

Carbothermic formation of boron nitride

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Received 10 August 2002; received in revised form 27 January 2003; accepted 8 February 2003

Abstract

Formation of boron nitride by reaction of boric oxide with carbon and nitrogen was studied. It was found from the results of experiments conducted by holding B₂O₃-activated C mixtures under a flowing nitrogen atmosphere that formation of boron nitride was complete in 120 min at 1500 °C. After cleaning the reaction product from the ash of the activated carbon and from the unreacted B₂O₃ pure BN powder was obtained. B₄C was found to exist as an intermediate species in the reaction products of the experiments in which BN formation was not complete. The results of experiments conducted with the objective of gaining an insight into the reaction mechanism by using different geometrical arrangements show that liquid B₂O₃ and solid carbon need not be in contact in the formation of BN from B₂O₃, C and N₂ and indicate that the reaction proceeds through a gaseous boron containing species which is most probably B₂O₃(g).

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Keywords: BN; Carbothermic nitridation; Powder preparation; Reaction mechanisms

1. Introduction

This study is concerned with the production of hexagonal boron nitride. There are a number of different methods used to produce hexagonal boron nitride, which is a white, soft, lubricous, non-toxic refractory compound.^{1–5} One of the oldest production methods is carbothermic reduction of boric oxide in the presence of nitrogen. Few studies exist on the mechanism of formation of boron nitride by carbothermic reduction of boric oxide,^{6–8} however. This study has been undertaken with the objective of studying the mechanism of formation of boron nitride by carbon reduction of boric oxide in presence of nitrogen gas.

2. Experimental

Formation of boron nitride was studied by subjecting pellets prepared from boric oxide–carbon mixtures to nitrogen gas in a horizontal tube furnace having a 49

mm inside diameter, 58 mm outside diameter and 800 mm long alumina tube placed inside a 600 mm long, 60 mm inside diameter and 75 mm outside diameter spiral silicon carbide heating element. The Al₂O₃ tube was closed at both ends by water-cooled brass heads having gas inlet and outlet tubes, thermocouple insertion and observation tubes. The boric oxide–carbon pellet was contained in a 40-mm deep graphite crucible having an inside diameter of 23 mm and an outside diameter of 32 mm placed in the hot zone of the furnace. The interior of the graphite crucible was lined by a boron nitride layer having a thickness of approximately 0.5-mm to avoid contact of the pellet with the graphite crucible. Temperature of the hot zone of the furnace was kept constant at ±1 °C by an electronic temperature controller activated by a Pt–Pt13%Rh thermocouple in an Al₂O₃ protection tube inserted into the furnace from the gas inlet end of the furnace tube with the tip of the protection tube in touch with the graphite crucible. The gas outlet was on the other end of the Al₂O₃ furnace tube from where the graphite crucible containing the boric oxide–carbon pellet was introduced into the furnace at the start of the experiment and removed at the end. Additional details are presented elsewhere.⁹ Calcined extra-pure boric acid and pure activated charcoal, both supplied by Merck Company, were used in the

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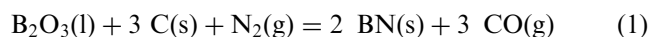
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preparation of the boric oxide–carbon pellets. Boric acid was calcined in a graphite crucible at 900 °C in a pot furnace for 30 mins. The product of calcination was molten boric oxide, which was taken from the system by immersing a cold iron rod and quickly removing it out when a layer of solid boric oxide formed around the iron rod. B₂O₃ was then ground in an agate mortar. It was established from weight gain determinations when the product of calcination was subjected to water that it was completely boric oxide. The ash content of the activated charcoal was determined as 4.14% after complete burning by keeping it at 600 °C for 40 h. Ar of 99.998% purity and N₂ of 99.999% purity were used in the experiments with no additional gas cleaning.

In a given run appropriate weights of boric oxide and activated charcoal were mixed in an agate mortar and a cylindrical pellet was prepared by pressing this mixture in a die with a pressure of 58.9 MPa. The pellet contained in the boron nitride coated graphite crucible was then placed into the cold end of the heated furnace while nitrogen was flowing through the system at a rate of 200 ml/min. After 10 min of waiting period the graphite crucible with its contents was slowly pushed into the hot zone of the furnace by an iron rod and nitrogen gas flow rate was decreased to 20 ml/min. Time was taken as zero at the point when the system reached steady state at the desired temperature. After keeping the graphite crucible with its contents in the hot zone of the furnace under 20 ml/min nitrogen flow for a pre-determined time, it was quickly pulled to the cold end of the furnace and removed from the furnace. The reaction product removed from the graphite crucible was weighed and subjected to X-ray diffraction, microscopic examination and chemical analysis studies. Experiments were conducted at 1100, 1200, 1300, 1400, and 1500 °C for 2 h and also at 1500 °C for 15, 30, 60, 90, 180, and 240 min.

Formation of BN from boric oxide, carbon, and nitrogen proceeds according to the overall reaction:



and is accompanied by weight loss. The weight loss encountered in the preliminary experiments made with pellets prepared by stoichiometric amounts of B₂O₃ and carbon was more than that stoichiometrically expected. Appreciable quantities of B₂O₃ was observed in these experiments to be lost from the reaction mix due to evaporation and some carbon was observed to be carried away from the system by the furnace gases; solid B₂O₃ and carbon were observed to have been deposited on the furnace tube, on the brass head on the gas outlet end, and also in the tubing used for gas outlet.

Evaporation of B₂O₃ was studied by keeping and determining the weight loss of B₂O₃ contained in a boron nitride coated graphite crucible in the hot zone of the tube furnace described above at 1500 °C under 20

ml/min argon flow for 15, 30, 60, and 120 min. The weight loss of B₂O₃ was found to vary almost linearly with time after 15 min and to be 23% in 120 min. Due to evaporation loss, excess B₂O₃ was decided to be used, and, in the experiments reported, 0.0287 mole B₂O₃ and 0.0574 mole activated charcoal were used in the preparation of the B₂O₃–C pellets. The weight of B₂O₃ was thus 50% in excess of the amount calculated in accord with the stoichiometry of reaction (1); carbon loss from the system mentioned above and ash content of the activated carbon was not taken into consideration in this calculation.

3. Results

B₂O₃ + C pellets subjected to N₂(g) were observed to have retained their original pellet forms at the end of the experiments- although their dimensions have changed and some swelling has taken place- and could therefore be easily taken out from the graphite crucibles. The B₂O₃ + C pellets were found to have lost weight when subjected to N₂(g) and their colours were observed to progressively turn into white from the original black colour which were indications of formation of BN. Weight lost by B₂O₃ + C pellets, expressed as the percentage of the original pellet weight, are given in Table 1 as a function of time and temperature. Experiments in which weight loss was significant were repeated to check reproducibility; each number appearing in Table 1 for a given temperature–time combination is the weight loss result of a separate experiment. Reproducibility is seen to be excellent considering loss of B₂O₃ due to evaporation and carbon loss mentioned above.

X-ray diffraction patterns and microscopic examinations revealed presence of BN in all of the reaction products. H₃BO₃ (which forms by reaction of unreacted B₂O₃ with moisture in air during specimen preparation) peaks were also present on the X-ray diffraction patterns of all of the reaction products in accord with expectation due to excess amount of B₂O₃ used. No other species could be detected in the reaction products of the experiments conducted at 1500 °C for 2, 3 and 4 h by X-ray and microscopic studies. Unreacted charcoal was observed to be present in microscopic examination

Table 1
Percentage loss in weight of B₂O₃ + C pellets kept under N₂(g) as a function of time and temperature

Temperature (°C) → Time (min) ↓	1100	1200	1300	1400	1500
15					36.0
30					55.0, 54.4, 53.9
60					70.7, 69.7, 69.4
90					74.7, 73.0, 73.8
120	8.1	11.6	35.0, 33.5	66.7, 65.3	74.5, 74.1, 73.9, 74.8
180					74.0, 73.3, 74.9
240					75.1, 73.9

of the products of the experiments conducted at 1100, 1200, 1300 and 1400 °C for 2 h and at 1500 °C for 30, 60 and 90 min. B_4C peaks were seen on the X-ray diffraction patterns of the products of the experiments conducted at 1400 °C for 2 h and at 1500 °C for 30 and 60 min. These results indicate that carbon in the $B_2O_3 + C$ mixtures subjected to nitrogen gas at 1 atmosphere pressure at 1500 °C is completely used and the reaction product consists of BN, unreacted B_2O_3 and ash of the reacted activated charcoal at the end of 2 h and that BN formation is not complete at 1500 °C in shorter times and also in 2 h at lower temperatures.

After trial of different solutions the ash of the activated charcoal was found to completely dissolve in 1:1 HCl solution. Removal of water-soluble B_2O_3 and ash of the activated charcoal from the reaction product should therefore be possible by HCl leaching. As expected, HCl leaching of the reaction product of the experiment conducted at 1500 °C for 2 h completely removed the unreacted B_2O_3 and ash of the activated charcoal leaving behind pure BN as can be seen from the X-Ray diffraction patterns shown in Fig. 1. No additional check was done on the purity of BN. HCl leaching additionally resulted the reaction product in pellet form to disintegrate and transform into powder form. Specific surface areas of the products obtained at the end of the experiments conducted at 1500 °C for 2 and 4 h and later leached with 1:1 HCl solution were determined as 14.13 and 12.25 m^2/g , respectively, by the 3 point BET method using nitrogen gas as the adsorbate. The results indicate that the particle size of BN increases with time.

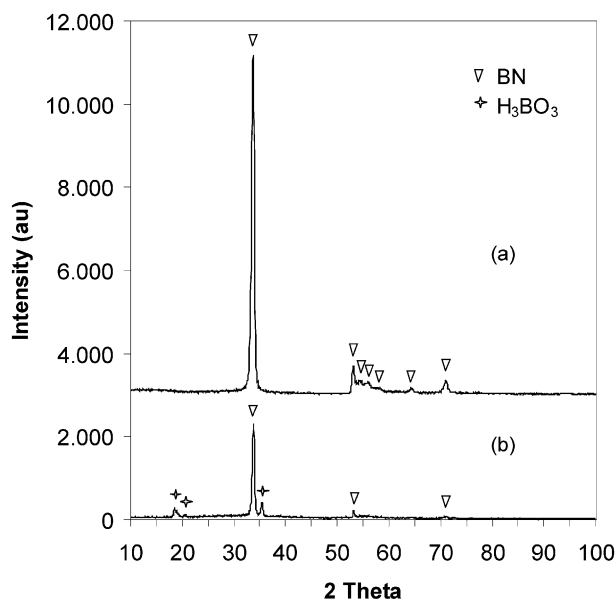


Fig. 1. X-ray diffraction pattern of the product of the experiment conducted at 1500 °C for 2 h (b) and after leaching with 1:1 HCl solution (a).

The products of the experiments in which BN formation is not complete are expected to be composed of boron nitride, boron carbide, unreacted boron oxide, unreacted charcoal and ash of the reacted charcoal. Charcoal can be burned and accordingly removed from the reaction product by subjecting the reaction product to an oxidizing atmosphere at a suitable temperature but BN and B_4C could also get oxidized. Pure BN and pure B_4C samples contained in alumina boats were held in a muffle furnace at 600 and 800 °C; weight change in the BN sample was negligibly small for both temperatures but a significant weight gain (60%) was detected in the B_4C sample at the end of 1 h at 800 °C. It was found that the product of oxidation of B_4C could be leached with water and that the weight gain during oxidation and the weight loss during leaching were stoichiometrically equivalent for B_4C getting oxidized to B_2O_3 . From these experiments it was concluded that BN does not get oxidized in air at 800 °C but B_4C gets oxidized to B_2O_3 . With this conclusion samples cut from the products of the BN formation experiments were subjected to the sequence of events schematically in Fig. 2. In the first step the sample was leached with 1:1 HCl solution which removed the ash of the reacted activated charcoal and the B_2O_3 contained in the sample. In the second step the product obtained at the end of leaching was oxidized in a muffle furnace at 800 °C to burn the activated charcoal and oxidize B_4C to B_2O_3 . The product of the oxidation step was observed under an optical microscope and oxidation was continued until no black particle (C or B_4C) could be observed under the microscope. In the third step the ash of the activated charcoal and B_2O_3 formed from the oxidation of B_4C were removed by leaching with 1:1 HCl at the end of which pure BN was obtained. W_1 in Fig. 2 is the weight of the sample cut from the reaction product and was determined immediately after removal of the reaction product from the furnace before any B_2O_3 gets converted into H_3BO_3 by reaction with moisture in air. W_2 and W_4 are the dry weights of the residues separated from the leach solutions by filtration after the first and the second leaching steps, respectively. W_3 is the weight of the product of the oxidation step and was determined immediately after removal of the product from the oxidation furnace before any conversion of B_2O_3 into H_3BO_3 . Ash in the reaction product originates from carbon that has reacted which was assumed to be the stoichiometric quantity necessary for formation of BN and B_4C . With simple mass balance considerations the formulae given in Fig. 2 were derived from which the weight percentages of the constituents of the products of the BN formation experiments given in Table 2 could be calculated. No B_4C was found to exist in the reaction products of the experiments conducted at 1100 and 1200 °C for 2 h and those conducted at 1500 °C for 2 and 4 h. Great care was exercised in determining

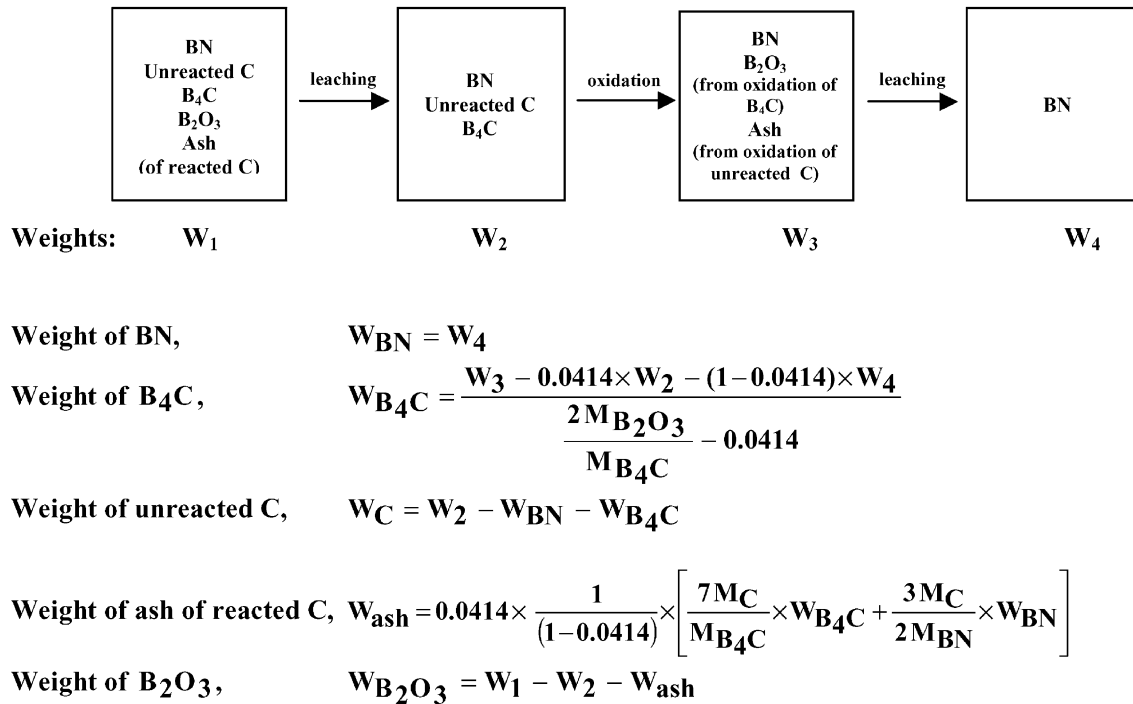


Fig. 2. Schematic representation of the leaching-oxidation-leaching method and mass balance equations for determination of the quantities of the constituents of the reaction products.

Table 2
Weight percentages of the constituents of the reaction products

Temperature (°C)	Time (min)	BN (%)	B ₄ C (%)	Charcoal (%)	B ₂ O ₃ (%)	Ash (%)
1100	120	2.22	–	19.75	77.96	0.07
1200	120	2.62	–	21.94	75.35	0.09
1300	120	13.15	0.86	20.24	65.29	0.46
1400	120	45.27	8.03	3.62	41.13	1.94
1500	15	7.49	5.79	19.70	66.41	0.61
1500	30	21.10	13.92	12.11	51.29	1.58
1500	60	63.79	8.79	1.57	23.28	2.56
1500	90	85.95	2.55	3.06	5.58	2.86
1500	120	92.31	–	–	4.80	2.89
1500	240	90.19	–	–	6.99	2.82

weights of samples at the end of each step but considering that there are successive filtration and drying steps in addition to the leaching and oxidation steps in the method and that sample sizes are small, very small errors in weight determinations could give rise to magnified errors in the relative proportions of the different constituents of the reaction products. In view of this fact, then, weight percentages of the different constituents in the reaction products determined by the method should be considered to be approximate.

Weight percentages of the constituents of the reaction products given in Table 2 are shown graphically as a function of temperature and as a function of time, respectively, in Figs. 3 and 4. It is seen from Table 2 and

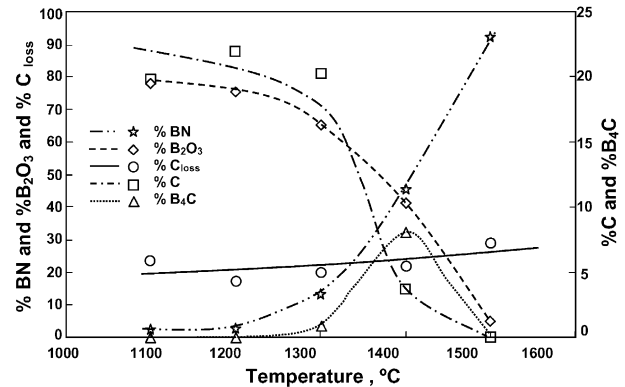


Fig. 3. Variation of weight percentages of the constituents of the products and carbon loss from the system in the experiments conducted for 2 h with temperature.

Fig. 3 that the quantity of BN in the reaction products of the experiments conducted for 2 h increases whereas the quantity of B₂O₃ decreases with increasing temperature; unused charcoal in the reaction products is seen not to vary significantly up to 1300 °C but to decrease drastically at higher temperatures. These results indicate that the quantity of B₂O₃ and charcoal reacting and of BN forming in 2 h increase with increasing temperature. Table 2 and Fig. 3 indicate that the quantity of B₄C in the reaction products of the experiments conducted for 2 h increases with increasing temperature at temperatures above 1200 up to 1400 °C and then decreases reaching zero at 1500 °C.

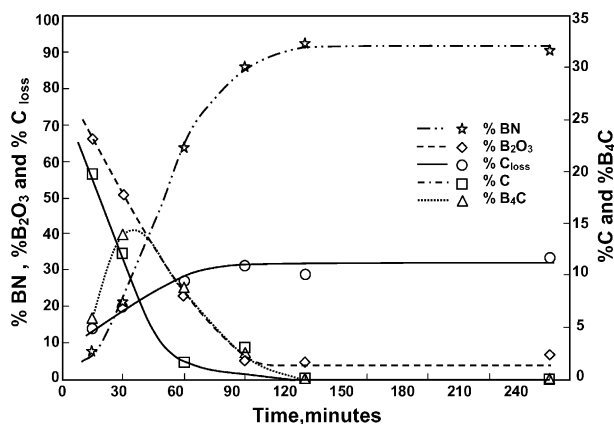


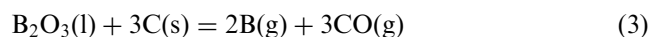
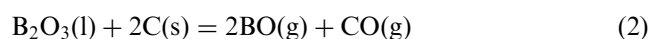
Fig. 4. Variation of weight percentages of the constituents of the products and carbon loss from the system in the experiments conducted at 1500 °C with time.

It is seen from Table 2 and Fig. 4 that the quantity of BN in the reaction products of the experiments conducted at 1500 °C increases with time up to 120 min beyond which it is almost constant. The quantities of B₂O₃ and unused charcoal in the reaction products of the experiments conducted at 1500 °C decrease with increasing reaction time with carbon reaching zero at the end of 2 h. Table 2 and Fig. 4 indicate that quantities of B₄C in the reaction products of experiments conducted at 1500 °C increases with time up to 30 min and then decreases reaching zero at the end of 2 h.

BN production experiments were conducted with pellets prepared from a mixture of 2 g B₂O₃ and 0.69 g activated charcoal, which should stoichiometrically yield 0.9117 g of BN if activated charcoal is considered to be completely used. Weights of BN in the reaction products of all of the experiments were less than 0.9117 g with highest BN weight (0.6485 g) obtained in the experiment conducted at 1500 °C for 2 h. The fact that there is no unused carbon left in this reaction product and that the weight of BN produced is less than the stoichiometrically calculated amount indicates that some carbon is lost during the experiment. Carbon loss, defined as the difference between the weight of carbon used in the preparation of the (B₂O₃+C) pellet and the sum of the weight of carbon in the reaction product and the weight of carbon necessary for formation of BN of weight W_{BN} and B₄C of weight W_{B_4C} , calculated using the results presented in Table 2 and expressed as percentage of the charcoal weight used in the preparation of (B₂O₃+C) pellets is also shown graphically in Figs. 3 and 4 as functions of temperature and time, respectively. Fig. 3 indicates that carbon loss from the system in 2 h increases with increasing temperature and Fig. 4 indicates that carbon loss at 1500 °C increases with time up to 90 min beyond which it is constant.

It was mentioned above that some carbon was observed to have been carried away from the pellet with

the furnace gases. This physical carbon loss from the system was observed to take place during and just after the placement of the (B₂O₃+C) pellet contained in the graphite crucible in the hot zone of the furnace. Accordingly, it takes place during the period when the (B₂O₃+C) pellet gets heated and probably during the melting of B₂O₃. Carbon loss originating from this source is expected not to vary significantly from one experiment to the other. The fact that carbon loss increases with temperature and with time as shown in Figs. 3 and 4 may be taken as indications that carbon loss from the system is not entirely due to the amount carried away from the pellet with the furnace gases (physical loss) but may also be due to some C consuming reactions (chemical loss) like:



4. Reaction mechanism

The overall reaction in the formation of BN from B₂O₃, C, and N₂, given by Eq. (1) involves four phases and as such cannot represent its mechanism. Therefore, reaction (1) is expected to proceed through gaseous intermediates. To gain a better insight into the mechanism of the BN formation reaction, some experiments using different geometrical arrangements were conducted.

In the first of these experiments, a graphite pellet was placed onto B₂O₃ contained in a graphite crucible the interior surface of which was coated with BN. The graphite crucible with its contents was kept at 1500 °C under flowing N₂(g) for 2 h and then removed out from the furnace. The graphite pellet at the end of the experiment was observed to have leaned on one side and touched the wall of the graphite crucible as schematically shown in Fig. 5. BN was observed to have formed on the lower regions of the surface of the carbon pellet as shown by the hatched area in Fig. 5. The carbon pellet was cut longitudinally into two pieces. Microscopic examination of area indicated as 1 in Fig. 5 showed that white colored BN had formed on the surface of the pellet but there was no BN in the interior regions. Deep cracks were observed to have formed at the bottom of the carbon pellet and there was no BN formed on the surface of the carbon pellet in contact with liquid B₂O₃, except within the cracks. This result may be taken as an indication that B₂O₃ and carbon need not be in contact for the formation of BN from B₂O₃ and carbon under N₂ atmosphere and that BN formation reaction proceeds through gaseous intermediate species as suggested above. Formation of BN within the cracks on the bottom face of the carbon pellet in contact with

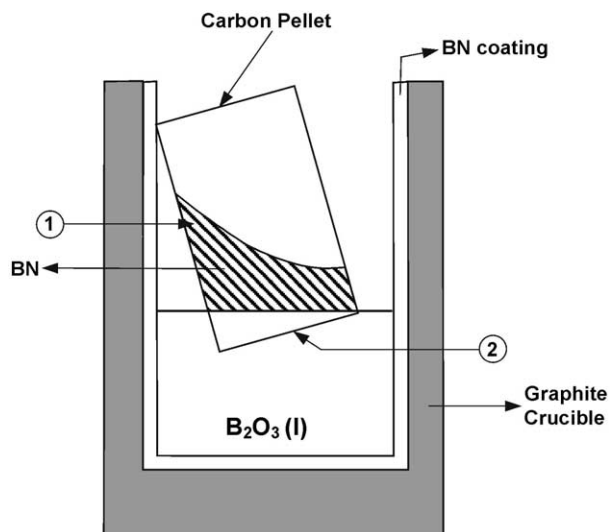
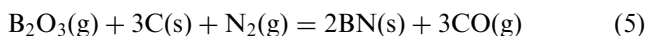


Fig. 5. Schematic representation of the position of the carbon pellet placed on $B_2O_3(l)$ contained in a graphite crucible at the end of the experiment.

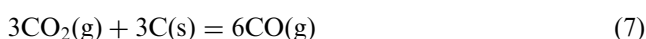
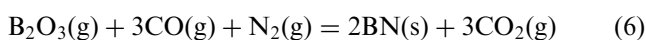
liquid B_2O_3 could be that liquid B_2O_3 has not completely penetrated into the crack. To check whether BN would form in a system when liquid B_2O_3 and solid carbon are not in contact, an experiment was made in which B_2O_3 was contained in a graphite crucible the interior of which was coated with BN and a carbon pellet was contained in an adjacent separate graphite crucible. After keeping this system under flowing $N_2(g)$ at $1500\text{ }^\circ\text{C}$ for 2 h the graphite crucibles were removed from the furnace and cooled. BN was seen to have formed on the top face and the upper lateral surface of the carbon pellet; there was some BN formed also on the wall of the graphite crucible in which the carbon pellet was contained and some on the bare (not coated with BN) upper face of the wall of the graphite crucible in which B_2O_3 was contained. These results indicate that B_2O_3 and carbon need not be in contact for the formation of BN from B_2O_3 and carbon under N_2 atmosphere and that the reaction proceeds through a gaseous intermediate boron containing species which may be $B_2O_3(g)$ or $BO(g)$ or even $B(g)$. Considering the boron containing gaseous species to be $B_2O_3(g)$, BN formation reaction is expected to be:



followed by



Analogous to carbon reduction of oxides to take place through $CO(g)$ and $CO_2(g)$, reaction (5) may be considered to proceed by the following successive reactions:



To check whether BN formation would be possible in a system where there is no C by the successive reactions (4) and (6), an experiment was conducted in which B_2O_3 contained in a graphite crucible coated with BN was contacted with a gas containing 20%CO and 80% N_2 at $1500\text{ }^\circ\text{C}$. There was seen no BN formed except on the upper face of the wall of the graphite crucible which was not coated with BN. This result indicates that C is necessary in the formation of BN.

In view of the above-mentioned results, it is expected that BN forms by the reaction of $B_2O_3(g)$ and $N_2(g)$ with solid carbon and it forms on carbon. To gain a better insight into the reaction mechanism, the products of the experiments in which BN formation was not complete were examined microscopically. Figs. 6 and 7, respectively, show an optical micrograph and a scanning electron microscope micrograph of the product of the experiment conducted at $1500\text{ }^\circ\text{C}$ for 1 h. There are

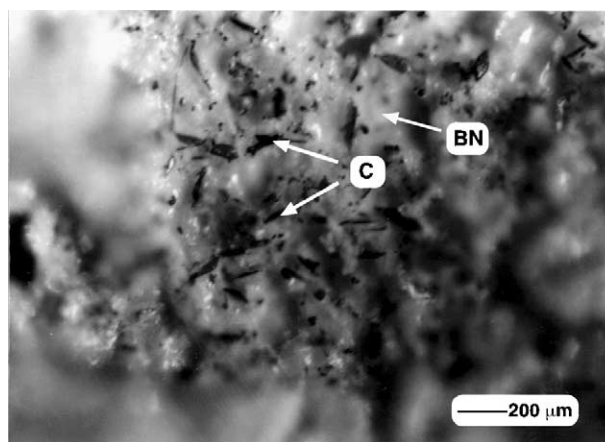


Fig. 6. Optical micrograph of the product of the experiment conducted at $1500\text{ }^\circ\text{C}$ for 1 h.

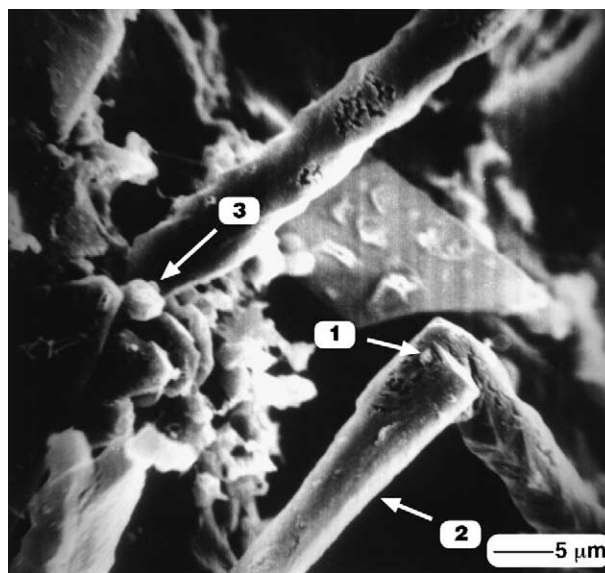


Fig. 7. SEM micrograph of the product of the experiment conducted at $1500\text{ }^\circ\text{C}$ for 1 h.

black-colored rod-like particles and a white-colored phase predicted to be BN in Fig. 6. The activated charcoal used was found to be composed of rod-like particles and equiaxed particles by microscopic examination. The rod-like particles seen in Fig. 6 are probably as yet unreacted carbon particles. The product is seen to be composed of rod-like particles and equiaxed particles from the scanning electron microscope micrograph given in Fig. 7. The rod-like particles in Fig. 7 are probably as yet unreacted carbon particles again. The large equiaxed particles predicted to be BN in optical microscope studies are also apparent in the SEM micrograph. Additionally, small spherical particles, which are not resolvable under optical microscope, are seen from SEM micrograph to be present on the rods. Energy dispersive analysis by X-ray (EDAX) energy profiles obtained from spot analysis of small and large particles on the rod, indicated as points 1 and 3, respectively, in Fig. 7 were found to exhibit only boron and nitrogen peaks; these particles were concluded to be BN. EDAX energy profile obtained from spot analysis of a point on the rod itself, indicated as point 2 in Fig. 7, was found to exhibit C and O peaks; presence of a B peak was not clear in view of the fact that heights of the peaks of the light elements do not directly correspond to relative amounts of these elements. These results suggest that the rod like particles are as yet unreacted carbon particles on which BN particles, unreacted B_2O_3 , and perhaps also B_4C exist. The results of the microscopic examinations, accordingly, also indicate that C is necessary for formation of BN and that BN forms on carbon.

Formation of BN from $B_2O_3 + C$ mixtures subjected to $N_2(g)$ was considered to take place by successive reactions involving gaseous B_2O_3 as an intermediate species. Formation of gaseous BO and B is possible in the system due to reaction of B_2O_3 and C as was mentioned above. Accordingly, BN formation in the system may take place through these intermediate gaseous species also. Consequently, although it is clear that formation of BN proceeds through gaseous intermediates in accord with what is presented above, it is not clear whether the boron containing gaseous species is B_2O_3 or BO or B. Bartnitskaya et al⁸ concluded that B_2O_3 first gets reduced to B by carbon and then B reacts with $N_2(g)$ to form BN in production of BN by carbothermic reduction of B_2O_3 with simultaneous nitridation; state of aggregation of B is not explicitly stated in their study. To get some idea as to how important B(g) is in the formation of BN, an experiment was made in which a B(s) pellet prepared by pressing fine boron powder supplied by HCST firm contained in a graphite crucible coated with BN was subjected to $N_2(g)$ at 1500 °C for 2 h. After removal of the graphite crucible from the furnace, BN was observed to have formed on the surface of the boron pellet but there was no BN formed on the

graphite crucible. It appears, therefore, that BN forms in this system by the



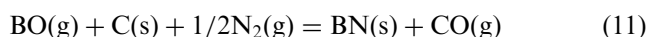
reaction taking place on the surface of the boron pellet and gaseous B originating from evaporation of B(s),



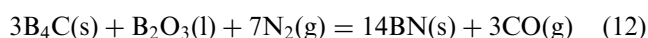
does not have a significant contribution to the formation of BN by the



reaction when solid boron is contacted with $N_2(g)$. This is not an unexpected result as the equilibrium vapor pressure of B(s), calculated from the standard Gibbs Free Energy change for reaction (9), $\Delta G_{(9)}^\circ = 570,150 - 147.82 T$ joules,¹⁰ is very low; 8.38×10^{-10} atm at 1500 °C and much lower at lower temperatures. Yoon and JHA⁶ have considered BN formation to proceed through the gaseous species BO in carbothermic reduction of B_2O_3 in presence of $N_2(g)$ and have concluded BO(g) formation by the overall reaction (2) and BN formation by the reaction



to take place successively. It is not possible to know the composition of the gas in the reaction system with the experimental arrangement used but simple thermodynamic calculations can be made. The experimental reaction system (neglecting the ash of the activated charcoal) is a four-component ($C=4$) system on which two restrictions, ($\delta=2$), T (= experimental temperature) and total pressure, P_{total} (= 1 atm) are imposed. Under these conditions the maximum number of phases that can exist in the system is 4 ($P=4$) when the degrees of freedom, F , of the system is 0 in accord with the phase rule, $F + P = C + 2 - \delta$. In presence of a gas phase, $B_2O_3(l)$ and C(s), then, one additional condensed phase can exist in the system at equilibrium. This analysis indicates that either BN(s) or $B_4C(s)$ but not both can exist in the system at equilibrium. Thermodynamic analysis based on the



reaction indicates that $B_4C(s)$ is unstable in the system

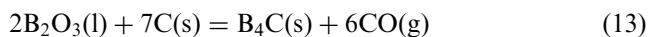
at a given temperature when the $\frac{P_{CO}^3}{P_{N_2}^7}$ ratio is less than a critical value. The $\frac{P_{CO}^3}{P_{N_2}^7}$ ratio in the experimental system

where there is a continuous flow of $N_2(g)$ is expected to be smaller than the critical ratio at any temperature when $B_4C(s)$ is expected not to be present in the system at equilibrium; the experimental findings related to $B_4C(s)$ presented above are in accord with this expectation. Under these conditions the equilibrium system will be composed of $B_2O_3(l)$, C(s), BN(s) and a gas phase

consisting of B_2O_3 , BO , B , CO and N_2 (CO_2 was neglected due to presence of $C(s)$ and temperature being high) in which the number of independent reactions is 4. Using reactions (2), (3), (4) and (10) as the independent reactions, the equilibrium partial pressures in atmospheres of the gaseous species at 1500 °C were calculated as: $P_{CO} = 0.8681$, $P_{B_2O_3} = 0.1317$, $P_{BO} = 1.23 \times 10^{-4}$, $P_B = 1.5 \times 10^{-10}$, $P_{N_2} = 7.64 \times 10^{-5}$ by simultaneous solution of the equations, $K_{(2)} = P_{BO}^2 \cdot P_{CO}$, $K_{(3)} = P_B^2 \cdot P_{CO}^3$, $K_{(4)} = P_{B_2O_3}$, $K_{(10)} = \frac{1}{P_B \cdot P_{N_2}^{1/2}}$ and $P_{CO} + P_{B_2O_3} + P_{BO} + P_B + P_{N_2} = 1$. The equilibrium constants appearing in these equations, K values, other than $K_{(4)}$ have been calculated from the standard Gibbs Free Energy change, ΔG° , values in joules for these reactions, $\Delta G_{(2)}^\circ = 1,106,840 - 473.42 T$, $\Delta G_{(3)}^\circ = 2,025,980 - 763 T$, $\Delta G_{(10)}^\circ = -820,780 + 235.43 T$, calculated from the data compiled by Turkdogan,¹⁰ $\Delta G_{(4)}^\circ = 359,995 - 186.2 T$ joules was taken from Yoon and JHA.⁶ The equilibrium nitrogen pressure in the system is seen to be very low which indicates that the efficiency of use of $N_2(g)$ is close to 100% in formation of $BN(s)$ by reaction (1) under equilibrium conditions. At the 20 ml/min flow rate used in the experiments in this study the quantity of $N_2(g)$ passed through the system in the experiment conducted at 1500 °C for 2 h is 0.0982 mol of N_2 . The quantity of N in the 0.6485 g of $BN(s)$ formed in this experiment is 0.0261 mol of N from which the overall percentage of $N_2(g)$ converted into $BN(s)$ is calculated as 13.3%. This is a reasonably high efficiency and is in accord with the simple equilibrium calculations presented above. Efficiency of use of $N_2(g)$ will be much higher than the overall efficiency of 13.3% during the initial periods of the experiment when the rate of formation of $BN(s)$ is higher. Yoon and JHA⁶ suggested CO pressure to be low in the system and based on this they considered $BO(g)$ pressure not to be very low. As 3 mol of $CO(g)$ are formed in reaction (1) when 1 mol of $N_2(g)$ reacts and as efficiency of use of $N_2(g)$ is high, the CO pressure in the system is not expected to be low, however; the equilibrium calculations presented above are in accord with this expectation. Equilibrium pressure of $B(g)$ at 1500 °C is seen to be very low and lower than the equilibrium vapor pressure of $B(s)$ from which it may be concluded that solid boron is not stable in the system and that gaseous B does not have a significant contribution to formation of BN . Equilibrium vapor pressure of $BO(g)$ is seen to be about 3 orders of magnitude lower than that of $B_2O_3(g)$. Some $BO(g)$ is expected to form in the system by the overall reaction (2) in view of the carbon loss from the system mentioned above. All of the $BO(g)$ forming is not expected to form $BN(s)$ by reaction (11), however, in which case there should be no chemical carbon loss from the system. The calculations and the related considerations presented above

suggest that the important boron containing intermediate gaseous species in the formation of $BN(s)$ in the system is $B_2O_3(g)$.

The result that $B_4C(s)$ is present in the reaction products of the experiments in which BN formation is not complete directs one to consider the possibility of B_4C being an intermediate species in the formation of BN from $B_2O_3 + C$ mixtures subjected to $N_2(g)$ in which case $BN(s)$ formation will be expected to proceed according to the overall reaction



followed by the overall reaction (12). Both of reactions (13) and (12) are also expected to proceed through the intermediate $B_2O_3(g)$ species in view of the discussion presented above; this expectation is in accord with the findings of Pikalov.⁷ To check the possibility of formation of BN proceeding through the intermediate species B_4C , an experiment was made in which a pellet prepared from a mixture of B_2O_3 and B_4C supplied by the HCST company was subjected to $N_2(g)$ at 1500 °C for 2 h in a graphite crucible the interior of which was coated with BN . The size of the $B_2O_3 + B_4C$ pellet used in this experiment was the same as those of the $B_2O_3 + C$ pellets used in the previous experiments and the amount of B_2O_3 in the pellet was 50% in excess of that required by the stoichiometry of Reaction (12). X-ray diffraction pattern of the reaction product of this experiment indicated that it consisted of BN , B_4C , and B_2O_3 . By the leaching-oxidation-leaching method, the quantity of B_4C that has reacted was calculated to be 20% of the amount used in the preparation of the pellet. Considering that the reaction of $B_2O_3 + C$ mixtures with N_2 is complete in 2 h at 1500 °C whereas there is a significantly high quantity of unreacted B_4C in the reaction of $B_2O_3 + B_4C$ mixture with N_2 at 1500 °C in the same time period, it may be stated that formation of BN from $B_2O_3 + B_4C$ mixtures is slower than that from $B_2O_3 + C$ mixtures. The sizes of the $B_2O_3 + B_4C$ and the $B_2O_3 + C$ pellets used in the experiments were identical but the weights were different. Accordingly the stoichiometric weight of BN to form from the $B_2O_3 + B_4C$ pellet (4.988 g BN from 2.38 g B_4C and 1.5 g B_2O_3) is much higher than that from the $B_2O_3 + C$ pellet (0.9117 g BN from 2 g B_2O_3 and 0.69 g C). This might have given rise to the reaction of the $B_2O_3 + B_4C$ pellet with N_2 not reaching completion in 2 h at 1500 °C.

To obtain additional data on the relative rates of BN formation from $B_2O_3 + C$ and $B_2O_3 + B_4C$ mixtures subjected to $N_2(g)$ an experiment was made in which equal sized C and B_4C pellets placed onto B_2O_3 contained in a BN -coated graphite crucible were subjected to $N_2(g)$ at 1500 °C for 2 h. The weights of the carbon and the B_4C pellets were 0.89 and 1.33 g, which should stoichiometrically yield 1.18 and 2.79 g of BN respectively. After removal of the graphite crucible with its

contents from the furnace, BN was seen to have formed on both the carbon and the B₄C pellet. It was also seen that the reaction was not complete with either the carbon pellet or the B₄C pellet. It was estimated by visual examination, that the weight of BN on the carbon pellet was about 10 times as large as that on the B₄C pellet. From this result that less BN has formed on the B₄C pellet than on the carbon pellet when more would be expected to have formed from a stoichiometric point of view, and the result of the previous experiment that the reaction of B₂O₃ + B₄C pellet with N₂(g) is not complete in 2 h at 1500 °C whereas the reaction of B₂O₃ + C pellet is complete, it may be concluded that formation of BN from B₂O₃ + B₄C mixtures is slower than that from B₂O₃ + C mixtures.

Specifications provided by the producers indicate that the specific surface area of the boron carbide powder used in the above experiments is 9 m²/gm which is very small compared to the 588 m²/gm specific surface area of the activated charcoal. This may be a reason why formation of BN from boric oxide-boron carbide mixtures subjected to N₂(g) is slower than that from boric oxide-activated charcoal mixtures.

A possible explanation for the presence of B₄C(s) in the pellets in which BN(s) formation is not as yet complete is that nitrogen pressure across the pellet is not uniform in spite of its high porosity and in regions where nitrogen pressure is too low or $\frac{P_{CO}^3}{P_{N_2}^2}$ ratio is too high for BN formation, B₄C(s) forms which later reacts with B₂O₃ and N₂(g) to give BN. The variation of the B₄C(s) content of the products of the experiments conducted with (B₂O₃ + C) pellets at 1500 °C with time, given in Fig. 4 is in accord with this explanation.

5. Conclusions

Formation of boron nitride by reaction of boric oxide with carbon and nitrogen gas has been studied by subjecting boric oxide-activated carbon mixtures, in which the quantity of boric oxide was 50% more than the stoichiometric amount, to nitrogen gas at 1100, 1200, 1300, and 1400 °C for 2 h and at 1500 °C for 15, 30, 60, 90, 120, 180, and 240 min. The reaction products of the experiments in which formation of BN was not complete were found to consist of BN, unreacted B₂O₃, unreacted charcoal, B₄C and ash of the charcoal used. A method, called as the leaching-oxidation-leaching method, was found with which all species other than BN present in the reaction products could be removed and

their quantities could be determined. The experimental results indicate that the quantity of BN forming increases with increasing temperature in 2 h and increases at 1500 °C with increasing time and that formation of boron nitride is complete in 2 h at 1500 °C.

Experiments employing different geometries were conducted with the objective of determining the mechanism of the reaction of boric oxide with carbon and nitrogen. It was shown that liquid B₂O₃ and carbon need not to be in contact for formation of BN(s) from B₂O₃(l) and C(s) under N₂(g) atmosphere and it was concluded that the reaction proceeds through gaseous intermediates. Based on the experimental results, formation of BN(s) from (B₂O₃ + C) mixtures subjected to N₂ gas is proposed to take place by the following two mechanisms:

1. Evaporation of B₂O₃(l) and reaction of B₂O₃(g) with C(s) and N₂(g) forming BN(s) on the carbon particles (overall reaction 5).
2. Formation of B₄C(s) with reaction of B₂O₃ (probably gaseous B₂O₃) and C(s) in regions where N₂(g) pressure is too low for BN formation (overall reaction 13) followed by reaction of B₂O₃ (probably gaseous B₂O₃) with B₄C(s) and N₂(g) forming BN(s) (overall reaction 12).

References

1. Taylor, K. M., Boron nitride. *Materials and Methods*, 1956, **88**, 88–91.
2. Niedenzu, K. and Dawson, J. W., *Boron-Nitrogen Compounds*. Springer-Verlag, 1965 pp. 147–158.
3. Brotherson, R. J. and Steinberg, H., *Progress in Boron Chemistry*, Vol. 2. Pergamon Press, 1970 pp. 173–230.
4. Schwetz, K.A. and Lipp, A., Boron carbide, boron nitride and metal borides. In *Ullmann's Encyclopedia of Industrial Chemistry*. Verlag Chemie GmbH, Weinheim FRG, 1985, pp. 295–307.
5. Lipp, A. and Schwetz, K. A., Hexagonal boron nitride: fabrication, properties and applications. *J. Eur. Ceram. Soc.*, 1989, **5**, 3–9.
6. Yoon, S. J. and Jha, A., Vapour-phase reduction and the synthesis of boron-based ceramic phases, part II, the synthesis of hexagonal boron nitride phase. *Journal of Materials Science*, 1996, **31**, 2265–2277.
7. Pikalov, S. N., Mechanism of formation of graphite-like boron nitride in the carbothermal process. *Soviet Powder Metall. Met. Ceram.*, 1988, **27**, 404–406.
8. Bartnitskaya, T. S., Kosolapova, T.Ya., Kurdyumov, A. V., Oleinik, G. S. and Pilyankevich, A. N., Structure and some properties of fine-grained graphite-like boron nitride. *Journal of the Less Common Metals*, 1986, **117**, 253–258.
9. Aydođdu, A., *Production of Boron Nitride*. PhD thesis, Middle East Technical University, Ankara, Turkey, 1993.
10. Turkdogan, E. T., *Physical Chemistry of High Temperature Technology*. Academic Press, London, 1980 pp. 5–24.