

# Effect of sodium carbonate on carbothermic formation of hexagonal boron nitride

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#### Abstract

The effect of sodium carbonate  $(Na_2 CO_3)$  on the formation of hexagonal boron nitride (h-BN) by the carbothermic method was studied by subjecting  $B_2O_3$ -C and  $Na_2CO_3$ -added  $B_2O_3$ -C mixtures to a  $N_2$ (g) atmosphere. The  $Na_2CO_3$  amount in the mixtures was changed in the range of 0-40 wt%. Time and temperature were used as experimental variables. Reaction products were analyzed by XRD and scanning electron microscope.  $Na_2CO_3$  was found to increase both the amount and the particle size of h-BN, similar to calcium carbonate (CaCO<sub>3</sub>).  $Na_2CO_3$  was found to be less effective than CaCO<sub>3</sub> in increasing the amount, while it was more effective than CaCO<sub>3</sub> in increasing the particle size of the formed h-BN.

Key Words: Hexagonal boron nitride, carbothermic formation, sodium oxide, particle size

# 1. Introduction

Hexagonal boron nitride (h-BN) is a unique material with a wide application area due to its high thermal conductivity, excellent solid lubricity, and good electrical insulation (Pikalov, 1988; Paine and Narula, 1990; Rudolph, 1994; Economics of Boron, 2002; Haubner et al., 2002; Zhao et al., 2009). h-BN was first synthesized in 1842 but took over 100 years to be produced commercially (Balmain, 1842). Generally, 1 of 3 production methods is used today: direct reaction of boric oxide and ammonia, reaction of boric acid with urea or melamine and ammonia, and carbothermic reduction of boric oxide under nitrogen atmosphere (Paine and Narula, 1990; Economics of Boron, 2002; Haubner et al., 2002; Zhao et al., 2009) according to:

$$B_2O_3(l) + 3C(s) + N_2(g) = 2BN(s) + 3CO(g).$$
(1)

Several studies have been done on the mechanism of the carbothermic formation of h-BN (Bartnitskaya et al., 1986; Pikalov, 1988). Aydoğdu and Sevinç (2003) stated that the h-BN formation proceeded by reaction of gaseous  $B_2O_3$  with  $N_2(g)$  on solid carbon particles. The reaction was found to be complete in 2 h at 1500

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 $^{\circ}$  C and B<sub>4</sub> C was found to exist in the reaction products for which h-BN formation was not complete. Çamurlu et al. (2006) indicated B<sub>4</sub> C to be an intermediate product and to slow the rate of h-BN formation.

Use of certain additives in  $B_2O_3$ -C mixtures subjected to  $N_2$  gas has been found to increase the yield and particle size of h-BN in carbothermic formation. Bartnitskaya et al. (1996) conducted experiments with Li<sub>2</sub>CO<sub>3</sub> and LiOH-added B<sub>2</sub>O<sub>3</sub>-C or boric acid-carbamide mixtures under nitrogen or ammonia atmospheres and found these additives to increase the yield of h-BN formation. Camurlu et al. (2009) investigated the addition of MgO, BaCO<sub>3</sub>, and CaCO<sub>3</sub>, separately, to B<sub>2</sub>O<sub>3</sub>-C mixtures subjected to N<sub>2</sub> gas, and found that these additives increased the amount and the particle size of the formed h-BN. In another study on the effect of  $CaCO_3$  on the carbothermic formation of h-BN, 10 wt% addition was found to be the optimum amount; the yield and the grain size of the h-BN formed were higher than those obtained from plain mixtures (Çamurlu et al., 2008). The amount of  $B_4C$  in the products was also found to decrease considerably by the addition of 10 wt% CaCO<sub>3</sub> in the same study. Camurlu et al. found reaction products of CaCO<sub>3</sub>-added  $B_2O_3$ -C mixtures to be more porous than those of the plain mixtures and suggested increased porosity to increase the rate of formation of h-BN. They also proposed that an additional BN formation mechanism, referred to as the ionic mechanism and involving nitrogen dissolution in and BN formation from the calcium borate melt, may be operative in the experiments conducted with CaCO<sub>3</sub> additions. Özkenter (2009) studied the effects of CaO and CaCO<sub>3</sub> on the carbothermic formation of h-BN, found h-BN formation to take place in C-free calcium borate melts containing h-BN, and concluded the ionic mechanism to be operative.

All of the additives,  $Li_2CO_3$ , LiOH, CaO, CaCO<sub>3</sub>, MgO, and BaO, exist as oxides of the respective metals at experimental temperatures since the carbonates and the hydroxides of these metals decompose at much lower temperatures.  $Li_2O$ , CaO, MgO, and BaO, which affect carbothermic h-BN formation favorably, are all basic oxides. This study was a continuation of previous studies done in the Department of Metallurgical and Materials Engineering of Middle East Technical University (Aydoğdu and Sevinç, 2003; Çamurlu et al., 2008; Çamurlu et al., 2009), and it was undertaken to find the effect of Na<sub>2</sub>O, which is also a basic oxide, on the carbothermic formation of h-BN by using Na<sub>2</sub>CO<sub>3</sub>-added B<sub>2</sub>O<sub>3</sub>-C mixtures. A favorable effect would allow borax (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>.10H<sub>2</sub>O), which is readily available in reasonable purities and prices, to be used as a substance in the carbothermic production of h-BN.

#### 2. Experimental

Experiments were conducted by subjecting pellets prepared from  $B_2O_3$ -C,  $B_2O_3$ -  $Na_2CO_3$ -C, and  $B_2O_3$ - $Na_2CO_3$ -C pellets to nitrogen atmosphere at different temperatures and times. The furnace was a horizontal furnace consisting of an inner diameter of 50.0 mm, an outer diameter of 60.0 mm, and an alumina tube 800.0 mm in length, heated by SiC heating elements and used in previous studies (Çamurlu, 2006; Özkenter, 2009). Both ends of the tube were closed with silicon stopples having gas inlet and outlet tubes and a thermocouple insertion hole. The reactant pellet was placed in a graphite boat, the interior of which was lined by a boron nitride layer approximately 0.5 mm thick to avoid contact of the pellet with the graphite boat. The graphite boat containing the reactant pellet was slowly pushed into the hot zone of the furnace from the gas outlet end under  $N_2$  (g) flowing at the rate of 1 L/min. It was then held in the hot zone of the furnace under  $N_2$  (g) flowing at a rate of 200 mL/min at a certain temperature and was quickly removed from the furnace at the end of a predetermined time from the gas outlet end. The temperature of the furnace was kept constant at  $\pm 1$  °C and was measured by a Pt-Pt-13% Rh thermocouple, the tip of which was nearly touching the graphite

boat. Experiments were conducted with mixtures containing 0-40 wt% Na<sub>2</sub>CO<sub>3</sub> at 1500 °C for 30 min and with mixtures containing 40 wt% Na<sub>2</sub>CO<sub>3</sub> for 0.5, 1, 1.5, 2, 2.5, and 3 h at 1500 °C, and also for 3 h at 1300 and 1400 °C. 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 qualitative analysis software. The grain size and morphology of the products were investigated by scanning electron microscope (SEM; JEOL JSM-6400).

Addition of  $Na_2 CO_3$  is expected to result in the formation of sodium borate in view of the phase diagram given in Figure 1. In order to determine if sodium borate is soluble in dilute HCl, a mixture of 1 g of  $Na_2 CO_3$ and 2 g of  $B_2O_3$  was prepared and kept in a BN-coated graphite boat at 1500 °C for 1 h. After removing it from the furnace and cooling it, the content of the crucible was placed into a 1:1 (v/v) HCl and water solution. It was found that sodium borate was completely soluble in the 1:1 (v/v) HCl and it was concluded that it was possible to remove sodium borate from the reaction products by leaching with the 1:1 (v/v) HCl solution.



Figure 1. Phase diagram of B<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>O (Morey and Merwin, 1936).

In view of the results from previous studies (Aydoğdu and Sevinç, 2003; Çamurlu, 2006; Ozkenter, 2009) and the preliminary experiments in this study, the reaction products for which BN formation is not complete are known to contain Na<sub>2</sub>O, B<sub>2</sub>O<sub>3</sub>, B<sub>4</sub>C, unreacted C, and h-BN. Amounts of the constituents of the reaction products were determined by a quantitative chemical method consisting of successive leaching, oxidation, and leaching steps developed by Aydoğdu and Sevinç (1993); this was also used with slight modifications in other

subsequent studies (Çamurlu et al., 2008; Çamurlu et al., 2009; Özkenter, 2009). In this method, the reaction product is first leached with 1:1 HCl, which removes sodium borate (Na<sub>2</sub>O + unreacted B<sub>2</sub>O<sub>3</sub>). The residue of the leaching is oxidized at 800 °C, which results in the burning of the unreacted carbon and the conversion of B<sub>4</sub>C into B<sub>2</sub>O<sub>3</sub>. The product of oxidation is then leached with 1:1 HCl, which removes the B<sub>2</sub>O<sub>3</sub>, leaving behind only BN. The quantities of Na<sub>2</sub>O + unreacted B<sub>2</sub>O<sub>3</sub>, B<sub>4</sub>C, unreacted C, and h-BN in the reaction products are then determined by simple mass balances.

#### 3. Results and discussion

# 3.1. Effect of $Na_2CO_3$ addition on formation of BN and $B_4C$

Experiments were conducted with plain  $B_2O_3$ -C mixtures at 1500 °C for 0.5, 1, 1.5, 2, 2.5, and 3 h at the beginning of the study to obtain results to be used as the basis for the effect of sodium carbonate on the carbothermic formation of h-BN. The results were in very good agreement with those of previous studies (Çamurlu et al. 2006; Özkenter, 2009). Çamurlu et al (2008) investigated the effect of calcium carbonate addition on the formation of h-BN. They found the amount of h-BN to increase with the addition of CaCO<sub>3</sub> up to an amount of 10 wt% of the activated carbon-boric oxide mixture and to decrease afterwards in their experiments conducted at 1500 °C for 30 min. They chose a time of 30 min because, as the h-BN formation is not yet complete at that time, the reaction mixture contains both the reactants and the phases forming in the system. Additionally, the amount of B<sub>4</sub>C, which forms as an intermediate phase and slows the h-BN formation, is about at its maximum value at this time (Çamurlu et al., 2006). For the same reasons and also due to the possibility of comparison of the effect of sodium carbonate with that of calcium carbonate, experiments were conducted with B<sub>2</sub>O<sub>3</sub>-C-Na<sub>2</sub>CO<sub>3</sub> mixtures at 1500 °C for 30 min. The amounts of Na<sub>2</sub>CO<sub>3</sub> in the mixtures were 5%, 10%, 15%, 20%, 25%, 30%, 35%, and 40% of the weight of the B<sub>2</sub>O<sub>3</sub>-C mixtures.

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 0-40 wt% Na<sub>2</sub>CO<sub>3</sub> additions are presented in Figure 2. All of the reaction products obtained from Na<sub>2</sub>CO<sub>3</sub>-added pellets were seen to contain higher amounts of h-BN than that obtained from the plain mixture. It was seen that the amount of h-BN increased steadily with an increase in the amount of Na<sub>2</sub>CO<sub>3</sub> added to the activated carbon-boric oxide mixtures, while the amount of B<sub>4</sub>C increased with increases in the amount of Na<sub>2</sub>CO<sub>3</sub> up to 10 wt% but decreased beyond 10 wt%.



Figure 2. Amounts of the constituents in the reaction products for 30 min at 1500  $^{\circ}$  C with B<sub>2</sub>O<sub>3</sub>-C mixtures containing 0-40 wt% Na<sub>2</sub>CO<sub>3</sub> additions.

The effect of Na<sub>2</sub>CO<sub>3</sub> on the carbothermic formation of h-BN was found to be different from the effect of CaCO<sub>3</sub> reported by Çamurlu et al. (2008), who found that the amount of h-BN increased with the addition of CaCO<sub>3</sub> up to an amount of 10 wt% of the activated carbon-boric oxide mixture and decreased afterwards with the amount of B<sub>4</sub>C presenting an almost opposite behavior. They decided a 10 wt% CaCO<sub>3</sub> addition to be the optimum amount. The results presented in Figure 2 show that an optimum of Na<sub>2</sub>CO<sub>3</sub>, similar to CaCO<sub>3</sub>, does not exist in the 0-40 wt% range and that the highest amount of BN amount was obtained with a 40 wt% addition. The quantity of activated carbon-boric oxide was kept constant at 2.5 g (1.986 g B<sub>2</sub>O<sub>3</sub> and 0.514 g C) in these experiments and the addition of Na<sub>2</sub>CO<sub>3</sub> to this mixture resulted in an increase in the weight and the dimensions of the pellet prepared from it. Difficulty was encountered in keeping the pellet containing 40% Na<sub>2</sub>CO<sub>3</sub> additions above 40%. Because of this, and also because use of Na<sub>2</sub>CO<sub>3</sub> in amounts higher than 40% was considered to be impractical, it was decided to conduct experiments aimed at the investigation of the catalytic effect of Na<sub>2</sub>CO<sub>3</sub> for longer durations at 1500 °C with a 40 wt% addition.

Amounts of the constituents of the reaction products of the experiments conducted with Na<sub>2</sub>CO<sub>3</sub>-added B<sub>2</sub>O<sub>3</sub>-C mixtures at 1500 °C for times from 30 min to 3 h are given in Table 1. The quantities of h-BN and B<sub>4</sub>C formed in the experiments conducted with plain and 40 wt% Na<sub>2</sub>CO<sub>3</sub>-added mixtures at 1500 °C from 30 min to 3 h are presented in Figure 3. Quantities of h-BN and B<sub>4</sub>C found in the reaction products of CaCO<sub>3</sub>-added B<sub>2</sub>O<sub>3</sub>-C mixtures obtained in the study by Çamurlu et al. (2008) are also shown in Figure 3 for comparison purposes. It can be seen that the quantities of h-BN formed in the mixtures containing Na<sub>2</sub>CO<sub>3</sub> or CaCO<sub>3</sub> addition is known to increase the amount of h-BN formed (Çamurlu et al., 2008; Özkenter, 2009). Na<sub>2</sub>CO<sub>3</sub> also increases the amount of h-BN formation. The effect of Na<sub>2</sub>CO<sub>3</sub> in increasing the amount of h-BN formed is seen to be very pronounced for short times but less so for longer times; Na<sub>2</sub>CO<sub>3</sub> is seen to be more effective than even CaCO<sub>3</sub> for times up to about 0.5 h, but the reverse is true for longer times. Figure 3 additionally shows that there is almost no BN formation after 2 h. This is an expected result in view of Table 1, in which the amount of B<sub>2</sub>O<sub>3</sub> + Na<sub>2</sub>O in the reaction product of the experiment for 2 h is seen be about 0. No BN can, obviously, form after 2 h due to the absence of B<sub>2</sub>O<sub>3</sub> in the system. B<sub>4</sub>C is not entirely consumed and its amount does not change after 2 h, again due to the absence of B<sub>2</sub>O<sub>3</sub> in the system.



Figure 3. Quantities of  $B_4 C$  and h-BN formed in the experiments performed with plain, CaCO<sub>3</sub>-added, and Na<sub>2</sub>CO<sub>3</sub>-added mixtures (Çamurlu et al., 2008).

| Time (h) | $B_2O_3 + Na_2O(g)$ | C(g)   | $B_4C(g)$ | h-BN(g) |
|----------|---------------------|--------|-----------|---------|
| 0        | 2.5705              | 0.5140 | 0         | 0       |
| 0.5      | 0.2703              | 0.1227 | 0.0940    | 0.3195  |
| 1        | 0.0260              | 0.1123 | 0.0817    | 0.3707  |
| 2        | 0.0100              | 0.0948 | 0.0442    | 0.4450  |
| 3        | 0                   | 0.0927 | 0.0313    | 0.4785  |

Table 1. Amounts of constituents of the reaction products of experiments conducted with  $Na_2 CO_3$ -added mixtures at 1500 °C for from 30 min to 3 h.

There is a loss of  $B_2O_3$  from the system in the carbothermic formation of h-BN due to evaporation, and the quantity of  $B_2O_3$  used in the preparation of the  $B_2O_3 + C$  mixtures with or without additives was 100% in excess of the stoichiometric amount dictated by Eq. (1) to account for evaporation loss in the previous studies conducted in the Department of Metallurgical and Materials Engineering of Middle East Technical University (Aydoğdu, 1993). A higher amount of loss of  $B_2O_3$  and also some loss of  $Na_2O$  from the system due to evaporation was expected at the beginning of the study in view of the results of Cole and Taylor, who found  $B_2O_3$ ,  $Na_2O$ , and sodium borates like  $Na_2B_4O_7$  to evaporate from liquid  $Na_2O$ - $B_2O_3$  systems at high temperatures (Cole and Taylor, 1935; Brewer et al., 1955). The possibility of loss of  $Na_2O$  from the system due to the following reaction,

$$Na_2O(l) + C(s) = 2Na(g) + CO(g),$$
 (2)

was also considered, but these losses were not expected to reach the point where there would not remain any  $Na_2O$  or  $B_2O_3$  in the system.

These results indicate that Na<sub>2</sub>CO<sub>3</sub> significantly increases the rate of carbothermic formation of h-BN, but loss of Na<sub>2</sub>O and B<sub>2</sub>O<sub>3</sub> is severe, which makes its use impractical at 1500 °C. The possibility of the use of Na<sub>2</sub>CO<sub>3</sub> as a catalytic additive into B<sub>2</sub>O<sub>3</sub> + C mixtures at lower temperatures was studied and experiments were again conducted with a 40 wt% Na<sub>2</sub>CO<sub>3</sub> addition at 1300 and 1400 °C. Amounts of the constituents of the reaction products of these experiments together with those at 1500 °C are given in Table 2. The only study, to the knowledge of the authors, on the effect of temperature on carbothermic formation of h-BN was that done by Aydoğdu and Sevinç (2003) with plain B<sub>2</sub>O<sub>3</sub>-C mixtures. Direct comparison of their results with those of this study is not possible because the quantities of B<sub>2</sub>O<sub>3</sub> and C in the 2 studies were different. However, while the quantity of h-BN that formed at 1500 °C, the quantity of h-BN formed at 1500 °C in the present study was about 30% more than that formed at 1300 °C. This may be taken as an indication that Na<sub>2</sub>CO<sub>3</sub> may be used as an additive to produce h-BN at lower temperatures, which may be of practical interest.

Table 2. Amounts of the constituents in the experiments conducted for 3 h at 1300-1500  $^{\circ}$ C.

| Temperature (°C) | $B_2O_3 + Na_2O(g)$ | $B_4C(g)$ | Carbon (g) | BN(g)  |
|------------------|---------------------|-----------|------------|--------|
| 1300             | 0.4639              | 0.1059    | 0.1538     | 0.3764 |
| 1400             | 0.0014              | 0.0701    | 0.1149     | 0.4195 |
| 1500             | 0.0000              | 0.0313    | 0.0927     | 0.4785 |

## 3.2. Effect of $Na_2CO_3$ addition on particle size of h-BN

Substances such as  $CaCO_3$ , when added to  $B_2O_3$ -C mixtures, increase the particle size in addition to the quantity of h-BN formed. Samples taken from all of the reaction products removed from the furnace as well as samples after the leaching-oxidation-leaching process were subjected to XRD analysis. The results were the same as those of the previous studies and are therefore not shown in this study. Samples after the leaching-oxidation-leaching process were also examined by SEM and particle sizes of the samples were calculated.

SEM micrographs are shown in Figures 4a-4g, respectively, for samples obtained after subjecting the reaction products of the experiments conducted with the plain  $B_2O_3$ -C mixture at 1500 °C for 3 h; Na<sub>2</sub>CO<sub>3</sub>-added mixtures at 1500 °C for 0.5, 1, 2, and 3 h; and Na<sub>2</sub>CO<sub>3</sub>-added mixtures at 1300 and 1400 °C for 3 h to the leaching-oxidation-leaching process. SEM micrographs of the samples from plain and CaCO<sub>3</sub>-added



Figure 4. SEM micrographs of h-BN powders obtained from experiments conducted with a) plain  $B_2O_3$ -C mixture at 1500 °C for 3 h;  $Na_2CO_3$ -added mixtures at 1500 °C for b) 30 min, c) 1 h, d) 2 h, and e) 3 h; f)  $Na_2CO_3$ -added mixture for 3 h at 1400 °C; g)  $Na_2CO_3$ -added mixture for 3 h at 1300 °C; and  $CaCO_3$ -added mixtures h) for 2 h and i) 3 h.

mixtures taken from Çamurlu et al. (2008) and Özkenter (2009) are also shown in Figures 4h and 4i, respectively. The average particle sizes of the h-BN appearing in Figure 4 are tabulated in Table 3. Particle sizes of h-BN obtained from  $B_2O_3$ -C mixtures containing  $Na_2CO_3$  or  $CaCO_3$  were larger than those obtained from the plain  $B_2O_3$ -C mixture at any temperature and for any time. Average particle sizes of h-BN obtained from the  $Na_2CO_3$ -added mixture at 1500 °C for 2 h were not different from those for 3 h, which was expected in view of the fact that no  $B_2O_3$  was found to exist in the system at the end of 2 h, as stated above. Comparison of the particle size of h-BN obtained from the  $Na_2CO_3$ -added mixture at 1500 °C for 2 h (1.17 ± 0.27  $\mu$ m) with that from the  $CaCO_3$ -added mixture (0.70 ± 0.14  $\mu$ m) indicates  $Na_2CO_3$  to be much more effective than  $CaCO_3$  in increasing the particle size of h-BN.

**Table 3.** Average particle size of the samples obtained from the experiments conducted with 40 wt% Na<sub>2</sub>CO<sub>3</sub>-added plain mixtures for different times and temperatures, with CaCO<sub>3</sub>-added plain mixtures at 1500 °C for 2 and 3 h, and plain mixtures for 3 h at 1500 °C (Çamurlu et al., 2008; Özkenter, 2009).

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#### 4. Conclusion

The effect of  $Na_2CO_3$  addition on the carbothermic formation of h-BN was investigated by adding  $Na_2CO_3$  to a B2O3-C mixture in the range of 0-40 wt%. It was found from the experiments performed for 30 min at 1500 °C that the amount of h-BN increased steadily with an increase in the amount of  $Na_2CO_3$  added. It was found from experiments conducted with 40 wt%  $Na_2CO_3$  for from 0.5 to 3 h at 1500 °C that  $Na_2CO_3$  is even more effective than  $CaCO_3$  in increasing the amount as well as the particle size of the h-BN formed, but there was a significant loss of  $B_2O_3$  and  $Na_2O$  from the system. This would make the use of  $Na_2O_3$  impractical unless ways of decreasing this loss can be found.

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