The effects and roles of CaCO₃ and CaO in the carbothermic formation of h-BN

Ali Arda Özkenter, Hasan Erdem Çamurlu and Naci Sevinç

Abstract

The effects of CaCO₃ and CaO on the carbothermic formation of h-BN were investigated by subjecting plain, CaCO₃-added, and CaO-added B₂O₃-activated C mixtures to N₂ gas at 1500 °C. Both additions were found to result in the formation of more BN with larger particle sizes in a given time. It was shown that BN forms in the absence of carbon in CaO-B₂O₃ melts but not in a plain B₂O₃ melt subjected to N₂ by a mechanism involving nitrogen dissolution in and formation of BN from the melt. This mechanism, in addition to the reaction of B₂O₃ with C and N₂, results in more BN formation in CaCO₃-added and CaO-added B₂O₃-activated C mixtures subjected to N₂. BN particles were also found to grow in carbon-free CaO-B₂O₃ melts not only in the presence of N₂ when additional BN forms but also in the absence of N₂ (under Ar) when no additional BN forms.

Key words: Grain growth, Powders-chemical preparation, Nitrides, Alkaline earth oxides, Boron nitride.

Introduction

Hexagonal boron nitride (h-BN) is a white non-toxic refractory compound which has a large application area in industry due to its excellent solid lubricity, high thermal conductivity, good electrical insulation properties, low density, high thermal shock resistance, low thermal expansion, inertness to and non-wettability by many metallic melts such as Al, Cu, Fe, Zn and non-metallic melts such as B, Si and glasses [1-6].

There are principally 3 methods for the production of h-BN. One of these methods is based on the direct reaction of boric oxide and ammonia [1]. Another method is through the reaction of boric acid with urea or melamine and ammonia [3, 7]. The third method, which is the concern of this study, is the carbothermic reduction of boron oxide in the presence of N₂(g) [4, 5, 8, 9] when h-BN forms according to the overall reaction:

\[ \text{B}_2\text{O}_3(l) + 3\text{C}(s) + \text{N}_2(g) = 2\text{BN}(s) + 3\text{CO}(g) \]  \hspace{1cm} (1)

Studies done on the mechanism of carbothermic formation of h-BN [10-13] indicate that reaction (1) proceeds through intermediate species. Bartnitskaya et al. [10] concluded that B₂O₃ first gets reduced to B by carbon and then B reacts with N₂ (g) to form BN while Joon and Jha [11] considered h-BN formation to proceed through gaseous BO. Pikalov [12] suggested h-BN formation proceeded in two consecutive steps with B₄C forming by the reaction of B₂O₃ and C in the first step and h-BN forming by the reaction of B₄C with B₂O₃ and N₂(g) in the second step. Aydoğdu and Sevinç [8] subjected pellets prepared from B₂O₃-activated C mixtures to N₂ gas and found B₄C in addition to unreacted B₂O₃, unreacted C and BN formed, to exist in the reaction products of their experiments in which h-BN formation was not complete. They concluded that carbothermic h-BN formation proceeds by the evaporation of B₂O₃(l) and the reaction of B₂O₃(g) with N₂(g) and C(s) and/or B₄C(s). The role of B₄C in the carbothermic formation of h-BN was studied by Çamurlu et al. [9] who concluded B₄C not to be a necessary intermediate species and that it forms in regions where the N₂ pressure is too low due to insufficient penetration of N₂(g) into the B₂O₃(l)-C(s) mixture and that it retards h-BN formation. Certain additives have been found to favorably affect h-BN formation. Bartnitskaya and co-workers [13, 14] found Li₂CO₃ and LiOH additions into B₂O₃-C or boric acid-carbamide mixtures subjected to nitrogen gas or ammonia gas to increase the amount and the crystallinity of h-BN forming. They suggested h-BN crystallized from the resulting lithium borate melt without giving a specific mechanism. Çamurlu et al. [15, 16] investigated the effects of the addition of MgO, BaCO₃ and CaCO₃, separately, into B₂O₃-C mixtures subjected to N₂ gas and found that these additives increased the amount and the particle size of the h-BN forming. In their study of the effect of CaCO₃ on carbothermic formation of h-BN, B₂O₃-C mixtures containing 0-50 wt % CaCO₃ were subjected to N₂ (g) at 1500 °C for 0.5-3 h [15]. It was seen from the experiments conducted for 30 minutes at 1500 °C that the amount of h-BN in the reaction products increased up to 10 wt.% CaCO₃ addition and then decreased...
while the amount of $\text{B}_2\text{C}$ presented an almost opposite behavior and 10 wt.% $\text{CaCO}_3$ addition was decided to be the optimum amount. They observed the products of the experiments conducted with $\text{CaCO}_3$ additions to be more porous than those of the plain mixtures and suggested increased porosity of the pellet, probably resulting from calcination of the added $\text{CaCO}_3$, to increase the rate of $\text{h-BN}$ formation by reaction (1) by easing the access of $\text{N}_2(\text{g})$ into the pellet. They also proposed that an additional $\text{BN}$ formation mechanism, to be referred to as the ionic mechanism, involving nitrogen dissolution in and $\text{BN}$ formation from the calcium borate melt may be operative in the experiments conducted with $\text{CaCO}_3$ additions. This study is a continuation of the study of Çamurlu et al. [15] and was undertaken with the objective of gaining further information on the role of $\text{CaO}$ or $\text{CaCO}_3$ in the carbothermic formation of $\text{BN}$, in general, and on the formation of $\text{h-BN}$ by the ionic mechanism, in particular.

Experimental

Materials and method

Pellets prepared from $\text{B}_2\text{O}_3$-$\text{C}$ (Exp. #1-3), $\text{B}_2\text{O}_3$-$\text{C}$-$\text{CaCO}_3$ (Exp. #4, 5), $\text{B}_2\text{O}_3$-$\text{C}$-$\text{CaO}$ (Exp. #6, 7), and carbon-free $\text{B}_2\text{O}_3$-$\text{CaO}$ (Exp. #8-10), $\text{B}_2\text{O}_3$-$\text{CaO}$-$\text{BN}$ (Exp. #11-13), $\text{B}_2\text{O}_3$-$\text{BN}$ (Exp. #14), $\text{BN}$ (Exp. #15) reaction ingredients 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 quantity of $\text{B}_2\text{O}_3$ in the preparation of $\text{B}_2\text{O}_3$ and $\text{C}$ containing pellets was 100% in excess of the amount calculated in accord with the stoichiometry of reaction (1) to account for loss due to vaporization. The pellet contained in the boron nitride coated graphite boat was placed into the cold end of the furnace heated to 1500 °C while nitrogen was flowing through the system at a rate of 1 ml.minute⁻¹. After ten minutes waiting the graphite boat with its contents was slowly pushed into the hot zone of the furnace by an aluminia rod and the nitrogen gas flow rate was decreased to 200 ml.minute⁻¹. Time was taken as zero at the point when the system reached a steady state at 1500 °C. After keeping the graphite boat with its contents in the hot zone of the furnace under a $\text{N}_2$ gas flow at the rate of 200 ml.minute⁻¹ for a predetermined time it was quickly pulled to the gas outlet end and removed from the furnace. Most of the experiments were repeated at least once more and reproducibility was found to be very good.

Analyses

Reaction products were weighed and subjected to X-ray diffraction, microscopic examination and chemical analysis studies. X-ray analyses were done by a Rigaku Multiflex powder X-ray diffractometer with Cu-Kα radiation in the 2θ range of 20° to 80° with 0.02° steps at a rate of 2°.minute⁻¹. Software including qualitative analysis program was utilized during operations performed on XRD patterns. Morphological examinations and particle size calculations were conducted with the aid of a Jeol JSM 6400 scanning electron microscope (SEM). Particle size distributions of $\text{BN}$ powders were determined by a Malvern Zetasizer Nano-ZS unit. The quantities of the constituents of the reaction products were determined by and pure $\text{BN}$ was obtained at the end of a quantitative chemical method consisting of successive leaching, oxidation and leaching steps developed by Aydoğdu and Sevinç [8] and used also with slight modifications in subsequent studies [9, 15, 16]. In this method the reaction product is first leached with 1:1 HCl which removes unreacted $\text{B}_2\text{O}_3$, calcium borate and the ash of the carbon that has reacted. The residue of leaching is oxidized at 800 °C which results in burning of the unreacted carbon and conversion of $\text{B}_2\text{C}$ into $\text{B}_2\text{O}_3$. The product of oxidation is then leached with 1:1 HCl which removes $\text{B}_2\text{O}_3$ and the ash of the carbon burnt leaving behind only $\text{BN}$. The quantities of the constituents of the reaction products are then determined by simple mass balances.

Results

Effect of $\text{CaCO}_3$ and $\text{CaO}$ on $\text{hBN}$ yield

Pellets of weight 2.5 g prepared from $\text{B}_2\text{O}_3$-$\text{C}$ mixtures (0.514 g active C and 1.986 g $\text{B}_2\text{O}_3$) were
subjected to N\textsubscript{2} gas for 2, 3 and 4 hours at the beginning of the study. h-BN formation was found to be complete (when no unreacted C and B\textsubscript{4}C was found to exist in the reaction product) in 4 h in these experiments and the amounts of h-BN formed were found to be 0.37 g in 2 h, 0.47 g in 3 hours and 0.49 g in 4 hours (Exp. 1-3). Çamurlu et al. [15] found a CaCO\textsubscript{3} addition to favorably affect BN formation and found the optimum CaCO\textsubscript{3} weight to be 10\% of the weight of the B\textsubscript{2}O\textsubscript{3}-C mixture. In view of this result, pellets prepared from 0.514 g of active C, 1.986 g of B\textsubscript{2}O\textsubscript{3} and 0.25 g CaCO\textsubscript{3} (or 0.14 g CaO) were subjected to N\textsubscript{2}(g) for 2 and 3 hours. Reaction was found to be complete in 3 hours in these experiments with formation of 0.59 g and 0.56 g BN, respectively, in the CaCO\textsubscript{3}-added and CaO-added pellets (Exp. #5 and #7, respectively). The amounts of h-BN which have formed in 2 hours were 0.41 g and 0.43 g, respectively, in the CaO-added and CaCO\textsubscript{3}-added pellets (Exp. #6 and #4 respectively). These results are in accord with the results of Çamurlu et al. [15] in that CaCO\textsubscript{3} additions into B\textsubscript{2}O\textsubscript{3}-C mixtures subjected to N\textsubscript{2} gas increase the amount of BN forming. The results indicate CaO additions to favorably affect BN formation also; the beneficial effect of CaO is seen to be less than that of CaCO\textsubscript{3}. The result that CaCO\textsubscript{3} is more effective than CaO in increasing the amount of BN forming may be related to the higher porosity of the CaCO\textsubscript{3}-added reaction aggregate as was suggested by Çamurlu et al. [15]. This point will be discussed further below.

**Suggested mechanism and results of CaO-B\textsubscript{2}O\textsubscript{3} mixture experiments**

As stated above, Çamurlu et al. [15] proposed that a second mechanism of BN formation may be operative in the experiments conducted with CaCO\textsubscript{3} additions. In this mechanism, N\textsubscript{2}(g) is considered to dissolve in the calcium borate melt forming from B\textsubscript{2}O\textsubscript{3} and CaO originating from calcination of CaCO\textsubscript{3} and BN forming by reaction of borate and nitride ions existing in the melt. Nitrogen dissolution is governed by reaction (2):

\[
\frac{1}{2}N_{2}(g) + 3/2O^{2-} = N^{3-} + 3/4 O_{2}(g) \quad (2)
\]

in basic slags [17] and by reaction (3):

\[
1/2N_{2}(g) + 2O^{'} = N^{'} + 1/2O^{2-} + 3/4 O_{2}(g) \quad (3)
\]

with nitrogen considered to be incorporated to the complex borate ions in the form of (B\textsubscript{2}O\textsubscript{3}N\textsuperscript{5-}), (B\textsubscript{3}O\textsubscript{4}N\textsuperscript{6-}) etc. in acidic slags [17, 18]. The composition and hence basicity of the calcium borate melt forming in CaO-added or CaCO\textsubscript{3}-added B\textsubscript{2}O\textsubscript{3}-C mixtures during carbothermic formation of BN is variable due to the loss of B\textsubscript{2}O\textsubscript{3} from the system by reaction (1) and also by evaporation. BN may form from the calcium borate melt by a reaction such as:

\[
(BO_{3})^{3-} + (N^{5-}) = BN(s) + 3O^{2-} \quad (4)
\]

if the melt is basic and by reactions such as:

\[
(B_{2}O_{4}N)^{5-} = BN(s) + (BO_{3})^{3-} + O^{2-} \quad (5)
\]

\[
(B_{3}O_{6}N)^{6-} = BN(s) + (BO_{3})^{4-} + O^{2-} \quad (6)
\]

if the melt is acidic. There is no C in formation of BN by reactions (2) and (4) or reactions (3) and (5) and/or (6) taking place successively. BN formation should therefore be possible in C free CaO-B\textsubscript{2}O\textsubscript{3} mixtures subjected to N\textsubscript{2} gas if the mechanism outlined above is operative. With this understanding CaO-B\textsubscript{2}O\textsubscript{3} mixtures contained in BN-coated graphite boats were subjected to N\textsubscript{2} gas under conditions the same as those used in the carbothermic BN formation experiments. Dissolution of nitrogen in oxide melts by reactions (2) and (3) is seen to depend on the oxygen pressure. The oxygen pressure is low in carbothermic BN formation experiments due to the presence of C in the system. To achieve a comparable oxygen pressure in the experiments where CaO-B\textsubscript{2}O\textsubscript{3} mixtures are subjected to N\textsubscript{2} gas, active carbon contained in a second graphite boat was placed on the gas inlet side a few centimetres away from the BN coated graphite boat containing the CaO-B\textsubscript{2}O\textsubscript{3} mixture.

The first experiment on this topic (Exp. #8) was conducted with a 4 g pellet prepared from a CaO-B\textsubscript{2}O\textsubscript{3} mixture having a weight ratio of CaO to B\textsubscript{2}O\textsubscript{3} equal to that used in the carbothermic BN formation experiments conducted with CaO-added B\textsubscript{2}O\textsubscript{3}-C mixtures (0.14/1.986). The original composition of the CaO-B\textsubscript{2}O\textsubscript{3} sample was 6.58 wt\% B\textsubscript{2}O\textsubscript{3} and is in the two liquids, a’ + b’, region at 1500 °C on the B\textsubscript{2}O\textsubscript{3}-CaO phase diagram shown in Fig. 1 [19]. The two liquids in this CaO-B\textsubscript{2}O\textsubscript{3} composition are pure B\textsubscript{2}O\textsubscript{3} and calcium borate. No BN was found to have formed from the XRD analysis in this experiment.

B\textsubscript{2}O\textsubscript{3} melts completely covering and hence preventing contacting of N\textsubscript{2} gas with the calcium borate melt could be the reason for no formation of BN in this experiment.
The next experiment (Exp. #9) to be conducted was decided to be with a B₂O₃-CaO mixture having one liquid phase at 1500 °C and the composition chosen was 25 wt % CaO. The experiment described above was conducted with a pellet prepared from 3 g B₂O₃ and 1 g CaO. No BN was found to have formed in the reaction products. Nucleation was considered to be a barrier to BN formation and the experiment was repeated under the same conditions but the reaction mix was furnace cooled (Exp. #10) under N₂ gas flow at the rate of 5 K.minute⁻¹. The result was no different and no BN has formed.

**Formation hBN without carbon from B₂O₃-CaO-BN mixtures**

It was considered that nucleation barrier could be avoided by the presence of BN in the B₂O₃-CaO system and an experiment (Exp. #11) was done with a pellet prepared from 3 g B₂O₃, 1 g CaO and 0.25 g BN; BN used was taken from the products of the carbothermic BN formation experiments conducted with CaCO₃-added B₂O₃-C mixtures. The pellet was kept for 3 hours at 1500 °C under flowing N₂ gas and was then quickly removed from the furnace as usual. After removal of the calcium borate from the reaction product by 1:1 HCl leaching the weight of the solid remaining undissolved, BN, was determined as 0.30 g. As with most of the experiments reported above, this experiment was repeated and the weight of BN in the reaction product was determined as 0.31 g. A similar experiment (Exp. #12) was then done with again a pellet prepared from 3 g B₂O₃, 1 g CaO and 0.25 g BN but the BN used in this experiment was obtained from the products of BN formation experiments conducted with plain B₂O₃-C mixtures. The weight of BN in the reaction product was determined as 0.32 g in this experiment. So, 0.05-0.07 g of BN has formed in these experiments which clearly indicate that there is BN formation in calcium borate melts subjected to N₂ gas without the use of carbon by ionic reactions like those suggested above. The results indicate also that there is a nucleation barrier to BN formation by the ionic mechanism and that the presence of BN in the calcium borate is necessary for the mechanism to be operative. This mechanism should be operative in the formation of BN by the carbothermic method in which B₂O₃-CaO or B₂O₃-CaCO₃ mixtures are subjected to N₂ gas as BN forming by the overall reaction (1) can act as nucleation site for BN formation by the ionic mechanism.

An experiment was later done in which a pellet prepared from 4 g B₂O₃-0.25 g BN was subjected to N₂ gas for 3 hours (Exp. #14). After 1:1 HCl leaching of the product, the weight of the solid remaining undissolved was determined to be 0.24 g (Some loss of BN should not be unexpected considering that the reaction product is subjected to processes like leaching, filtration etc. There may be some dissolution of BN also in the initially nitrogen-free B₂O₃ melt.) indicating that there is no BN formation in liquid B₂O₃ by the ionic mechanism.

In addition to the chemical analysis and purification method consisting of successive leaching, oxidation and leaching processes, reaction products were subjected to SEM and XRD analyses in the as-removed from the furnace condition as well as after purification. The SEM micrographs of BN obtained in 3 h from the experiments (Exp. #3, 5, 7) conducted with plain B₂O₃-C, B₂O₃-CaCO₃ and B₂O₃-CaO pellets, to be referred to as BN(plain), BN(CaCO₃) and BN(CaO), are shown in Figures 2a, 2b and 2c, respectively. The BN particles are seen to have a plate-like morphology with BN(CaCO₃) and BN(CaO) particles significantly larger than BN(plain) particles. The average particle sizes of BN(plain), BN(CaCO₃) and BN(CaO) particles were calculated as 0.49 ± 0.11 µm, 1.19 ± 0.37 µm and 1.30 ± 0.45 µm, respectively. Average particle size values were obtained by measuring the size of at least 50 grains, and by calculating their average and standard deviation. CaCO₃ addition into B₂O₃-C mixtures was found to increase the particle size of h-BN in the carbothermic formation [15, 16]; CaO is seen to be slightly more effective than CaCO₃ in increasing the particle size of BN.

![SEM micrographs of BN](image)

**Fig. 2.** SEM micrographs of BN (a) obtained from plain B₂O₃-C mixture; (b) obtained from CaCO₃-added B₂O₃-C mixture; (c) obtained from CaO-added B₂O₃-C mixture; (d) obtained from plain B₂O₃-C mixture and (e) obtained from CaCO₃-added B₂O₃-C mixture contained in a C-free CaO-B₂O₃ melt under N₂; (f) obtained from CaCO₃-added B₂O₃-C mixture contained in a C-free CaO-B₂O₃ melt under Ar.
Growth of hBN particles in C-free CaO-B₂O₃-hBN mixtures in N₂ atmosphere

The most important objective of this study was to find whether BN forms by the ionic mechanism in C-free CaO-B₂O₃ melts subjected to N₂ gas. BN formation was found not to take place in a plain C-free CaO-B₂O₃ melt but to take place in a BN-added C-free CaO-B₂O₃ melt as stated above. In order to investigate the effect of CaO on the growth behavior of hBN, the hBN particles obtained in the previous experiments conducted with plain and CaCO₃ added mixtures, were mixed with B₂O₃ and CaO and were subjected to a N₂ atmosphere for 3 h at 1500 °C. The SEM micrographs of BN obtained in the experiments in which pellets prepared from 3 g B₂O₃, 1 g CaO and 0.25 g BN(plain) (Exp. #12) and BN(CaCO₃) (Exp. #11) were reacted, are shown in Figs. 2d and 2e, respectively. Comparison of Fig. 2a with 2d and Fig. 2b with 2e shows that the plate-like morphology of BN particles have been preserved and the average particle sizes have significantly increased in both of these experiments with the calculated average particle size of BN(plain) increasing to 1.58 ± 1.04 µm from 0.49 ± 0.11 µm and BN(CaCO₃) increasing to 2.37 ± 0.61 µm from 1.19 ± 0.37 µm.

In addition to visual particle size measurements on SEM micrographs, the BN powders obtained were subjected to particle size distribution analysis, results of which are presented in Fig. 3 and Table 1. The particle sizes of BN formed from B₂O₃-C-CaCO₃ mixtures (Exp. #5) were seen to be considerably larger than that of BN formed from plain B₂O₃-C mixture

Table 1. Summary of experiments

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<th>Exp. #</th>
<th>B₂O₃</th>
<th>C</th>
<th>CaO</th>
<th>CaCO₃</th>
<th>BN</th>
<th>Gas Type</th>
<th>Duration of Experiment (h)</th>
<th>Amount of BN (g) in products</th>
<th>Av. Particle Size (from SEM measurements (µm))</th>
<th>Av. Particle Size (from part. size dist. meas. (nm))</th>
<th>Av. Crystallite thickness, Lc (nm)</th>
<th>Relative Intensity of (002) peak</th>
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<td>0.24, 0.53 ± 0.15</td>
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</table>

*Cooled in furnace at a rate of 5 °C/min.
(Exp. #2). When BN which was obtained from these experiments was mixed with CaO and reacted again in a N$_2$ atmosphere at 1500 °C, a significant increase in the particle size was observed (Exp. #11 and 12). These results are in parallel with those inferred from SEM observations. Average particle size values determined by particle size distribution analysis were smaller than those calculated from SEM observations, as presented in Table 1. This may be due to the fact that in the SEM observations the diameters of the BN plates which could be visualized were measured and averaged, however in the particle size distribution analyses the thickness of BN plates may have also been included. The particle size data obtained from the SEM observations and the particle size distribution measurements show that particles having larger initial sizes grow to larger final sizes which should be expected.

**Growth of hBN particles in C-free CaO-B$_2$O$_3$-hBN mixtures in an Ar atmosphere**

The formation of BN by the ionic mechanism necessitates presence of BN in the system, the newly forming BN should form on already existing BN particles with a consequent increase in particle size. So an increase in the particle size of BN particles in these experiments should be an expected result. 0.05-0.07 g of newly forming BN may not be sufficient for the growth seen in Figures 2d and 2e, however, in which case another growth mechanism should also be operative. To check whether another growth mechanism exists, an experiment (Exp. #13) was done by subjecting a pellet prepared from 3 g B$_2$O$_3$, 1 g CaO and 0.25 g BN(CaCO$_3$) to Ar gas for 3 hours. The reaction aggregate was subjected to 1:1 HCl leaching for removal of calcium borate and 0.24 g BN was left after filtration and drying. Comparison of the SEM micrograph of this BN, shown in Figure 2f with those in Figure 2b clearly shows that the particle size of BN subjected to Ar gas in calcium borate melt has increased (from 1.19 ± 0.37 µm to 1.94 ± 0.54 µm) indicating that BN particles grow in a calcium borate melt even when there is no new BN forming.

0.25 g of BN(plain) contained in a BN-coated graphite boat was then subjected to N$_2$ gas for 3 h (Exp. #15) to find whether growth will occur under these conditions. An insignificant growth resulting in an increase of the average particle size to 0.53 ± 0.15 µm from 0.49 ± 0.11 µm was found in this experiment. A slightly larger increase in the particle size, from 0.49 ± 0.11 µm to 0.65 ± 0.16 µm, was found when 0.25 g BN(plain) mixed with 4 g of B$_2$O$_3$ was subjected to N$_2$ gas for 3 h (Exp. #14). These results indicate that a calcium borate melt is quite effective in the growth of BN particles. As the growth of BN particles in a calcium borate melt is possible even when there is no new BN forming, the growth may be suggested to take place by dissolution of perhaps small BN particles in the melt followed by crystallization on larger particles.

**XRD analyses and crystal thickness calculations**

The XRD patterns of the products of the experiments conducted with plain B$_2$O$_3$-C, B$_2$O$_3$-CaCO$_3$, B$_2$O$_3$-CaO, B$_2$O$_3$-CaO-BN(plain), B$_2$O$_3$-CaO-BN(CaCO$_3$) mixtures subjected to N$_2$ gas and B$_2$O$_3$-CaO-BN(CaCO$_3$) mixture subjected to Ar gas for 3 h are given in Figures 4a, 4b, 4c, 4d, 4e and 4f, respectively (Exp. #2, 5, 7, 11, 12, 13). As all of these products have been subjected to the chemical analysis and purification method, they are expected to contain no species other than BN; the XRD patterns given in Fig. 3 are in accord with this expectation.

Intensity values of the peak in the XRD patterns given in Fig. 4 pertaining to the (002) plane of h-BN were calibrated by assigning the highest peak (Exp. #12 or Fig. 4 (e)) to the value of 100. The (002) peaks of all of the samples given in Fig. 4 were calibrated relative to the (002) peak of h-BN obtained in Exp. #12. Relative intensity values of h-BN powders obtained in different experimental conditions are presented in Table 1. The relative intensities of the products of the experiments conducted with B$_2$O$_3$-CaO-BN(plain), B$_2$O$_3$-CaO-BN(CaCO$_3$) mixtures are highest, with the relative intensity values of 86 and 100, respectively. The particle sizes of BN obtained at the end of these two experiments are larger than those obtained in the other experiments as seen in SEM micrographs.

Average crystal thickness values of the h-BN formed in the c-axis direction, Lc, were calculated by the Scherrer formula [20, 21], in order to investigate the effect of CaCO$_3$ or CaO additions on the growth of h-BN crystallites. Lc is defined as the mean height of a pack of parallel and crystallographically connected hexagonal layers. It was reported that comparatively rough measurements can be done in the range of 0-500 Å with the Scherrer formula [20]. In this

![Fig. 4. XRD patterns of BN (a) obtained from plain B$_2$O$_3$-C mixture; (b) obtained from CaCO$_3$-added B$_2$O$_3$-C mixture; (c) obtained from CaO-added B$_2$O$_3$-C mixture, (d) obtained from plain B$_2$O$_3$-C mixture and (e) obtained from CaCO$_3$-added B$_2$O$_3$-C mixture contained in a C-free CaO-B$_2$O$_3$ melt under N$_2$; (f) obtained from CaCO$_3$-added B$_2$O$_3$-C mixture contained in a C-free CaO-B$_2$O$_3$ melt under Ar.](image-url)
calculation, full width at half maximum (FWHM) values of the peaks pertaining to the (002) planes of h-BN ($2\theta = 26.7^\circ$), presented on the XRD patterns given in Fig. 4 were utilized. The calculated Lc values of the h-BN formed in the experiments conducted for 3 h at 1500 °C with plain, CaCO$_3$ added and CaO added B$_2$O$_3$ + C mixtures, and with B$_2$O$_3$ + BN + CaO mixtures are presented in Table 1. It can be seen that as a result of a CaCO$_3$ or CaO addition to the plain mixture, the average crystal thickness of the h-BN powder formed increases from 15.74 nm (Exp. #2) to 22.69 nm (Exp. #5) and 22.03 nm (Exp. #7), respectively. When BN(plain) and BN(CaCO$_3$) powders, obtained from Exp. #2 and Exp. #5 were mixed with B$_2$O$_3$ and CaO and kept at 1500 °C for 3 h in N$_2$, the average crystallite thickness values were seen to increase from 15.74 to 22.78 nm (Exp. #11) and 22.69 to 30.11 nm (Exp. #12), respectively. The average crystallite thickness values, calculated by the Scherrer formula from XRD data are in parallel with the average particle size data obtained from SEM measurements and particle size distribution analyses. These results indicate quantitatively that CaO and CaCO$_3$ are effective in increasing the crystallite size and particle size of h-BN.

**Discussion**

The results presented above indicate that the carbothermic formation of h-BN proceeds by two different mechanisms, by the overall reaction (1) and by the ionic mechanism, when CaO or CaCO$_3$ containing B$_2$O$_3$-C mixtures are subjected to N$_2$ gas. The particle size of BN forming by the overall reaction (1) is small and the particle size increases by the ionic BN formation mechanism and an additional growth mechanism. There is some C loss from the system due to reaction of B$_2$O$_3$ with C, with formation of gases such as BO, B etc which, referred to as chemical C loss, increases with time [8]. The rate of formation of BN by the overall reaction (1) appears to be related to the access of N$_2$ into the reaction aggregate and to depend on the porosity of the aggregate. The rate of formation of BN by the overall reaction (1) is expected to be higher in CaCO$_3$-addition B$_2$O$_3$-C mixtures, in view of their higher porosity, than that in CaO-added B$_2$O$_3$-C mixtures which should result in more BN formation of a small particle size in CaCO$_3$ added B$_2$O$_3$-C mixtures by the overall reaction (1) in a given time before carbon is completely used. If the amounts of BN forming by the ionic mechanism are considered to be the same in both of the mixtures, the higher amount and smaller particle size of BN which form in CaCO$_3$-added B$_2$O$_3$-C mixtures may be attributed to more BN formation by the overall reaction (1) in these mixtures compared to those in CaO-added B$_2$O$_3$-C mixtures.

**Conclusions**

The effects of CaCO$_3$ and CaO on the carbothermic formation of h-BN were studied by subjecting B$_2$O$_3$-C, B$_2$O$_3$-C-CaCO$_3$, B$_2$O$_3$-C-CaO mixtures to N$_2$ gas at 1500 °C. Both additions were found to result in the formation of more BN with larger particle sizes in a given time. The possibility of formation of BN by a mechanism, referred to as the ionic mechanism, involving dissolution of nitrogen as nitride ions in and formation of BN from the calcium borate melt by reaction of borate and nitride ions, was investigated by holding carbon-free B$_2$O$_3$ and B$_2$O$_3$-CaO reaction ingredients under flowing N$_2$ gas at 1500 °C. BN was found to form in B$_2$O$_3$-CaO melts into which BN has been added but no BN formation was observed in the absence of BN. BN was found not to form in B$_2$O$_3$ in the absence or in the presence of BN. It was concluded on the basis of these results that there is BN formation without the use of carbon by the ionic mechanism in B$_2$O$_3$-CaO melts subjected to N$_2$ gas but there is a nucleation barrier to the process and BN should be present in the system for the mechanism to be operative. BN particles forming in the experiments conducted with all of the B$_2$O$_3$-C, B$_2$O$_3$-C-CaCO$_3$, B$_2$O$_3$-C-CaO mixtures were found to have a plate-like morphology and these particles were found to significantly grow in B$_2$O$_3$-CaO melts in the presence as well as in the absence (under Ar) of N$_2$ gas. Based on the experimental results, it is concluded that BN forms only by the overall reaction (1), which is known to consist of steps, in plain B$_2$O$_3$-C mixtures while BN forms both by the overall reaction (1) and by the ionic mechanism in CaO-added and CaCO$_3$-added B$_2$O$_3$-C mixtures subjected to N$_2$ gas with the BN particles forming by the overall reaction (1) acting as nucleation sites for BN formation by the ionic mechanism.

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**References**