. Two ways to crystallization were revealed by further heating depending on the urea ratio in the starting mixture. Above 70%, the system remained monophasic and consisted of only one turbostratic phase. Below this ratio the system split into three phases at temperatures above 700°C. These were assigned as turbostratic boron nitride, boron oxynitride, and crystalline boric oxide. Boron oxynitride has been interpreted as an interfacial zone between turbostratic boron nitride crystallites and residual boric oxide resulting from an imperfect nitriding of starting oxidic precursors. Existence of this transition zone promotes the crystallization when heated at elevated temperatures. © 1994 Academic Press, Inc.

1. INTRODUCTION

Hexagonal boron nitride (hBN) is a typical layered substance, as planar hexagonal networks are stacked with van der Waals force to form a three-dimensional, graphite-like structure. In contrast to a crystalline phase prepared at high temperature (1650°C and above), low-temperature forms prepared at about 1000°C often have a disordered structure (1). The disorder, resulting from weak attractive forces between layers, consists in irregularities of the layers arranging within the c crystallographic axis (2). In accordance with disordered carbons, such a structure is called "turbostratic" (3). The structural imperfectness, on the other hand, is an important technological requirement, as such powders have good sinterability, when compared with the crystalline material (4).

An effective method to prepare sinteractive, turbostratic boron nitride powder by heating a mixture of boric acid and urea was developed and patented by O'Connor in the sixties. By using this method a powder having the lowest possible content of impurities relative to the starting oxidic compounds of boron was obtained when using a sufficient ratio of urea in the starting mixture (68.75%), together with ammonia as a reactive medium (5). Such a material is a so-called soft form of boron nitride, as this can crystallize (graphitize) rather easily in contrast to a powder having similar crystallographic properties but prepared by pyrolyzing nonoxide compounds carrying both boron and nitrogen (6). During the graphitization boron nitride crystallites grow, and finally their width is approximately sevenfold (11 and 78 nm, resp.) (7).

Oxygen-containing impurities, thus, were believed to promote graphitization of turbostratic boron nitride. Boron oxynitride was supposed to be especially effective. Its existence is derived from the fact that the low-temperature forms of boron nitride prepared using oxidic compounds exhibited extra lines in their infrared patterns in comparison with those of boron nitride (8). Existence of such a compound, however, has never been confirmed by other authors, unless other oxynitridic systems, such those based on silicon and aluminum, rank among important ceramic materials. The high-temperature behavior of turbostratic boron nitride can be summarized by the statement that elevating temperature leads to a more ordered arrangement of layers in the boron nitride crystallites, while their size increases as well. Boron oxide released during the high-temperature treatment is easy to purify by water or ethanol, in contrast to the starting turbostratic powder (9). The boron oxide is supposed to be amorphous, as no lines relating to crystalline boric oxide have been found in X-ray diffraction patterns. The turbostratic system was found to be basically monophasic, as only shifting and sharpening of the (002) line, together with the gradual appearance of further lines relating to hexagonal boron nitride, was observed (10). Vacuum, nitrogen, or noble gas are the media under which these phenomena have been observed. On the other hand, the use of ammonia, and especially its mixture with halogenated hydrocarbons, hinders the crystallization of turbostratic boron nitride. This phenomenon has been explained by the formation of new nuclei of turbostratic boron nitride, lowering the mobility of layers in original crystallites for rearrangements (11,12).

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TABLE 1
Chemical Composition of Boron Nitride Samples

Symbol of sample	c_{urea}		Item of procedure			
			1	2	3	4
A	33.33	^{c}N	7.77	7.17	49.81	7.39
		^{c}O	66.87	63.82	19.82	62.06
B	61.54	^{c}N	13.17	28.38	48.57	49.94
		^{c}O	44.12	35.91	19.17	4.45
C	68.75	^{c}N	27.94	44.45	32.50	53.78
		^{c}O	34.23	19.34	30.85	3.48
D	70.59	^{c}N	27.81			
		^{c}O	29.19			
E	100.00	^{c}N	53.23			
		^{c}O	10.90			

Note. c_{urea}, content of urea in the starting boric acid–urea mixture (% in mass); ^{c}N, nitrogen concentration in a product (% in mass); ^{c}O, oxygen concentration in a product (% in mass); 1, precursor prepared at 220°C; 2, precursor heated in nitrogen at 1100°C; 3, product No. 2, after leaching in ethanol; 4, precursor heated in ammonia at 1100°C.

In the present paper, the graphitization of turbostratic boron nitride and its coexistence with boric oxide were studied by using precursors with different nitrogen-to-oxygen ratios controlled by the amount of nitrogen active for nitriding.

2. EXPERIMENTAL AND ANALYTICAL METHODS

Turbostratic boron nitride (tBN) was prepared by a modified method according to O'Connor (10). In the first stage a precursor was prepared: A mixture of boric acid (GR Grade, with minimum content higher than 99.5%, Kanto Chemical Co.) and urea (GR grade, with minimum content higher than 99%, Wako Pure Chemical Co.) was pulverized in a porcelain mortar and then put in a Pyrex beaker placed in a stainless-steel container, which was closed up and linked to vibratory vacuum pump. The mixture was heated up to 150°C for 1 hr and then the temperature was raised to 220°C for the next 2 hr; the pressure in the system was maintained at 8 kPa. Through the treatment, the mixture was completely melted and gradually solidified and dehydrated. After cooling, the prepared boron nitride precursor was ground in the mortar. In the second stage the precursor was charged into a sintered-alumina boat, inserted in a quartz-glass tube, and heated in a stream of either nitrogen or ammonia at a flow rate of 1.5 cm/sec in Kanthal-wire furnace for 3 hr. As noted below, some portions of the preparations were further leached in ethanol for another 3 hr, and filtered and dried at 105°C, to remove free boric oxide.

Nitrogen and oxygen were determined by using a TC 136 automatic analyzer (LECO, USA). Phases were identified from X-ray diffraction patterns obtained by a PW 1130 diffractometer (Philips, Netherlands), using Cu$K\alpha$ radiation and a scan speed of 1°/min. Infrared spectra were obtained by using a FTS-65 spectrometer (BIO-RAD, Japan).

3. RESULTS

3.1. *Boron Nitride Precursor*

X-ray diffraction patterns of precursors prepared at 220°C with different boric acid–urea ratios (see Table 1), are shown in Fig. 1a. The products had diffraction patterns similar to tBN with a two-dimensional structure. It can be seen that when the content of urea in the starting mixture was increased, the interlayer spacing $\mathbf{d}_{002}$ decreased slightly. For up to 68.75% of urea ratio in a mixture, no other phase than tBN was noticed (A, B, C). However, a slight increase of urea (70.59%) resulted in the appearance of a new crystalline phase. This new phase had a different character from the phase obtained by thermal decomposition of urea itself (E). This fact was confirmed by the infrared spectra shown in Fig. 1b. The IR peaks can be ascribed to boron nitride, the decomposition product of urea (E), and others which later are interpreted as boron oxynitride. Judging from the change of peak intensity, the mutual ratio between boron nitride and "boron oxynitride" remains approximately the same in all samples regardless of the different urea ratio in the starting mixture. However, the concentration of the urea-derived products increases without any drastic change in the spectra between C and D in contrast with the X-ray diffraction patterns. This phenomenon might be explained by saturation of the boron nitride precursor with a urea. Above this saturation point, a urea-related decomposition product represents an independent phase.

3.2. *Crystallization of Boron Nitride*

Figure 2 shows the relationship between the composition of the starting mixture and the nitrogen-to-oxygen molar ratio (N/O) in the products obtained by heating the precursor at various temperatures. It can be seen that in the case when the urea content was rather low (A), the N/O ratio was almost constant. Increasing the urea content resulted in an increase in the N/O molar ratio with temperature (B, C).

Figure 3 shows the changes of interlayer spacing derived from (002) diffraction lines of turbostratic phases after heat treatment. When the ratio of urea was sufficient to saturate the precursor, a shortening of the interlayer distances was observed with elevating temperature over 500°C probably due to the specimen being monophasic (C). In the opposite case, when a low urea-containing

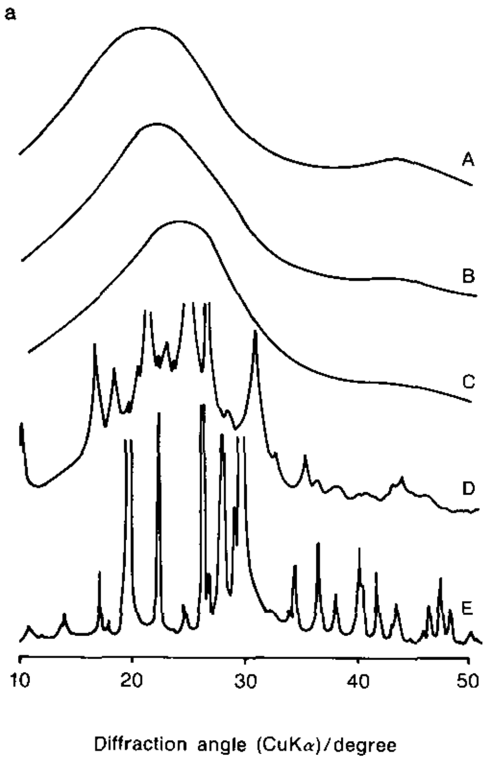

FIG. 1a. X-ray diffraction patterns of the precursors prepared at 220°C with varying urea-to-boric acid ratios (see Table 1).

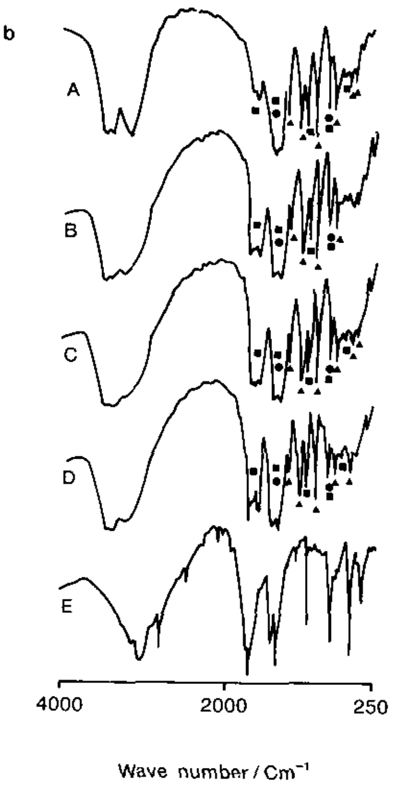

FIG. 1b. Infrared spectra of the precursors prepared at 220°C with varying urea-to-boric acid ratio (see Table 1) (●, boron nitride; ■, boric oxide; ▲, unknown substance).

preparation was heated above 700°C, a different behavior was noticed (A). The originally monophasic system was split into two phases after heat treatment: tBN with the interlayer spacing reaching the standard value 0.333 nm (I), and another turbostratic phase having larger interlayer distances than the same material treated at 500°C (II). Occurrence of both these turbostratic phases together with a third phase — crystalline boric oxide is demonstrated in Fig. 4, procedure 2, samples A, B. This shows the diffraction patterns of the three types of precursors after heating at 1100°C in a stream of either nitrogen. In contrast to the gradual arranging of layers in urea-sufficient samples described above (sample C), the newly observed phase of tBN suddenly reached the standard value of spacing, and this process was accompanied by the release of crystalline boric oxide. When samples A and B are compared, it can be seen that the ratios of the close-packed tBN and released boric oxide were roughly proportional, while the loose-packed turbostratic phase showed an inverse tendency compared to the both former phases.

Preparation of crystalline boric oxide by dehydration of boric acid or by growing it from boric oxide melt is well known to be rather difficult. The system, investigated in the present work, thus, represents a stabilizing medium, preventing the formation of amorphous boric oxide, even when the temperature of heat treatment is higher than the melting point of boric oxide.

Furthermore, the ratio between the two kinds of turbostratic phases was dependent on the N/O ratio. When the urea content was low, the relative amount of the loosely packed phase (II) was higher. With increasing content of urea, the closely-packed phase (I) occurred prevailingly, and so the amount of released boric oxide increased. And then, diffraction lines corresponding to boric oxide suddenly disappeared. This transition point was found to be at 70% of urea content, which corresponds to the critical point of the changing X-ray diffraction patterns of the precursors as has already been shown in Fig. 1.

The middle row in Fig. 4 shows the results after ethanol treatment (procedure 3). With the treatment it was easy to leach out boric oxide from the samples (B3 in Fig. 4). In addition to boric oxide, the loosely packed turbostratic phase also showed poor stability against this agent, as the relative amount of the closely-packed phased increased after leaching in ethanol (patterns A3, B3). Additionally, in the case of the monophasic system (C), the leaching led to a sharpening of the (002) on the low 2θ side, and to a shift in the maximum to a higher value of the diffraction angle. This suggests that tBN is not in fact mono-

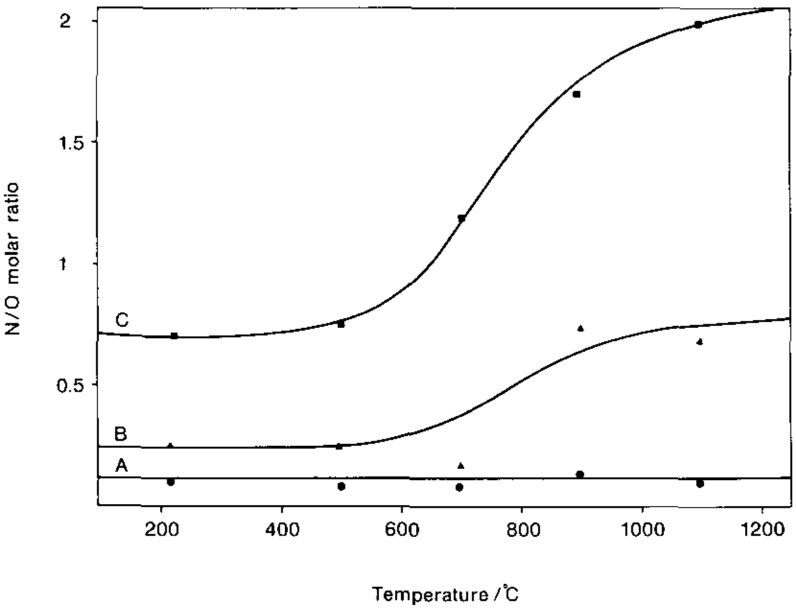

FIG. 2. Nitrogen-to-oxygen molar ratio vs temperature of the precursor heat treatment (precursors A, B, C: see Table 1).

phasic, but represents a continuous spectrum of various *d*-spacings. These constituent subpolytypes differ from each other in chemical stability, as is suggested from the above-mentioned change of the (002) line shape, which is in good agreement with the results obtained by leaching the biphasic samples. Partial decomposition of the biphasic system by leaching resulted in a decrease of the oxygen content. In contrast, after leaching the monophasic specimen, the oxygen content was decreased as shown in Table 1.

Heating the powders in a stream of ammonia led to similar results, as far as the existence of both the types of crystallization is concerned (procedure 4, the lowest row in Fig. 4). By the reducing effect of ammonia, the formation of boric oxide was suppressed, so that only in specimen A, prepared from the mixture with the lowest amount of urea, 33.33%, a weak line of boric oxide could be observed, and in samples B4 and C4 only that phase corresponding to tBN was found. Despite the fact that the difference in oxygen content is only 1% (see Table 1), the shape of the (002) diffraction line is rather different. In sample B, the line is rather broadened at the low 2θ side with its maximum position corresponding to the theoretical value (0.333 nm), while that of sample C shows a

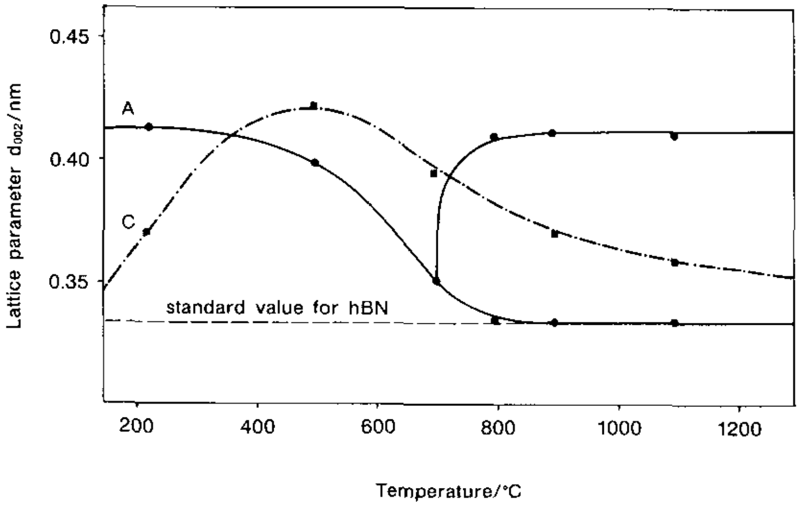

FIG. 3. The interlayer spacing parameter vs temperature of the precursor heat treatment (precursors A, C: see Table 1).

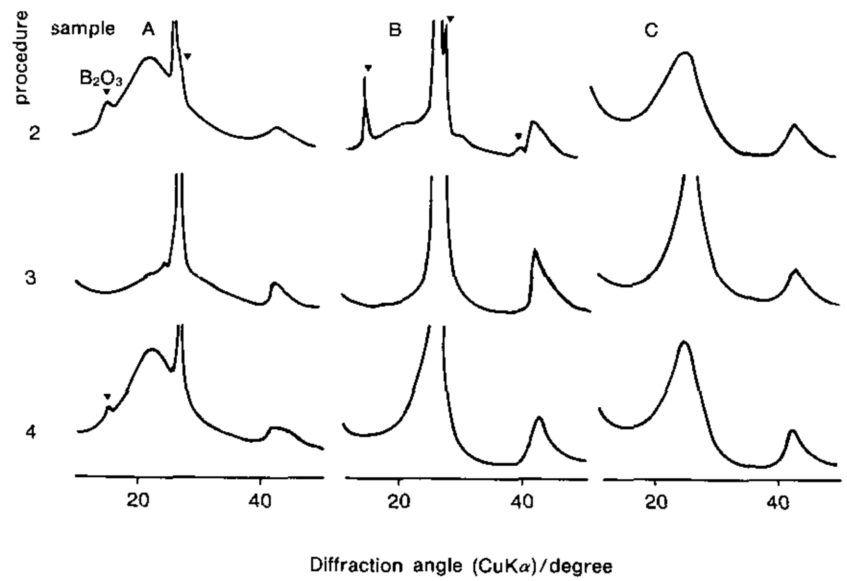

FIG. 4. X-ray diffraction patterns of the precursors heated at 1100°C in nitrogen (procedure 2) and then leached in ethanol (procedure 3), and heated at 1100°C in ammonia (procedure 4) (▼, boric oxide).

Lorentzian shape with the maximum shifted to lower value of 2θ angle.

Figure 5 shows infrared absorption spectra of the heat-treated samples. The IR peak found in the precursor at around 1500 cm^{-1} became gradually sharp and the peak at around 800 cm^{-1} became clearly observable after heating at 1100°C. Thus we confirmed the formation of boron nitride; at the same time we can assume the existence of boron nitride layers even in the precursor, confirming the previous suggestion based on the XRD patterns. Thus with raising temperature, boron nitride was purified by releasing accompanying residue, making the latter peak in infrared spectra clearly observable.

Other phases besides boron nitride were detected in

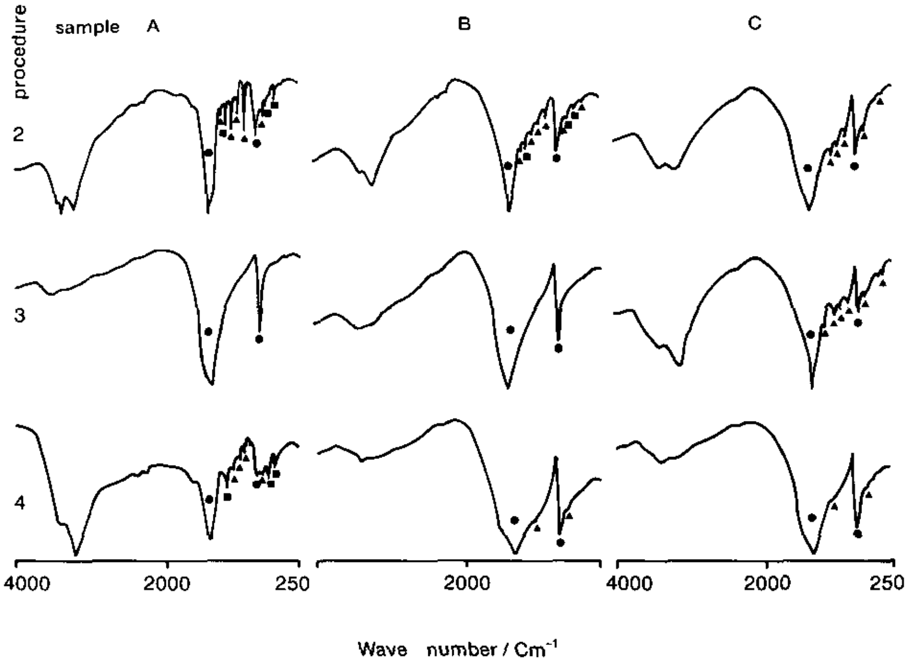

FIG. 5. Infrared spectra of the precursors heated at 1100°C in nitrogen (procedure 2) and then leached in ethanol (procedure 3), and heated at 1100°C in ammonia (procedure 4) (●, boron nitride; ■, boric oxide; ▲, unknown substance).

the spectra after heating the precursors in nitrogen: In the case of the samples prepared from the starting material with a low urea content, boric oxide and unidentified lines were observed (A2, B2). The sample prepared from the mixture with a high content of urea (C2) showed only the unidentified lines and those of boron nitride.

After leaching in ethanol, the infrared lines of boric oxide were not observable, and the intensity of the unidentified lines was drastically suppressed in samples A and B, leaving only the lines corresponding to boron nitride. In sample C, no substantial changes were observed in the spectra and the unidentified lines remained clear. From these facts, it is suggested that the structural properties of tBN, such as the size of the crystallites and the interlayer spacing, closely determine the ability to leach the phase showing the observed unidentified lines.

The lowest row in Fig. 5 shows the results after using ammonia instead of nitrogen. The spectrum of sample A4 showed the presence of all three phases, while spectra of samples B4 and C4 were free of boric oxide, and the unknown phase was poorly detected. This may be caused by the excellent nitriding ability of ammonia. As shown in Table 1, the oxygen content was low in samples B and C, and the changes in N/O ratio correspond with the changes of the infrared spectra. It is therefore considered that ammonia reduced the oxygen-containing phases, including the unknown phase.

4. DISCUSSION

By summarizing the above results it can be assumed that the turbostratic structure of the precursor basically consists of small nitride layers with significantly expanded interlayer distances. They are accompanied with other phases, as urea-related residue and products of an uncompleted conversion of the starting source of boron. After the decomposition of the uric remainders (approximately 500°C), oxygen-containing phases are exclusively considered to coexist with tBN.

A model of hBN planar network has been presented in a previous paper (7). By this model, the chemical character of trivalent peripheral nodal points of the network is explained. The third bonding electrons at the peripheral boron and nitrogen atoms, which do not participate in forming the network, are compensated with OH group and hydrogen in the case of boron and nitrogen, respectively. Thus the B–OH and N–H bonds terminate the boron nitride planar macromolecule, and concentration of them is inversely proportional to the macromolecule size, as the circumference-to-area ratio decreases when the macromolecule grows. This model has been applied for the case of tBN free of boric impurities. A similar model considering the presence of remainders of the mother phase located at the peripheral dangling bonds of oligomeric boron nitride molecules has been used to explain the presence of leaving groups in boron nitride products (13). In the powders prepared here, boric impurities were allowed to form when the conversion into boron nitride was intentionally limited by decreasing the urea ratio in the starting mixture and avoiding ammonia usage.

Boron nitride and boric oxide are substances having common origin in boric acid. Both phases can be interconnected with the dangling bonds at the periphery of boron nitride planar macromolecules. Such a zone terminates the boron nitride macromolecules and represents a natural transition from boron nitride to boric oxide. It is considered that specific character of the transition phase results in the excess lines in infrared spectra, and its ratio is inversely proportional to the crystallite size of boron nitride.

A sharp transition between the two crystallization mechanisms effected by the ratio of urea strongly suggested to us that when the content of residual boric oxide is sufficient to saturate the dangling bonds in boron nitride macromolecules, their interplanar spacing can reach the theoretical value starting at temperatures as low as 800°C. Thus the presence of the zone positively influences the mobility of the crystallites as they can appropriately rearrange for consecutive coalescence. During coalescence, the number of nodal points decreases and boric oxide is liberated. As the crystallites grow, cavities are formed as the result of a better arrangement of boron nitride layers. The cavities are filled with the released boric oxide, and at the same time they stabilize its crystallinity, as a formation of free crystalline boric oxide under these experimental conditions is practically excluded. The presence of the loose-packed turbostratic phase might be explained by the existence of isolated islettes that did not participate in the coalescence process. They can be ascribed to the tBN subpolytypes with extremely disordered crystal lattice and small size, thus having an abundant relative number of peripheral bonds and strong adhesion to the oxidic phase. These properties, then, are the reason for their poor stability against the leaching agents.

In an opposite case, when the content of oxidic "intercrystallite lubricant" was low, crystallization of boron nitride occurred as usual process generally described for boron nitride, consisting in gradual growth of the crystallites and simultaneous decreasing of the mean interlayer spacing parameter.

5. CONCLUSIONS

Turbostratic boron nitride precursors were prepared by heating mixtures of boric acid and urea at 220°C. Oxygen-to-nitrogen ratio was controlled by changing the ratio of the starting components. The precursor was heated in nitrogen and ammonia, and was leached in ethanol; the following conclusions can be stated:

1. Turbostratic boron nitride represents a coherent spectrum of structural subpolytypes of the hexagonal type, differing in their crystallite size, interlayer distance, and chemical stability. The smaller the crystallite is, and the looser the packing of its layers, the lower the stability is, as the concentration of the peripheral dangling bonds which mediate a reaction with an aggressive environment is higher.

2. Boron oxynitride is not an individual compound; it represents just an interfacial zone joining boric oxide and turbostratic boron nitride networks in their trivalent peripheral bonds, in products resulting from imperfect nitridation of oxidic boron compounds. However, this zone has a distinctive chemical character, possessing an unambiguous response in infrared spectra.

3. The transition oxynitridic zone ensures high mobility of boron nitride crystallites, which can be easily rearranged and become coalescent when being thermally exposed. The released boric oxide is then concentrated in cavities of the boron nitride grains, resulting from the contraction of the phase during the rearrangement of the crystallites. Furthermore, boron nitride environment stabilizes the crystallinity of the released boric oxide, which is kept even after heating high above the melting point.

4. When the oxygen content is too low to build a transition oxynitridic zone to a sufficient extent, the graphitization process is more restrained and gradually proceeds with the temperature elevation. This is why the layered system keeps the apparent coherency of the substructural polytypes within the entire range of the temperature.

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