The Formation and Crystalline Nature of Boron Nitride in the Reaction of Boron Oxide with Sodium Amide

By Hiroaki TAGAWA and Otokichi ITOUJI

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Boron nitride has extremely interesting chemical properties and physical characteristics. As the structure is very similar to that of graphite, it is sometimes called white graphite. Boron nitride is an excellent refractory material and is used as a thermal insulator in high frequency induction vacuum furnaces, as a material for the manufacture of refractory crucibles, and as an anti-sticking agent in contact with molten glass or metals. It is also an excellent lubricant and is used as a heat-resistant lubricant.

Boron nitride has been known for the more than one hundred years since it was first prepared by Balmain in 1842[1]. Since then it has been investigated by many researchers, and many methods of fabrication have been described in the literature and by patents.

Boron nitride is prepared by the reactions of a compound containing boron with a compound containing nitrogen; it the many processes by which it is produced may be summarized by the following equations:

$4NH_3+BCl_3=BN+3NH_4Cl$[2-4]

$2B+N_2=2BN$[5]

$B_2O_3+2NH_3=2BN+3H_2O$[6-8]

$B_2O_3+3NaNH_2=2BN+NH_3+3NaOH$[9]

$B_2O_3+2NH_4Cl=2BN+2HCl+3H_2O$[10]

As with carbon, the physical and chemical properties of this material may vary considerably according to the nature of the starting materials and of the fabricating condition, but they may be thought of as depending mainly on such structural factors as the crystallinity and the state of the condensed system of the triboron-triazin ring.

In this article, boron oxide and sodium amide were selected as the starting materials in the preparation of boron nitride. Sodium amide is a chemically strong reducing agent; its great reactivity is coupled with the relatively low melting point of 210°C. The boron nitride which was formed in the reaction of boron oxide with sodium amide was investigated for the effect of the producing conditions on its structure and properties. The behavior of the reaction was examined by differential thermal analysis and thermogravimetry, and the crystalline nature of the boron nitride thus formed

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[3] I. E. Compbell et al., *J. Electrochem. Soc.*, **96**, 318 (1948).

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[6] E. Podzus, *Z. angew. Chem.*, **30**, 156 (1917); German Pat. 282701, 282748 (1913).

[7] The British Thomson Houston Co., Ltd., Brit. Pat. 483201 (1938).

[8] K. M. Tayler, U. S. Navy, Bureau of Ordnance Research Contract NOrd 10982 (1945).

[9] J. Kamlet, U. S. Pat. 2865715 (1958).

[10] R. Heyder, *J. Soc. Chem. Ind.*, **32**, 600 (1913).

was investigated by X-ray analysis and infrared absorption measurement.

The Nature of the Reaction of Boron Oxide with Sodium Amide

Experimental.—*Material.*—Boron oxide (Junsei Chemicals Co.) was dehydrated at 1000°C for 1hr., and then pulverized and screened with a 16 to 32 mesh sieve in a dry box. The sodium amide used in this experiment was obtained from the Kongo Chemicals Co.; it was pulverized below a 100 mesh sieve. The purity of this material was 93%; the rest was sodium hyroxide.

Differential Thermal Analysis.—A specimen, mixed to a 1 : 3 (by mol.) ratio of boron oxide to sodium amide was examined by differential thermal analysis with a three-hole nickel holder within an atmosphere of nitrogen. The difference in temperature between the sample and the reference (aluminium oxide) was measured by a thermocouple of chromel-alumel with two pairs in series. The differential thermoelectric motive force was recorded on the chart of electric recorder.

The temperature of the electric furnace was elevated continuously at a constant heating rate of 5°C/min.

Thermogravimetry.—The behavior of the reaction of boron oxide with sodium amide was also examined by using a thermogravimetric apparatus, which allowed a continuous measurement of the weight loss against the time. The apparatus consisted of a torsion type thermobalance (Shimadzu Manufacturing Co.) using a fine tungsten wire and of an electric furnace. The weight changes were measured by the rotation of the wheel, which applied sufficient torsion to the fiber to restore the arm to the null position. Its capacity and sensitivity were 1 g. and 5 mg. respectively. The thermobalance system could be evacuated.

The specimen used in this experiment was a mixture of boron oxide and sodium amide (mixing ratio, 1 : 3 by mol.). The powdered sample was placed in a nickel crucible and was suspended from the arm by a molybdenum wire. The weight changes by dehydration and nitridation were observed during the elevation of the sample temperature at a constant rate of heating of 5°C/min, within an atmosphere in nitrogen.

Results and Discussion.—*Differential Thermal Analysis.* — Differential thermograms of the reaction of boron oxide with sodium amide and of that of only sodium amide are shown in Fig. 1. The reaction of boron oxide with sodium amide in Fig. 1 (a) shows two peaks at 163 and 205°C, while in the reaction of boron oxide with sodium amide, involving 65% of sodium hydroxide, only one peak appears, at 163°C. Although the melting point of sodium amide is 210°C, it may be found in Fig. 1 (c) that the melting point is lowered in the presence of sodium hydroxide to about 165°C. The endothermic peaks at 155 and 201°C correspond with the melting of the sodium amide containing large amounts of sodium hydroxide and pure sodium amide respectively. The reaction peak at 205°C shows that the reaction of boron oxide with sodium amide occurs as soon as the sodium amide melts, which agrees with finding of Kamlet⁹⁾. It may therefore be concluded that this reaction needs the melting of sodium amide and that the reaction temperature is lowered in the presence of sodium hydroxide, as sodium amide appears to make a solid solution with sodium hydroxide. The several peaks at about 300°C in the reaction of boron oxide with sodium amide involving large amounts of sodium hydroxide in Fig. 1 (b), seem to be due to the formation of sodium borates by the reaction of sodium hydroxide with the unreacted boron oxide.

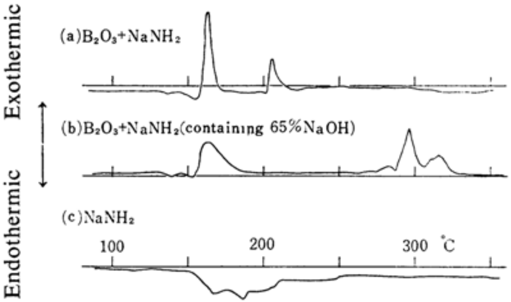

Fig. 1. DTA curves of a mixture of boron oxide and sodium amide (mixing ratio by mol. = 1 : 3).

Thermogravimetry. — The thermogravimetric curve of a mixture of 1.5 g. of boron oxide (16∼32 mesh) and 2.5 g. of sodium amide is shown in Fig. 2. In this curve the weight loss observed is plotted against the temperature

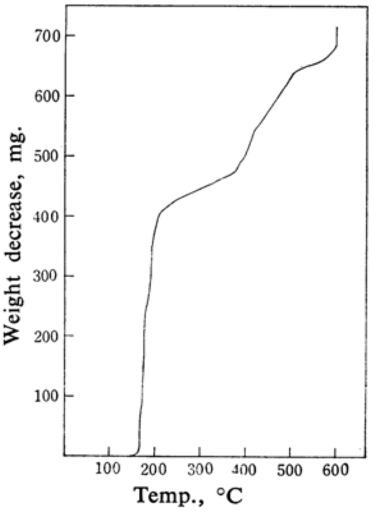

Fig. 2. Thermogravimetric curve of a mixture of boron oxide and sodium amide in hydrogen. B_2O_3; 1.5 g., $NaNH_2$; 2.5 g., heating rate; 5°C/min., retention time at 600°C; 30 min.

up to 600°C. A steep weight loss occurs in the temperature range from 170 to 200°C. The finding of this decrease in weight above 170°C is correspondent with that of the differential thermal analysis. The weight of the sample decreases gradually with the raising of the temperature, even above 200°C. At temperatures above 400°C, some sodium amide was condensed at the cold part of the quartz tube.

The mixing ratio of boron oxide was chosen as 1 : 3 by mole according to the following equation :

$$B_2O_3 + 3NaNH_2 = 2BN + NH_3 + 3NaOH$$

Theoretically, 1.5 g. of boron oxide reacts with 2.5 g. of sodium amide to form 1.1 g. of boron nitride and 0.36 g. of ammonia. The actual weight decrease is two times larger than the calculated quantity of evolved ammonia. Chemical analysis indicates that only 29.9% of the boron oxide changes into boron nitride. Consequently, this large weight loss may be due to the reaction of the sodium hydroxide formed with the amide and to the sublimation of the amide.

Crystalline Nature of the Boron Nitride Formed

Experimental.—*Preparation of Boron Nitride.*— Boron nitride for X-ray analysis and for infrared absorption measurement was produced by heating a mixture of boron oxide and sodium amide (mixing ratio, 1 : 3 by mole) at a desired temperature between 200 and 800°C in an ammonia atmosphere. The apparatus consisted of a quartz tube 50 mm. in inner diameter, a suspended crucible 30 mm. in diameter and 40 mm. in height, and an electric furnace. The tube containing the mixture could be evacuated for the exchange of atmosphere. The sample was suspended in a nickel bucket in the hot zone of the tube with fine tungsten wire from the top of the tube.

Five grams of boron oxide and 13.3 g. of sodium amide were ground together, charged into the nickel crucible, and heated in the electric furnace at temperatures from 200 to 800°C. In order to examine the behavior of the reaction during heating, a thermocouple was put in the mixture. The reaction commenced at about 170°C and proceeded vigorously at about 210°C with the evolution of ammonia. When the furnace temperature stood at 210°C, it was shown that the temperature of the mixture was temporarily brought up to 350°C. The reaction mixture was kept at the desired terminal temperature between 200 and 800°C for more than 30 minutes. The product in the crucible was obtained as a gray porous material. The substance was broken up and vigorously stirred into ice water. The insoluble boron nitride was filtered off, washed free of soluble matter with water, and then dried. The yields of boron nitride based on boron oxide were always about 30 percent in the top temperature range from 200 to 800°C. This boron nitride was analyzed for boron and nitrogen using the method mentioned by Finlay et al.[11]

X-Ray Measurement.—Changes in the interlayer spacing and crystallite growth were observed as a function of the terminal temperature. The diffraction patterns were recorded by an automatic recording X-ray spectrometer (Rigaku Denki Co.) and were calibrated by referring to a standard quartz specimen. The diffraction maximum did not directly give the true interlayer spacing for the polarization and absorption, as in the case of carbon[12], but the measured values were used.

The crystallite size was obtained from the broadening of the X-ray diffraction lines according to the procedure described by Klug and Alexander[13]. The crystallite dimension was calculated according to the following equation :

$$L = K\lambda/\beta\cos\theta$$

where L is the average effective dimension of the crystallite in a direction perpendicular to the reflecting plane at the glancing angle θ, λ is the wave length of the X-ray, K is a shape factor, and β is defined as the half-maximum line breadth. The Lc-dimension, the thickness of the parallel packets of layers, was obtained from the (002) line by using $K=0.9$. The La-dimension could not be obtained because of the obscure shape of the (10) band.

The diffraction conditions employed were as follows ; the target was copper filtered by nickel, the filament voltage and current were 30 kV. and 15 mamp. respectively, the divergent slit was 1°, the receiving slit, 1° and 0.1 mm., the time constant, 4 sec., and the scanning speed, 2°/min.

Infrared Absorption Spectra.—The infrared spectra in the 4000 to 650 cm^{-1} region of boron nitride were obtained by using a Nippon Bunko model DS-301 spectrophotometer (with a potassium bromide prism) and by using potassium bromide pellet techniques.

Results and Discussion.—*X-Ray Analysis.*— The X-ray diffraction patterns of boron nitride formed at several temperatures between 200 and 800°C are shown in Fig. 3. Geometrically, the structure is very similar to that of graphite[14]. The peak at about 26° of the Bragg angle corresponds with the interlayer spacing. A terminal temperature of 800°C for the reaction mixture scarcely affects the yield of boron nitride, but the crystallinity increases with an increase in the top temperature. The X-ray diagrams of the boron nitride formed at 200 to 600°C show diffuse bands corresponding to the positions of the (002) and (100) lines, indicating a two-dimensional structure. In the case of boron nitride produced at 800°C, the deformation of the (10) band is already visible, and the

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[11] G. R. Finlay and G. H. Fetterley, *Ceram. Bull.*, **31**, 141 (1952).

[12] W. R. Ruston, *Fuel*, **31**, 52 (1953).

[13] H. P. Klug and L. E. Alexander, "X-Ray Diffraction Procedures", John Wiley, New York (1954), p. 491.

[14] R. S. Pease, *Acta Cryst.*, **5**, 356 (1952).

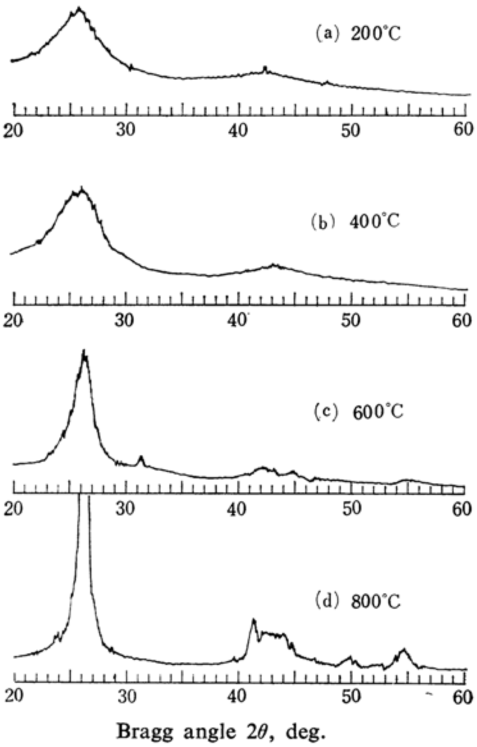

Fig. 3. X-ray patterns of boron nitride of various terminal temperatures.

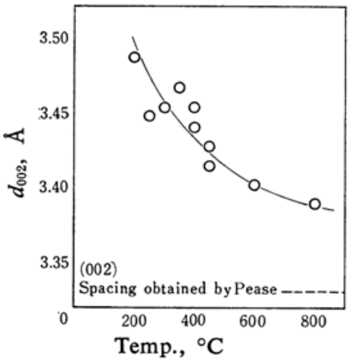

Fig. 4. Relationship between the apparent interlayer spacing and the terminal temperatures.

separation of the (100) and (101) reflexions may be clearly recognized.

By increasing the terminal temperature of the reaction mixture, the diameter of the boron nitride layers and the number of layers per parallel packet is increased, and the (002) spacing decreases. The results of these measurements are shown in Figs. 4 and 5. In the case of carbon, a decrease in the interlayer spacing, which accompanies an increase in the degree of graphitization, has already been shown by Rooksby[15], Bacon[16] and Franklin[17]. The different graphitizing behavior of carbon may be a result of the nature of the original carbonaceous material and of the conditions under which they have been carbonized. On the other hand, the crystallization of boron nitride, like that of carbon, seems to be due to the processes and conditions of various methods of production. The increase of crystallite above 400°C, as shown in Fig. 5, is thought to be accelerated in the presence of molten salts, such as boric anhydride and sodium hydroxide.

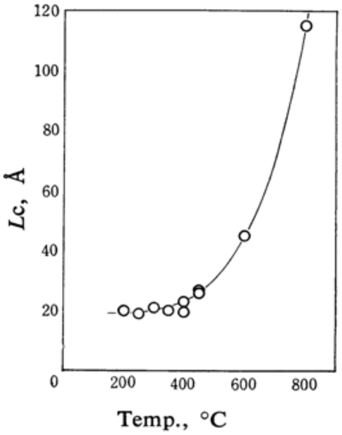

Fig. 5. Relationship between the Lc-dimensions of the parallel layer groups and the terminal temperature.

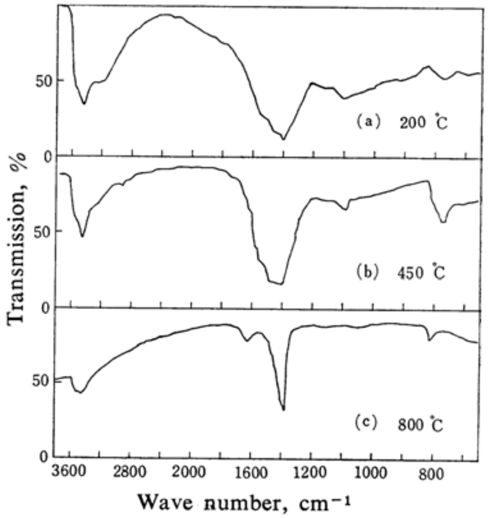

Fig. 6. Infrared absorption spectra of boron nitride of various terminal temperatures.

Infrared Absorption Spectra. — The infrared absorption spectra of boron nitride formed at

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15) H. P. Rooksby, *Elect. Times*, **102**, 19 (1942).
16) G. E. Bacon, *Acta Cryst.*, 3, 137, (1950).
17) R. E. Franklin, ibid., **4**, 153 (1951).

200, 450 and 800°C are shown in Fig. 6. The absorption band at about 1400 cm^{-1} for boron nitride may be assigned as an in-plane B–N ring deformation. The spectrum of boron nitride obtained at 200°C, especially the B–O streching vibration at 1450 cm^{-1}, is different from the infrared absorption spectrum of boron oxide[18]. The absorption spectrum of boron nitride formed at 800°C agrees with the finding of Miller[19] and Brame[20]. The broadness of the absorption band at 1400 cm^{-1} and the O–H stretching band due to boron nitride hydrolyzed become somewhat smaller with an increase in the terminal temperature. The fundamental infrared absorption spectrum of boron nitride is scarcely influenced by the fabrication temperature. Although the melting point of boron nitride is above 3000°C, the skeletal structure of B–N hexagonal layers is complete even in the formation at 200°C, which finding agrees with the results of X-ray diffraction.

Summary

The reaction of boron oxide with sodium amide has been investigated using differential thermal analysis and thermogravimetry. The reaction occurs at 210°C, the melting point of sodium amide, while in the presence of a large amount of sodium hydroxide, the reaction temperature is lowered to 165°C. It has been shown from the results of the differential thermal analysis that the reaction of boron oxide with sodium amide commences as soon as the sodium amide melts.

The boron nitride formed completes the skeletal structure of B–N hexagonal layers even at 200°C. The fundamental infrared absorption spectra of boron nitride is very little influenced by the fabrication temperature. The crystallinity of boron nitride as shown by the interlayer spacing and the crystallite size increases with the reaction temperature.

Research Laboratory
Nippon Carbide Industries Co., Inc.
Uozu, Toyama

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[20] E. G. Brame, *J. Inorg. Nucl. Chem.*, **5**, 48 (1957).