

Crystallization Behavior and Characterization of Turbostratic Boron Nitride

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Abstract

X-ray diffraction studies of boron nitride powders synthesized from boric oxide and ammonia at 900°C indicates a turbostratic structure which is characterized by the absence of ordering in the third dimension. Turbostratic boron nitride (t-BN) powders are found to be unstable and decompose into ammonium borate compound ($\text{NH}_4\cdot\text{B}_5\text{O}_8\cdot 4\text{H}_2\text{O}$) after long storing periods. Thermal transformation of t-BN into the stable, hexagonal ordered layer lattice structure was promoted with heat treatments at 1500–1800°C for 15 min–5 h. The transformation and degree of crystallization was observed with X-ray diffraction analysis. The effect of crystallization period and temperature on the particle sizes and shapes of the powders was examined with transmission electron microscope. BET surface area measurements of the powders were also performed for the characterization of powder properties. © 1997 Elsevier Science Limited.

1 Introduction

Boron nitride (BN) is a widely used ceramic material with attractive properties such as high thermal-shock resistance due to its high thermal conductivity and low coefficient of thermal expansion, and high electrical resistivity at a wide temperature range. In addition, it is chemically inert to most molten metals and glasses, organic solvents and acids, and also it keeps its chemical stability at high temperatures.^{1,2} As in all other materials, these excellent properties of BN are essentially related to its crystal structures and the bond types between B–N atoms. Boron and nitrogen are neighbors to carbon in the periodic table, which leads them to form

a compound, boron nitride, isoelectronic with the structure of C–C bonds, and display crystallographic transformations analogous to carbon. Under normal conditions, the graphite-like hexagonal form (h-BN) is stable but the other two main forms zinc blende cubic structure (c-BN) and wurtzite-like close packed hexagonal structure (w-BN), with a tetrahedral distribution of atoms, are stable at high pressures and temperatures. However, they can also be found in a metastable state under normal conditions.³ In addition to these main polymorphs, stacking faults in (001) plane of h-BN cause them to form a structure analogous to a ‘rombohedral’ lattice, which is also presented as a structural modification of h-BN and can be present in small quantities in the h-BN powder.³

The hexagonal structure of boron nitride, first proposed by Pease,^{4,5} is constructed from layers consisting of a flat or nearly flat network of B_3N_3 hexagons with a bond length of 1.446 Å and strong covalent bonds between boron and nitrogen atoms within the hexagons. Unlike graphite, in boron nitride these hexagons are packed in the third ‘c’ dimension in such a way that the atoms stack in an orderly array on top of each other with alternating B and N atoms in each layer (Fig. 1). Because of this alternation, the interlayer spacing is $1/2c = 3.33$ Å and the bonds between layers are weak Van der Waals bonds. The lattice dimension in the ‘a’ direction is also given as $a = 2.504$ Å.⁵ This packing of BN, which is different than graphite, may be attributed to the electrical dipole moment of the B–N bond and the interlayer interaction of these poles.⁵

In addition to the structures mentioned above, BN has a semi-crystalline structure called ‘turbostratic boron nitride (t-BN)’. This structure is analogous to turbostratic carbon black, and it can be defined as B_3N_3 hexagon layers stacked roughly parallel to each other with a random rotation and translation about the layer normal⁶ which indicates

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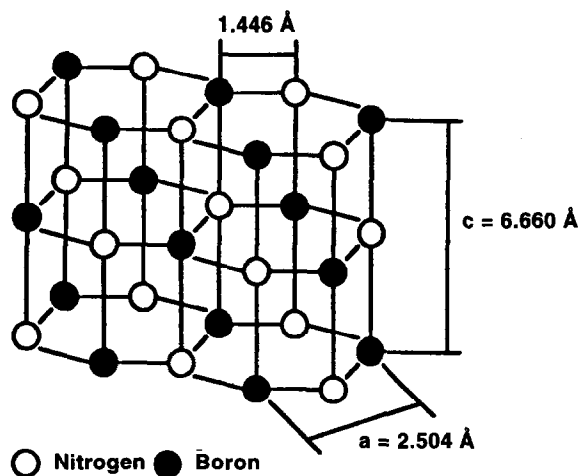


Fig. 1. Schematic crystal structure of hexagonal boron nitride.

a two-dimensional order of atoms. In recent years, with its activity due to the incomplete bonds, large surface area and impurities, the turbostratic structure of boron nitride has attracted an increasing interest⁷⁻¹¹ and has been proposed as a solution for the pressureless sintering problems of h-BN. However, with its two-dimensional structure and the absence of strong interlayer bonds, t-BN is not a stable modification of the boron nitride compound. Turbostratic BN is reported to dissolve in water with increasing temperatures and dissociates into its components at $\sim 2000^\circ\text{C}$ under inert atmosphere,¹² which is a lower temperature compared to h-BN. Therefore, it is the purpose of this paper to investigate the formation of fully stabilized hexagonal BN powders from the turbostratic BN powder, in order to improve the stability of boron nitride.

2 Experimental Studies

Turbostratic boron nitride powders were obtained by nitridation of boric oxide (B_2O_3) under the flow of ammonia (NH_3) gas at 900°C in 2 h. The synthesis experiments were carried out under the dynamic conditions of a stainless steel rotary tube furnace that contained an intimate mixture of boric oxide and an inert filler material. Two different sizes of rotary furnaces were used for small and large quantities (less than 10 g and more than 500 g, respectively) of turbostratic boron nitride production to evaluate potential problems with the scale-up process. Tri-calcium phosphate [$\text{Ca}_3(\text{PO}_4)_2$], with a specific surface area of $60\text{ m}^2\text{ g}^{-1}$ was used as an inert filler material to provide sufficient reaction surface to the boric oxide, which is a viscous fluid at the reaction temperatures. Unreacted boric oxide and inert filler material were removed from the reaction products with an HCl acidic leaching process at $\text{pH}=0.5$, $T=20^\circ\text{C}$ with a pulp density of 10%.

Crystallization heat treatments of the turbostratic BN powders were carried out in graphite boats and crucibles under argon gas atmosphere. The turbostratic BN powders that were obtained by utilizing the small reactor were heat-treated only at a temperature of 1500°C . On the other hand, all of the powders heat-treated above 1500°C were obtained from the same batch of the large-scale production operation. Duration of heat treatments varied between 15 min and 5 h, depending on the crystallization temperature employed.

The three-dimensional ordering of the structure with increasing heat-treatment times and temperatures was investigated with utilization of X-ray diffraction (XRD) analysis. All the XRD analyses were carried out by using a Rigaku Rint X-ray diffractometer, with a horizontal goniometer and a $\text{Cu-K}\alpha$ radiation tube. Effect of crystallization on the shapes and sizes of the powder particles was examined with a JEM-2000 EX-type transmission electron microscope (TEM). Specific surface area of the heat-treated samples were also measured by a 3-point BET method with a Quantachrome Autosorb1 instrument.

3 Results and Discussion

3.1 X-ray diffraction studies

The XRD analysis of the powders after the reaction and purification steps reveals a broad peak between 23° and 29° , 2θ angles with a low relative peak intensity and another very broad peak between 40° and 44° , 2θ angles as shown in Fig. 2(a). The bragg angles of these peaks are coincident with the bragg angles of (001) and (10) reflections of hexagonal boron nitride and indicate the presence of a turbostratic structure, as was also illustrated by Thomas *et al.*⁶ During the course of the XRD analysis of the uncrystallized powders, observation on the instability of the turbostratic structure was also obtained. In Fig. 2(b), from the XRD patterns of powders synthesized and stored under atmospheric conditions for one year, it was found that turbostratic boron nitride decomposes into an ammonium borate compound ($\text{NH}_4\cdot\text{B}_5\text{O}_8\cdot 4\text{H}_2\text{O}$). This decomposition presumably took place due to the instability of this semi-crystalline structure, and has not been reported in the literature previously. To form a fully stabilized h-BN crystallization, heat-treatments were conducted at $1500\text{--}1800^\circ\text{C}$ for various time periods.

The relative degree of crystallization for the turbostratic BN powders that were produced from the small-scale operation increases with crystallization time at 1500°C . The comparative diffraction patterns of these experiments are given in Fig. 3.

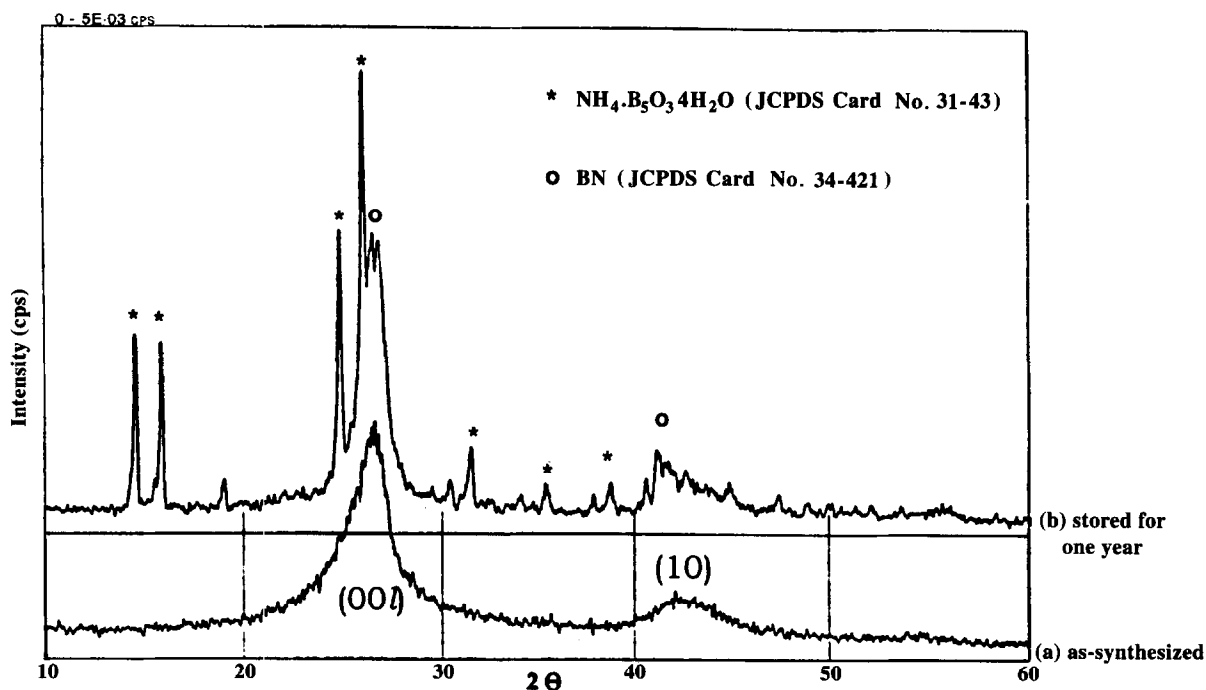


Fig. 2. XRD patterns of the samples (a) as-synthesized, and (b) stored for one year under atmospheric conditions.

An increase in the intensities of the (00l) reflection, which means an ordering of structure in basal planes, and a constriction in peak broadness with increasing time of heat-treatment were detected. Similar effects of time on the broad (10) reflection were also observed. Diffraction from the (100) and (101) peaks, which indicates the formation of a three-dimensional crystal structure, was observed with increasing crystallization periods. However, the crystallization was not fully completed with 5 h of heat treatment at 1500°C, as indicated by the

lack of (h0l) type of reflections in diffraction pattern. The results of these experiments indicate a transition mesographitic structure of boron nitride, which was defined by Thomas *et al.*⁶ as the transition phases with incomplete three-dimensional crystal structures which were formed during the phase transformation from turbostratic to hexagonal structures.

The rate of crystallization decreased significantly after the first hour. This is shown in Fig. 4, which is based on the calculations of the *relative degree of crystallization* from the half intensities of the (002)

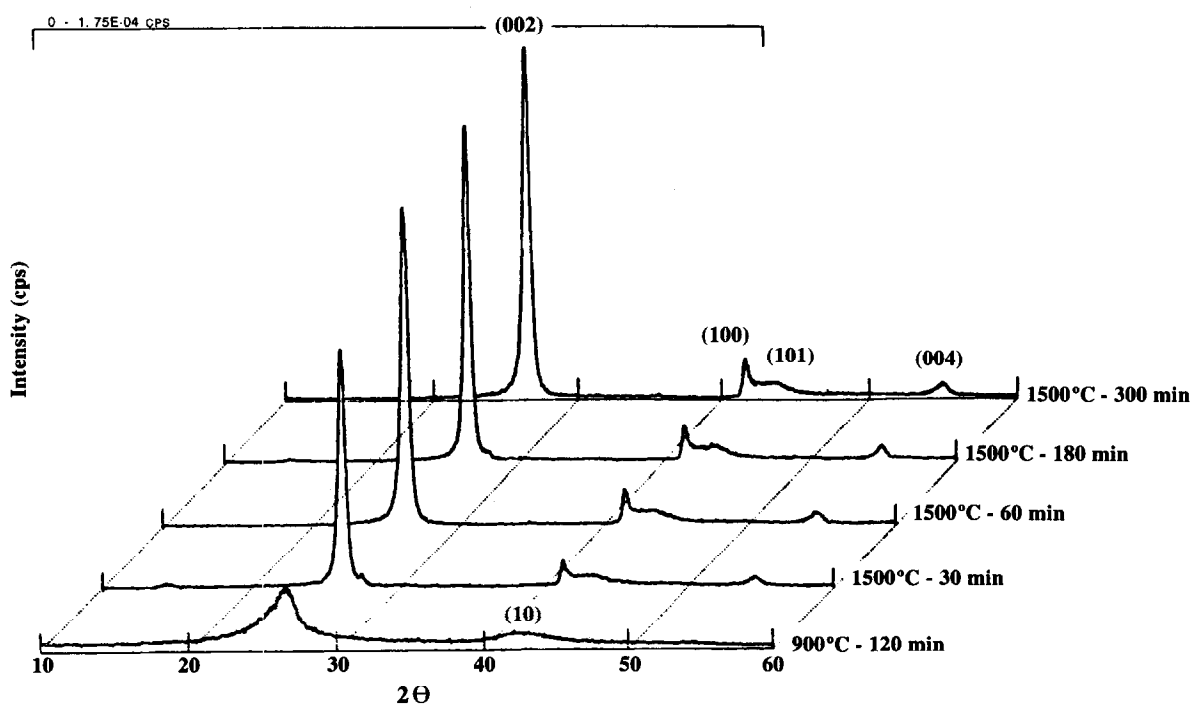


Fig. 3. X-ray diffraction patterns of samples before and after heat treatment at 1500°C for various times (small batch operation).

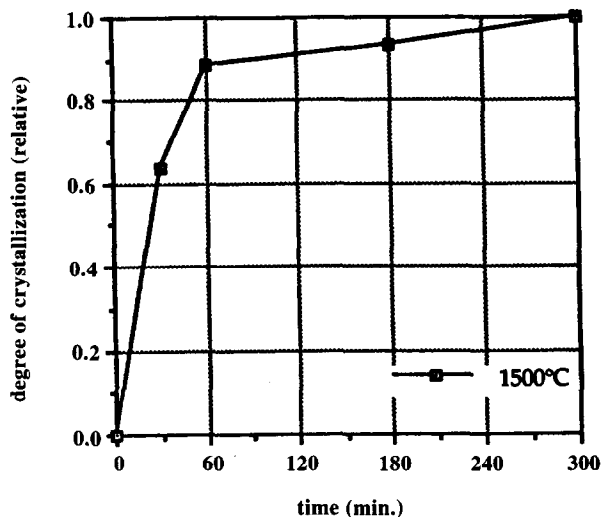


Fig. 4. Degree of t-BN crystallization for 1500°C heat treatment at various times.

peaks in X-ray diffraction patterns. The half intensity value of the (002) peak of the uncrystallized powders was assumed to be '0' and the half intensity value of the highest (002) peak of the crystallized powders was assumed to be '1'.

Higher temperature crystallization experiments were carried out on turbostratic structured BN powders between 1600 and 1800°C. A master batch of turbostratic powder that was obtained after a large-scale powder production was used for these crystallization experiments. As is seen in Fig. 5, for 1 h the intensities of (002) peaks and (10) reflections increase by the increasing temperature of crystallization. Also, the (004) and (102) reflections become visible at higher temperatures.

The crystallization period is less affected by time than increased temperature. Figure 6 illustrates the results of higher temperature crystallization at 1800°C. Relatively, 80% of the crystallization is completed in the first 15 min of the process at 1800°C and further treatment for 1 h seems to be sufficient for the complete formation of hexagonal structure.

The interlayer spacing values (d_{002}) of the powders, which were obtained from the XRD analysis, were also examined, and an expressive relation between the progress of the ordering and the interlayer spacing was searched for. Since an exact d_{002} value could not be determined for the uncrystallized powders because of the broadness of the (002) peak and the influence of the (310) reflection of boric oxide on this peak, an initial interlayer spacing value for uncrystallized powders could not be given in this discussion.

In Fig. 7, the interlayer spacing of the (002) atomic plane of the samples crystallized at 1500°C shows a continuous decrease with increasing periods of crystallization, i.e. increasing degree of ordering, and approach to a value of 3.35 Å, which is closer to the ideal value of 3.3306 Å⁴ for hexagonal BN. These findings are consistent with the literature,^{6-8,13,14} where d_{002} values higher than the ideal value were assumed as an indicator in assigning the turbostratic structure, and a decrease of this value by heat treatments was accepted to indicate an ordering in the crystal structure. Again from Fig. 7, for the samples that are heat-treated at temperatures over 1500°C, an expressive relation between the d_{002} values and the crystallization

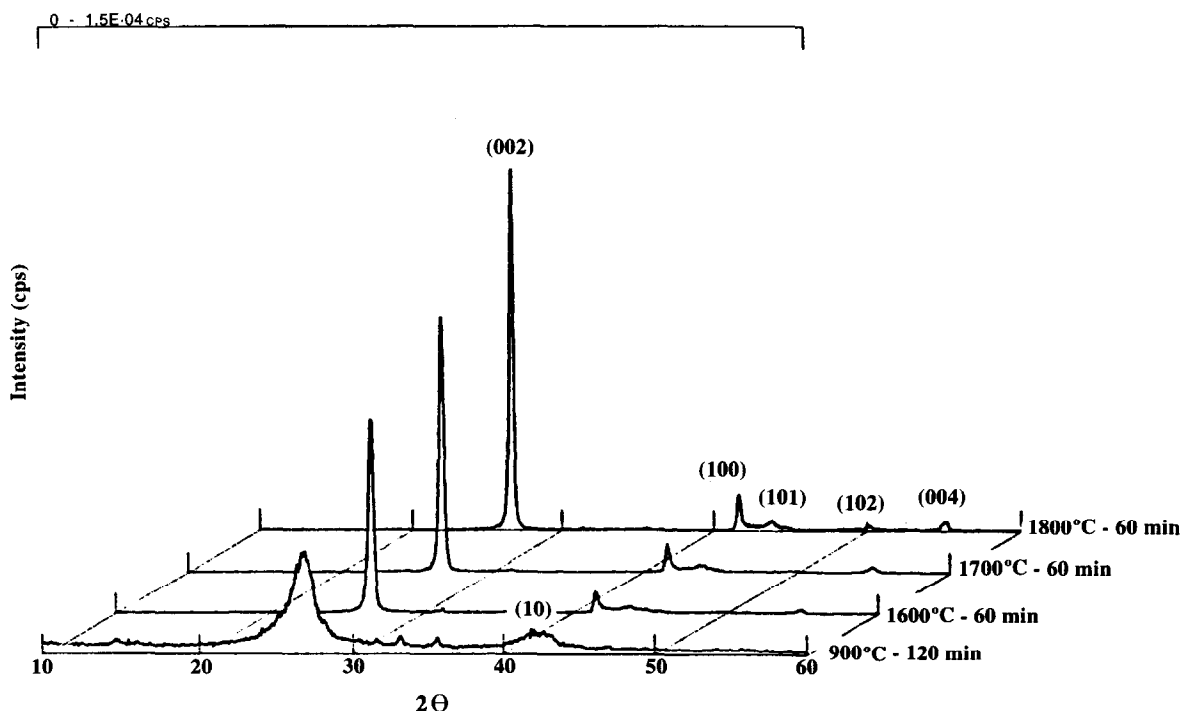


Fig. 5. X-ray diffraction patterns of the samples before crystallization and after heat treatment for 1 h at various temperatures (large batch operation).

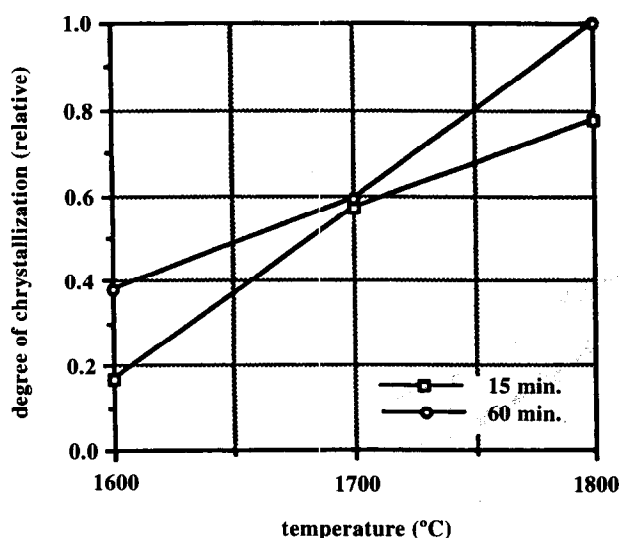


Fig. 6. Degree of turbostratic BN crystallization for heat treatments at 1600–1800°C for 15 and 60 min crystallization periods.

parameters was not found. However, the variation of the d_{002} values was found to be within a narrow range which is especially close to the ideal value for the samples heat-treated at 1700 and 1800°C. These results also support the idea that the crystallization process is nearly completed at the temperatures of 1700–1800°C, and a crystallization period longer than 1 h does not have a very pronounced effect on the ordering of the structure.

3.2 Transmission electron microscope studies

In our previous work¹⁵ on crystallization of turbostratic BN at temperatures below 1500°C, TEM studies indicated that BN particles, obtained with the method utilized in this study, have a round, plate-like shape, where the (002) atomic planes of the hexagonal structure of BN align parallel to the

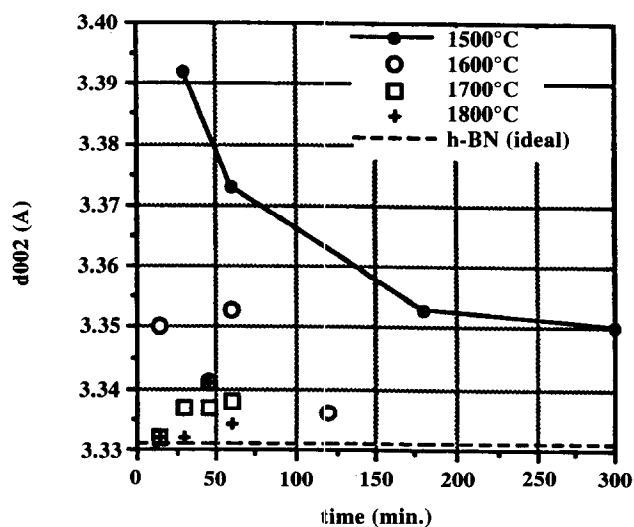


Fig. 7. Variation of the interlayer spacing (d_{002}) values of the BN powders with the crystallization parameters.

particle's major round, flat surface. Similar observations on the particle morphologies and texture of the particles were also reported by Bartnitskaya *et al.*¹⁶ Our previous study¹⁵ found that, while the crystallization parameters do not have a pronounced effect on the thickness of the plate-like particles, they do strongly affect the diameter of the particles, and showed an increase in diameter consistent with the ordering of the structure. The similar round-shaped BN particles are also determined to form above 1500°C and, based on the argument given above, the diameters of these round, face-on particles are considered to be the particle size in this study, as shown in Figs 8 and 9. Although these TEM studies cannot give accurate values of particle size distributions, approximate values of particle size limits can be obtained.

From Fig. 8, for the isothermal heat treatment of the t-BN powders at 1500°C, an increase in the particle sizes of BN powders in the first hour of the crystallization period was observed, whereas heat treatments longer than 1 h were not found to have any pronounced effect on particle size. Mean particle sizes determined from the TEM examinations can be given as follows; < 50 nm for t-BN powders, 50–100 nm for powders heat-treated for 30 min and 50–150 nm for powders having a heat treatment period over 30 min.

Figure 9 shows the TEM micrographs of the powders representing the samples taken from large-scale operations and heat-treated at temperatures over 1500°C. From Fig. 9(a), before crystallization, t-BN powders have a very wide range of particle size distribution, which is different from the powders synthesized in the small-scale operation. This might be due to a precrystallization of some particles during the synthesis operation on the large scale. However, this wide particle size distribution seemed to become more homogeneous and narrow by increasing the temperature of the heat-treatment.

Further TEM examinations revealed that, for high crystallization temperatures, time variations do not have a pronounced effect on particle size and shape of the powders. From TEM examinations, mean particle sizes of the fully crystallized powders can be estimated in the following ranges; ~ 0.2 to 2.0 μm in diameter, and 50 to 150 nm in thickness.

3.3 Surface area measurements

BET analysis was also performed on powder samples in order to find the variation of the specific surface area values by changing heat-treatment parameters. The value for synthesized powder before any heat treatment is 19.94 $\text{m}^2 \text{g}^{-1}$ and, for samples crystallized at 1600–1800°C for various times, the values

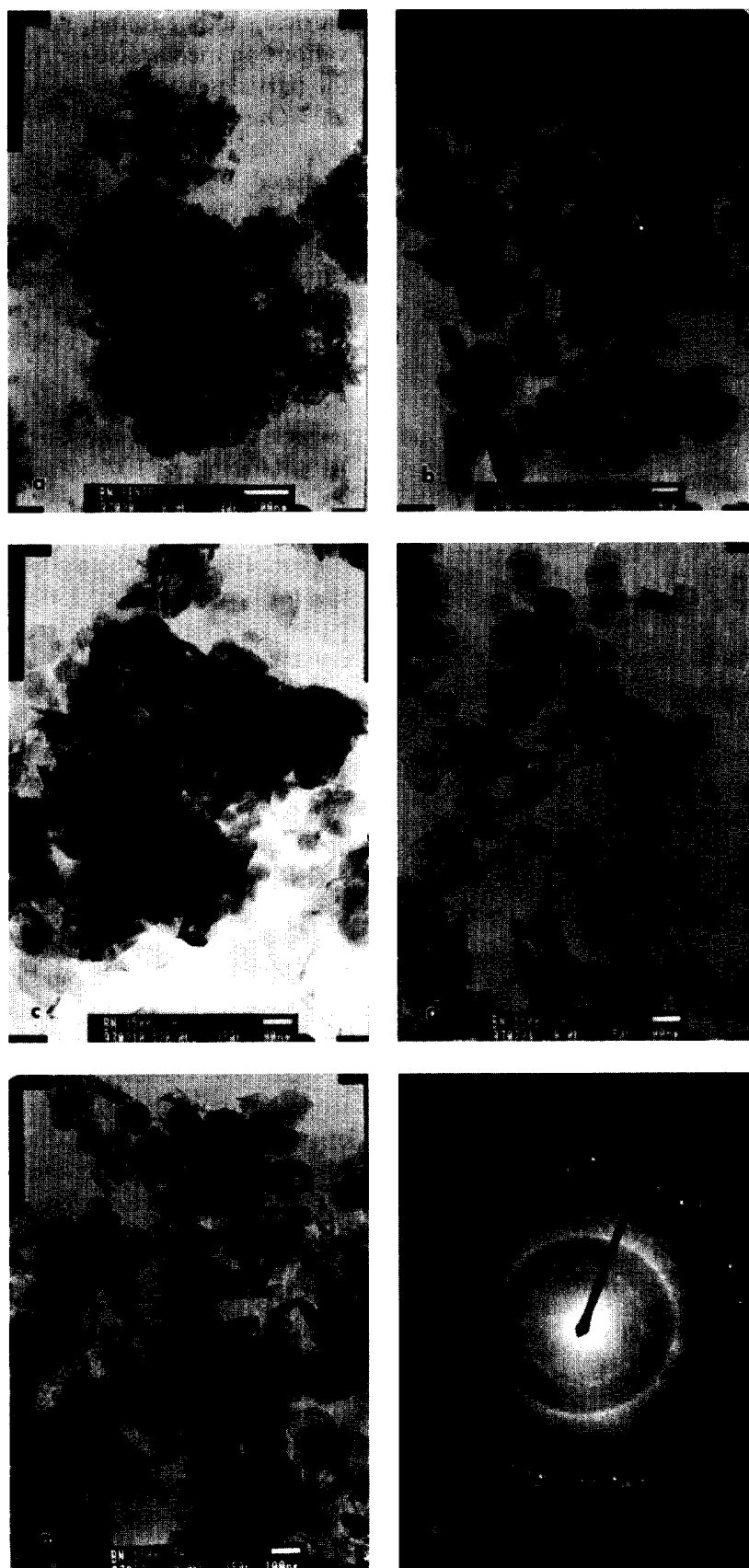


Fig. 8. Transmission electron micrographs of boron nitride powders heat treated at 1500°C for various periods. (a) t-BN (before heat treatment), (b) 1500°C—30 min, (c) 1500°C—60 min, (d) 1500°C—180 min, (e) 1500°C—300 min, (f) electron diffraction of the sample 1500°C—60 min.

are found to vary between 3.10 and $11.71 \text{ m}^2 \text{ g}^{-1}$, but the results do not indicate any relation between specific surface area values and crystallization conditions for these temperatures. However, the

values for the 1500°C experiments indicate a continuous decrease in the specific surface area with the increasing periods of crystallization and they are found to vary from $13.1 \text{ m}^2 \text{ g}^{-1}$ to $5.42 \text{ m}^2 \text{ g}^{-1}$.

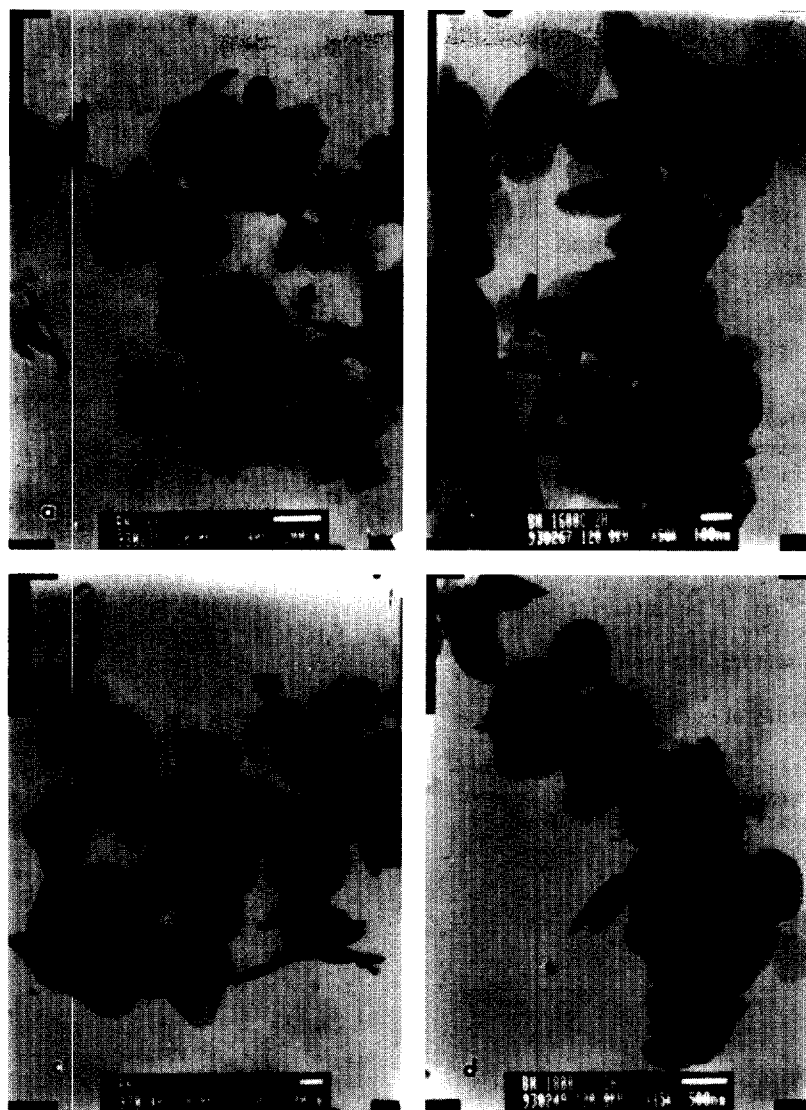


Fig. 9. Transmission electron micrographs of boron nitride powders before crystallization and after heat-treatment under different conditions. (a) t-BN (before heat treatment), (b) 1600°C—120 min, (c) 1700°C—60 min, (d) 1800°C—90 min.

These decreases are thought to be the result of the increasing crystallinity of the powders, which yields a powder product with fewer active surfaces.

4 Conclusion

Studies on the synthesis of hexagonal boron nitride from boric oxide and ammonia gas in the presence of an inert filler material yields a semi-crystalline boron nitride, so-called turbostratic BN, with a layered crystal structure which is basically characterized by the absence of ordering in the third dimension. Under atmospheric conditions for long storing periods, turbostratic boron nitride was determined to decompose into an ammonium borate compound, namely $(\text{NH}_4)_2\text{B}_5\text{O}_8 \cdot 4\text{H}_2\text{O}$. Because of the instability of the t-BN structure, crystallization heat-treatments are required at elevated temperatures.

From the results of the X-ray diffraction analysis of heat-treated samples, it is determined that the

practical heat-treatment has a meaningful effect on degree of crystallization for the first hour, or less, depending on the crystallization temperature. With increasing temperature of crystallization, optimum treatment time for the crystallization process can be as short as 15 min. High order diffraction planes can also be detected for the high temperature crystallization process at 1800°C.

From the transmission electron microscopy examinations, the t-BN powders are determined to have a plate-like, flat, rounded shape. Crystallization parameters are shown to have a considerable effect on the particle size for lower crystallization temperatures, whereas increases in crystallization temperature and time are determined to lead to a narrow particle size distribution. Individual particle sizes are shown to be varied between 50 nm and 2 μm in diameter and 50 and 150 nm in thickness.

BET surface-area measurements indicate an overall decrease in the specific surface of the powders with crystallization which results from the

formation of ideal crystalline structure and increasing particle size.

Acknowledgements

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