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Catalytic effect of potassium carbonate on carbothermic production of hexagonal boron nitride

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Abstract

Effect of potassium carbonate addition on the carbothermic formation of hexagonal boron nitride (hBN) was investigated by keeping the K_2CO_3 added B_2O_3+C mixtures in nitrogen atmosphere at 1400 °C for 40–160 min. K_2CO_3 amount was varied in the range of 10–60 wt% of the B_2O_3+C mixture. Products were subjected to XRD and quantitative analyses, SEM and TEM observations, and particle size measurement. Amount of hBN increased considerably with K_2CO_3 addition; also particle size and crystallinity improved. Catalytic role of K_2CO_3 was suggested as forming a potassium borate melt in which hBN particles form, in addition to carbothermic formation reaction. Effect of K_2CO_3 on increasing the hBN amount decreased when it was used over 40%. This was attributed to the rapid evaporation of the formed potassium borate liquid.

Keywords: A. Powders: chemical preparation; D. Hexagonal boron nitride

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1. Introduction

Boron nitride can be found in various crystallographic forms such as cubic, hexagonal, wurtzitic, rhombohedral or turbostratic. The crystal structure of hexagonal boron nitride (hBN) resembles that of graphite. hBN has attracted much attention due to its superb high temperature and lubricating properties, in addition to its chemical stability, and non-reactivity with molten metals [1]. hBN has been used in ceramic matrix composites for decreasing the thermal expansion coefficient and enhancing thermal shock resistance of the composite [2]. It was also reported to improve machinability in ceramic systems [3]. In addition, hBN has been used in polymer matrix composites in order to improve various properties such as flame retardancy [4], toughness [5] or wear properties [6].

hBN can be produced by a number of techniques such as carbothermic reduction and nitridation [7–9], reaction of boron oxide and ammonia [10] or reaction of urea and boric acid [11]. In the carbothermic method, boron oxide is reduced by carbon and simultaneous nitridation occurs, resulting in the formation of hBN. Effect of catalysts on formation and crystal structure of hBN has been investigated in various production routes [8,9,11–13]. Role of lithium carbonate on the formation of hBN from boric acid and carbon mixture was studied by Bartnitskaya et al. [12]. Lithium carbonate was found to have a positive role in increasing the quantity and enhancing the crystal structure of the formed hBN. A lithium borate melt was suggested to form and the formed hBN was suggested to dissolve and to crystallize in the melt [12]. In further studies conducted by Çamurlu et al. in order to clarify the formation mechanism of hBN in the presence of catalysts, alkaline earth oxides have been added to the boron oxide–carbon starting mixture and the reactions were conducted at 1500 °C in nitrogen atmosphere [8,9]. It was suggested that some of the hBN is formed in the products by the carbothermic process, and some hBN forms through an ionic mechanism. In that mechanism, an alkali borate or alkaline earth borate melt formed by the reaction of alkali or alkaline earth oxides and boron oxide. hBN formation was suggested to take place in the melt by the reaction of the borate anions and dissolved nitrogen [8,9]. The ionic mechanism is operative in the presence of alkali or alkaline earth oxides [8,9,12].

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hBN is an industrially important material that has been utilized in various applications, with increasing consumption. Catalysts play a key role in the production and property control of hBN. In this study, the catalytic effect of K_2CO_3 on carbothermic formation of hBN, which has not been reported previously, was investigated.

2. Material and methods

B_2O_3 (Eti Mine, >98%), C (Merck >99%) and K_2CO_3 (Merck, >99%) were mixed thoroughly in dry form in a planetary ball mill for 30 min with 20 mm steel balls at 250 rpm. Amount of B_2O_3 in the mixture was 100% in excess of the stoichiometry of Reaction (1). Weight of B_2O_3+C mixture was kept constant at 12.5 g in the samples and K_2CO_3 was added into this mixture in varying percentages. Reactant mixtures were placed in a graphite crucible and the crucible was pushed into the hot zone of a SiC resistance tube furnace, which was preheated to 1400 °C. This was the upper working temperature of the mullite tube of the furnace. The inner and outer diameters of the tube were 50 mm and 60 mm, respectively. Reactants were kept under flowing N_2 for predetermined duration. Amounts of K_2CO_3 in the samples and duration of the experiments are presented in Table 1. N_2 flow was kept constant during the experiments at 200 ml/min. After the predetermined duration, the crucible was quickly pulled out of the furnace and the products were cooled under Ar.

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

XRD analyses were performed by a Rigaku Multiflex unit. Interplanar spacing and crystallite thickness of the formed hBN were calculated from the XRD data by the Scherrer formula [14]. The quantitative analysis and purification of hBN were performed as described previously [7,8]. This method involves leaching the products in 1/1 HCl/water, oxidation of C and B_4C in the leached products at 800 °C and again leaching the oxidized products in water. Particle size of the formed hBN was determined by a Malvern Zetasizer ZS particle size analyzer.

3. Results and discussion

3.1. XRD and quantitative analyses

XRD patterns of the products obtained by reacting the mixtures containing 20–60 wt% K_2CO_3 for 40 min are presented in Fig. 1. The products are composed of hBN, H_3BO_3 (which is formed due to hydration of boron oxide in the products during sample preparation) and potassium borate hydrate ($KB_5O_8 \cdot 4H_2O$ (ICDD #25-0624), (which is formed due to hydration of potassium borate in the products during sample preparation). XRD patterns of the products obtained by reacting the mixtures containing 10–60 wt% K_2CO_3 for 80 min are presented in Fig. 2. XRD pattern of the product of a sample which did not contain K_2CO_3 is also given for comparison (Fig. 2a). It can be inferred from the increase in intensity of the (002) peaks in the given XRD figures that the amount of hBN in the products increases with the increase in the addition of K_2CO_3.

For a clearer interpretation on the amounts of formed hBN, quantitative analyses were performed. Amounts of hBN

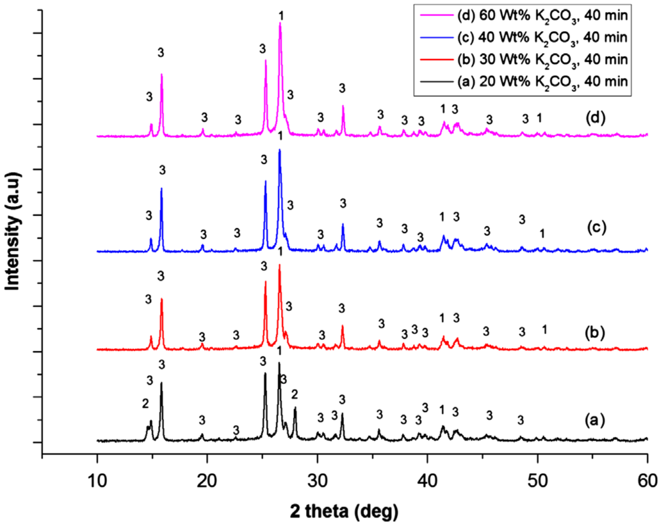

Fig. 1. XRD patterns of the products of the experiments conducted for 40 min (1: hBN, 2: H_3BO_3 and 3: $KB_5O_8 \cdot 4H_2O$).

Table 1
Weight% of K_2CO_3 in the samples, duration of the experiments, and initial weight of (B_2O_3+C+K_2O), initial wt% of K_2O in K_2O–B_2O_3 system in the reactants as well as amount and average particle size of the formed hBN.

Sample no.	K_2CO_3 in the sample (wt%)	Experiment duration (min)	Initial total weight of reactants B_2O_3+C+K_2O (g)	Initial K_2O in K_2O–B_2O_3 system (wt%)	Amount of formed hBN (g)	Average particle size of formed hBN (nm)
1	–	80	12.5	–	0.15	–
2	–	160	12.5	–	0.57	150
3	10	80	13.35	7.8	0.40	222
4	20	40	14.20	14.5	0.37	154
5	20	80	14.20	14.5	0.84	247
6	30	40	15.05	20.3	0.86	160
7	30	80	15.05	20.3	1.25	295
8	40	40	15.91	25.4	0.87	218
9	40	80	15.91	25.4	1.35	292
10	60	40	17.61	33.8	0.51	221
11	60	80	17.61	33.8	1.16	301

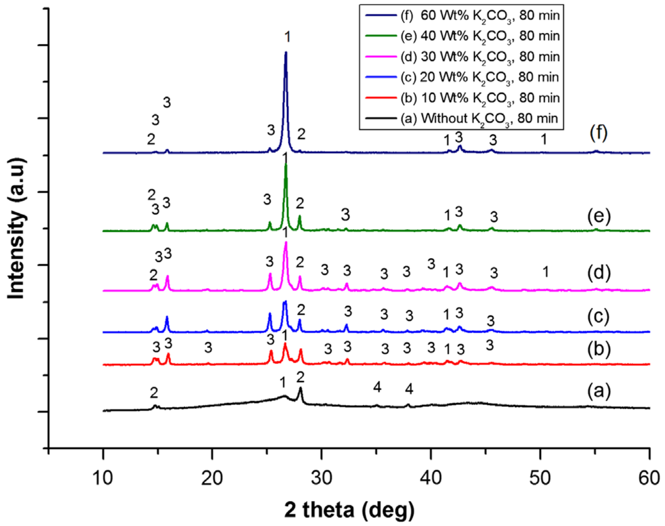

Fig. 2. XRD patterns of the products of the experiments conducted for 80 min (1: hBN, 2: H_3BO_3, 3: $KB_5O_8 \cdot 4H_2O$ and 4: B_4C).

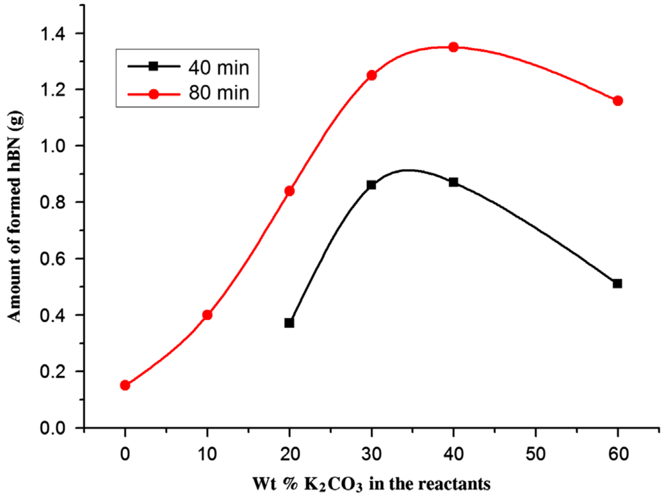

Fig. 3. Variation of the amounts of hBN formed as a function of K_2CO_3% in the reactants.

formed in the products, which were determined by leaching, oxidation and again leaching of the products [7,8], are presented in Table 1 and Fig. 3. Amount of hBN in the experiment conducted for 40 min without K_2CO_3 addition could not be determined due to its very low amount. Addition of K_2CO_3 was seen to enhance the hBN formation to a great extent. In all the experiments conducted with 10–60% K_2CO_3 addition, amount of formed hBN was higher than that formed without addition. Amount of hBN formed at the end of 80 min duration without K_2CO_3 was 0.15 g, whereas 1.35 g of hBN formed in the same duration when 40% K_2CO_3 was added into the reactant mixture. It can be seen in Fig. 3 that in both series of the experiments which were conducted for 40 min and 80 min, the increase in the amount of hBN formation continues up to 40% addition. When 60% addition was used, formed hBN was less than that formed when 40% K_2CO_3 was added. In addition, there was only a slight increase in the amount of formed hBN when K_2CO_3 amount was increased from 30% to 40%. In view of these results, the optimum amount of K_2CO_3 can be suggested to be 30%.

It can be seen that boron nitride formed without addition of K_2CO_3 has a wide (002) peak, indicating its low crystalline structure (Fig. 2a). In general the increase in the K_2CO_3 amount resulted in an enhancement in the crystallinity of hBN, as visualized from the narrowing and increasing in intensity of the (002) peaks at 26.7°. Average crystallite thicknesses and L_c values of the formed hBN were calculated by the Scherrer formula [14]. L_c is the mean height of the crystallographically connected hexagonal layers of an hBN particle, along the *c*-axis. L_c values of the hBN obtained without K_2CO_3 in 80 and 160 min were 9 and 18.3 nm, respectively. hBN obtained from K_2CO_3 added samples in 80 min exhibited L_c values in 25–34 nm range. This result indicates that K_2CO_3 is effective in increasing the crystallinity of the formed hBN.

3.2. *TEM and particle size analyses*

SEM and TEM images of some samples prepared without and with K_2CO_3 addition are presented in Figs. 4 and 5, respectively. At 1400 °C, amount of sample prepared without addition was very low in 80 min and it could not be separated from the filter paper. Thus, hBN powder obtained in the experiment conducted for 160 min without K_2CO_3 was subjected to SEM examinations. It was seen that the particle size of hBN was in the range of 100–200 nm when no K_2CO_3 catalyst was used (Figs. 4 and 5a). When 10% K_2CO_3 was introduced, and the experiment was conducted for 80 min, the particle size distribution was in the same range (Figs. 4 and 5b, note the difference in magnification in SEM). Similarly, when the K_2CO_3 amount was increased to 40% and the experiment was conducted for 40 min, hBN of similar particle size was obtained (Fig. 5c).

In addition to SEM observations, the particle size distributions of hBN powders were determined by dynamic light scattering and the results are presented in Table 1 and Fig. 6. The particle size data given in Table 1 and Fig. 6 is in agreement with the SEM and TEM observations. These results indicate that increasing catalyst amount while decreasing the duration provided the growth of the formed hBN particles, resulting in similar particle size in shorter duration. Increasing K_2CO_3 amount in the starting mixture was seen to increase the hBN particle size when the duration was fixed at 80 min (Fig. 4b–d). The hBN particles had irregular morphology. Particle size was about 300 nm and more round particles were seen when 40% K_2CO_3 was used (Figs. 4 and 5d).

Average particle size data is presented in the last column of Table 1 and particle size distribution of hBN powder obtained from the experiments conducted for 80 min is presented in Fig. 6. Data pertaining to the hBN prepared without K_2CO_3 addition in 160 min is also given in the same figure. Average particle size was 150 nm when no catalyst was used in 160 min. In all the experiments conducted for 40 or 80 min, particle size of hBN obtained by K_2CO_3 addition was higher than that obtained from plain B_2O_3+C mixture, as shown in

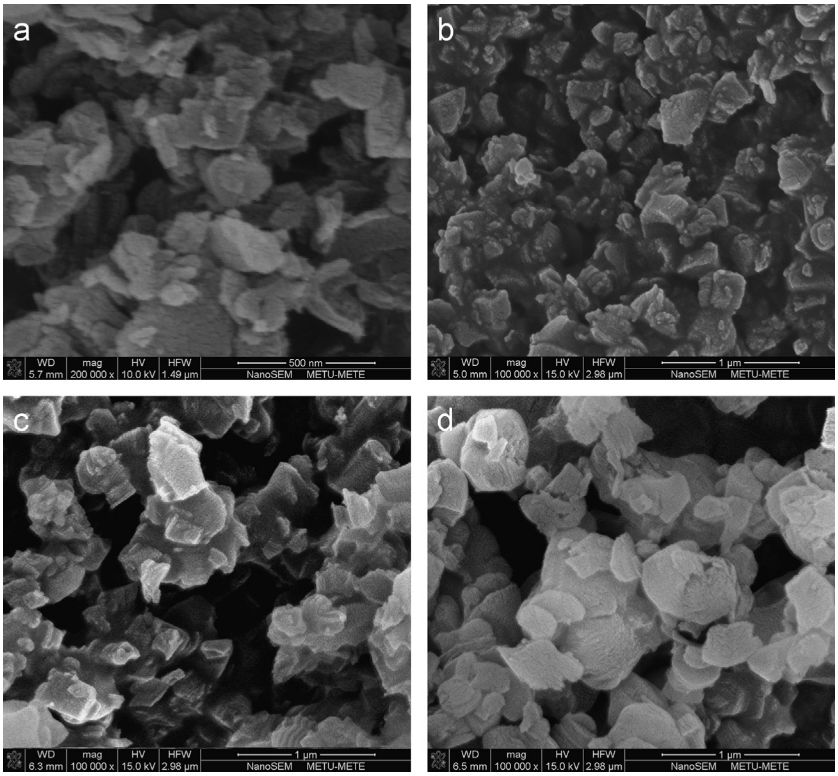

Fig. 4. SEM images of the samples obtained from the experiments conducted (a) without K_2CO_3, for 160 min; (b) with 10% K_2CO_3, for 80 min; (c) with 20% K_2CO_3, for 80 min and (d) with 40% K_2CO_3, for 80 min.

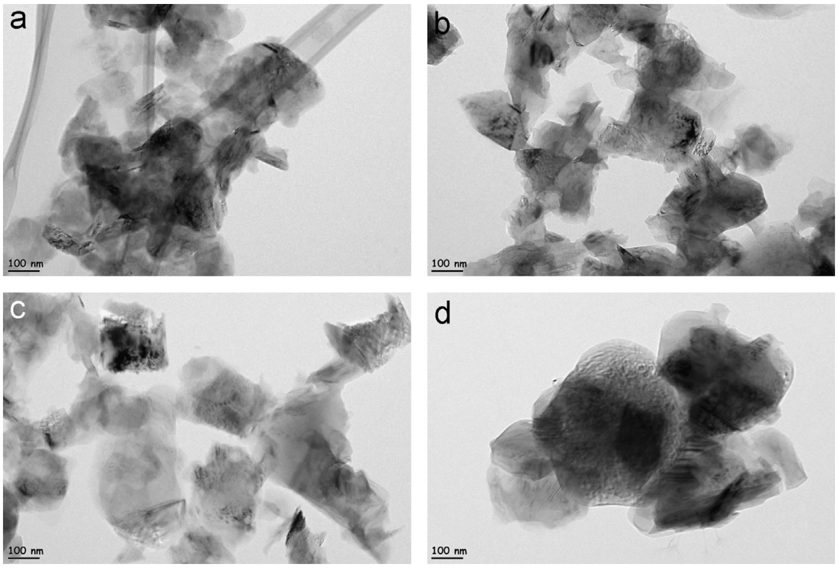

Fig. 5. TEM images of the samples obtained from the experiments conducted (a) without K_2CO_3, for 160 min; (b) with 10% K_2CO_3, for 80 min; (c) with 40% K_2CO_3, for 40 min and (d) with 40% K_2CO_3, for 80 min.

Table 1. When 10% K_2CO_3 was added, average particle size was 200 nm, with a relatively broad distribution when the experiment was conducted for 80 min (Fig. 6). Increasing the K_2CO_3 amount shifted the average particle size over 200 nm and it was about 300 nm when 30 or 40% K_2CO_3 was used. These results indicate the catalytic effect of K_2CO_3 on enhancing the growth of hBN particles.

3.3. Phases and reaction mechanism

K_2CO_3 is expected to decompose into K_2O in the initial moments of the experiment, when the reactants are placed into the preheated furnace at 1400 °C. The decomposition temperature of K_2CO_3 is 898 °C [15]. After decomposition, K_2O is expected to dissolve in the B_2O_3 melt, resulting in the

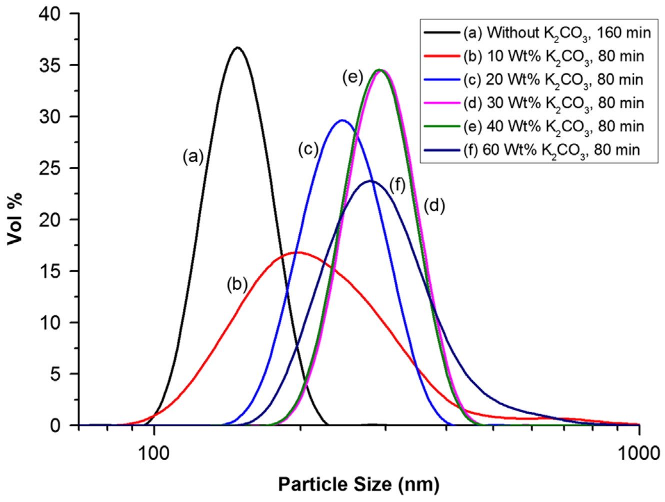

Fig. 6. Particle size distribution graphs of some of the obtained hBN powder.

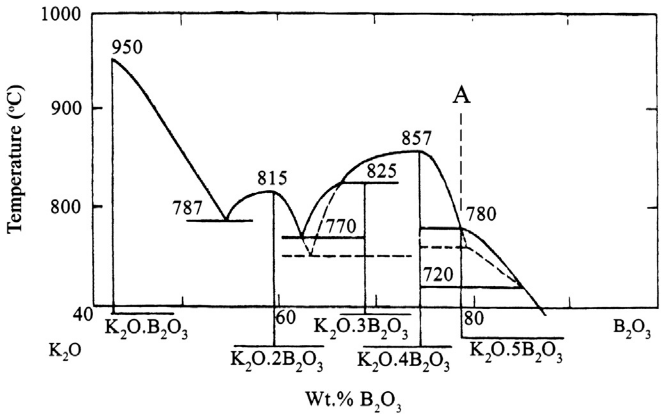

Fig. 7. K_2O–B_2O_3 phase diagram [16].

formation of a potassium borate liquid. In the studied range, no solid compound is expected in the system above 857 °C. Upon cooling, formation of potassium borate compounds takes place as shown in the K_2O–B_2O_3 phase diagram given in Fig. 7. These compounds are expected to be in amorphous form, due to fast cooling of the products after they are taken out of the furnace. If the composition of the K_2O–B_2O_3 system is to the left of the line A (wt% $K_2O > 22\%$ in the K_2O–B_2O_3 system), upon cooling only solid borate compounds are expected to be present in the system, and if the composition is to the right of the line A, solid boron oxide and a borate phase are expected. The initial weight% of K_2O in the K_2O–B_2O_3 system in the prepared samples is presented in Table 1. The composition of the system is expected to change as a result of the consumption of the species due to hBN formation reaction and also due to evaporation. For compositions including and lower than 30% K_2CO_3, the initial composition of the system is to the right of the line A; therefore in the products boron oxide and a borate phase are expected upon cooling, and for compositions higher than 30% K_2CO_3, only borate phases are expected. However, due to reaction and evaporation, the B_2O_3 composition changes and the discussion on these changes which have been followed by XRD analyses can be given as follows.

It was seen in the experiments conducted for 40 min that products of the compositions having equal to and higher than 30% K_2CO_3 contained boron oxide in the products, in addition to the borate phase (Fig. 1). This indicates that the composition of the system up to 30 wt% K_2CO_3 content is in 2 phases region (to the right of line A) at the end of 40 min, where boron oxide and potassium borate exist. Higher addition of K_2CO_3 resulted in formation of potassium borate, and no boron oxide was present in the products at the end of 40 min.

Products of all the experiments conducted with mixtures having 10–60 wt% K_2CO_3 for 80 min were seen to contain boron oxide together with potassium borate (Fig. 2). The fact that boron oxide is present in all the systems indicates that the composition of the systems after 80 min falls to the right of line A in the phase diagram. This can be taken as an indication of the high evaporation rate of the borate phases. As a result of rapid evaporation of borates, composition of the system shifts to higher boron oxide side at the end of 80 min for all compositions, resulting in the coexistence of boron oxide with potassium borate after solidification. In addition, it can be seen in the XRD patterns of the samples containing 40% and 60% K_2CO_3 that amount of both boron oxide and borate phases decrease with increasing K_2CO_3 amount in the mixtures, as can be seen in Fig. 2. This also supports the inference about the fast evaporation rate of the borate phases.

In order to investigate the effect of K_2CO_3 addition on evaporation of the borates, weights of the reaction products and also weights of boron oxide+potassium borate in the reaction products were determined. In acid leach (1/1 HCl/water) step of the employed quantitative analysis method, boron oxide and potassium borate in the products are removed [8,9]. Therefore, their amount in the products can be calculated from the weight difference of the products before and after leaching. It can be seen in Fig. 8 that weight of the reaction products and also weight of boron oxide+potassium borate in the reaction products decreases with the increase in the K_2CO_3 amount in the reactants, for both 40 min and 80 min series.

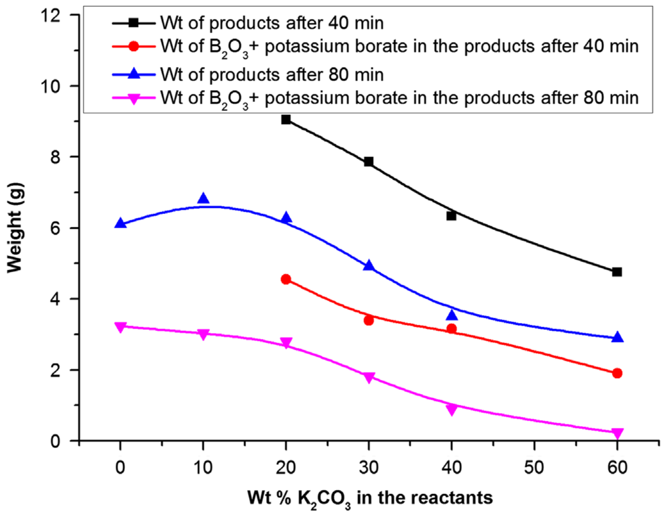

Fig. 8. Weight of products and weight of B_2O_3+potassium borate in the products after 40 and 80 min of reaction.

K_2CO_3 decomposes into K_2O in the initial moments of the reaction when the samples are placed into the preheated furnace and the weight of K_2O+B_2O_3+C at the beginning of the reaction is of concern. The initial weight of B_2O_3+C+K_2O increases with the increase in the addition of K_2CO_3 in the reactant mixture, as shown in Table 1. Therefore, the decrease in the product weight and boron oxide+potassium borate weight as a result of increasing K_2CO_3 addition indicates that the rate of evaporation of liquid potassium borate increases with the increase in the addition of K_2CO_3. Heat of vaporization of alkali borates was found to be lower than that of boron oxide, which results in higher vaporization of alkali borates [17]. In addition, in a study conducted on nuclear waste glass containing boron oxide and alkali oxides, major alkali loss was found to occur by alkali metaborate vaporization [18].

It is known that in the B_2CO_3+C system at 1400 °C in nitrogen atmosphere, hBN formation takes place through the carbothermic mechanism, which includes reduction of B_2O_3 and nitridation [7]. It was also shown that with the addition of basic oxides into B_2CO_3+C mixture, such as CaO [8,13] or MgO [9], an alternative mechanism of hBN formation becomes operative. In the so called ionic mechanism, borate ions form in the melt due to the oxygen ions supplied to the boron oxide melt by K_2O, which form through dissociation of K_2CO_3. Nitrogen ions form as a result of dissolution of nitrogen in the borate melt [8,9]. In that mechanism, hBN formation can be suggested to take place via the reaction of borate and nitrogen ions in the melt, according to the reactions such as [8,13]

$$(\mathrm{BO}_3)^{3-} + \mathrm{N}^{3-} = \mathrm{BN} + 3\mathrm{O}^{2-} \quad (2)$$

$$(B_2O_4N)^{5-} = \mathrm{BN} + (\mathrm{BO}_3)^{3-} + \mathrm{O}^{2-} \quad (3)$$

Formation of hBN particles by the ionic mechanism alone was investigated recently by keeping CaO containing B_2O_3 melts (without C) in nitrogen atmosphere at 1500 °C [13]. No hBN formation took place in the borate melt, indicating a nucleation barrier for the homogenous nucleation of hBN in this mechanism. Diffusion rate of the species is expected to be sufficiently high, given that the medium is in the liquid state and that the temperature is high. The nucleation barrier, arising from the energy required for creating a new interface, can be overcome by the introduction of a pre-existing interface. When the experiment was repeated by adding hBN particles into the CaO–B_2O_3 melt (without C), amount of added hBN increased [13], indicating that the ionic mechanism is operative in the presence of existing hBN nuclei. The increase in the amount and the particle size of the seed hBN particles suggests that they act as heterogeneous nucleation sites and thus they eliminate the nucleation barrier for the ionic mechanism. In the carbothermic formation of hBN with the addition of basic catalysts, then, the hBN particles which form initially by the carbothermic reduction and nitridation of boron oxide become the heterogeneous nuclei and initiate the ionic mechanism, through which further formation and growth of hBN particles can take place.

Therefore, in the present study the role of K_2CO_3 in increasing the amount, particle size and crystallinity of hBN can be explained by the introduction of the ionic mechanism, which occurs in addition to, and also with the contribution of the carbothermic mechanism.

4. Conclusion

K_2CO_3 addition was found to be effective in carbothermic formation of hexagonal boron nitride. Amount, particle size and crystallinity of the formed hBN were seen to increase with the addition of K_2CO_3 into B_2O_3+C starting mixtures. Amount of formed hBN was seen to increase up to 40% addition and then decreased. Amount of K_2O–B_2O_3 in the products and therefore the weight of the products decreased with increasing K_2CO_3 additive in the starting mixture. This was attributed to the rapid vaporization of the potassium borate melt. Rapid vaporization of potassium borate may be the reason for decrease in the rate of hBN formation with the increase in K_2CO_3 amount over 40%.

Acknowledgments

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