J Mater Sci (2006) 41:4921–4927
DOI 10.1007/s10853-006-0339-6

Role of boron carbide in carbothermic formation of hexagonal boron nitride

H. E. Çamurlu · N. Sevinç · Y. Topkaya

Received: 14 April 2005 / Accepted: 29 September 2005 / Published online: 27 May 2006

Abstract Formation of hexagonal boron nitride by carbothermic reduction of boric oxide under nitrogen atmosphere at 1500 °C was investigated. Experiments were performed for durations in the range of 15 min to 3 h. Reaction products were subjected to powder X-ray diffraction analysis, chemical analysis and were examined by scanning electron microscope. Formation of hexagonal boron nitride was found to be complete in 3 h with most forming in the initial 2 h. Boron carbide was found to exist in the reaction products of the experiments in which hexagonal boron nitride formation was not complete. The aim of this study was to investigate the role of boron carbide in the carbothermic production of hexagonal boron nitride. For this purpose, conversion reaction of boron carbide into hexagonal boron nitride was studied. Boron carbide used in these experiments was produced in the same conditions that hexagonal boron nitride was formed, but under argon atmosphere. It was found that formation of hexagonal boron nitride from boron carbide—boric oxide mixtures was slower than activated carbon—boric oxide mixtures. It was concluded that boron carbide is not a necessary intermediate product in the carbothermic production of hexagonal boron nitride.

Introduction

Hexagonal boron nitride (h-BN) is a unique ceramic material with superior high temperature properties. Due to its thermal shock resistance, thermal conductivity, electrical insulation and lubricating property; it finds a large application area in industry [1]. Carbothermic formation of h-BN is stated to be the most widely used industrial production method [2]. In this method, boric oxide reacts with carbon and nitrogen gas to form h-BN:

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

Few studies have been done on the mechanism of carbothermic formation of h-BN [3–6]. Bartnitskaya et al. [3] concluded that B_2O_3 first gets reduced to B by carbon and then B reacts with $N_2(g)$ to form BN while Yoon and Jha [4] considered h-BN formation to proceed through gaseous BO. Pikalov [5] suggested h-BN formation to proceed in two consecutive steps with B_4C forming in the first step according to the overall reaction:

$$2B_2O_3(l) + 7C(s) = B_4C(s) + 6CO(g) \qquad (2)$$

and h-BN forming by reaction of B_4C with B_2O_3 in the second step according to the overall reaction:

$$3B_4C(s) + B_2O_3(l) + 7N_2(g) = 14BN(s) + 3CO(g) \qquad (3)$$

Aydoğdu and Sevinç [6] studied formation of h-BN by subjecting pellets prepared from B_2O_3-activated C mixtures to N_2 gas at temperatures ranging from1100 °C to 1500 °C for durations ranging from 15 min to 4 h and found the reaction to be complete in 2 h at 1500 °C and B_4C, in addition to unreacted B_2O_3, unreacted C and BN formed, to exist in the reaction products of the experiments in which h-BN formation was not complete. They found from the results of experiments directed to the mechanism of the reaction by use of different geometrical arrangements that liquid B_2O_3 and solid carbon need not be in contact in the

---

H. E. Çamurlu · N. Sevinç (✉) · Y. Topkaya
Department of Metallurgical and Materials Engineering, Middle East Technical University, Ankara 06531, Turkey
e-mail: nsevinc@metu.edu.tr

formation of BN from B_2O_3, C and N_2 and concluded the overall reaction (1) to proceed by evaporation of $B_2O_3(l)$ and reaction of $B_2O_3(g)$ with C(s) and $N_2(g)$ on C(s). By thermodynamic analysis based on reaction (3), they showed that either BN(s) or $B_4C(s)$ but not both can exist in the system at equilibrium and that $B_4C(s)$ is unstable in the system when the $\frac{P_{CO}^3}{P_{N_2}^7}$ ratio is less than a critical value at a given temperature which can be calculated to be 6.7×10^{34} for 1500 °C by employing the data used by them. They stated the $\frac{P_{CO}^3}{P_{N_2}^7}$ ratio in their experimental system, where there is a continuous flow of N_2 gas, to be expected to be less than the critical ratio when B_4C is expected not to be present in the system and suggested B_4C to form in regions of the pellet where N_2 pressure is too low due to insufficient penetration of nitrogen gas. They concluded that some h-BN forms according to the overall Reaction (1) and some according to Reactions (2) and (3) taking place successively and found from experiments conducted by subjecting commercial B_4C–B_2O_3 mixtures to N_2 gas the rate of Reaction (3) to be lower than that of Reaction (1). While B_4C appears to be a necessary intermediate product according to Pikalov, the results of Aydoğdu and Sevinç imply B_4C formation not to be necessary in carbothermic formation of BN. This study is a continuation of the study of Aydoğdu and Sevinç and was undertaken with the objective of gaining further information as to the role of B_4C in carbothermic formation of BN. For this purpose in addition to carbothermic h-BN formation experiments according to Reaction (1), experiments were conducted to study B_4C formation according to Reaction (2) by subjecting B_2O_3–C mixtures to argon atmosphere. B_4C powder produced in these experiments, expected to have similar properties such as grain size and morphology to the boron carbide forming during carbothermic production of h-BN was mixed with B_2O_3 and subjected to $N_2(g)$ to study BN formation according to reaction (3).

Experimental procedure

Preliminary experiments were conducted by reacting activated carbon–boric oxide mixtures at 1500 °C under nitrogen atmosphere using the same set up used by Aydoğdu and Sevinç [6] in which similar results were obtained. The furnace in this system was a horizontal tube furnace in which the service life of the furnace tube and the heating elements was rather short due to attack of the boric oxide vapor. In the current study the configuration of the furnace was altered in order to increase the lifetime of the furnace elements and the experiments were conducted in a vertical tube furnace which had an 800 mm long mullite tube of 50 mm inner and 60 mm outer diameters. The mullite tube was closed at both ends by water-cooled brass heads having thermocouple insertion, gas inlet and outlet tubes. Nitrogen gas was introduced into the furnace from the bottom and the exit gas was removed from the top. Temperature of the furnace, kept constant at ±1 °C by a digital temperature controller, was measured with an S type thermocouple inserted into the system from the bottom. Before the experiments the furnace was heated to and stabilized at 1500 °C.

Experiments were performed using boric oxide–activated carbon mixtures containing 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 vaporization. The mixtures consisted of 1.9861 g boric oxide and 0.5140 g activated carbon.

Activated carbon–boric oxide mixtures were prepared by grinding and thoroughly mixing in acetone in an agate mortar and pestle. Activated carbon was over 99% purity. Its XRD pattern revealed no peaks indicating that it had an amorphous structure. It was found after complete burning by keeping at 600 °C for 40 h in a muffle furnace that the activated carbon contained 0.3% ash. Boric oxide was produced by calcination of boric acid of 99.8% purity at 900 °C in an alumina crucible for 1 h and then by pouring the melt onto the surface of a stainless steel plate. During cooling and solidification, boric oxide separated itself from the surface of the stainless steel plate due to shrinkage. It was then collected and stored as bulk pieces in a closed jar in a desiccator. No other phase was detected by powder X-ray diffraction (XRD) analysis in the produced boric oxide.

At the beginning of the experiments, the activated carbon–boric oxide mixture was placed into a graphite crucible the interior of which was lined with a thin (~0.5 mm) h-BN layer. The furnace tube was flushed with N_2 for 5 min and the graphite crucible with its contents was lowered from the top end of the tube into the hot zone of the furnace by hanging to an alumina bar. Then, the top end of the tube was closed airtight. Time was taken as zero when the furnace regained its stable state at 1500 °C, which was about 3–5 min after the positioning of the sample in the furnace. At the end of the experiments the crucible was removed from the furnace. The crucible and the contents were cooled to room temperature under flow of argon gas in a closed jar. The reaction product was in the form of an aggregate, which was then cut longitudinally into two pieces. One of the pieces was ground in agate mortar and pestle and subjected to XRD analysis and chemical analysis. The other piece was used for scanning electron microscopy (SEM) examinations on fracture surfaces.

Nitrogen flow rates of 50 cc/min, 100 cc/min, 200 cc/min and 400 cc/min were tested in the preliminary experiments in order to determine a suitable rate for investigation of the formation of h-BN. It was seen in most of the experiments conducted with 50 cc/min N_2 flow rate that there was popping of a flame when the top brass head of the furnace was opened for taking the sample out. Also, the amount of hexagonal boron nitride as well as boron carbide was observed to be less than the amounts obtained at higher flow rates. These results were taken as indications that there could be a high concentration of carbon monoxide in the system when 50 cc/min N_2 flow rate was used, which might have slowed down the reactions. It was observed that nitrogen flow rates above 100 cc/min did not have a significant effect on the amount of boron nitride formed. Based on these findings it was decided to use a nitrogen gas flow rate of 200 cc/min in the experiments. The BN-coated graphite crucible used to contain the B_2O_3- activated carbon mixtures had an ID of 2.5 cm, an OD of 3 cm and a depth of 3 cm while the reaction products in aggregate form had depths of 1 to 1.5 cm. Holes close to the circumference of the bottom of the BN-coated graphite crucible used to contain the B_2O_3-activated C mixtures were drilled in some of the preliminary experiments to have better contacting of N_2 gas with the B_2O_3-activated C mixtures contained in the crucible and to find if the unoccupied volume above the reaction mix in the crucible to have any effect on the reaction. This geometry was found not to have a significant effect on the quantity of BN and B_4C forming but resulted in higher evaporation loss of B_2O_3. All of the experiments reported were conducted by subjecting B_2O_3-activated C mixtures contained in a BN-coated graphite crucible having no holes at the bottom to nitrogen gas introduced into the system at a flow rate of 200 cc/min.

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. XRD data was processed and phases were identified by the Qualitative Analysis program. It is a software embedded in the computer of the XRD device, where smoothing, background subtraction, Ka2 elimination and phase identification operations were performed on the XRD patterns. Grain size and morphology were examined by SEM. The amounts of the constituents of the products were determined by following a method, which is very similar to the method used by Aydoğdu and Sevinç [6]. The method is schematically shown in Fig. 1 and explained below.

The product of each experiment was ground in an agate mortar and pestle and moisturized in order to convert all of the boric oxide into boric acid and dried at 40 °C until constant weight. In the products, only boric acid was soluble in water. Therefore, the product was dissolved in water and filtered. Amount of unreacted boric oxide, $W_{B_2O_3}$, was determined volumetrically by titrating the filtrate with NaOH. The residue containing boron carbide, boron nitride and unreacted carbon was placed in a small alumina boat and oxidized at 800 °C for 15 h, as a result of which boron carbide was completely converted into boric oxide and unreacted carbon was completely burned. It was found in our previous study [6] that boron carbide gets oxidized but h-BN does not at 800 °C. The oxidized product was analyzed by powder XRD and it was verified that no boron carbide remained in the sample. The oxidized products were weighed and dissolved in water and then filtered. Amount of boric oxide, $W_{B_2O_3^*}$, which was formed by the oxidation of boron carbide was determined volumetrically, from which the amount of boron carbide was calculated by use of the equation: $W_{B_4C} = \frac{W_{B_2O_3^*}}{69.62\times 2} \times 55.25$. The final product contained only h-BN. Amount of boron nitride was calculated by subtracting the amount of boric oxide, $W_{B_2O_3^*}$, formed by the oxidation of boron carbide from the weight of the products after oxidation: $W_{BN} = W_3 - W_{B_2O_3^*}$. Calculated weight of boron nitride was also verified by weight of the final product. Amount of unreacted carbon was calculated by subtracting the weight of boron carbide and boron nitride from the weight of the product before oxidation: $W_C = W_2 - W_{B_4C} - W_{BN}$.

In all the filtering operations, Whatman #42 filter was used, which is the slowest filter paper and specifically used for filtering fine crystalline particles. A vacuum pump was used in the filtering system to speed up the process. No solid particle passed to the filtrate, which would cause blurring and difficulties in the titration process. All of the titrations and analysis of the samples were conducted twice in parallel. The values from two analyses were compared

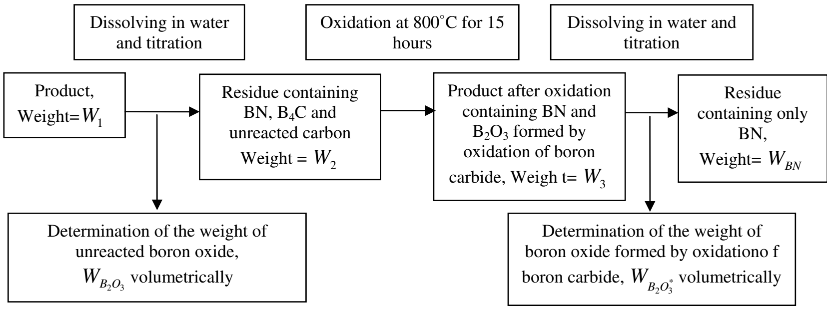


Fig. 1 Method of analysis for determination of the constituents of the products

and repeated if they were inconsistent. The average of the two values was reported, if the two analyses were consistent with each other.

Boron carbide formation experiments were performed by the same procedure as h-BN formation, but argon atmosphere was used instead of nitrogen. In order to investigate the conversion of B_4C into h-BN, the produced B_4C was then mixed with boric oxide, the amount of which was 150% more than the stoichiometric amount according to Reaction (3). The mixture was reacted under nitrogen atmosphere at 1500°C for 3 h and the reaction products were examined.

Results and discussions

Experiments were conducted in order to investigate the formation of hexagonal boron nitride and to determine the duration for the completion of the reaction. In the initial runs the weight of boric oxide in the activated carbon-boric oxide mixtures was 50 mole % in excess of the amount, calculated in accord with the stoichiometry of Reaction (1) to account for loss of boric oxide by vaporization. This quantity of boric oxide was found more than adequate for completion of h-BN formation in the preliminary experiments conducted in the horizontal furnace used by Aydoğdu and Sevinç [6] but the products of experiments conducted in the vertical furnace described above were found to contain boron carbide and h-BN but no boric oxide at 1500 °C for durations longer than 2 h. It is known that some boron carbide forms in carbothermic production of h-BN according to Reaction (2), which is then converted into h-BN by reacting with boric oxide and nitrogen according to Reaction (3) [3, 6]. Reaction (3) is known to proceed in the presence of N_2 gas until at least one of B_4C or B_2O_3 is completely used [6]. Presence of B_4C but absence of B_2O_3 in the reaction products stated above indicated that 50 mole% excess boric oxide was not sufficient and that more boric oxide would be necessary for complete conversion of B_4C into h-BN. The higher loss of boric oxide was attributed to the vertical position of the furnace used in the current study. Later experiments were conducted with activated carbon-boric oxide mixtures having 100-mole% excess boric oxide.

Formation of h-BN was followed by powder XRD analysis. The XRD patterns of the products of the experiments conducted with 100-mole% excess boric oxide for 15 min to 3 h are given in Fig. 2. h-BN phase (ICDD card # 34-0421) was identified in the XRD patterns and it was seen that B_4C peaks (ICDD card # 35-0798) were present up to 2 h. The decrease in the peak broadening (full width at half maximum, FWHM) of the (002) peak of the formed h-BN with increasing duration may be taken as an indication that the average crystal thickness of h-BN increased with duration [7].

Amounts of the constituents of the products of the experiments conducted with 100-mole% excess boric oxide for durations in the range of 15 min to 3 h at 1500 °C are presented in Figs. 3 and 4. It is seen from the results that the amounts of unreacted activated carbon and boric oxide decreased with increasing duration. Amount of h-BN in the reaction products increased with time and was constant after 2.5 h. Amount of boron carbide in the reaction products increased in the first 30 min and then decreased. This behavior may be as a result of two competing reactions. The first one is Reaction (2), where B_4C formation occurred and the second is Reaction (3), where consumption of B_4C took place. It can be inferred from Fig. 4 that rate of formation of B_4C was higher by Reaction (2) in the initial stages, i.e. up to 30 min, most probably due to the high concentration of carbon in the reactants. As the amount of carbon decreased, the rate of Reaction (3) became higher than Reaction (2) and consumption of B_4C dominated, resulting in a decrease in the amount of B_4C after the first half hour. It can be suggested therefore that the overall formation of h-BN took place by two parallel reactions. Some of the total h-BN formed by Reaction (1), where boric oxide was directly reduced by carbon in the presence of nitrogen in order to form h-BN. Additionally, some of it formed as a result of combination of Reactions (2) and (3), where B_4C first formed from boric oxide and carbon and simultaneously converted into h-BN.

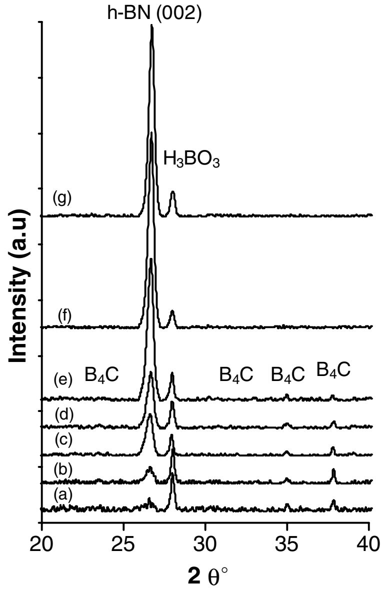


Fig. 2 XRD patterns of the products of the experiments conducted for (**a**) 15 min, (**b**) 30 min, (**c**) 1 h, (**d**) 1.5 h, (**e**) 2 h, (**f**) 2.5 h and (**g**) 3 h

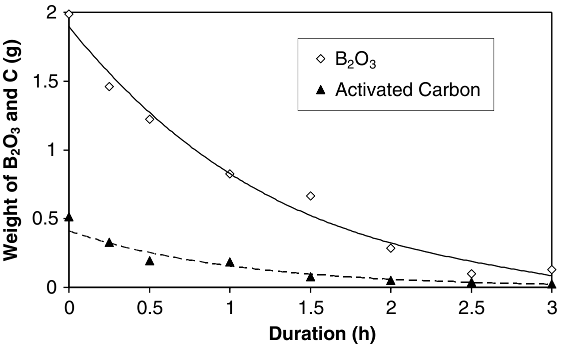


Fig. 3 Amounts of B_2O_3 and activated carbon in the products of the experiments conducted for 15 min to 3 h

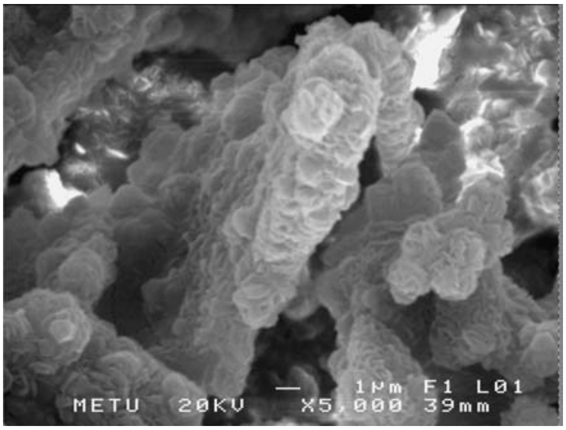


Fig. 5 SEM micrograph of h-BN formed in 3 h

SEM micrograph of the product of the experiment conducted for 3 h is given in Fig. 5. It was observed in this micrograph that h-BN particles forming by reaction of gaseous B_2O_3 and nitrogen gas on C(s) had flaky structure; and were below 1 μ size.

The reaction products were in the form of solid aggregates which were kept together by the solidified boric oxide and in which some small and large pores existed. It was observed by visual examination of these aggregates that B_4C formation mostly took place in the core and bottom regions. It can be suggested from this observation that B_4C formed at points where nitrogen gas could not penetrate into the aggregate and where N_2 partial pressure was too low for h-BN formation. This observation may be taken as an indication that B_4C may not be a necessary intermediate product in the carbothermic production of h-BN under nitrogen atmosphere.

SEM micrographs of boron carbide rich parts of the products of the experiments conducted for 1 h are given in Fig. 6a and b. It can be seen that boron carbide forming in the system had various shapes such as whisker like formations as in Fig. 6(a) and blocky–angular grains as in Fig. 6(b).

In order to investigate the conversion of B_4C into h-BN, B_4C was produced in the same experimental conditions that h-BN formation was studied, but under argon atmosphere. SEM micrograph of the boron carbide powder produced by reacting activated carbon–boric oxide mixtures under argon at 1500°C for 2.5 h is given in Fig. 7. A mixed morphology of boron carbide grains was observed. There were some rod-like or whisker-like formations, also blocky and angular grains of 2–7 microns were present. It was realized from SEM examinations that the size and

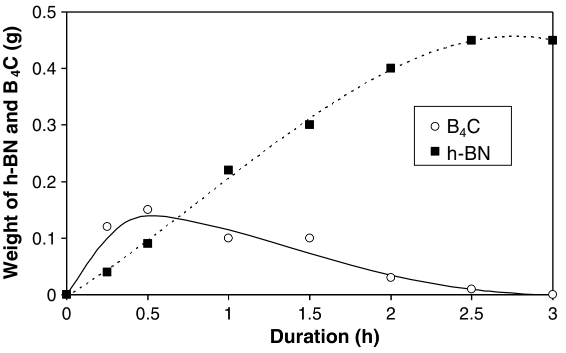


Fig. 4 Amounts of h-BN and B_4C in the products of the experiments conducted for 15 min to 3 h

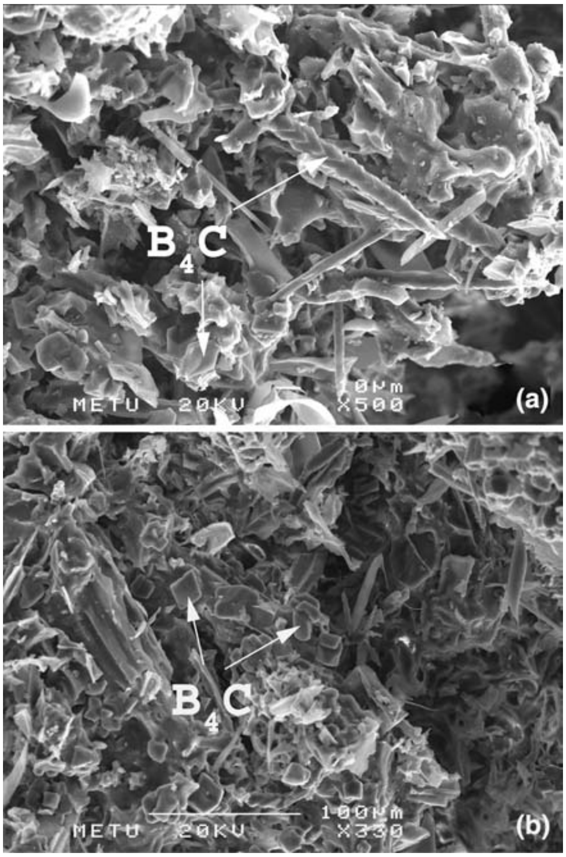


Fig. 6 (**a**) and (**b**) SEM micrographs of boron carbide rich parts of the product of the experiment conducted for 1 h

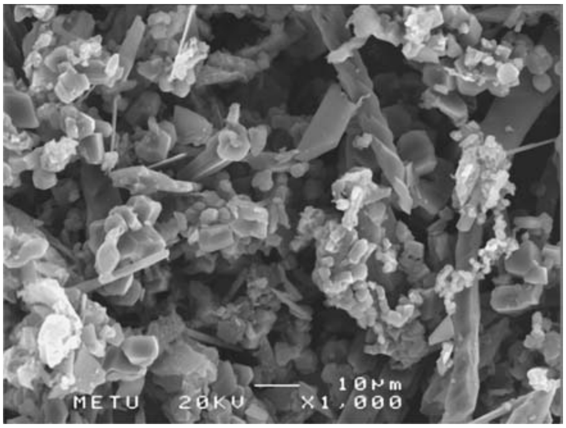


Fig. 7 SEM micrograph of the produced boron carbide powder

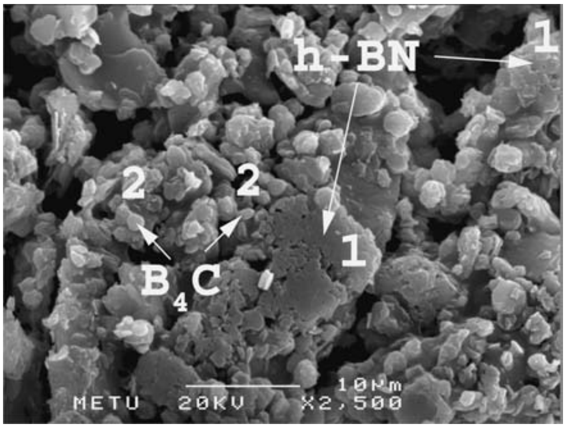


Fig. 9 SEM micrograph of the product of the experiment conducted by reacting boron carbide–boric oxide mixtures at 1500 °C for 3 h under nitrogen

morphology of the B_4C grains produced under argon were comparable to those formed during h-BN formation.

Produced boron carbide phase was clearly detected by XRD analysis given in Fig. 8a. It was also realized from this XRD pattern that some graphite might have been formed by the graphitization of activated carbon. Similar results were observed in other studies [8].

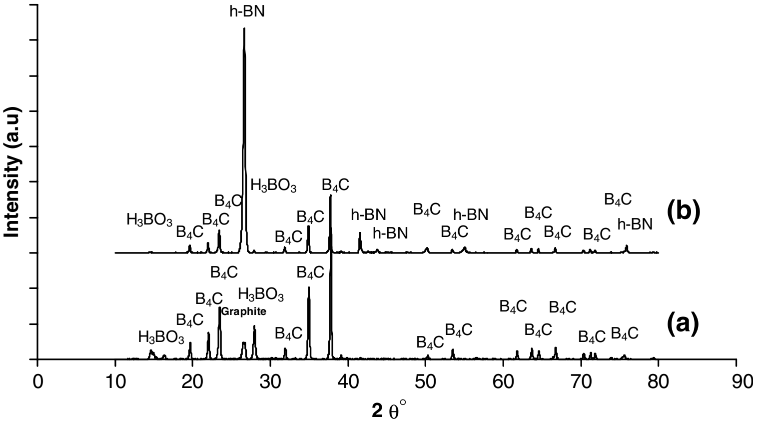
The produced boron carbide was mixed with boric oxide and the mixture was reacted under nitrogen atmosphere for 3 h. It can be seen in the XRD pattern given in Fig. 8b that h-BN was formed; however boron carbide phase was also present with h-BN, indicating that the conversion of boron carbide into h-BN was not complete. This may be taken as an indication that reaction of boron carbide and boric oxide under nitrogen (Reaction 3) in order to form h-BN requires longer durations than 3 h.

SEM micrograph of the product of the experiment conducted by reacting boron carbide–boric oxide mixtures at 1500 °C for 3 h under nitrogen atmosphere is given in Fig. 9. Unreacted B_4C grains could be distinguished in the reaction products. It was inferred from the boron and nitrogen peaks in the energy dispersive analysis by X-ray (EDX) that the points indicated as (1) in Fig. 9 were h-BN; and from the carbon and boron peaks, the grains indicated as (2) were B_4C.

Conclusions

The aim of this study was to investigate the role of B_4C forming during carbothermic production of h-BN. It was found from the experiments conducted at 1500 °C under nitrogen atmosphere that activated carbon in boric oxide–activated carbon mixtures was completely converted into h-BN in 3 h. In order to investigate the conversion of B_4C into h-BN, B_4C was produced in the same conditions of h-BN formation but under argon atmosphere. It was determined by XRD and SEM analysis that the produced boron carbide was not completely converted into h-BN in 3 h. Therefore, it could be concluded that formation of h-BN from boron carbide by Reaction (3) was slower than formation of h-BN from carbon by Reaction (1). This result may be taken as an indication that boron carbide is not a necessary intermediate product in formation of hexagonal

Fig. 8 XRD patterns of (**a**) produced boron carbide, (**b**) after reacting produced boron carbide–oric oxide mixtures under nitrogen at 1500 °C for 3 h



boron nitride and that formation of boron carbide slows the rate of formation of boron nitride. One important point to be taken into account in carbothermic production of boron nitride is the very high losses of boric oxide. This loss primarily arises from evaporation of boric oxide and some boric oxide is lost due to formation of gaseous BO and B and increases with time. Increasing the rate of formation of boron nitride is expected to decrease the boric oxide losses. Prevention or minimization of boron carbide formation during carbothermic production of boron nitride appears not only to increase the rate of formation of boron nitride but to decrease the boric oxide losses also. Studies directed to this objective should be useful. B_4C was found to have formed in the core and bottom regions of the reaction mixture where nitrogen partial pressure was probably too low for h-BN formation. Better contacting of the boric oxide–carbon reaction mixture with nitrogen gas may be helpful to decrease the quantity of B_4C forming in carbothermic formation of boron nitride.

Acknowledgements This project was supported by the State Planning Organization of the Turkish Government through the Academic Human Resources Program and by Middle East Technical University grants.

References

1. Haubner R, Wilhelm M, Weissenbacher R, Lux B (2002) Boron nitrides – properties, synthesis and applications. Springer-Verlag, Berlin Heidelberg, p 14
2. The Economy of Boron (2002) Roskill information services, London, p 250
3. Bartnitskaya TS, Ya Kosolapova T, Kurdyumov AV, Oleinik GS, Bilyankevich AN (1986) J Less-Common Met 117:253
4. Yoon SJ, Jha A (1996) J Mater Sci 31:2265
5. Pikalov SN (1988) Powder Metall Met C+ 27:404
6. Aydoğdu A, Sevinç N (2003) J Eur Ceram Soc 23:3153
7. Cullity BD, Stock SR (2001) Elements of X-ray diffraction. Prentice Hall, New Jersey, p 169
8. Sinha A, Mahata T, Sharma BP (2002) J Nucl Mater 301:165