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Catalytic effect of alkaline earth oxides on carbothermic formation of hexagonal boron nitride

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Abstract

Effect of MgO, CaO and BaO on carbothermic formation of hexagonal boron nitride (h-BN) was investigated. B_2O_3–C mixtures containing alkaline earth oxide additives were reacted at 1500 °C for 30–120 min in nitrogen atmosphere. Formed phases in the reaction products were determined by powder-XRD analyses, and amounts of the constituents were determined by chemical analyses. Particle size and morphology of the formed h-BN powders were examined by FESEM and particle size distributions were determined by particle size analyzer. Addition of alkaline earth oxides was found to increase the amount and grain size of h-BN significantly and to decrease the amount of B_4C formed in the system. Investigated alkaline earth oxides presented similar catalytic effects according to chemical analyses and FESEM observations. While the average particle size of h-BN powder obtained from plain mixture was 149 nm, those obtained from MgO, CaO and BaO containing mixtures were 297, 367 and 429 nm, respectively.

Keywords: A. Grain growth; A. Powders: chemical preparation; D. Alkaline earth oxides; D. Nitrides

1. Introduction

Hexagonal boron nitride (h-BN) is one of the key advanced ceramics with excellent solid lubricity, high thermal conductivity, good electrical insulation properties and low density 2.27 g/cm^3 [1–6]. It is stable in air up to 1000 °C, non-wettable and inert to many metallic melts such as Al, Cu, Zn, Fe and non-metallic melts such as Si, B and glasses [1,2]. In addition, it has high thermal shock resistance and low thermal expansion which make it an indispensable material for refractory and crucibles in molten metal handling. h-BN is applied in high temperature lubrication and used as insulators and coolers in electronic circuits, as well as additives in other ceramics and polymers [1,3,4,6–10]. It is possible to utilize h-BN in many forms including hot pressed solids, powders, fibers, in aerosols and as dispersed powders in liquid media [1,2].

Formation of h-BN was achieved by various processes, starting from boron and nitrogen bearing solid and gaseous reactants. Mainly 3 methods are employed industrially [3–5]. First is based on direct reaction of boric oxide and ammonia [1]. The other method is through the reaction of boric acid with urea or melamine and ammonia [3,11]. The third one is carbothermic reduction and simultaneous nitridation of boric oxide [4,5,12,13] according to Reaction (1).

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

It was previously found that [12], carbothermic formation of h-BN takes place through the reaction of gaseous B_2O_3 and solid C. B_4C was observed to form during this process; however it was shown that B_4C is not a necessary intermediate compound and that it retards the completion of formation of pure h-BN [13]. Reduction of the amount of forming B_4C in this process was therefore stated as a critical issue.

In industry, there is an increasing demand on h-BN due to its growing utilization. Additionally, large grain size and high crystallinity of h-BN is required in order to have better

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lubricating properties and high temperature stability [2,3,14]. However, the above mentioned production processes require high temperatures, and particle size of the formed h-BN is too small. As a result, research on increasing the rate of h-BN formation reactions and the size of h-BN particles has been ongoing. Bartnitskaya et al. studied the effect of Li_2CO_3 addition to h-BN formation by different methods like subjecting B_2O_3–C mixtures, boric acid–carbamide mixtures to N_2(g) or ammonia gas [15,16]. They have found Li_2CO_3 to favorably affect h-BN formation and h-BN crystallinity and have suggested h-BN to crystallize from the lithium borate melt. 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, the effect of addition of $CaCO_3$ as a catalyst has been investigated [17]. Addition of $CaCO_3$ was found to provide h-BN powder with low specific surface area and high crystallinity. Recently, Çamurlu et al. studied the effect of $CaCO_3$ on carbothermic formation of h-BN by holding B_2O_3–C mixtures containing 0–50 wt% $CaCO_3$ at 1500 °C for 0.5–3 h [18]. They found from the experiments conducted for 0.5 h that when $CaCO_3$ addition was in 5–20 wt% range, the amount of h-BN was higher and the amount of B_4C was lower in the products than when no $CaCO_3$ was added. 10 wt% $CaCO_3$ was found as the optimum value to keep the amount of B_4C as low as possible and h-BN as high as possible in the reaction products. $CaCO_3$ addition yielded h-BN powder with larger particle size and the amount of h-BN formed was 50% higher than the experiments without $CaCO_3$.

In the present study catalytic effect of alkaline earth oxides, namely MgO, CaO and BaO (in the form of carbonates), was investigated on the formation of h-BN by the reaction of boric oxide and carbon under nitrogen atmosphere. Alkaline earth oxides or carbonates are low cost materials and they are easily available. Thus, they are candidate catalyst materials for carbothermic formation of h-BN.

2. Experimental procedure

Experiments were performed by holding the activated carbon–boric oxide (alkaline earth oxide) mixtures under nitrogen atmosphere in a tube furnace. Activated carbon (Merck, 99.0%) boric oxide mixtures were prepared by grinding and thoroughly mixing in acetone in an agate mortar and pestle. Boric oxide was produced by calcination of boric acid (Merck, 99.8%) in a nickel crucible for 2 h at 900 °C. The mixtures contained B_2O_3 100 mole% in excess of the amount calculated in accord with the stoichiometry of Reaction (1) to account for loss due to evaporation. In each experiment, a total mixture of 2.5 g was used, which consisted of 1.986 g boric oxide and 0.514 g activated carbon. 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 furnace tube had 50 mm inner and 60 mm outer diameters. The graphite crucible in which the reactants were contained during the experiments had 2.5 cm inner and 3 cm outer diameters, and a depth of 3 cm. The nitrogen gas flow rate was kept at 200 cm^3/min during the experiments. The reaction product was in the form of an aggregate, which was weighed and then ground in agate mortar and pestle and subjected to XRD and chemical analyses.

Effect of alkaline earth oxide additives, namely CaO, MgO, BaO (Merck Chemicals) was investigated by mixing them with the $B_2O_3 + C$ mixtures and performing the experiments as described above. MgO was used as oxide and CaO and BaO were used in the form of carbonates, $CaCO_3$ and $BaCO_3$, which decompose into oxides at reaction temperature. Durations of the experiments were 0.5, 1 and 2 h. Amounts of additions were kept at 10 wt% of the initial $B_2O_3 + C$ mixtures.

Reaction products were analyzed by a Rigaku Multiflex Powder X-ray diffractometer with Cu Kα radiation in the 2θ range of 10° to 80° with 0.02° steps at a rate of 2° min^{-1}. The amounts of the constituents of the products were determined by following a quantitative chemical analysis method, which consisted of successive leaching-oxidation and leaching of the products. A brief description of the method is given here, details of it can be found elsewhere [11,12,18]. The first leaching step was performed in 1/1 (v/v) HCl solution. In this step, calcium borate and boric oxide phases are dissolved and removed by filtering. In the case of plain mixtures, amount of unreacted boric oxide in the products is found volumetrically by titrating the filtrate with NaOH, and in the case of mixtures containing additives, total amount of unreacted boric oxide and formed borates is found from the weight difference between the initial product and the residue. The residue contains B_4C, h-BN and unreacted C. The oxidation step is performed by holding the residue in a muffle furnace in air at 800 °C for 15 h. At 800 °C h-BN does not get oxidized, but C in the residue is oxidized and B_4C is converted into B_2O_3. The final leaching step is performed in deionized water, when the boric oxide in the oxidized product is dissolved and removed by filtering. Amount of B_4C is calculated after volumetric determination of boric oxide, which was formed due to oxidation of B_4C, by titrating the filtrate with NaOH. The residue after filtering is pure h-BN. The pure h-BN powders obtained at the end of the described chemical analysis method were examined by a field emission scanning electron microscope (FESEM, Jeol 6335F). Particle size distributions were determined by particle size analyzer (Zetasizer Nano-ZS, Malvern Instruments).

3. Results and discussion

Experiments aiming for the investigation of the catalytic effect of MgO, CaO and BaO were performed at 1500 °C for 0.5–2 h. Amounts of h-BN and B_4C formed in the experiments conducted with plain $B_2O_3 + C$ mixtures and with mixtures containing additives are given in Fig. 1. For all durations, the quantities of h-BN forming in the mixtures containing additives are considerably higher than those without additive. Amounts of h-BN formed in 1 h with different additives are higher than that formed in 2 h without additive. At the end of 2 h, amounts of formed h-BN from mixtures containing additives are over 50% higher than that obtained from plain mixtures. Moreover, alkaline earth oxide additions decrease the amount of formed B_4C in the reaction products. All the additives appear to have

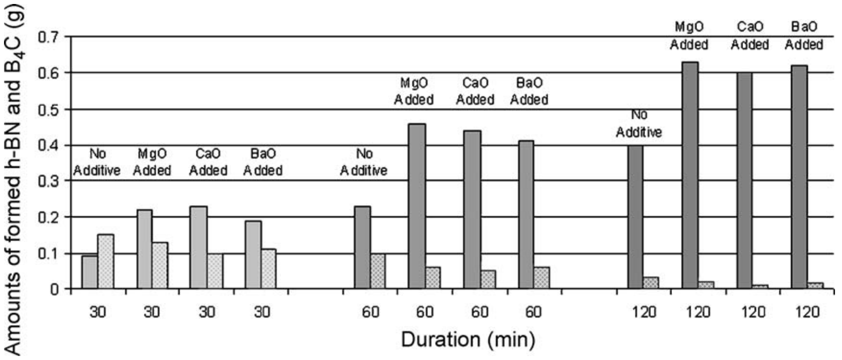

Fig. 1. Amounts of h-BN and B_4C formed in the products of the experiments conducted for 0.5, 1 and 2 h using plain $B_2O_3 + C$ mixtures, and compositions containing MgO, CaO and BaO (full bars represent h-BN, crossed bars represent B_4C).

similar effect on increasing the amount of h-BN and decreasing the amount of B_4C in the products. Efficiency of h-BN formation was calculated from the chemical analysis data. When no alkaline earth oxide was used efficiency of h-BN formation according to carbon utilization was calculated as 63% at the end of 3 h, when the entire C was consumed. On the other hand, it was found that all C in the initial mixture was consumed in 2 h when additives were used and over 80% of C was calculated to be utilized in formation of h-BN. It can be concluded from these results that addition of alkaline earth oxides increases the reaction rate and reduces the loss of carbon.

XRD patterns of the samples obtained from the experiments conducted for 1 h with plain and MgO, CaO and BaO containing mixtures are presented in Fig. 2. XRD analyses of the products are in accord with the results of the quantitative analysis. The h-BN peaks of the products obtained from mixtures containing additives were higher than those of the products obtained from plain mixtures. On the contrary, B_4C peaks were lower, thus they were below the detection limit of XRD analysis when additives were used. The relative heights of the boric acid peaks present in the XRD patterns are proportional to the amount of unreacted boric oxide in the products, since boric acid forms due to hydration of boric oxide during specimen preparation of XRD analyses. The boric acid peaks of the products obtained from mixtures containing additives are seen to be lower than the ones obtained from plain $B_2O_3 + C$ mixture, indicating higher consumption of B_2O_3.

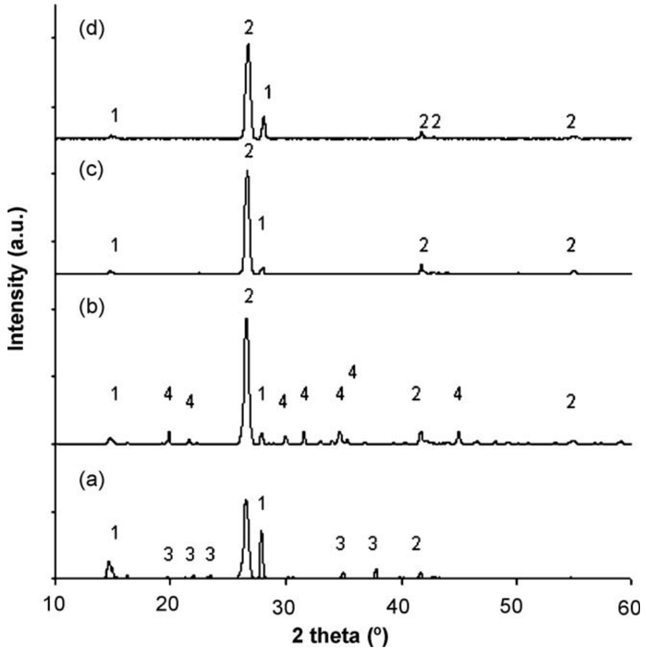

Fig. 2. XRD patterns of the products of the experiments conducted for 1 h with (a) plain mixture, and mixtures containing (b) MgO, (c) CaO and (d) BaO. (1) H_3BO_3, (2) h-BN, (3) B_4C and (4) $Mg_2B_2O_5$.

No alkaline earth carbonate peak is expected to be present on the XRD patterns of the products after conducting the experiments at 1500 °C, since the normal calcination temperature of $CaCO_3$ is 902 °C and that of $BaCO_3$ is 1431 °C [19]. There are no alkaline earth oxide peaks on the XRD patterns indicating a reaction between alkaline earth oxides and boric oxide, according to which alkaline earth borates are expected to form. During the experiments, amount of B_2O_3 decreases by Reaction (1) and by evaporation, which is believed to change the compositions of the formed alkaline earth borates. The XRD patterns of the products obtained from CaO containing mixtures were similar to those obtained from BaO containing samples (Fig. 2(c) and (d)), where it can be seen that no peaks related to any Ca or Ba containing species are present. Due to the fast cooling rate of the samples, these phases may be in amorphous form and may have not been detected by the XRD analyses. Only in the case of MgO addition, $Mg_2B_2O_5$ ($2MgO \cdot B_2O_3$) was detected as a crystalline borate phase (Fig. 2(b)), which has formed by the reaction of MgO with B_2O_3. After leaching with 1/1 (v/v) HCl/water solution for 15 h, the $Mg_2B_2O_5$ phase was removed.

High magnification FESEM micrographs of reaction products formed in the experiments conducted for 2 h with plain and alkaline earth oxide added mixtures are presented in Fig. 3. It is seen that h-BN particles formed from the mixtures containing additives are significantly larger than those formed from plain mixes. Particle size and shape of h-BN powder formed with additives appear to be similar. The plate-like morphology of h-BN particles can be clearly seen in these micrographs. BET specific surface area measurements were performed on samples obtained from plain and CaO containing

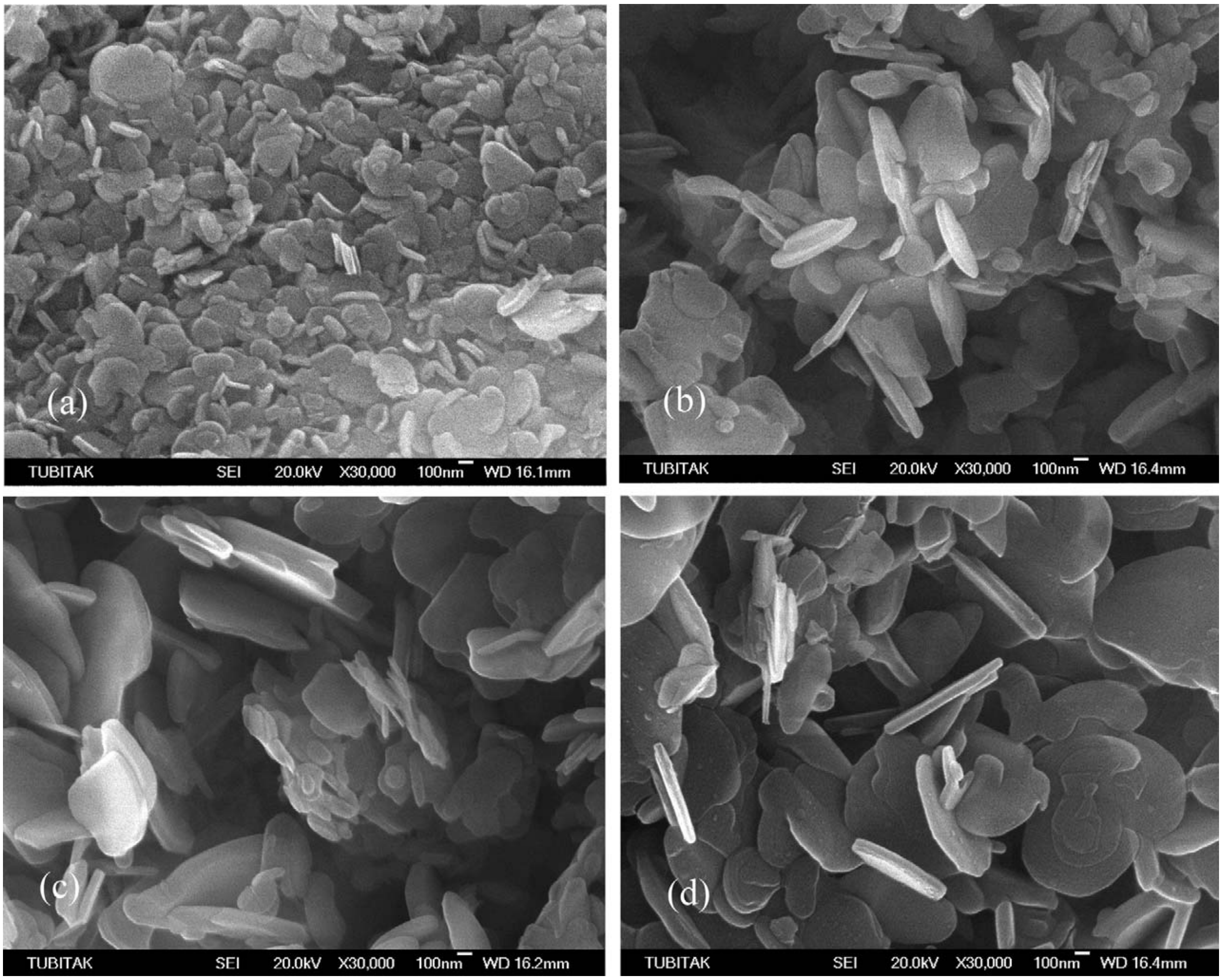

Fig. 3. FESEM micrographs of h-BN powders obtained in 2 h from (a) plain mixture, and mixtures containing (b) MgO, (c) CaO and (d) BaO.

mixtures, where it was found that h-BN powder formed from plain mixes in 2 h had a specific surface area of 31.7 m^2/g, while that of the h-BN produced by CaO addition was 21 m^2/g, confirming the increase in the grain size.

Particle size distribution graphs of h-BN powders obtained form plain and alkaline earth oxide containing mixtures are presented in Fig. 4. The average particle size of h-BN powder obtained from plain mixture was 149 nm; and those obtained from MgO, CaO and BaO containing mixtures were 297, 367 and 429 nm, respectively. The results of particle size distribution analyses are in agreement with the SEM observations, from which it can be seen that addition of alkaline earth oxides gives rise to significant growth of h-BN particles. According to particle size analysis, CaO appears to be slightly more effective than MgO, and BaO appears to be slightly more effective than CaO on growth of h-BN particles.

From the results of chemical analysis, FESEM observations and particle size analysis it can be concluded that alkaline earth oxides increase the rate of h-BN formation and also particle size of the formed h-BN powder, and that all of the alkaline earth oxides investigated in the present study presented similar effects to each other. There are 2 possible means by which alkaline earth oxide additions may improve the formation of h-BN from B_2O_3 + C mixtures. One is easing the access of $N_2(g)$ into the reaction mixture. The product pellets obtained from mixtures containing additives were observed to be more porous than the ones obtained from plain mixtures. Therefore, addition

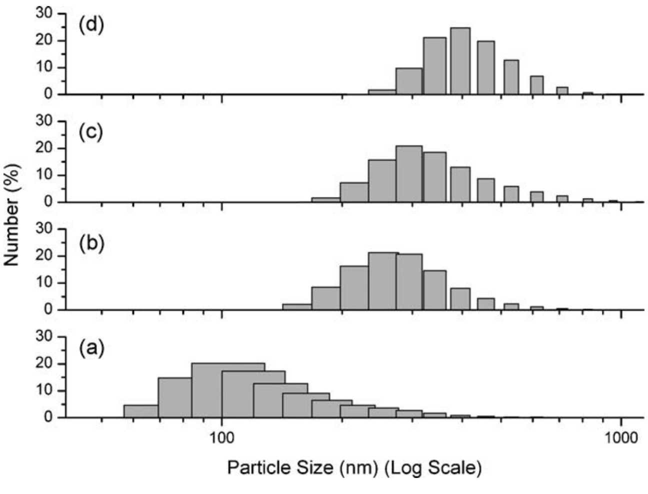

Fig. 4. Particle size distribution graphs of h-BN powders obtained in 2 h from (a) plain mixture, and mixtures containing (b) MgO, (c) CaO and (d) BaO.

of alkaline earth oxides appear to have a positive effect as providing a more porous structure in the reaction pellet, leading to better nitrogen penetration. However, this can not be the only reason, as this effect is expected to increase the rate of h-BN formation, but not the total amount of h-BN at the end of the reaction since the amount of C in the initial mixtures were kept constant. This observation brings about the possibility of another mechanism, which can be suggested to proceed without the need of C. In formation of h-BN from B_2O_3 + C + alkaline earth oxide mixtures subjected to N_2 gas, a precipitation from the melt mechanism may be suggested to apply.

The mechanism of precipitation of h-BN from the melt relies on the fact that h-BN is soluble in oxide melts and its solubility depends on composition. Alkaline earth oxides are basic oxides. It was shown that the solubility of h-BN in B_2O_3-basic oxide binary systems increases with increase in the concentration of the basic oxide up to 0.1–0.2 mole fraction of the basic oxide and then decreases [20,21]. Formation of h-BN may take place in a B_2O_3 containing oxide melt in which nitrogen is dissolved, if the solubility product of h-BN is exceeded. Nitrogen in the oxide melt may remain as free [22] or as incorporated into the borate anions in B_2O_3-basic oxide binary systems [22,23]. Therefore, in addition to Reaction (1) which uses C, formation of h-BN from nitrogen and B_2O_3-alkaline earth oxide containing melts may be suggested to take place through non-C consuming reactions between dissolved nitrogen and borate anions [18,20,21].

4. Conclusion

Addition of alkaline earth oxides into B_2O_3–C mixtures was found to significantly increase the amount and particle size of h-BN and to decrease the amount of B_4C formed in the system. Investigated alkaline earth oxides showed similar effects on enhancing the rate of formation of h-BN. According to particle size analysis, CaO appeared to be slightly more effective than MgO, and BaO to be slightly more effective than CaO on growth of h-BN particles. It was suggested that addition of alkaline earth oxides increased the rate of h-BN formation by easing the access of N_2 into the reaction mixture. Additionally, h-BN may be suggested to form by precipitation from the B_2O_3-alkaline earth oxide containing melt in which N_2(g) dissolves.

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