

## Effect of calcium carbonate addition on carbothermic formation of hexagonal boron nitride

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### Abstract

Effect of CaCO<sub>3</sub> on formation of hexagonal boron nitride (h-BN) was investigated by holding CaCO<sub>3</sub> free and CaCO<sub>3</sub> added activated carbon–boric oxide mixtures under nitrogen atmosphere at 1500 °C for 30–120 min. Amount of CaCO<sub>3</sub> addition was varied in the range of 0–50 wt.% of the initial mixture. Products were characterized by powder X-ray diffractometry, FT-IR analysis, quantitative chemical analysis, scanning electron microscopy and BET specific surface area analysis. It was observed that calcium carbonate addition led to an increase in the amount and the grain size of hexagonal boron nitride and a decrease in the amount of boron carbide forming. Ten weight percent calcium carbonate addition was found to be the optimum value for increasing the yield of hexagonal boron nitride and decreasing the formation of boron carbide.

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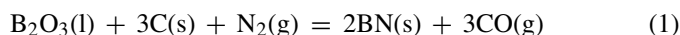
**Keywords:** Hexagonal boron nitride; Powders-solid state reaction; Grain growth; Grain size; Nitrides; BN

### 1. Introduction

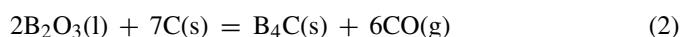
Hexagonal boron nitride (h-BN) is a versatile ceramic material, with unique properties and a wide application area in industry. Some important properties of h-BN are resistance to oxidation up to higher temperatures (~1000 °C) than graphite (~400 °C), lubricity,<sup>1</sup> high corrosion resistance, high thermal conductivity and high electrical resistivity. It is used mostly as a high temperature lubricant, an electrical insulator and a mold release agent. It can be shaped by hot-pressing with some additives and mechanically worked easily. In the shaped form it is primarily used as molds for molten metal handling and evaporation. In the last decade, the consumption of h-BN has increased due to its use in composite materials with other ceramics or polymers.<sup>2</sup> h-BN, when added into plastics, reduces friction

coefficient, increases thermal conductivity, decreases thermal expansion and increases use temperatures, depending on the type of the plastic.<sup>3</sup>

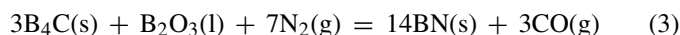
There are three commonly used methods for production of h-BN in industrial scale.<sup>2,4,5</sup> One is based on direct reaction of boric oxide and ammonia. Another method is through the reaction of boric acid with urea or melamine and ammonia.<sup>2,5</sup> The third one is the carbothermic reduction and simultaneous nitridation of boric oxide<sup>4,6</sup> according to Reaction (1).



Few studies have been done on the mechanism of carbothermic formation of h-BN.<sup>7–9</sup> Bartnitskaya et al.<sup>7</sup> concluded that B<sub>2</sub>O<sub>3</sub> first gets reduced to B by carbon and then B reacts with N<sub>2</sub> (g) to form BN while Joon and Jha<sup>8</sup> considered h-BN formation to proceed through gaseous BO. Pikalov<sup>9</sup> suggested h-BN formation to proceed in two consecutive steps with B<sub>4</sub>C forming in the first step according to the overall reaction:



and h-BN forming by reaction of B<sub>4</sub>C with B<sub>2</sub>O<sub>3</sub> in the second step according to the overall reaction:



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Aydoğdu and Sevinç<sup>6</sup> found Reaction (1) to be completed in 2 h at 1500 °C in their system and found B<sub>4</sub>C, in addition to unreacted B<sub>2</sub>O<sub>3</sub>, unreacted C and h-BN formed, to exist in the reaction products of the experiments in which h-BN formation was not complete. They found that liquid B<sub>2</sub>O<sub>3</sub> and solid carbon need not be in contact in the formation of BN from B<sub>2</sub>O<sub>3</sub>, C and N<sub>2</sub> and concluded the overall Reaction (1) to proceed by evaporation of B<sub>2</sub>O<sub>3</sub>(l) and reaction of B<sub>2</sub>O<sub>3</sub>(g) with C(s) and N<sub>2</sub>(g) on C(s). By thermodynamic analysis based on Reaction (3), they showed that either BN(s) or B<sub>4</sub>C(s) but not both can exist in the system at equilibrium and suggested B<sub>4</sub>C to form in regions of the pellet where N<sub>2</sub> pressure is too low due to insufficient penetration of nitrogen gas. They concluded that some h-BN forms according to the overall Reaction (1) and some according to Reactions (2) and (3) taking place successively. In a study<sup>10</sup> it was later reported that B<sub>4</sub>C was not a necessary intermediate compound in the carbothermic formation of h-BN and that it retarded the completion of the formation of pure h-BN due to the longer time required to convert the formed B<sub>4</sub>C into h-BN by Reaction (3) than formation of h-BN directly from boric oxide and carbon according to Reaction (1). It can therefore be stated that the reduction of the amount of forming B<sub>4</sub>C is a critical issue in this process.

The increase of the demand on h-BN and the requirement of high temperatures in the mentioned production processes have led to further research on finding ways to increase the rate of h-BN formation reaction. For this purpose catalytic effect of some lithium compounds such as Li<sub>2</sub>CO<sub>3</sub> and LiOH on the yield and three-dimensional crystallographic ordering of h-BN was investigated.<sup>11,12</sup> It was found from the experiments conducted at 1500 °C for 3 h in nitrogen atmosphere that when Li<sub>2</sub>CO<sub>3</sub> was added to boric acid–carbon black mixture at an amount of 12%, the amount of h-BN formed was about twice the amount formed in the experiments without Li<sub>2</sub>CO<sub>3</sub>. The crystal structure of the formed h-BN was also seen to be improved by the addition of Li<sub>2</sub>CO<sub>3</sub>.

Use of CaCO<sub>3</sub> as a catalyst has been investigated<sup>13</sup> in processes where nitrogen containing compounds such as urea or melamine and boric acid are reacted at 1800–2200 °C under ammonia or inert atmosphere. It was reported that addition of CaCO<sub>3</sub> into the starting mixture yielded h-BN powder with high crystallinity and low specific surface area. Larger grain size and higher crystallinity lead to better lubricating properties and high temperature stability of h-BN.<sup>2,14,15</sup>

No study has been encountered in the literature on the role of CaCO<sub>3</sub> addition on carbothermic formation of h-BN. The abundance and low cost of CaCO<sub>3</sub> makes it a candidate catalyst material for this process. This study was undertaken in order to investigate the catalytic effect of CaCO<sub>3</sub> on the formation of h-BN by the reaction of boric oxide and carbon under nitrogen atmosphere.

## 2. Experimental procedure

Activated carbon (Merck, 99% purity)–boric oxide mixtures, each having a weight of 2.5 g were prepared with 100 mole %

more boric oxide than the stoichiometric amount required for Reaction (1). The amount of excess boric oxide was determined in a previous study<sup>10</sup> and was necessary to compensate for the loss of boric oxide due to evaporation. Boric oxide, used in the preparation of the mixtures, was produced by calcination of boric acid (Merck, 99.8% purity) at 900 °C for 2 h. Experiments were performed with both plain (activated carbon–boric oxide mixtures without CaCO<sub>3</sub> addition) and CaCO<sub>3</sub> added mixtures. In each experiment, reactant mixtures contained 0.514 g activated carbon and 1.986 g boric oxide. CaCO<sub>3</sub> was added into these mixtures in amounts of 5, 10, 20, 30, 40 and 50 wt.% of the initial activated carbon-boric oxide mixtures. The ingredients were mixed and ground in an agate mortar and pestle in acetone. Experiments were performed by subjecting these mixtures to high purity nitrogen atmosphere at 1500 °C in a vertical mullite tube furnace which was heated with SiC heating elements. The mullite furnace tube was 800 mm long, and had 50 mm inner and 60 mm outer diameters. The mixtures were placed in a graphite crucible which had a depth of 3 cm and inner and outer diameters of 2.5 cm and 3 cm, respectively. Inside of the graphite crucible was covered with a ~0.5 mm thick layer of h-BN in order to prevent reaction with its contents. The crucible containing the mixtures was placed into the hot zone of the furnace which was preheated to 1500 °C and the starting time was set to zero when the furnace was re-stabilized at this temperature, which was approximately 5 min after placing the sample. Before the experiments, inside of the furnace tube was flushed with flowing high purity nitrogen gas at a rate of 2 l/min for 10 min. The nitrogen gas flow rate was kept at 200 cc/min during the experiments. Experiments aiming for the determination of the optimum amount of CaCO<sub>3</sub> addition were conducted with mixtures containing 5–50 wt.% CaCO<sub>3</sub> at 1500 °C for 30 min. After determining the optimum amount for CaCO<sub>3</sub> addition, experiments were performed for 1/2, 1 and 2 h at 1500 °C with plain and CaCO<sub>3</sub> added mixtures. Reaction products were subjected to powder X-ray diffraction (XRD) analysis by a Rigaku-Multiflex unit at a scan speed of 2°/min with 0.02° steps. K $\alpha$ 2 and background subtraction operations were performed on these XRD patterns with the supplied software of the X-ray diffractometer in order to discern the crystalline phases. The phases were identified by the Qualitative Analysis software. Grain size and morphology of the products were investigated by scanning electron microscope (SEM) (Jeol JSM6400). The quantities of the constituents of the products were determined by a quantitative chemical analysis method, which is described briefly below. Further details of the method can be found elsewhere.<sup>6,10</sup>

Addition of CaCO<sub>3</sub> is expected to result in formation of calcium borates in view of the phase diagram given in Fig. 1. In order to determine if calcium borates were soluble in dilute HCl, two B<sub>2</sub>O<sub>3</sub>–CaO mixtures containing 20 and 35 wt.% CaO, respectively, were prepared and kept in a platinum crucible at 1150 °C for 2 h. It is known from the phase diagram given in Fig. 1 that calcium borate melt forms above 1100 °C for these compositions.<sup>16</sup> After removing from the furnace and cooling, the platinum crucible with its contents was placed into a 1/1 (v/v) HCl/water solution. It was found that both of the compositions were completely soluble in dilute HCl and it was concluded that

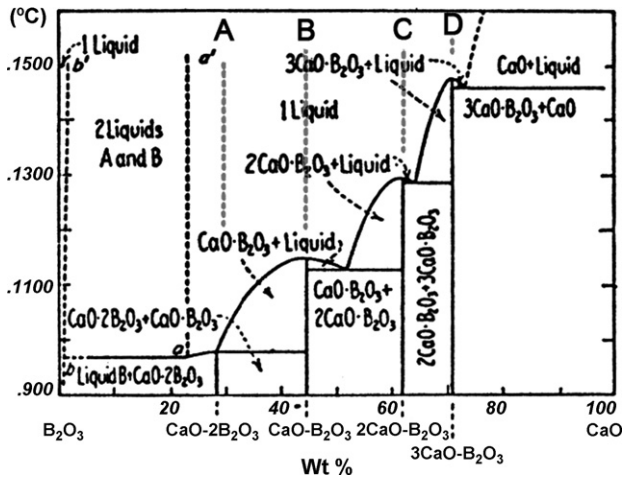


Fig. 1.  $B_2O_3$ –CaO phase diagram.<sup>16</sup>

it was possible to remove calcium borates by leaching in this solution. The leaching duration in the chemical analysis method used was fixed at 15 h for all the products obtained with additives.

The method used for quantitative analysis consists of consecutive leaching, oxidation and leaching steps. The reaction products containing unreacted  $B_2O_3$ , unreacted activated carbon, h-BN, (in some experiments)  $B_4C$ , and amorphous or crystalline calcium borate (in  $CaCO_3$  added experiments); were dissolved in 1/1 HCl solution and compounds which are soluble in dilute hydrochloric acid (calcium borate and unreacted boric oxide) were taken into solution and removed by filtering the solution; the leachant used for reaction products of plain mixtures was deionized water. Solid to liquid ratio in the leaching operations was 1 g/100 cc. Amounts of unreacted  $B_2O_3$  in the products obtained from plain  $B_2O_3 + C$  mixtures were determined volumetrically by titrating the filtrate with 1 N NaOH solution. Total amount of calcium borate + unreacted  $B_2O_3$  in the products obtained from  $CaCO_3$  added mixtures was determined from the weight difference of the products before and after leaching. On the basis of the assumption that no CaO is lost from the system, the overall composition of the ( $B_2O_3 + CaO$ ) system could be calculated. The leaching duration in the chemical analysis method used was fixed at 15 h for all the products obtained with  $CaCO_3$  additions. The removal of the calcium borate was also verified by Fourier transformed-infrared spectrometry (FT-IR) analysis. FT-IR analyses were performed by a Varian-1000 model unit after mixing the powders with KBr.

The residue from leaching containing only h-BN,  $B_4C$  and unreacted carbon was dried, weighed and then kept in air in a muffle furnace at 800 °C for 15 h in order to oxidize and remove all unreacted carbon and to oxidize all  $B_4C$  into  $B_2O_3$ . The oxidized product was dissolved in water and filtered. The filtrate was titrated with 0.5 N NaOH solution and amount of  $B_2O_3$  formed by the oxidation of  $B_4C$  in the reaction products was determined volumetrically. Amount of  $B_4C$  was calculated from the amount of  $B_2O_3$  according to:  $W_{B_4C} = (W_{B_2O_3}/69.62 \times 2) \times 55.25$ . The final residue was pure h-BN. Amount of h-BN was calculated by subtracting the weight of  $B_2O_3$  from the weight of the oxidized product. Weight of h-BN was checked by the amount

of the final residue. Leaching and oxidation steps were followed by XRD and FT-IR analysis and completeness of these processes were confirmed. Related results of FT-IR analysis are presented in Section 3.

Specific surface area measurements of the produced h-BN, which were obtained in pure form after the described chemical analysis, were performed by BET specific surface area analyzer (Carlo Erba, Sorptomatic 1900). Before the measurements, powders were subjected to ultrasonic bath in water in order to break up the soft agglomerates.

### 3. Results and discussion

#### 3.1. Effect of $CaCO_3$ addition on formation of BN and $B_4C$

Initial experiments were performed in order to determine the optimum amount of  $CaCO_3$  to be added into the activated carbon–boric oxide mixtures. The duration for these experiments was selected by considering two issues. First, as mentioned in the introduction part,  $B_4C$  also forms as an undesired side product together with h-BN during carbothermic production of h-BN. It was observed in this study and also in previous studies<sup>6,10</sup> that at 1500 °C the amount of  $B_4C$  in the reaction products increases in the first 30 min and then decreases by reacting with boric oxide and nitrogen; suggesting that formation of  $B_4C$  mainly takes place in the first 30 min. Therefore, in order to observe the effect of  $CaCO_3$  addition on formation of  $B_4C$ , duration of 30 min at 1500 °C was suitable. Secondly; the reaction products had to be analyzed at an intermediate stage before complete consumption of the reactants, to examine the effect of  $CaCO_3$  on the formation of h-BN. Duration of 30 min could serve well for both of these purposes.

The quantities of  $B_4C$  and h-BN in the reaction products of the experiments conducted for 30 min at 1500 °C with activated carbon–boric oxide mixtures containing 0–50 wt.%  $CaCO_3$  additions, are presented in Table 1 and Fig. 2. In the same table CaO percentages of the ( $CaO + B_2O_3$ ) system in the pellets at  $t=0$  and  $t=30$  min are also given. The amounts of h-BN in all of the reaction products obtained from pellets containing  $CaCO_3$  are seen to be higher than that obtained from plain mixtures. It is seen that amount of h-BN increases with addition of  $CaCO_3$  up to an amount of 10 wt.% of the activated

Table 1

Amounts of h-BN and  $B_4C$  in the products of the experiments conducted at 1500 °C for 30 min with  $CaCO_3$  additions; and CaO percentages of the ( $CaO + B_2O_3$ ) system in the pellets at  $t=0$  and  $t=30$  min

$CaCO_3$ (%)	Amounts in the Products (g)		CaO (wt.%) in ( $B_2O_3 + CaO$ )	
	h-BN	$B_4C$	$t=0$ min	$t=30$ min
0	0.09	0.15	0	0
5	0.15	0.08	3.4	5.2
10	0.26	0.11	6.6	10.8
10	0.23	0.10	6.6	10.8
20	0.21	0.14	12.4	19.6
30	0.16	0.16	17.5	26.1
40	0.13	0.16	22	30.8
50	0.15	0.17	26.1	35.9

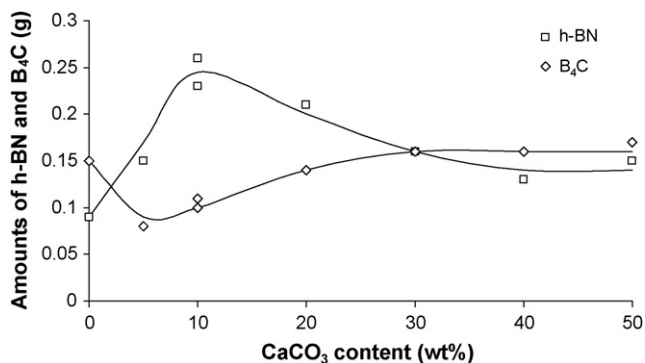


Fig. 2. Change in the amounts of h-BN and B<sub>4</sub>C in the products of the experiments conducted at 1500 °C for 30 min with CaCO<sub>3</sub> additions.

carbon-boric oxide mixture and decreases afterwards. It can be concluded from this figure that the positive effect of CaCO<sub>3</sub> on carbothermic formation of h-BN is the highest at 10 wt.%. Five to 10 weight percent CaCO<sub>3</sub> addition is effective in reducing the amount of B<sub>4</sub>C in the reaction products. The decrease in the amount of h-BN and increase in the amount of B<sub>4</sub>C in the reaction products of the experiments conducted with higher additions of CaCO<sub>3</sub> than 10 wt.% reveals that higher amounts of CaCO<sub>3</sub> is not as beneficial for this process.

Relative heights of the peaks of the phases appearing in the XRD patterns presented in Fig. 3 are in accord with the results of the quantitative chemical analysis. It can be discerned from these patterns that the h-BN peaks attain the highest values with 10 wt.% CaCO<sub>3</sub> addition and B<sub>4</sub>C peaks attain their lowest values at 5–10 wt.% CaCO<sub>3</sub> addition. H<sub>3</sub>BO<sub>3</sub> peaks, present in these XRD patterns are due to the formation of H<sub>3</sub>BO<sub>3</sub> by hydration of unreacted amorphous B<sub>2</sub>O<sub>3</sub> in the reaction products during specimen preparation for the XRD analyses, therefore their heights are proportional to the amount of B<sub>2</sub>O<sub>3</sub> in the reaction products. It is seen in Fig. 3 that H<sub>3</sub>BO<sub>3</sub> peaks become gradually shorter up to 20 wt.% CaCO<sub>3</sub> and then fade away, indicating that all of the B<sub>2</sub>O<sub>3</sub> was consumed upon addition of 30 wt.% CaCO<sub>3</sub> or more.

Addition of 10 wt.% CaCO<sub>3</sub> was found to be the optimum value to keep the amount of B<sub>4</sub>C as low as possible and h-BN as

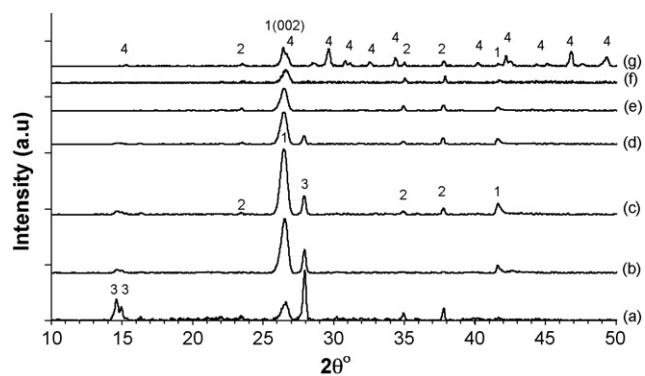


Fig. 3. XRD patterns of the products of the experiments conducted with 0–50 wt.% CaCO<sub>3</sub> addition for 30 min at 1500 °C. (a) No addition, (b) 5 wt.%, (c) 10 wt.%, (d) 20 wt.%, (e) 30 wt.%, (f) 40 wt.%, (g) 50 wt.% CaCO<sub>3</sub> addition. (1) h-BN, (2) B<sub>4</sub>C, (3) H<sub>3</sub>BO<sub>3</sub>, (4) CaB<sub>2</sub>O<sub>4</sub>.

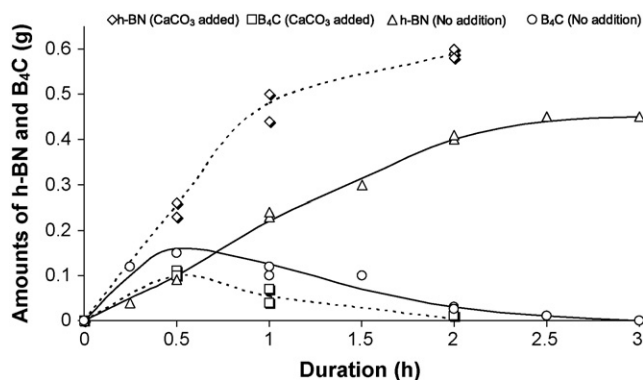


Fig. 4. Amounts of h-BN and B<sub>4</sub>C in the products of the experiments conducted for 30 min to 2 h at 1500 °C with plain and 10 wt.% CaCO<sub>3</sub> added mixtures.

high as possible in the reaction products. Therefore, experiments aiming for the investigation of the catalytic effect of CaCO<sub>3</sub> for longer durations at 1500 °C were performed with 10 wt.% CaCO<sub>3</sub> additions. The quantities of h-BN and B<sub>4</sub>C formed in the experiments conducted for 30 min to 2 h at 1500 °C with plain and 10 wt.% CaCO<sub>3</sub> added mixtures are presented in Fig. 4. It can be seen that the quantity of h-BN forming in the mixtures containing CaCO<sub>3</sub> as additive were significantly larger than those containing no CaCO<sub>3</sub>. CaCO<sub>3</sub> addition is also seen from Fig. 4 to decrease the quantity of B<sub>4</sub>C in the reaction products. The XRD patterns of these experiments given in Fig. 5 are in accord with the results of the quantitative analysis, where it can be observed that the B<sub>4</sub>C peaks of the samples obtained without CaCO<sub>3</sub> addition are higher than the ones with additions. Efficiency of h-BN formation was calculated from the chemical analysis data. It was found that all of the C was consumed in 2 h when CaCO<sub>3</sub> was added and 83% of C in the initial mixture was used in formation of h-BN. On the other hand, some unreacted carbon remained at the end of 2 h when no CaCO<sub>3</sub> was used and 56% of the C was consumed in h-BN formation. In these experiments, all of the C was consumed in 3 h and 63% of initial C was utilized. These results indicate that addition of 10 wt.% CaCO<sub>3</sub> increases the reaction rate and reduces the loss of carbon. Carbon loss, taking place during carbothermic production of h-BN was also reported in other studies.<sup>6,10</sup>

In order to investigate the effect of CaCO<sub>3</sub> addition on the growth of h-BN crystallites, average crystal thickness values in the *c*-axis direction, *L<sub>c</sub>*, of the formed h-BN were calculated by the Scherrer formula.<sup>17,18</sup> Relatively crude measurements can be done in the range of 0–500 Å with the Scherrer formula.<sup>17</sup> *L<sub>c</sub>* is defined as the mean height of a pack of parallel and crystallographically connected hexagonal layers. In this calculation, full width at half maximum (FWHM) values of the peaks originating from (002) planes of h-BN ( $2\theta = 26.7^\circ$ ), presented on the XRD patterns given in Fig. 5 were utilized. The calculated *L<sub>c</sub>* values of the h-BN formed in the experiments conducted for 30 min to 2 h at 1500 °C with plain and CaCO<sub>3</sub> added mixtures are presented in Table 2. It is seen that addition of CaCO<sub>3</sub> results in a moderate increase in the average crystal thickness of the formed h-BN powder.

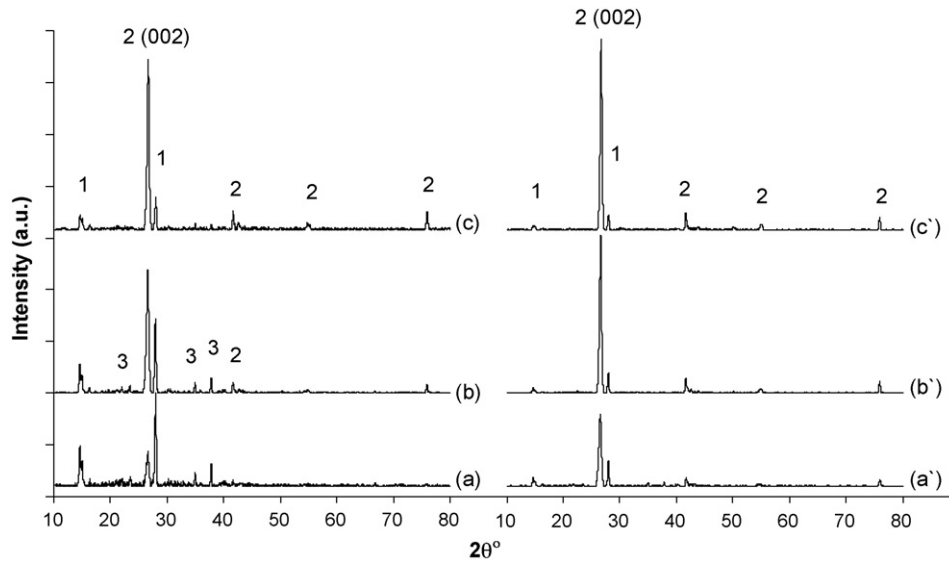


Fig. 5. XRD patterns of the products of the experiments conducted with plain and 10 wt.%  $\text{CaCO}_3$  added mixtures at  $1500^\circ\text{C}$ . (a) plain mixture—30 min, (a')  $\text{CaCO}_3$  added mixture—30 min; (b) plain mixture—1 h, (b')  $\text{CaCO}_3$  added mixture—1 h; (c) plain mixture—2 h, (c')  $\text{CaCO}_3$  added mixture—2 h. (1)  $\text{H}_3\text{BO}_3$ , (2) h-BN, (3)  $\text{B}_4\text{C}$ .

Table 2

Average crystal thickness values of h-BN formed from plain and  $\text{CaCO}_3$  added mixtures

Duration of experiment	Average crystal thickness, $L_c$ (nm)	
	Plain mixture	$\text{CaCO}_3$ added
30 min	15.13	16.55
1 h	17.90	21.14
2 h	22.02	23.85

SEM micrographs of reaction products formed in the experiments conducted for 2 h at  $1500^\circ\text{C}$  with plain and  $\text{CaCO}_3$  added mixture are presented in Figs. 6 and 7, respectively. These micrographs were taken from the spots inside the reaction products where definite grain structures could be visualized. It is measured on SEM micrographs that average grain diameter of h-BN formed in 2 h from plain mixtures is  $0.36 \pm 0.08 \mu\text{m}$  and addition of  $\text{CaCO}_3$  increases the grain diameter to  $0.70 \pm 0.14 \mu\text{m}$ .

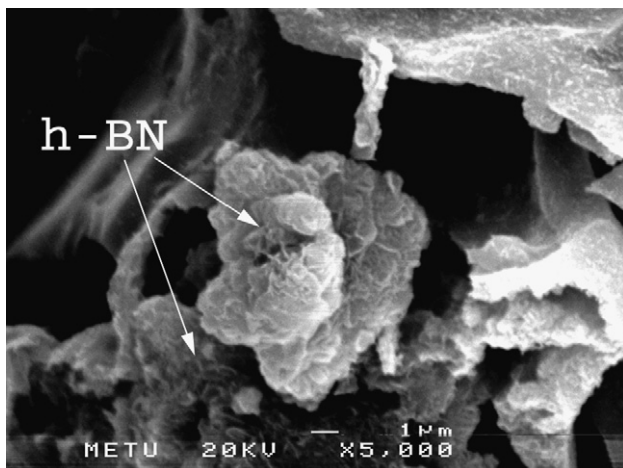


Fig. 6. SEM micrograph of h-BN formed from plain mixture at  $1500^\circ\text{C}$  in 2 h.

The effect of  $\text{CaCO}_3$  addition is seen to be that of formation of individual h-BN particles having separate surfaces with definite edges instead of a merged polycrystalline form observed in the h-BN produced without  $\text{CaCO}_3$  additions. The results of the BET specific surface area measurements are in accord with the observations made on the SEM micrographs. The specific surface area of the h-BN powder formed in the experiments conducted for 2 h with plain mixtures was determined as  $31.7 \text{ m}^2/\text{g}$ ; whereas the specific surface area of the h-BN powder obtained in the same experimental conditions with 10 wt.%  $\text{CaCO}_3$  added mixture was  $21 \text{ m}^2/\text{g}$ . This result indicates that  $\text{CaCO}_3$  has a positive function on the growth of h-BN grains.

### 3.2. Phase in the reaction mixtures

No peaks related to any Ca-containing species are seen on the XRD patterns of the reaction products of the mixtures into

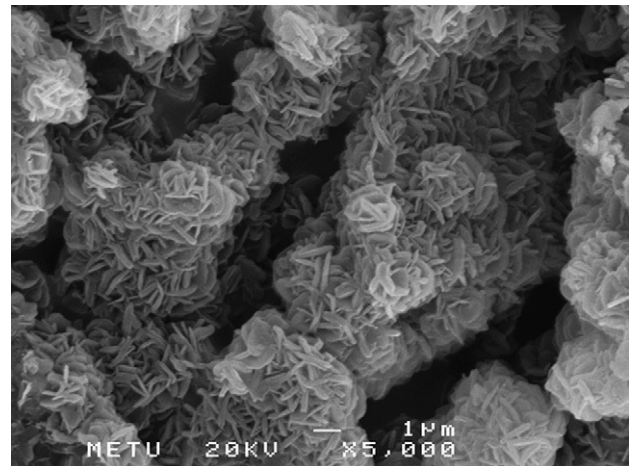
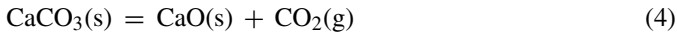
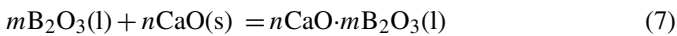
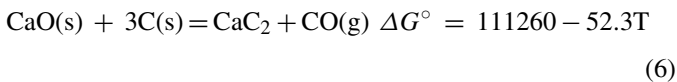
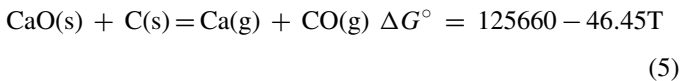


Fig. 7. SEM micrograph of h-BN formed from 10 wt.%  $\text{CaCO}_3$  added mixture at  $1500^\circ\text{C}$  in 2 h.

which  $\text{CaCO}_3$  has been added. No  $\text{CaCO}_3$  peak is expected to be present on the XRD patterns as  $\text{CaCO}_3$  decomposes in accord with the following reaction above a certain temperature.

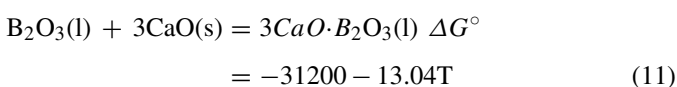
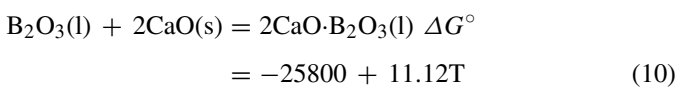
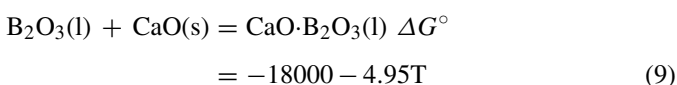
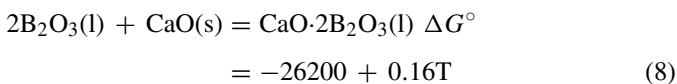


As the normal calcination temperature of  $\text{CaCO}_3$  is  $902^\circ\text{C}$ <sup>19</sup> and as the experimental temperature is  $1500^\circ\text{C}$ , there should not remain any  $\text{CaCO}_3$  in the reaction products. The fact that there are no CaO peaks on the XRD patterns may be taken as an indication that CaO has undergone a reaction during the experiments. The possibilities are reduction of CaO with carbon and formation of elemental calcium or  $\text{CaC}_2$  in accord with Reaction (5) and (6) or formation of calcium borate in accord with Reaction (7).



The equilibrium constant of Reaction (5),  $K_5 = P_{\text{Ca}} \cdot P_{\text{CO}}$ , is  $3.65 \times 10^{-6}$  at  $1500^\circ\text{C}$ . This low equilibrium constant indicates that Reaction (5) may take place only under very low pressures and is not expected to take place under the experimental conditions used. The equilibrium constant of Reaction (6),  $K_6 = P_{\text{CO}}$ , is  $6.45 \times 10^{-3}$  at  $1500^\circ\text{C}$  which again may be taken as an indication that this reaction also does not take place in the system. If either or both of Reactions (5) and (6) had taken place, carbon loss from the system would have increased. The fact that  $\text{CaCO}_3$  addition has resulted in a decrease of carbon loss also favors the conclusion that Reactions (5) and (6) do not take place in the system.

$\text{B}_2\text{O}_3$ –CaO phase diagram given in Fig. 1 shows that  $\text{B}_2\text{O}_3$  and CaO form the compounds  $\text{CaO}\cdot 2\text{B}_2\text{O}_3$ ,  $\text{CaO}\cdot \text{B}_2\text{O}_3$ ,  $2\text{CaO}\cdot \text{B}_2\text{O}_3$  and  $3\text{CaO}\cdot \text{B}_2\text{O}_3$  in the solid state and there is no solid phase in the system at  $1500^\circ\text{C}$  for CaO contents less than  $\sim 80\%$ . Standard free energy of formation of the compounds  $\text{CaO}\cdot 2\text{B}_2\text{O}_3$ ,  $\text{CaO}\cdot \text{B}_2\text{O}_3$ ,  $2\text{CaO}\cdot \text{B}_2\text{O}_3$  and  $3\text{CaO}\cdot \text{B}_2\text{O}_3$  indicate that all of these reactions are possible in the system:



So it is likely that a  $m\text{CaO}\cdot n\text{B}_2\text{O}_3$  compound has formed during heating of the reaction mix to  $1500^\circ\text{C}$ . If such a compound has formed during heating it would melt and exist in the liquid state at  $1500^\circ\text{C}$ . If such a compound has not formed during heating then CaO originating from calcination of  $\text{CaCO}_3$  is expected to dissolve in liquid  $\text{B}_2\text{O}_3$ . In either case, then,  $\text{B}_2\text{O}_3$  and CaO will exist in the liquid state (either as a single liquid or as two immiscible liquids) for CaO contents less than  $\sim 80\%$ . When the pellet is cooled to room temperature at the end of the experiment the liquid (or liquids) will solidify. There will be  $\text{B}_2\text{O}_3$  and  $\text{CaO}\cdot 2\text{B}_2\text{O}_3$  phases at room temperature if the overall composition is to the left of A,  $\text{CaO}\cdot 2\text{B}_2\text{O}_3$  and  $\text{CaO}\cdot \text{B}_2\text{O}_3$  phases if the overall composition is between A and B,  $\text{CaO}\cdot \text{B}_2\text{O}_3$  and  $2\text{CaO}\cdot \text{B}_2\text{O}_3$  phases if the overall composition is between B and C,  $2\text{CaO}\cdot \text{B}_2\text{O}_3$  and  $3\text{CaO}\cdot \text{B}_2\text{O}_3$  phases if the overall composition is between C and D and  $3\text{CaO}\cdot \text{B}_2\text{O}_3$  and CaO phases if the overall composition is to the right of D as seen in Fig. 1.  $\text{B}_2\text{O}_3$  ( $\text{H}_3\text{BO}_3$ ) peaks are seen in the XRD patterns of the pellets into which 20% or less  $\text{CaCO}_3$  has been added which indicates that the overall composition of the CaO– $\text{B}_2\text{O}_3$  melt is to the left of A in these pellets; the CaO contents given in Table 1 verify this indication. Quantity of  $\text{B}_2\text{O}_3$  is expected to decrease with increasing addition of  $\text{CaCO}_3$  in these pellets. The results presented in Fig. 3 are in accord with this expectation.  $\text{CaO}\cdot 2\text{B}_2\text{O}_3$  is also expected to be present in these pellets but no peaks related to this compound are seen on the XRD patterns given in Fig. 3. This may be due to  $\text{CaO}\cdot 2\text{B}_2\text{O}_3$  solidifying in amorphous state as rate of cooling is very fast.  $\text{CaO}\cdot \text{B}_2\text{O}_3$  peaks are observed in Fig. 3 to be present on the XRD pattern of the pellets into which  $\text{CaCO}_3$  higher than 40% have been added. There are no  $\text{B}_2\text{O}_3$  ( $\text{H}_3\text{BO}_3$ ) peaks on the XRD patterns of the pellets containing 30% or more  $\text{CaCO}_3$ . These results indicate that the overall composition of the CaO– $\text{B}_2\text{O}_3$  melt in these pellets is to the right of A.  $\text{CaO}\cdot \text{B}_2\text{O}_3$  phase is also expected to be present but no peaks related to this compound are seen on the XRD patterns given in Fig. 3. It appears therefore, that  $\text{CaO}\cdot \text{B}_2\text{O}_3$  has solidified in amorphous state in these pellets also.

It was seen in the XRD patterns of the products obtained by reacting 20 wt.% CaO–80 wt.%  $\text{B}_2\text{O}_3$  mixture and 35 wt.% CaO–65 wt.%  $\text{B}_2\text{O}_3$  mixture at  $1250^\circ\text{C}$  and then by cooling in air that both of the compositions were in amorphous structure. The product containing 35 wt.% CaO did not present any  $\text{B}_2\text{O}_3$  ( $\text{H}_3\text{BO}_3$ ) peaks, however  $\text{B}_2\text{O}_3$  ( $\text{H}_3\text{BO}_3$ ) peaks were present in the XRD pattern of the product obtained from 20 wt.% CaO–80 wt.%  $\text{B}_2\text{O}_3$  mixture. These results are in agreement with the previous statements and the phase diagram given in Fig. 3.

Due to the fact that amorphous calcium borate phases could not be detected by XRD analysis of the pellets containing less than 40%  $\text{CaCO}_3$ , FT-IR analyses were utilized. In order to distinguish the FT-IR peaks of the constituents of the products, FT-IR patterns of each constituent was determined separately in its pure form.  $\text{B}_4\text{C}$  used for this purpose was produced by the reaction of boric oxide and carbon under high purity argon (Fig. 8(a)). It has a characteristic peak at  $1095\text{ cm}^{-1}$ . h-BN was produced by carbothermic method and was purified by leaching and oxidation of the impurities (Fig. 8(b)).<sup>6,10</sup> h-BN has

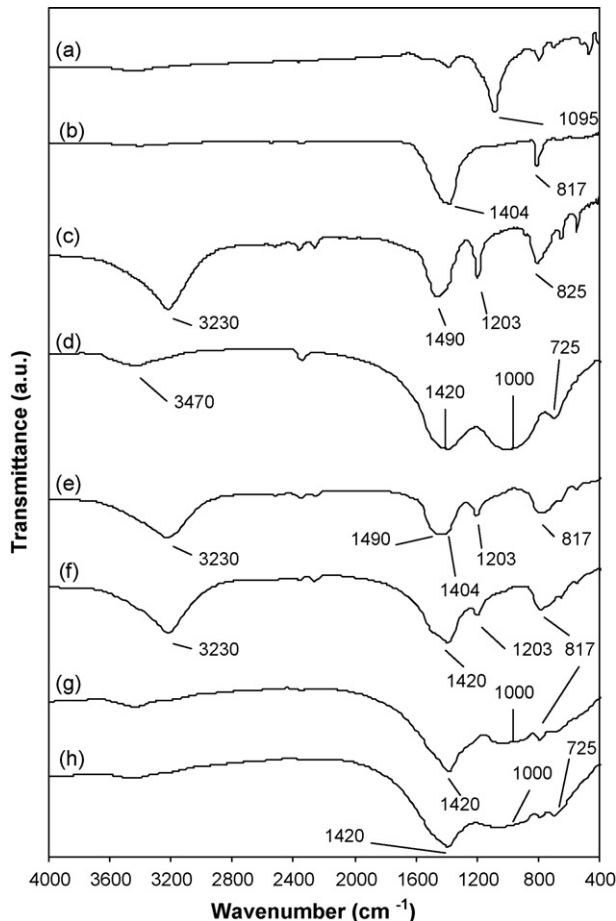


Fig. 8. FT-IR patterns of (a) B<sub>4</sub>C, (b) h-BN, (c) H<sub>3</sub>BO<sub>3</sub>, (d) calcium borate, (e) product obtained from plain B<sub>2</sub>O<sub>3</sub> + C mixtures in 30 min at 1500 °C, (f) product obtained from 10 wt.% CaCO<sub>3</sub> added B<sub>2</sub>O<sub>3</sub> + C mixtures, (g) product obtained from 30 wt.% CaCO<sub>3</sub> added B<sub>2</sub>O<sub>3</sub> + C mixtures, (h) product obtained from 50 wt.% CaCO<sub>3</sub> added B<sub>2</sub>O<sub>3</sub> + C mixtures.

peaks at 817 and 1404 cm<sup>-1</sup>. The pattern of H<sub>3</sub>BO<sub>3</sub> given in Fig. 8(c) belongs to a commercial boric acid (Merck Chemicals). It has peaks at 825, 1203, 1490, 3230 cm<sup>-1</sup>. The patterns of h-BN, B<sub>4</sub>C, BN and H<sub>3</sub>BO<sub>3</sub> are in agreement with the data in the literature.<sup>20</sup> Calcium borate was produced by reacting 35 wt.% CaO and 65 wt.% B<sub>2</sub>O<sub>3</sub> mixture (Fig. 8(d)) at 1150 °C. Due to the lack of FT-IR data on calcium borate in the literature, data obtained in the current study is used for the interpretation of product phases in the experiments.

In Fig. 8(e–h), FT-IR patterns of the products obtained from the experiments conducted at 1500 °C for 30 min with 0, 10, 30 and 50 wt.% CaCO<sub>3</sub> additions are presented. The peaks of h-BN, H<sub>3</sub>BO<sub>3</sub> and calcium borate at 1404–1490 cm<sup>-1</sup> overlap and make it difficult to make interpretations based on these peaks. In the sample produced without addition of CaCO<sub>3</sub>, presence of h-BN and H<sub>3</sub>BO<sub>3</sub> was detected (Fig. 8(e)). With addition of 10 wt.% CaCO<sub>3</sub> a peak at 1420 cm<sup>-1</sup> was observed and with increasing CaCO<sub>3</sub> contents, the hump at 1000 cm<sup>-1</sup> appeared indicating the presence of calcium borate phase (Fig. 8(g)). The consumption of B<sub>2</sub>O<sub>3</sub> during formation of calcium borate can be followed from the disappearance of the O-H peak at 3230 cm<sup>-1</sup> and also the peak at 1203 cm<sup>-1</sup>, which belong to H<sub>3</sub>BO<sub>3</sub>.<sup>20</sup>

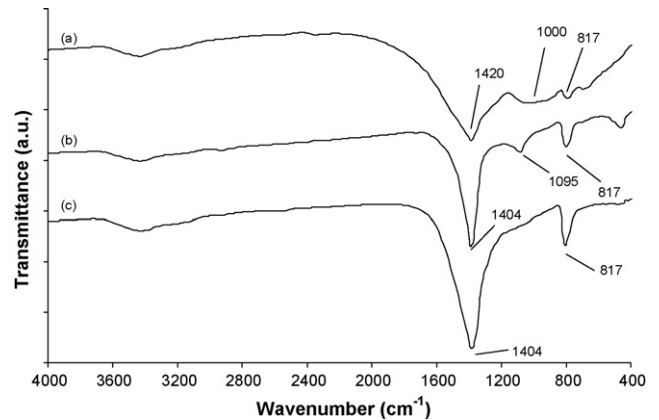


Fig. 9. FT-IR patterns of (a) product obtained from 30 wt.% CaCO<sub>3</sub> added B<sub>2</sub>O<sub>3</sub> + C mixture in 30 min at 1500 °C, (b) sample in (a) leached in dilute HCl, (c) sample in (b) oxidized at 800 °C and leached with water.

Peaks belonging to B<sub>4</sub>C are relatively small in Fig. 8(e) and (f); and are not distinguishable in Fig. 8(g) and (h). They may be masked by the other compounds.

In Fig. 9(b) it is seen that after leaching the sample containing 30 wt.% CaCO<sub>3</sub> with dilute HCl, the peaks belonging to calcium borate are removed and B<sub>4</sub>C peak is revealed. After holding the sample at 800 °C in air for oxidation and leaching with water, B<sub>4</sub>C was removed and only h-BN remained (Fig. 9(c)).

### 3.3. Reaction mechanism

Addition of CaCO<sub>3</sub> into (B<sub>2</sub>O<sub>3</sub> + C) mixtures in amounts in the 5–50 wt.% range increases the quantity of h-BN formed. It is known<sup>6</sup> that carbothermic formation of h-BN in B<sub>2</sub>O<sub>3</sub> + C mixtures subjected to N<sub>2</sub> gas takes place by reaction of B<sub>2</sub>O<sub>3</sub>(g) and N<sub>2</sub>(g) on solid C. B<sub>4</sub>C also forms<sup>6</sup> during the process which slows the h-BN formation as discussed in the previous sections. If this mechanism does not change with addition of CaCO<sub>3</sub> into B<sub>2</sub>O<sub>3</sub> + C mixtures, CaCO<sub>3</sub> should somehow be favoring of h-BN formation. B<sub>4</sub>C forms during carbothermic h-BN formation in regions of the pellet into which N<sub>2</sub> cannot penetrate. h-BN formation is expected to be accelerated by easing the access of N<sub>2</sub>(g) into the pellet. Accordingly, h-BN formation is expected to be favored by increased porosity of the pellet. Reaction products of the pellets containing lower than 20 wt.% CaCO<sub>3</sub> were observed to be more porous than those of the plain pellets. Based on this observation, CaCO<sub>3</sub> is concluded to increase the porosity of the pellets for additions of less than 20%. The effect of CaCO<sub>3</sub> in favoring the h-BN formation may therefore be due to increasing the porosity of the pellets. The increase in porosity of the pellet with addition of CaCO<sub>3</sub> may be due to CO<sub>2</sub>(g) evolution from the system associated with calcination of CaCO<sub>3</sub>. This cannot be the only reason, however, as porosity has been observed to be high with CaCO<sub>3</sub> additions up to 20% but low for higher additions. The properties like the viscosity, density, etc. of the liquid calcium borate existing in the system during the reaction also appears to affect the porosity of the pellets.

As stated above two liquids, a' and b' (essentially pure B<sub>2</sub>O<sub>3</sub>), exist in the system at 1500 °C (Fig. 1) for CaO contents of the

CaO–B<sub>2</sub>O<sub>3</sub> melts less than *a'* when the activity of B<sub>2</sub>O<sub>3</sub> as the standard state is about unity. With increase in the amount of CaCO<sub>3</sub> addition until the CaO content of the CaO–B<sub>2</sub>O<sub>3</sub> melt reaches *a'*, B<sub>2</sub>O<sub>3</sub> activity remains unchanged but the quantity of B<sub>2</sub>O<sub>3</sub> existing in the system decreases. Consequently, Δ*G* of Reaction (1), B<sub>2</sub>O<sub>3</sub>(l) + C(s) + N<sub>2</sub>(g) = 2BN(s) + 3CO(g) and equilibrium vapor pressure of B<sub>2</sub>O<sub>3</sub>(l) remain unchanged but due to the decrease in the quantity of B<sub>2</sub>O<sub>3</sub>(l) in the system, rate of evaporation of B<sub>2</sub>O<sub>3</sub>(l) decreases which decreases the rate of reaction. So, with CaCO<sub>3</sub> addition, porosity of the pellet increases (up to 20 wt.%) which increases the rate of Reaction (1) but the rate of evaporation of B<sub>2</sub>O<sub>3</sub>(l) decreases which decreases the rate of reaction. Depending on the relative importance of these opposing factors, rate of formation of h-BN may increase or decrease. For CaCO<sub>3</sub> additions up to 10 wt.% the increase in rate of the Reaction (1) due to increased porosity of the pellet appears to outweigh the decrease in the rate of the reaction due to decreased rate of evaporation of B<sub>2</sub>O<sub>3</sub>(l). For CaCO<sub>3</sub> additions more than 10 wt.%, the opposite appears to be true.

For larger CaCO<sub>3</sub> additions when the overall composition of the CaO–B<sub>2</sub>O<sub>3</sub> melt is to the right of *a'* in Fig. 1, there is no B<sub>2</sub>O<sub>3</sub>(l) in the system and the liquid existing in the system is a calcium borate in which activity of B<sub>2</sub>O<sub>3</sub> is less than 1. Under these conditions Δ*G* of Reaction (1) becomes less negative and equilibrium vapor pressure of B<sub>2</sub>O<sub>3</sub> becomes less than that of pure B<sub>2</sub>O<sub>3</sub>(l). Reaction (1) thus becomes less favorable which explains the decrease in the rate of formation of h-BN with the increase in CaCO<sub>3</sub> addition; the decrease in the porosity of the pellet also acts in the direction of decreasing rate of formation of h-BN.

Another reason for the increase in rate of formation of h-BN when CaCO<sub>3</sub> is added into B<sub>2</sub>O<sub>3</sub> + C mixtures could be that a different additional mechanism becomes operative with addition of CaCO<sub>3</sub>. Bartnitskaya et. al. studied the effect of Li<sub>2</sub>CO<sub>3</sub> addition to h-BN formation by different methods like subjecting B<sub>2</sub>O<sub>3</sub>–C mixtures, boric acid–carbamide mixtures to N<sub>2</sub>(g) or ammonia gas.<sup>11,12</sup> They have found Li<sub>2</sub>CO<sub>3</sub> to favorably affect h-BN formation and h-BN crystallinity and have suggested h-BN to crystallize from the lithium borate melt. A similar mechanism may apply in formation of h-BN from B<sub>2</sub>O<sub>3</sub> + C + CaO mixtures subjected to N<sub>2</sub> gas.

A SEM micrograph of the product pellet which was obtained from the experiment conducted at 1500 °C for 1 h with 10 wt.% CaCO<sub>3</sub> addition is given in Fig. 10. It is known from the presence of unreacted carbon and remaining boric oxide in this sample that reaction was not complete and formation of h-BN grains are in progress. It is seen from this figure that the h-BN grains are embedded in a solidified continuous matrix phase (pointed with arrows). The h-BN grains seem to be growing out from the matrix phase.

In accord with the discussion above, two liquids, *a'* (calcium borate) and *b'* (essentially pure B<sub>2</sub>O<sub>3</sub>) are expected to be present in the system at 1500 °C for CaCO<sub>3</sub> additions less than 40%. For 40 and 50% CaCO<sub>3</sub> additions there is a single liquid calcium borate in the system. As the different additional mechanism applies when CaCO<sub>3</sub> is added into the B<sub>2</sub>O<sub>3</sub> + C mixture, the

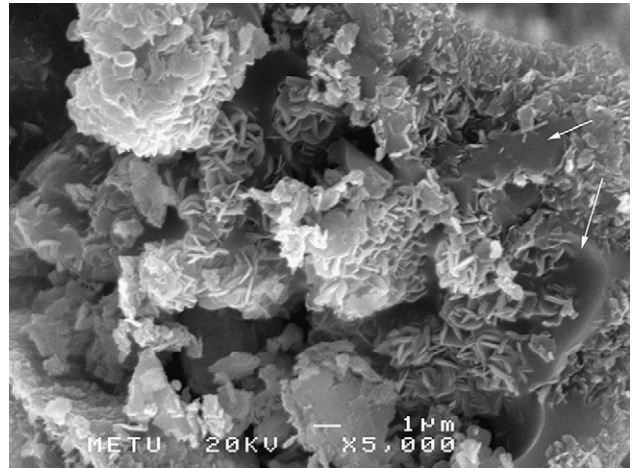
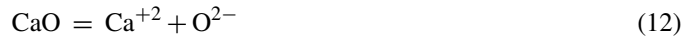


Fig. 10. SEM micrograph of h-BN formed from 10 wt.% CaCO<sub>3</sub> added mixture at 1500 °C in 1 h.

matrix phase through which the h-BN grains grow is expected to be the liquid calcium borate phase.

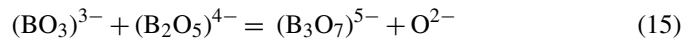
Nitrogen is soluble in oxide melts (slags) and the nitrogen solubility depends on slag basicity for given O<sub>2</sub> and N<sub>2</sub> pressures and temperature. Slag basicity depends on the relative proportions of basic and acidic oxides in the slag. A basic oxide like CaO dissolves in oxide solution in accord with the reaction<sup>21</sup>:



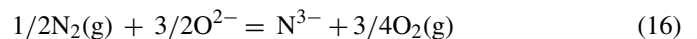
thereby providing O<sup>2-</sup> ions to the solution. An acidic oxide like B<sub>2</sub>O<sub>3</sub> consumes O<sup>2-</sup> during dissolution in oxide solutions. When sufficient O<sup>2-</sup> ions are present in the system B<sub>2</sub>O<sub>3</sub> is expected to form (BO<sub>3</sub>)<sup>3-</sup> according to:



A slag composed of basic and acidic oxides is basic when the O<sup>2-</sup> provided by basic oxides exceeds the O<sup>2-</sup> need of the acidic oxides when there will remain free O<sup>2-</sup> in the system. When the O<sup>2-</sup> need of the acidic oxide for formation of simple anions like (BO<sub>3</sub>)<sup>3-</sup> in Reaction (13) exceeds the O<sup>2-</sup> provided by the basic oxides, the slag will be acidic when the acidic oxides like B<sub>2</sub>O<sub>3</sub> form more complicated anions like (B<sub>2</sub>O<sub>5</sub>)<sup>4-</sup>, (B<sub>3</sub>O<sub>7</sub>)<sup>5-</sup>, etc. by polymerization (chain formation, network formation) reactions like:



Nitrogen dissolution in basic slags is governed by Reaction (16).<sup>21</sup>



The equilibrium constant of Reaction (16) is:

$$K_{16} = \frac{a_{\text{N}^{3-}} \times P_{\text{O}_2}^{3/4}}{P_{\text{N}_2}^{1/2} \times a_{\text{O}^{2-}}^{3/2}} = \frac{\gamma_{\text{N}^{3-}} \times (\%N) \times P_{\text{O}_2}^{3/4}}{P_{\text{N}_2}^{1/2} \times a_{\text{O}^{2-}}^{3/2}} \quad (1)$$

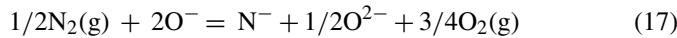


Activities and activity coefficients of single ions in slags cannot be determined. Rearranging Eq. (1), the relation

$$C_{N^{3-}} = K_{16} \times \frac{a_{O^{2-}}^{3/2}}{\gamma_{N^{3-}}} = (\%N) \times \frac{P_{O_2}^{3/4}}{P_{N_2}^{1/2}} \quad (2)$$

is obtained where the right hand side, defined as the nitride capacity  $C_{N^{3-}}$ , can experimentally be determined.

Nitrogen dissolution in acidic slags is more complicated as nitrogen has been observed<sup>22,23</sup> and is considered<sup>21</sup> to be combined to the acidic oxide anions. Fruehan<sup>24</sup> has suggested nitrogen dissolution in acidic slags to be governed by the reaction:

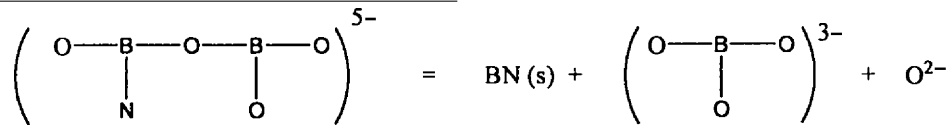


where  $O^-$  and  $N^-$  are non-bridging oxygen and non-bridging nitrogen, respectively. The equilibrium constant of Reaction (17) is:

$$K_{17} = \frac{a_{N^-} \times a_{O_2^{2-}}^{1/2} \times P_{O_2}^{3/4}}{P_{N_2}^{1/2} \times a_{O^-}^2} = \frac{\gamma_{N^-} \times (\%N) \times a_{O_2^{2-}}^{1/2} \times P_{O_2}^{3/4}}{P_{N_2}^{1/2} \times a_{O^-}^2} \quad (3)$$

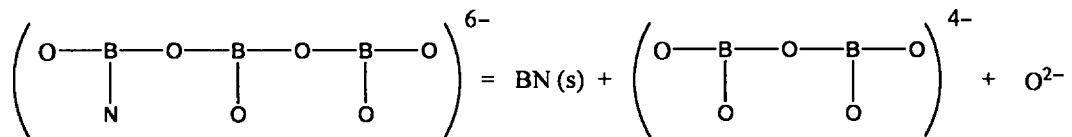
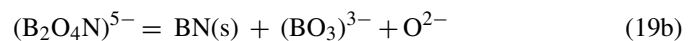
Rearranging Eq. (3), the relation

$$C_{N^-} = K_{17} \times \frac{a_{O^-}^2}{\gamma_{N^-} \times a_{O_2^{2-}}^{1/2}} = (\%N) \times \frac{P_{O_2}^{3/4}}{P_{N_2}^{1/2}} \quad (4)$$



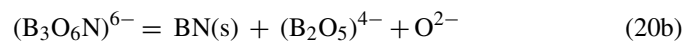
(19a)

which in condensed form can be written as:



(20a)

which in condensed form can be written as:

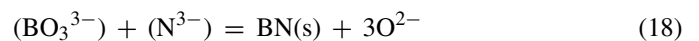


is obtained where the right hand side, defined as the incorporated nitride capacity,  $C_{N^-}$ , can experimentally be determined. The right hand side of Eqs. (2) and (4) in the definitions of  $C_{N^{3-}}$ , referred to as free nitride capacity, and  $C_{N^-}$  are identical. Nitride capacity, whether defined by Eq. (2) or by Eq. (4) is seen to depend on the composition of the oxide melt at a given temperature. Considering  $a_{O^{2-}}$  to be a measure of the basicity of the slag,  $C_{N^{3-}}$  is seen to increase while  $C_{N^-}$  is seen to decrease with increase in slag basicity. Accordingly, nitride capacity defined as:

$$C_N = (\%N) \times \frac{P_{O_2}^{3/4}}{P_{N_2}^{1/2}} \quad (5)$$

is expected to decrease with increase in slag basicity in acidic slags and to increase with increase in slag basicity in basic slags. Nitride capacities of several oxide melts have been measured. The results are not always in accord with the above stated expectations. It should be definite, however, that the nitride capacity of a slag of a given composition be a constant at a given temperature.

h-BN is soluble in oxide melts and its solubility depends on composition. Wakasugi<sup>25</sup> determined solubility of h-BN in several  $\text{B}_2\text{O}_3$ -basic oxide binary systems and found h-BN solubility to increase with increase in the concentration of the basic oxide up to 0.1–0.2 mole fraction of the basic oxide and to decrease with further increase in the concentration of the basic oxide. For a given slag composition h-BN solubility should be a constant at a given temperature. Nitrogen dissolved in  $\text{B}_2\text{O}_3$  containing oxide melts may result in formation of h-BN if the solubility product of h-BN is exceeded. What the reactions for dissolution of h-BN in oxide melts or for formation of h-BN from oxide melts are not known. One possible reaction for formation of h-BN from nitrogen and  $\text{B}_2\text{O}_3$  containing oxide melts may be:



If, as suggested by Martinez and Sano,<sup>21</sup> and Min and Fruehan<sup>24</sup>; nitrogen is considered to be incorporated into the borate anions, reactions like (19b) and (20b) may result in formation of h-BN.

Two liquids,  $a'$  and  $b'$  exist in the system at 1500 °C for 5, 10, 20 and 30%  $\text{CaCO}_3$  additions while a single calcium borate exists in the system at 1500 °C for 40 and 50%  $\text{CaCO}_3$  additions as stated above (Fig. 1). In the two liquids region thermodynamic properties of the calcium borate represented by  $a'$  in Fig. 1 are independent of composition and as such nitride capacity, activities of several species etc. do not change with change in the quantity of  $\text{CaCO}_3$  added. Driving force of Reactions (18), (19b) and (20b) will accordingly be independent of composition. If a certain amount of h-BN is considered to crystallize in a given

time from a certain quantity of calcium borate ( $a'$ ) phase, the total quantity of h-BN crystallizing in the system should increase with increase in the quantity of the calcium borate phase. As  $\text{CaCO}_3$  added to the reaction mix increases the quantity of calcium borate ( $a'$ ) phase, the quantity of h-BN forming in the system in a given time is expected to increase with  $\text{CaCO}_3$  addition. That the increase in the quantity of h-BN with the increase in the quantity of  $\text{CaCO}_3$  added continues up to 10% addition may be taken as an indication that crystallization of h-BN from the calcium borate phase is not the only mechanism of h-BN formation and that some h-BN forms by reaction of gaseous  $\text{B}_2\text{O}_3$  with  $\text{N}_2(\text{g})$  on carbon,<sup>6</sup> the rate of which was explained before to decrease with increase in the quantity of  $\text{CaCO}_3$  added.

For 40 and 50%  $\text{CaCO}_3$  additions there is a single calcium borate melt in the system, the composition of which is to the right of  $a'$ . Thermodynamic properties like the nitride capacity, activities of several species, etc. of this calcium borate phase depend on composition. Equilibrium vapor pressure of  $\text{B}_2\text{O}_3$  in the system will be less than that of pure  $\text{B}_2\text{O}_3(\text{l})$  when the rate of formation of h-BN by reactions of gaseous  $\text{B}_2\text{O}_3$  with  $\text{N}_2(\text{g})$  on carbon should be less than that for plain ( $\text{B}_2\text{O}_3 + \text{C}$ ) mixtures. That more h-BN forms for 40% and 50%  $\text{CaCO}_3$  additions compared to plain ( $\text{B}_2\text{O}_3 + \text{C}$ ) mixtures may be taken as an indication that some h-BN forms by crystallization from the borate melt. With increase in the quantity of  $\text{CaCO}_3$  added, the basicity of the borate melt will increase which is expected to decrease the activity of the borate anions making Reactions (18), (19b) and (20b) less favorable.

Reactions (18), (19b) and (20b) do not use C for formation of h-BN. C is nevertheless probably necessary, however, as dissolution of nitrogen in the calcium borate melt in accord with Reactions (16) and (17) and also formation of h-BN with Reactions (18), (19b) and (20b) are favored by low  $\text{O}_2$  pressures which is provided by C.

Quantity of h-BN forming in a given reaction depends on the quantity of C in the reaction mix as C is the limiting reactant for the overall reaction  $\text{B}_2\text{O}_3 + 3\text{C} + \text{N}_2 = 2\text{BN} + 3\text{CO}$  (Reaction (1)). Quantity of carbon in the ( $\text{B}_2\text{O}_3 + \text{C}$ ) mixtures and ( $\text{B}_2\text{O}_3 + \text{C} + \text{CaCO}_3$ ) mixtures were the same. The same amount of h-BN is therefore expected to form in different runs if the carbon loss from the system does not vary from run to run. As stated before, the quantity of h-BN forming in the mixtures containing  $\text{CaCO}_3$  as additive were significantly larger than those containing no  $\text{CaCO}_3$ . This may be taken as an indication that some h-BN forms according to Reaction (1) which uses C and some according to Reactions (18), (19b) and (20b) which do not consume C, on the conditions that C loss from the system does not change with addition of  $\text{CaCO}_3$ .

Bartnitskaya et al.<sup>11,12</sup> found in their study on h-BN formation from boric acid + carbamide mixtures that more C remains present at a given temperature while more h-BN forms when  $\text{Li}_2\text{CO}_3$  is added to the reaction mechanism. This result may also be taken as an indication that some h-BN forms without use of C when  $\text{Li}_2\text{CO}_3$  is added to the reaction mixture when a lithium borate is expected to form.

#### 4. Conclusions

Effect of  $\text{CaCO}_3$  addition on carbothermic formation of h-BN was investigated by adding  $\text{CaCO}_3$  to the activated carbon-boric oxide mixture in various amounts ranging in 5–50 wt.% of the initial mixture. It was seen from the experiments conducted for 30 min at  $1500^\circ\text{C}$  that amount of h-BN in the reaction products increases up to 10 wt.%  $\text{CaCO}_3$  addition and then decreases. The variation in the amount of  $\text{B}_4\text{C}$  presented an almost opposite behavior. Thus, 10 wt.%  $\text{CaCO}_3$  addition was found to be the optimum value and further experiments were performed with this amount of addition for longer durations at  $1500^\circ\text{C}$ . It was determined by analyzing the products of the experiments conducted with 10 wt.%  $\text{CaCO}_3$  addition by XRD, SEM, BET and quantitative chemical methods that the yield and grain size of formed h-BN was higher and specific surface area was lower than the products obtained from plain mixtures. Also, the amount of  $\text{B}_4\text{C}$  formed in the products decreased considerably by the addition of 10 wt.%  $\text{CaCO}_3$ . The role of  $\text{CaCO}_3$  at this amount was suggested to be that of increasing the porosity of the pellets thereby easing the access of  $\text{N}_2(\text{g})$  into the pellet. The  $\text{N}_2(\text{g})$  penetration increases the rate of h-BN formation by Reaction (1).

$\text{CaCO}_3$  addition into  $\text{B}_2\text{O}_3$ –C mixtures is suggested to result in an additional mechanism by which h-BN forms. CaO originating from calcination of  $\text{CaCO}_3$  forms a calcium borate liquid in which  $\text{N}_2(\text{g})$  dissolves as  $\text{N}^{3-}$  or as  $\text{N}^-$  depending on the basicity of the calcium borate phase. The dissolved nitrogen then reacts with  $(\text{BO}_3)^{3-}$  in basic melts or more complex anions like  $(\text{B}_2\text{O}_5)^{4-}$  in acidic melts to form h-BN.

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