EFFECT OF SODIUM CARBONATE ON CARBOTHERMIC FORMATION OF HEXAGONAL BORON NITRIDE

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

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IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
METALLURGICAL AND MATERIALS ENGINEERING

SEPTEMBER 2010

Approval of the thesis:

EFFECT OF SODIUM CARBONATE ON CARBOTHERMIC FORMATION OF HEXAGONAL BORON NITRIDE

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ABSTRACT

EFFECT OF SODIUM CARBONATE ON CARBOTHERMIC FORMATION OF HEXAGONAL BORON NITRIDE

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September 2010, 53 pages

Effect of Na_2CO_3 on formation of hexagonal boron nitride (h-BN) by carbothermic method has been studied by subjecting B_2O_3-C and Na_2CO_3-added B_2O_3-C mixtures to N_2 (g) atmosphere. 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 $CaCO_3$ [1]. Na_2CO_3 was found to be less effective than $CaCO_3$ in increasing the amount while it was more effective than $CaCO_3$ in increasing the particle size of h-BN forming.

Keywords: Hexagonal Boron Nitride, Carbothermic Formation, Sodium Oxide, Particle Size.

ÖZ

SODYUM CARBONATIN KARBOTERMİK YÖNTEMLE HEKZAGONAL BOR NİTRÜR OLUŞUMU ÜZERİNE OLAN ETKİSİ

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Tez Yöneticisi: Prof. Dr. Naci Sevinç

Eylül 2010, 53 sayfa

B_2O_3-C ve Na_2CO_3 eklenmiş B_2O_3-C karışımlar N_2 (g) atmosferinde tutalarak Na_2CO_3'ın karbotermik method ile hekzagonal bor nitrür oluşumu üzerindeki etkisi araştırıldı. Karışımlardaki Na_2CO_3 miktarı 0-40 ağırlık % arasında değiştirildi. Zaman ve sıcaklık deneysel değişkenler olarak kullanıldı. Reaksiyon ürünleri XRD ve SEM ile analiz edildi. Na_2CO_3'ın $CaCO_3$'a benzer şekilde h-BN'nin hem miktarını hem de tane boyutunu artırdığı bulundu [1]. Na_2CO_3'ın $CaCO_3$'a göre oluşan h-BN'lerin artışında daha az etkili olduğu ancak, tane boyutunun artışında daha fazla etkili olduğu gözlemlendi.

Anahtar Kelimeler: Hekzagonal Bor Nitrür, Karbotermik Oluşum, Sodyum Oksit, Tane Boyutu.

To My Family

ACKNOWLEDGEMENTS

It is a great pleasure to thank my supervisor Prof. Dr. Naci Sevinç for his valuable supervision, guidance and constant encouragement throughout the course of this study.

I am very grateful to M. Sc. Ali Arda Özkenter for their help and support during this work.

I would also like to thank Necmi Avcı for XRD analysis, Cengiz Tan for SEM analysis. I must also express my special thanks to Eylem Kahramansoy, Işıl Ertosun, Irmak Sargın and M. Sc. Güher Kotan for their support.

I should thank to Ajda for her endless love and support. I am also thankful to my friends Duygu Cantekin and Duygu Ergenç.

Finally, I wish to thank my parents Seher and Nadir Akyıldız for their support during this study and their endless love during my life.

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CHAPTER 1

INTRODUCTION

Ceramics are inorganic, non-metallic materials produced by the action of heat. Ever since ancient times ceramic materials evolve from clay to advanced ceramics and their uses area has grown. As technological improvements continue, necessity of enhanced properties becomes more significant. In the competition between oxide ceramics and non-oxide ceramics, the latter one is one step ahead by its higher hardness, higher mechanical strength, superior corrosion, oxidation and thermal shock resistance properties [1].

Hexagonal boron nitride (h-BN) is a white, soft and lubricous material which is often called as white graphite due to high resemblance of its crystal structure to that of graphite. Most important properties of h-BN are high thermal conductivity, excellent solid lubricity and good electrical insulation. It has a wide application area as a result of these advanced properties ranging from additive in cosmetic sector to insulator electronics [2, 3].

In the production of h-BN, carbothermic reduction of boric oxide in nitrogen atmosphere has an important place. Use of some additives is known to catalytically affect h-BN formation by carbothermic method. The aim of this study was to investigate the effect of Na_2CO_3 addition on carbothermic formation of h-BN and the possibility of use of cheap and readily available substances, boric acid and borax ($Na_2B_4O_7.10H_2O$), in carbothermic production of h-BN.

CHAPTER 2

LITERATURE REVIEW

Boron nitride is a unique material with excellent thermal, electrical and chemical properties. There are different methods for production of hexagonal boron nitride, and among these, carbothermic reduction is the most widely used one for industrial processes [4]. Addition of oxides like CaO, BaO, MgO, Li_2O into B_2O_3-C mixtures subjected to N2(g) is known to affect formation of h-BN. Turkey has large amount of Borax reserves, which consists of sodium oxide and boron oxide. Effect of Na_2CO_3 on carbothermic formation of h-BN and possibilities of production of h-BN by carbothermic reduction of B_2O_3-Borax mixtures was studied in this thesis.

In this chapter, information existing in literature on h-BN and its atomic structure, properties, application areas and production techniques with emphasis on carbothermic method will be briefly summarized.

2.1 Boron Nitride Phases

There are many forms of boron nitride, like cubic (cBN), hexagonal (h-BN), amorphous, turbostratic (tBN), wurtzitic (wBN) and rhombohedral (rBN)[3]. Two major allotropes are cubic and hexagonal BN, which are similar to the phases of carbon. Crystal structure of cubic BN is similar to diamond whereas crystal structure of hexagonal BN is similar to graphite. Since boron and nitrogen are on the right and left side of carbon in the periodic table, carbon and BN phases are isoelectronic and have four valence electrons for each atom [5]. Correspondence of phases broadens to properties, such as hexagonal BN is soft and lubricating like graphite and cubic BN is hard and abrasive like diamond. It is possible to produce cubic BN from hexagonal BN at temperatures above 1500 K and pressures above 6 GPa [3, 6].

Hexagonal BN has a hexagonal sheet layered structure, as shown in Figure 2.1. B and N atoms, forming B_3N_3 hexagons, compose layers of BN. Within these hexagons strong covalent (sigma) bonds arise from sp2 hybridization. On the other hand, among the planes of h-BN, there are weak van der Waals (pi) bonds. There are no free electrons and overlapping of pi bonds is not probable. Also, because of high electronegativity between boron and nitrogen atoms, localization of pi electrons is high. Therefore h-BN has a white color and it is a good electrical insulator [3, 5].

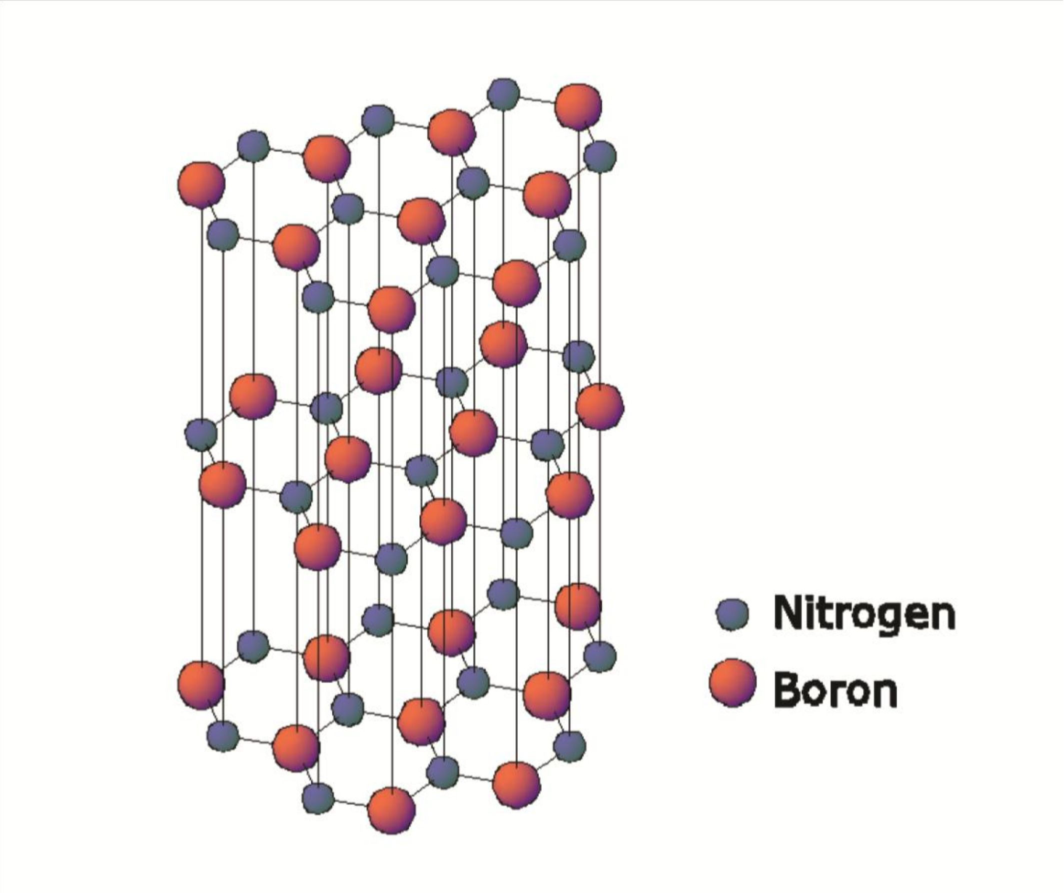

Figure 2.1 Crystal structure of hexagonal boron nitride.

2.2 Properties of Hexagonal BN

Properties of hexagonal BN largely depend on the production methods. Depending on the production methods, properties like crystallinity, particle size distribution, purity and shape of h-BN exhibit noticeable differences. The properties of h-BN determine the utilization area.

Hexagonal BN has high thermal conductivity, excellent solid lubricity and good electrical insulation. It is white, soft and non-toxic. Some physical, chemical electrical properties of h-BN compared to graphite, alumina and aluminum nitride are given in Table 2.1. It has low density and high melting point relative to Al_2O_3 and AlN. h-BN can be used up to 1000°C in oxidizing atmospheres, 1400°C under vacuum and 2800°C in inert atmospheres [3]. It is an excellent corrosion resistant material. It is inert to gasoline, benzene, acetone, alcohol, chlorinated hydrocarbons and other organic solvents [5]. It has outstanding thermal shock resistance and dielectric properties. It can withstand recurrent thermal shocks between 0-2000°C [7-10].

Table 2.1 Some physical, chemical electrical properties of h-BN, graphite, aluminum nitride and alumina [5, 11-14]

Properties	**h-BN**	**Graphite**	**Aluminum Nitride**	**Alumina**
Density, g/cm3	2.27	2.09-2.23	3.26	3.95-4.1
Hardness, Mohs	2	2	7	9
Melting Point, C	3000	3700	2200	2072
Electrical Resistivity, ohm-cm, RT	$1.17*E^{13}$	$109*E^{-6}$	$10*E^{14}$	$10*E^{15}$
Dielectric Strength (kV/mm)	35	-	14	9
Dielectric Constant	4.2	-	10	9.7
Coefficient of Thermal Expansion	0.7 ⊥ 7.5 //	32 ⊥ 46 //	4.1	7.1
Thermal Conductivity, Watt/Meter K	71 // 121 ⊥	95 // 138 ⊥	180-220	17-33
Working Temperature, °C				
In Air	1000	330	1350	1700
In inert atmosphere	3000	1650	-	2000

Easy sliding B_3N_3 hexagons provide a lubricating effect [7]. The lubricating properties do not depend on temperature contrary to other lubricants [7,8,15]. In Figure 2.2, some of the important lubricants are compared on friction coefficient versus temperature diagram.

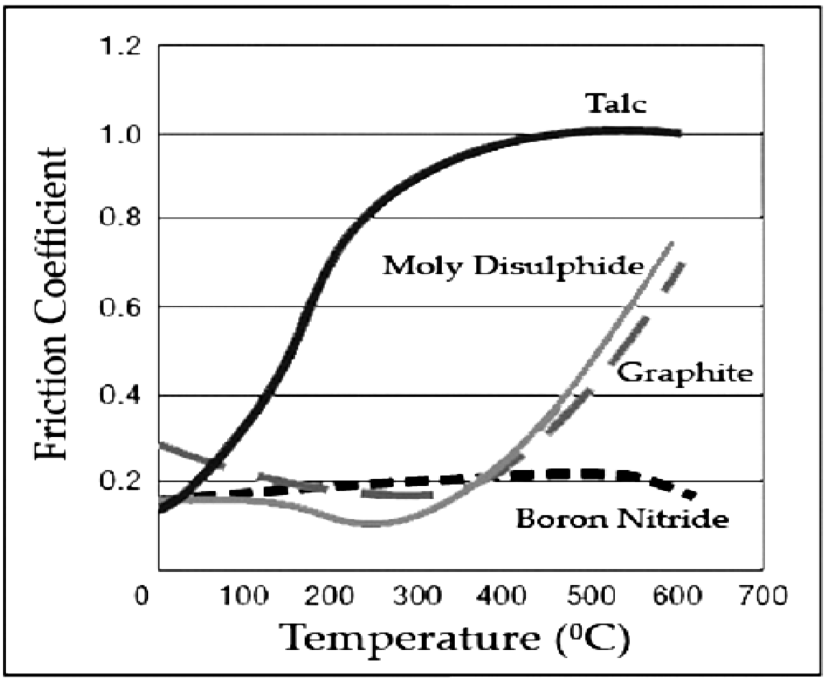

Figure 2.2 Change in friction coefficient of some important solid lubricants with temperature [16].

Hexagonal BN is not wetted by many molten metals such as aluminum, bronze, cadmium, bismuth, germanium, zinc and slags and non metallic melts such as boron, silicon and glasses [5, 9, 17, 18].

2.3 Applications of h-BN

Hexagonal BN is an exceptionally versatile material with excellent properties that makes it a desirable material for many industries. It is mainly used as a tablet lubricant or lubricant for moving parts at high temperatures, insulator or cooler in electronic parts, crucibles for molten metals in metal industry and additives to a variety of ceramic composite applications. It can be used as fibers, as source for cubic boron nitride, in sintered machine parts in severe conditions and in powders (in a liquid media or hot pressed). [2, 3, 6, 16, 19-21]

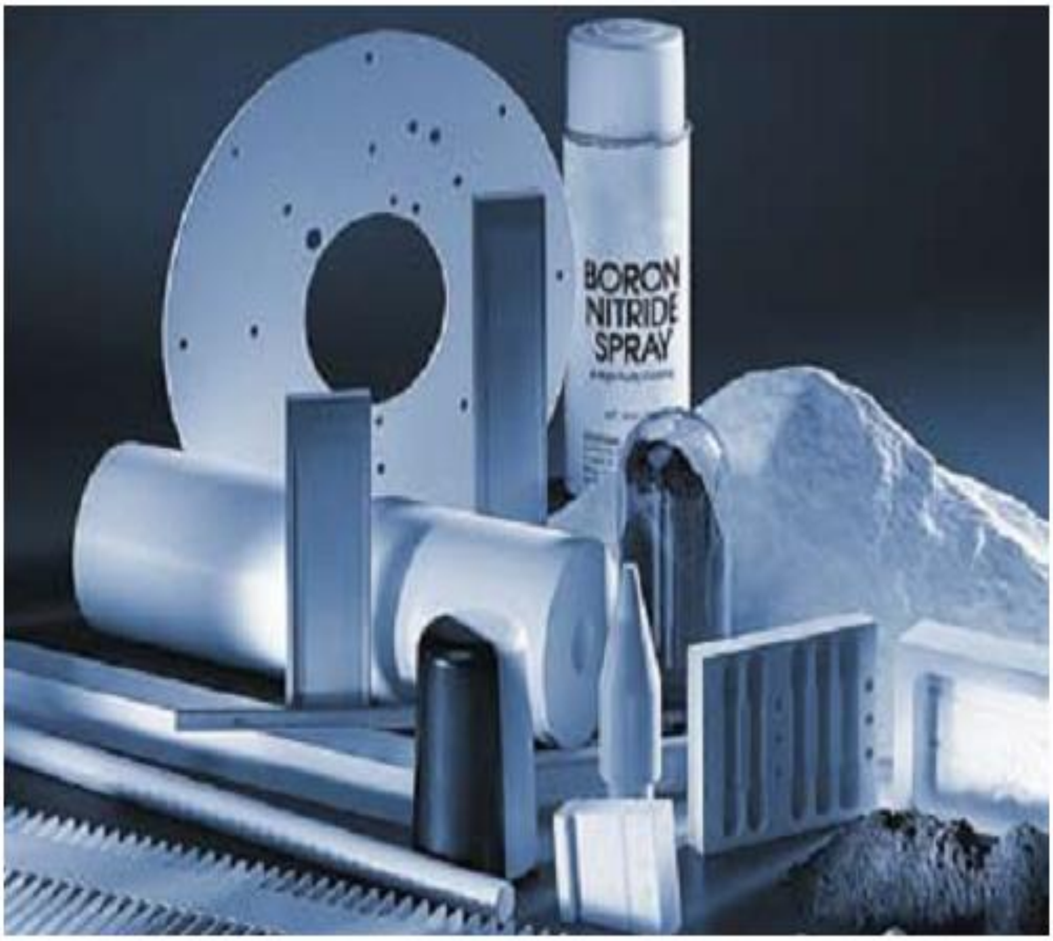

Figure 2.3 Various products of hexagonal boron nitride as powder, hot pressed shapes and pyrolytic shapes [22].

Manufactured goods of hexagonal BN can be summarized as follow;

- Solid lubricants
- Water and/or oil based lubricating dispersions
- Gas seals for oxygen sensors

- Break rings for casting
- Release agents
- Absorbent for benzene
- Isolators in glass and TV industry
- Filler for plastics
- Additives for ceramics and composites, like SiAlON, alumina and titanium diboride
- Radar windows and antennas
- Evaporater boats for aluminum and molecular beam epitaxy
- Masks for x-ray lithography
- Paints and coatings
- Fibers
- Insulator layers in MISFET semiconductors
- Electrodes in molten salt fuel cells
- Cosmetics
- Vessels for Czochralski crystal growth of III-V and II-VI compounds
- Seals in batteries [3, 5, 21, 23]

Depending on the application area, morphology of particles, purity and production method of h-BN must be determined delicately. For instance, ultra-high purity is the most important criterion for cosmetic industry whereas fine grain size is the main concern for hot pressing or hot isostatic pressing.

2.4 Synthesis Methods of h-BN

Hexagonal BN was first synthesized from potassium cyanide and boric acid in 1842 by W.H. Balmain but it took over 100 years to synthesise it commercially [24]. Today, there are several methods in synthesis of h-BN but three of them are used in industrial scale [3, 4, 6].

First one is reaction of boric acid and ammonia in the presence of a carrier substance such as calcium phosphate, calcium carbonate or calcium oxide, according to in Reaction 2.1;

$H_3BO_3 + NH_3 = BN + 3\ H_2O$ Reaction 2.1

Reaction temperatures exceed 900°C. In the process boric oxide melts and covers the carrier substance which provides a large surface area giving rise to increased reaction rate. Carrier substance is removed by subsequent leaching with HCl. In order to remove the impurities from the system and form hexagonal BN from amorphous structure, a heat treatment above 1500°C is required. [3, 6, 18]

Second synthesis method is the reaction of boric oxide or alkali borates with nitrogen containing organic substances like urea, melamine, cyanides or dicyanamide, in the nitrogen atmosphere. Overall reaction is given in Reaction 2.2;

$B_2O_3 + CO(NH_2)_2 = 2\ BN + CO_2 + 2\ H_2O$ Reaction 2.2

In this method also, a second treatment at 1500°C is needed to remove impurities and change the crystal structure from turbostratic to hexagonal. [3, 6, 14, 16, 18]

Third method is the carbothermic reduction method. In this method, boric oxide reacts with carbon and nitrogen according to Reaction 2.3;

$B_2O_3 + 3C + N_2 = 2BN + 3CO$ Reaction 2.3

Relevant literature on carbothermic formation of h-BN is summarized below:

Synthesis of boron nitride by the reaction of boric oxide with carbon and nitrogen gas was investigated by Aydoğdu and Sevinç [25]. They conducted experiments at 1100, 1200, 1300 and 1400°C for 2 hours and at 1500°C for 15, 30, 60, 90, 120, 180 and 240 minutes. h-BN formation was observed to have taken place at all temperatures. Amount of h-BN forming was found to steadily increase with increase in temperature. They concluded that formation of h-BN according to Reaction 2.3 was completed at 1500°C in 2 hours and found B_4C to exist in the reaction products of the experiments for which h-BN formation was not complete.

With the aim of determining the reaction mechanism of carbothermic reduction method, they conducted experiments with different geometries and concluded that liquid boric oxide and activated carbon need not to be in contact. They concluded that h-BN formation takes place by reaction between B_2O_3 (g) originating from evaporation of B_2O_3 (l) (Reaction 2.4) and N_2 (g) on C (s) according to Reaction 2.5.

B_2O_3 (l) = B_2O_3 (g) Reaction 2.4

B_2O_3 (g) + 3 C(s) + N_2(g) = 2 BN(s) + 3 CO(g) Reaction 2.5

Bartnitskaya et al. proposed Reaction 2.3 to take place in steps with formation of elemental boron in the first step and reaction of elemental boron with N2 (g) in the second step [26]. Yoon and JHA also suggested a step-wise reaction with formation of BO_3 in the first step and reaction of BO_3 and N_2 (g) in the second step [27]. Pikalov also considered a step-wise reaction and suggested B_4C to form according to Reaction 2.6 in the first step and BN to form according to Reaction 2.7 in the second step implying B_4C to be a necessary intermediate compound in carbothermic formation of BN [28].

2 B_2O_3 (l) + 7C (s) = B_4C (s) + 6 CO (g) Reaction 2.6

3 B_4C (s) + B_2O_3 (l) + 7 N_2 (g) = 14 BN (s) + 3 CO (g) Reaction 2.7

Aydoğdu and Sevinç [25] proposed that B_4C forms according to Reaction 2.6, in regions where there is insufficient penetration of N_2 (g). They indicated that both B_4C and BN cannot both exist in the system according to the phase rule and showed B_4C to be unstable in he system and to transform into BN according to Reaction 2.7 for P^3_{CO}/P^7_{N2} ratios smaller than a critical value.

Role of boron carbide in carbothermic formation of hexagonal BN was studied by Çamurlu et al.[29]. They concluded that B_4C is not a necessary intermediate product and its formation slows BN formation.

Use of certain additives into 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. [30, 31] conducted experiments with Li_2CO_3 and LiOH added B_2O_3-C or boric acid-carbamide mixtures under nitrogen or ammonia atmospheres and found these additives to increase the yield of h-BN forming. Çamurlu et al. [32] investigated the addition of MgO, $BaCO_3$ and $CaCO_3$, separately, into B_2O_3-C mixtures subjected to N_2 gas and found that these additives increase the amount and the particle size of the h-BN forming. In their study of the effect of $CaCO_3$ on carbothermic formation of h-BN, 10 wt.% addition was found to be the optimum amount; the yield and grain size of h-BN formed were higher than those obtained from plain mixtures [18]. The amount of B_4C in the products was found to decrease considerably also by addition of 10 wt.% $CaCO_3$ in the same study. They found reaction products of $CaCO_3$-added B_2O_3-C mixtures to be more porous than those of the plain mixtures and suggested increased porosity to increase rate of formation of h-BN. They also proposed that an additional BN formation mechanism, referred as the ionic mechanism, involving nitrogen dissolution in and BN formation from the calcium borate melt may be operative in the experiments conducted with $CaCO_3$ additions.

Özkenter [33] studied the effects of CaO and $CaCO_3$ on carbothermic formation of h-BN and found h-BN formation to take place in C-free calcium borate melts containing h-BN and concluded ionic mechanism to be operative.

CHAPTER 3

EXPERIMENTAL

This study concerns the possibility of BN formation by carbothermic reduction of borax and boric acid mixtures. Experiments were conducted in a tube furnace under nitrogen atmosphere at 1500°C. To start with, experiments were conducted by reacting boric acid-activated carbon mixtures at 1500°C for different durations to obtaine reference points to further experiments with sodium carbonate. Afterward, experiments were conducted with B_2O_3-C mixtures of varying Na_2CO_3 contents for 30 minutes. Experiments were also conducted with B_2O_3-C mixtures into which 40wt% sodium carbonate has been added at 1300 and 1400 for 3 hours and at 1500°C for 1, 1.5, 2, 2.5 and 3 hours were conducted. Experimental products were subjected to SEM and X-Ray analysis. In this chapter, set-up, materials and experimental procedure will be explained.

3.1 Set-Up

The tube furnace used in the experiments is schematically shown in Figure 3.1. The furnace was a horizontal furnace consisting of a 50.0 mm inside diameter, 60.0 mm outside diameter and 800.0 mm long alumina tube, heated by SiC heating elements and was that used in previous studies [33, 34]. Both ends of the tube were closed with silicon stopples having gas inlet and outlet tubes and a thermocouple insertion hole. To prevent degradation of silicon stopples that can be caused by radiated heat from hot zone of the furnace, radiation shields were positioned to both sides of the hot zone, which were shaped from isowool board made of ceramic fiber.

3.2 Materials

Boric oxide was used as the source for boron and obtained from calcination of boric acid (H_3BO_3) supplied by Merck Company. Boric acid was 99.8% pure and calcined in a nickel crucible which has an inside diameter and height of 60.0mm, supplied by Sigma-Aldrich, shown in Figure 3.1. Boric acid was charged into the nickel crucible and placed at the center of a pot furnace. The nickel crucible with its contents was kept in the furnace at 950°C for 1 hour. The resulting molten boric oxide was poured onto a stainless steel plate. After solidification, boric oxide separated itself from the surface of plate. Boric oxide was then ground in an agate mortar and placed in a desiccator to prevent rehydration.

Figure 3.1 Nickel Crucible.

Activated carbon used as a reducing agent was supplied by Merck Company, and it had purity exceeding 99%.

Nitrogen gas used in the experiments was supplied by BOS A.Ş. (Birleşik Oksijen Sanayi). Its purity was 99.998% and contained <50vpm oxygen and <30vpm moisture.

Na_2CO_3 used in the experiments was provided by Merck Company. Its purity was 99.9%Catalog numbers and purities of materials used during the experiments are tabulated in Table 3.1.

Table 3.1 Naming and purities of materials used.

Name	Brand	Catalog #	Purity (%)
H_3BO_3	Merck	1.00165	>99.8
Na_2CO_3	Merck	1.06392	>99
$CaCO_3$	Merck	102066	>99
Active Carbon	Merck	1.02186	>99
HCl (fuming)	Merck	1.00314	Extra pure 37-38

3.3 Experimental Procedure

The reactant pellet was placed in a graphite boat the interior of which was lined by an approximately 0.5 mm thick boron nitride layer to avoid contacting 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 flowing N2 (g) at the rate of 1 l/min. The graphite boat containing the pellet was held in the hot zone of the furnace under N2 (g) flowing at a rate of 200 ml/min at a certain temperature and was quickly removed out of the furnace at the end of a predetermined time from the gas outlet end. Temperature of the furnace was kept constant at ±1 °C and was measured by a Pt-Pt-13%Rh thermocouple the tip of which was about in touch with the graphite boat. Schematic representation of the furnace and general outlook of the experimental set-up is given schematically in Figures 3.2 and 3.3.

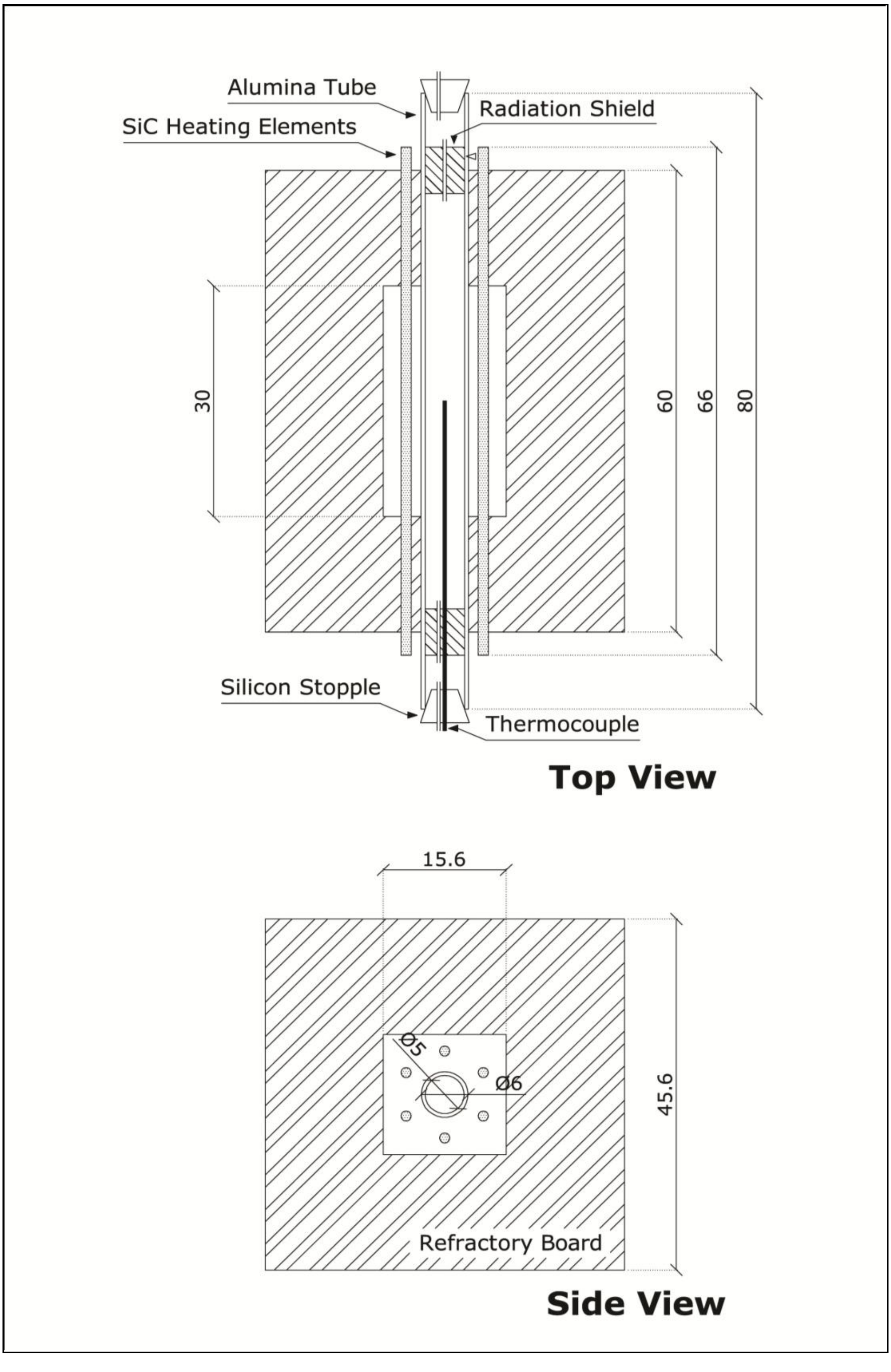

Figure 3.2 Schematic representation of the furnace.

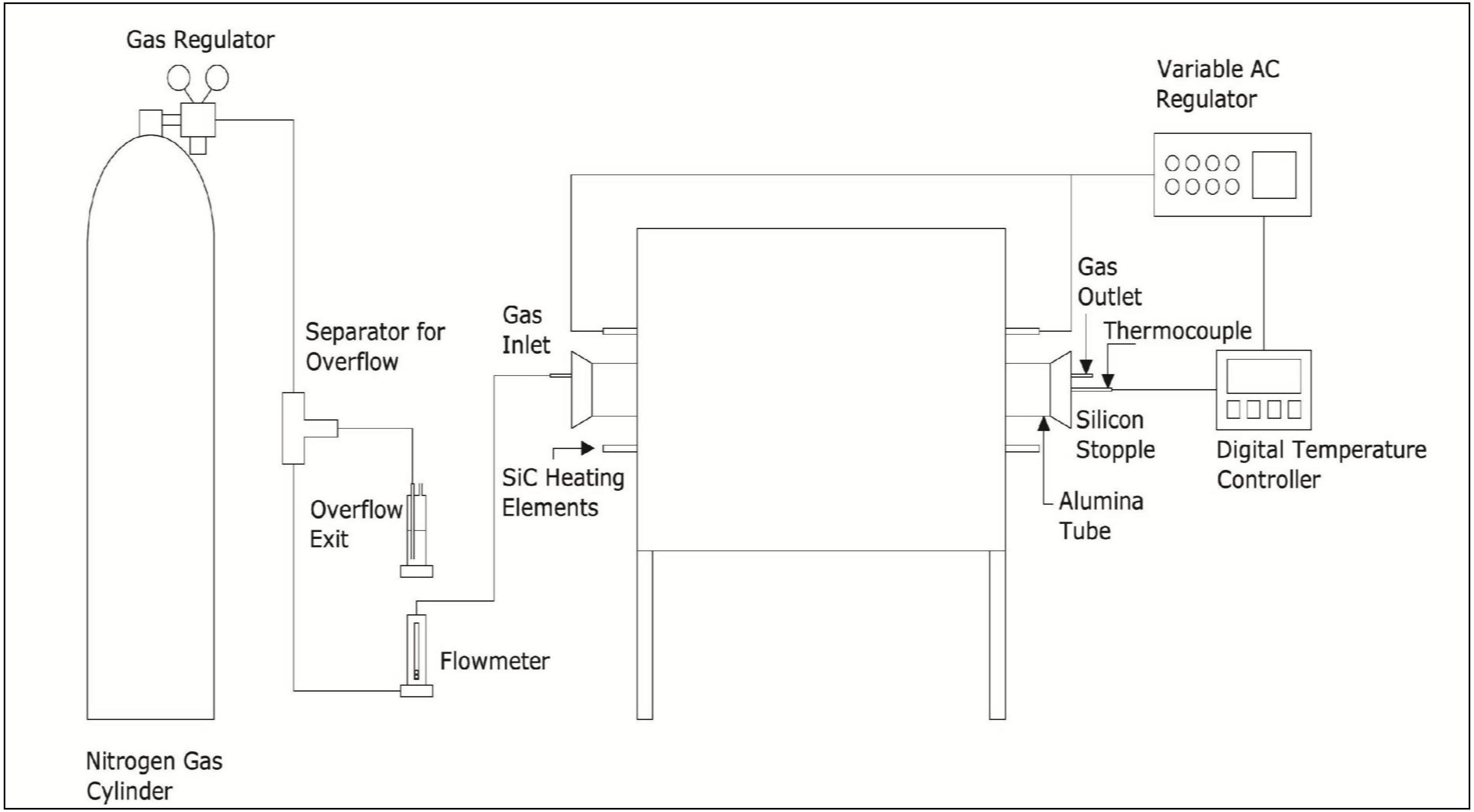

Figure 3.3 General outlook of the experimental set-up.

Boric oxide used was prepared in high energy planetary ball mill (Retsch PM 100) to form a powder and it was then put through a Tyler 80 mesh sieve, width of opening 175 µm, to prepare a uniform powder.

Experiments were conducted with mixtures containing 0-40 wt.% Na_2CO_3 at 1500°C for 30 minutes and with mixtures containing 40 wt.% Na_2CO_3 for ½, 1, 1.5, 2, 2.5 and 3h at 1500°C and also for 3h 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 degrees per minute 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 the Qualitative Analysis software. Grain size and morphology of the products were investigated by Scanning Electron Microscope (SEM) (Jeol JSM6400).

In order to determine if sodium borate is soluble in dilute HCl, a 1g Na_2CO_3 – 2g B_2O_3 mixture was prepared and kept in a BN-coated graphite boat at 1500° C for 1 hour. After removing from the furnace and cooling, the content of the crucible was placed into a 1/1 (v/v) HCl/water solution. It was found that sodium borate was completely soluble in 1/1 (v/v) HCl and it was concluded that it was possible to remove sodium borate from the reaction products by leaching with 1/1 (v/v) HCl solution.

In view of the results of the previous studies and the preliminary experiments in this study the reaction products for which BN formation is not complete are known to contain Na_2O, B_2O_3, B_4C, unreacted C and h-BN [14, 33, 34]. 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 [14] and used also with slight modifications in subsequent studies [33, 34]. In this method the reaction product is first leached with 1:1 HCl which removes sodium borate (Na_2O+ unreacted B_2O_3). The residue of leaching is oxidized at 800°C which results in burning of the unreacted carbon and conversion of B_4C into B_2O_3. The product of oxidation is then leached with 1:1 HCl which removes B_2O_3 leaving behind only BN. The quantities of (Na_2O+ unreacted B_2O_3), B_4C , unreacted C and h-BN in the reaction products are then determined by simple mass balances, as schematically shown in Figure 3.4.

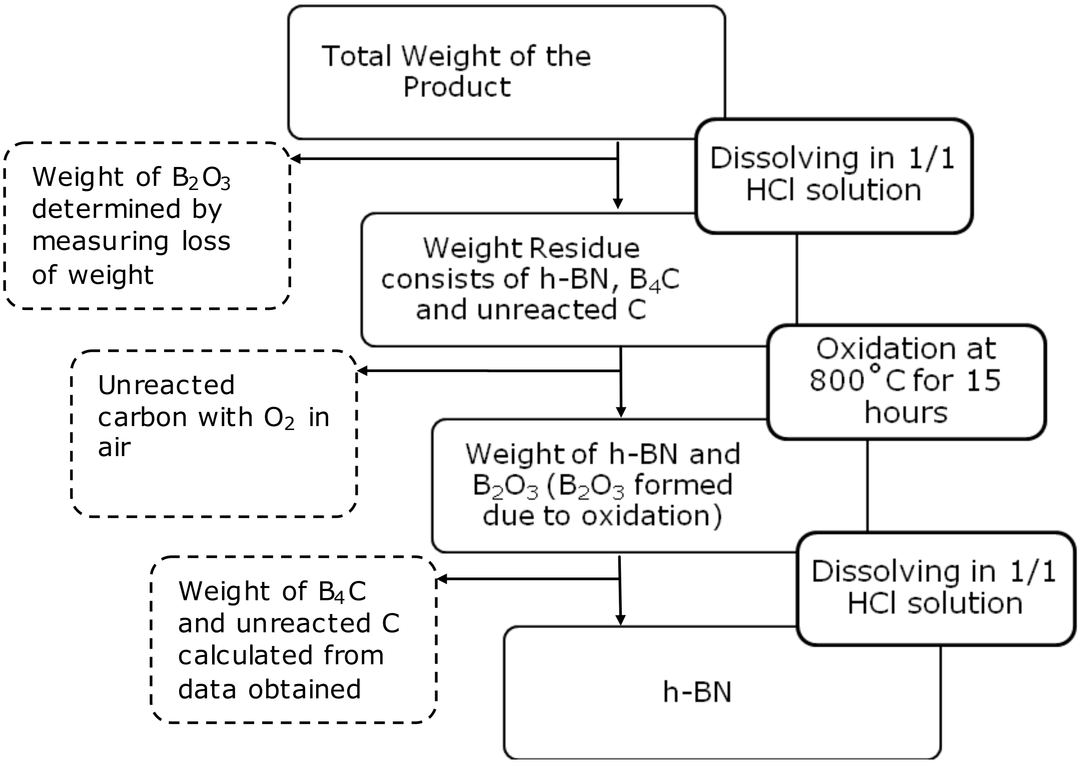

Figure 3.4 Schematic representation of leaching-oxidation-leaching method.

CHAPTER 4

RESULTS AND DISCUSSION

Initial experiments were made with plain B_2O_3-C mixtures to obtain data to be used as a basis for the effect of Na_2CO_3 addition. Experiments were then made with B_2O_3-C mixtures containing different amount of Na_2CO_3. Results and findings obtained from these experiments will be given and discussed in this section.

4.1 Experiments Conducted with B_2O_3-C Mixtures

Experiments were made with plain B_2O_3 – C mixtures at 1500°C for 0.5, 1, 1.5, 2, 2.5 and 3 hours at the beginning of the study to obtain results to be used as basis for the effect of sodium carbonate on carbothermic formation of h-BN. In each experiment, 1.986 gr B2O3 and 0.514 gr carbon were used as reactants. Amounts of each constituent of the reaction products were determined by the successive leeching, oxidation, leaching method. The results were in very good agreement with those of the previous studies [33, 34]. It is seen from Table 4.1 and Figure 4.1 that amount of hexagonal boron nitride increases with time and at the end of 3 hours h-BN reaches its highest amount. Amount of unreacted carbon and unused B_2O_3 in the reaction products decrease with time and all of the carbon is used up at the end of 3 hours.

It is also seen from the Table 4.1 and Figure 4.1 that boron carbide amount increases up to 30 minutes and then starts to decrease reaching zero at the end of 3 hours.

Table 4.1 Amounts of constituents in the reaction products changing with time.

Time (h)	**B_2O_3 (gr)**	**B_4C (gr)**	**Carbon (gr)**	**h-BN (gr)**
0	1.986	0	0.516	0
0.5	1.2009	0.0885	0.2804	0.0940
1	0.6780	0.0523	0.1393	0.2947
1.5	0.5841	0.0432	0.1017	0.3029
2	0.4946	0.0322	0.0443	0.3585
2.5	0.3542	0.0262	0.0240	0.4400
3	0.1614	0.0000	0.0000	0.4600

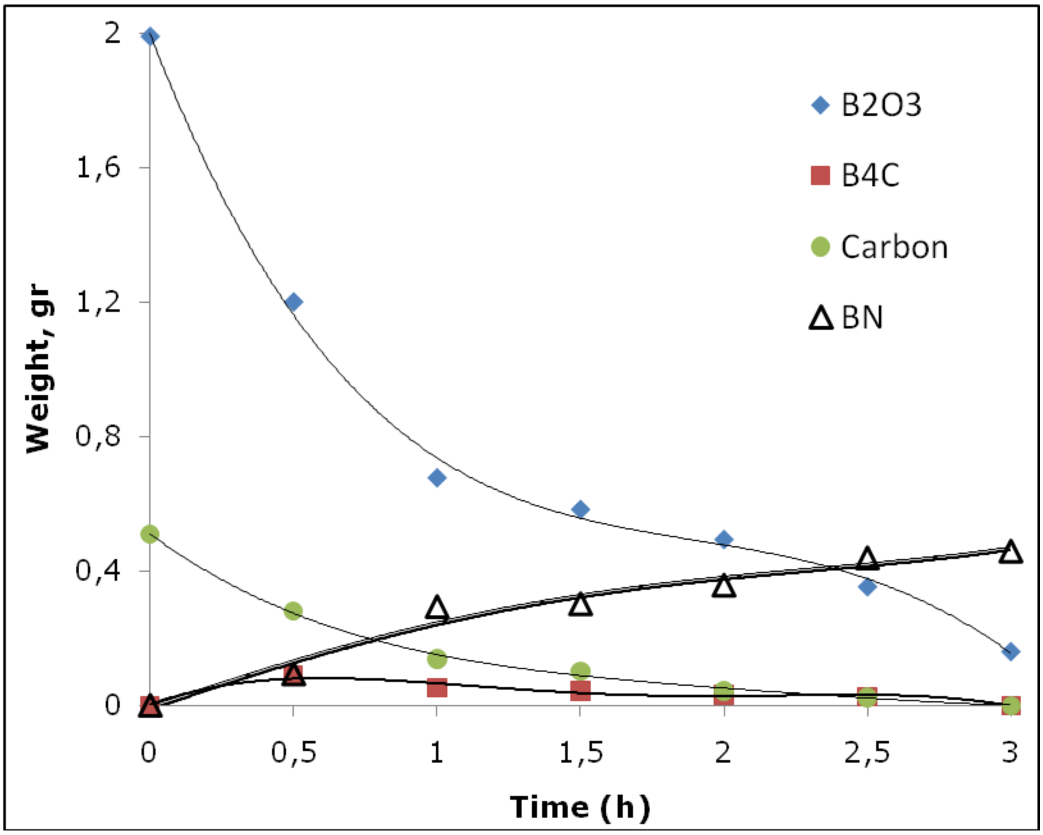

Figure 4.1 Variation of the amounts of the reaction products with time.

4.2 Experiments Conducted with Sodium Carbonate added B_2O_3-C Mixtures

Experiments with B_2O_3-C mixtures containing different amounts of Na_2CO_3 were made to study the effect of Na_2CO_3 on carbothermic formation of BN.

Experiments were made with B_2O_3 – C – Na_2CO_3 mixtures at 1500°C for 30 minutes. Amounts of Na_2CO_3 in the mixtures were 5, 10, 15, 20, 25, 30, 35 and 40% of the weight of the B_2O_3 – C mixtures.

The quantities of B_4C and h-BN in the reaction products of the experiments conducted for 30 minutes at 1500°C with boric oxide-carbon mixtures containing 0 – 40 wt.% Na_2CO_3 additions are presented in Table 4.2 and Figure 4.2. All of the reaction products obtained from Na_2CO_3 – added pellets are seen to contain higher amounts of h-BN than that obtained from plain mixture. It is seen that amount of h-BN increases steadily with increase in the amount of Na_2CO_3 added to the boric oxide-carbon mixtures while the amount of B_4C increases with increase in the amount of Na_2CO_3 up to 10 wt.% but decreases beyond 10%.

Table 4.2 Variation of amounts of constituents in the reaction products for 30 minutes at 1500°C with increasing NaCO3 content in the plain mixture.

Na_2CO_3 %	**B_2O_3-Na_2O (gr)**	**B_4C (gr)**	**Carbon (gr)**	**h-BN (gr)**
Without addition	1.0101	0.0885	0.4712	0.0940
5	0.7760	0.1488	0.1472	0.1622
10	0.6460	0.1690	0.1560	0.1643
15	0.4980	0.1682	0.1928	0.1888
20	0.5260	0.1456	0.1754	0.1978
25	0.3500	0.1210	0.1510	0.2295
30	0.3710	0.1125	0.2255	0.2455
35	0.2914	0.1067	0.1309	0.2813
40	0.2703	0.0940	0.1227	0.3195

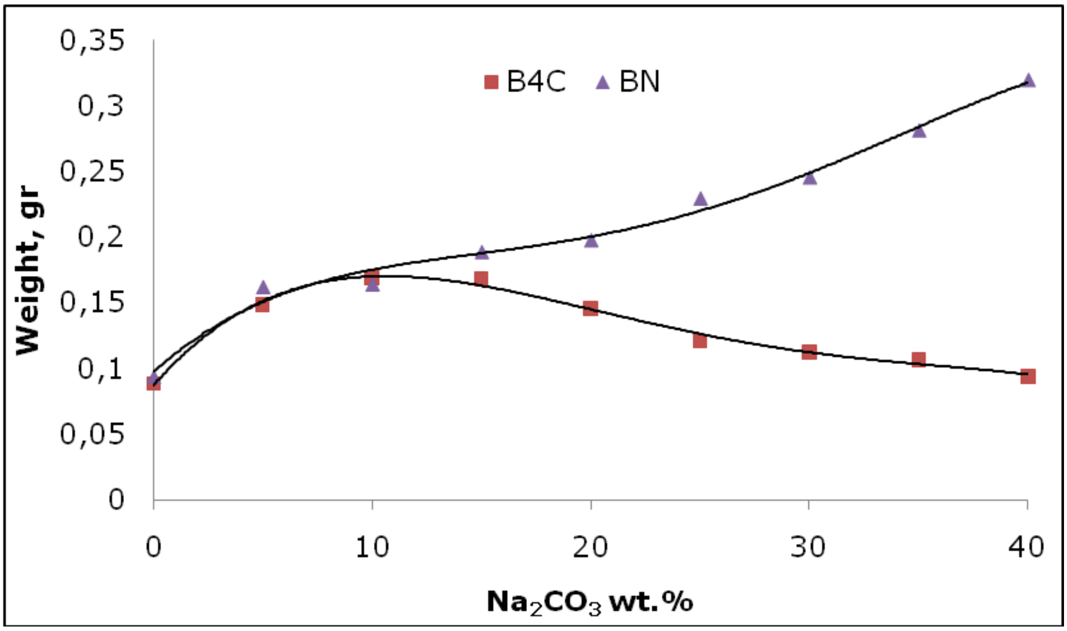

Figure 4.2 Variation of amounts of B4C and h-BN in the reaction products for 30 minutes at 1500°C with increasing Na_2CO_3 content in the plain mixture.

The effect of Na_2CO_3 on carbothermic formation of h-BN is found to be different from the effect of $CaCO_3$ studied by Çamurlu et al. who found amount of h-BN to increase with addition of $CaCO_3$ up to an amount of 10 wt.% of the activated carbon-boric oxide mixture and to decrease afterwards with the amount of B_4C presenting an almost opposite behaviour [18, 34]. They decided 10 wt.% $CaCO_3$ addition to be the optimum amount. The results presented in Figure 4.2 show that an optimum of Na_2CO_3, similar to $CaCO_3$, does not exist in the 0-40 wt.% range and that the highest amount of BN amount is obtained at 40% addition. Quantity of activated carbon-boric oxide was kept constant at 2.5 g (1.986 g B_2O_3 and 0.514 g C) in these experiments and addition of Na_2CO_3 into this mixture resulted in increase in the weight and dimensions of the pellet prepared from it.

Difficulty was encountered in keeping the pellet containing 40% Na_2CO_3 in the graphite boat and modification of the system would be necessary to conduct experiments for Na_2CO_3 additions above 40%. Because of this and also because use of Na_2CO_3 in amounts higher than 40% was considered to be impractical, to it was decided to conduct experiments aiming the investigation of the catalytic effect of Na_2CO_3 for longer durations at 1500°C with 40 wt.% addition.

Amounts of the constituents of the reaction products of the experiments conducted with Na_2CO_3-added B_2O_3–C mixtures at 1500°C for 30 min to 3 h are given in Table 4.3. The quantities of h-BN and B_4C formed in the experiments conducted with plain and 40 wt.% Na_2CO_3 added mixtures at 1500°C for 30 minutes to 3 hours are presented in Figure 4.3. Quantities of h-BN and B_4C found in the reaction products of $CaCO_3$ - added B_2O_3 – C mixtures obtained in the study of Çamurlu et al. are also shown in Figure 4.5 for comparison purposes [18, 34]. It can be seen that the quantities of h-BN forming in the mixtures containing Na_2CO_3 or $CaCO_3$ as additives are larger than those containing no additive.

Table 4.3 Amounts of constituents in the reaction product with 40 wt.% Na_2CO_3 added mixtures and amounts of B_4C and h-BN in the plain mixtures conducted at 1500°C for 30 minutes to 3 hours.

	40 wt.% Na_2CO_3 added Plain Mixture				**Plain Mixture**	
Time(h)	B_2O_3+Na_2O(gr)	C(gr)	B_4C (gr)	h-BN(gr)	B_4C (gr)	h-BN(gr)
0	2,5705	0.5140	0	0	0	0
0.5	0,2703	0.1227	0.0940	0.3195	0.0885	0.0940
1	0.0260	0.1123	0.0817	0.3707	0.0523	0.2947
1.5					0.0432	0.3029
2	0.0100	0.0948	0.0442	0.4450	0.0322	0.3585
2.5					0.0262	0.4400
3	0	0.0927	0.0313	0.4785	0.0000	0.4600

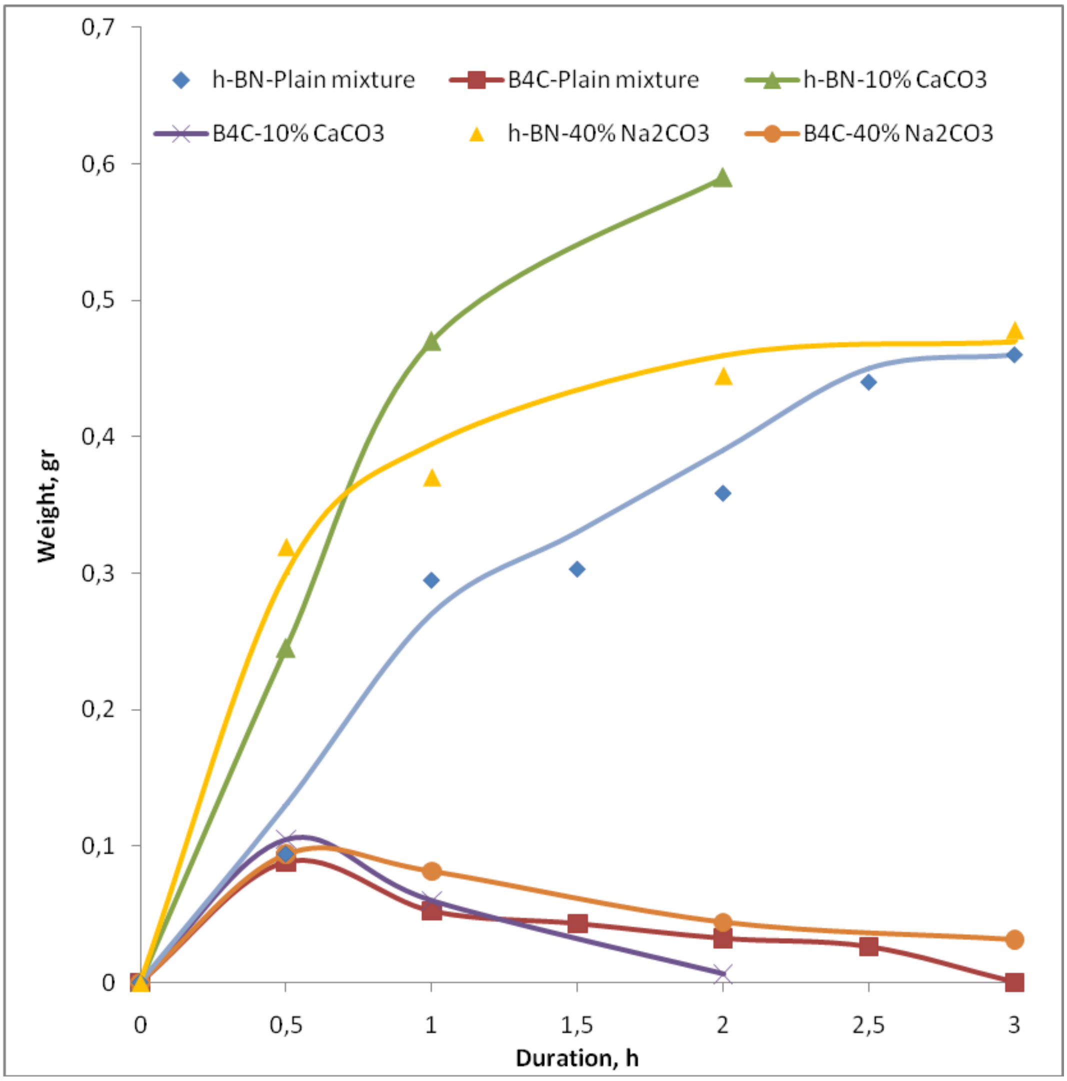

Figure 4.3 Quantities of B_4C and h-BN in the experiments conducted with $CaCO_3$ added and Na_2CO_3 added and plain mixtures conducted at 1500°C for 30 minutes to 3 hours [34].

$CaCO_3$ addition is known to increase the amount of h-BN forming from previous studies [33, 34]. The reason for increase in the amount of h-BN forming in $CaCO_3$-added mixtures was stated to be due increased porosity of the pellet resulting from calcination of $CaCO_3$ and also due to the formation of additional h-BN by ionic mechanism. Na_2CO_3 also increases the amount of h-BN formation. Calcination temperature of Na_2CO_3 is 850°C. Therefore it decomposes during heating of the pellet made from the reaction mix and increases the porosity of the pellet.

Na_2O originating from calcination and B_2O_3 form a homogeneous liquid at 1500°C according to the phase diagram given in Figures 4.4 and 4.5. Increase in the amount of h-BN with Na_2CO_3 addition is suggested to arise from increased porosity of the pellet and additional h-BN formation by the ionic mechanism similar to the effect of $CaCO_3$ [33].

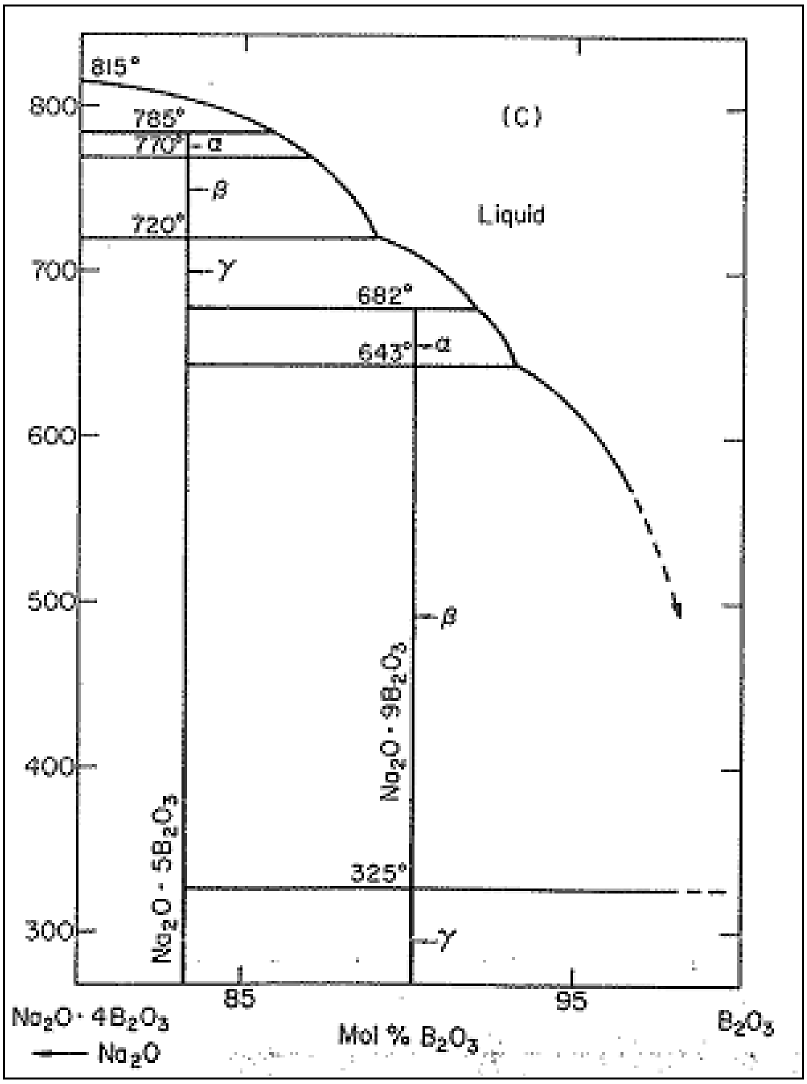

Figure 4.4 B_2O_3-Na_2O phase diagram [35]

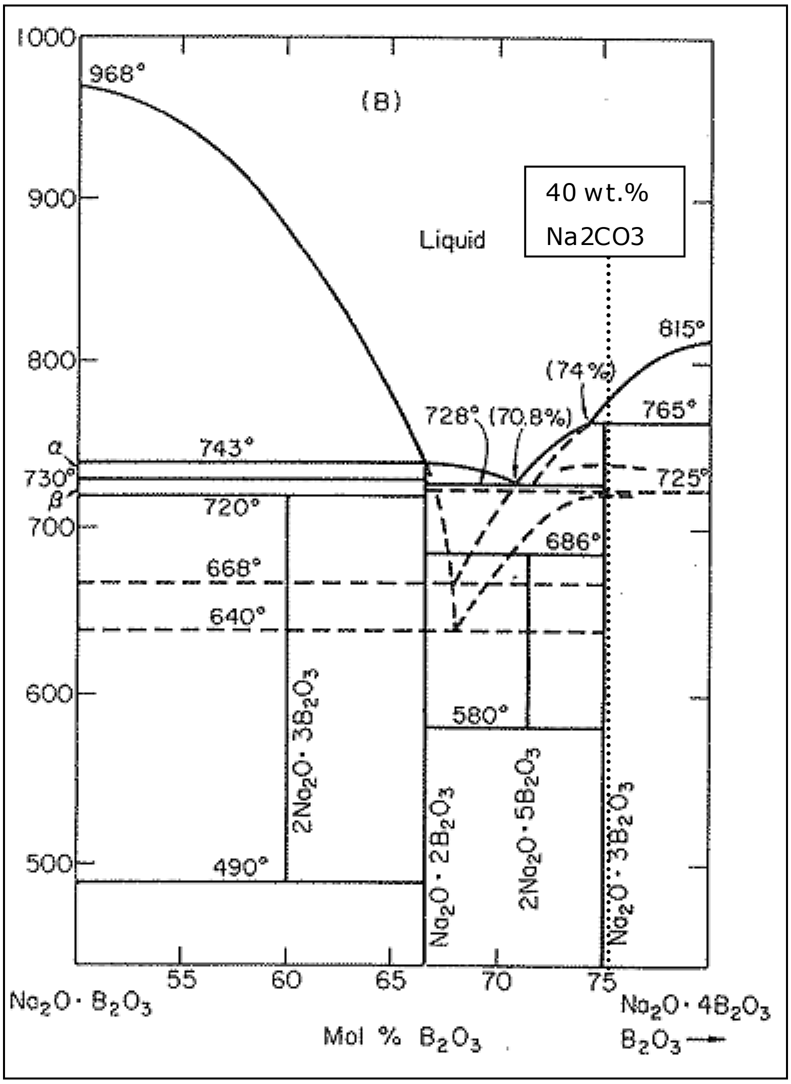

Figure 4.5 B_2O_3-Na_2O phase diagram [35].

The effect of Na_2CO_3 in increasing the amount of h-BN forming is seen to be very pronounced for short times but less so for longer times; Na_2CO_3 is seen to be more effective than even $CaCO_3$ for times up to about 0.5 h but the reverse is true for longer times. Figure 4.5 additionally shows there is almost no BN formation after 2 h. This is an expected result in view of Table 4.2 from where the amount of B_2O_3 + Na_2O 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 absence of B_2O_3 in the system. B_4C is not entirely consumed and its amount does not change after 2h again due to absence of B_2O_3 in the system.

There is loss of B_2O_3 from the system in 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 Reaction 4.1 to account for evaporation loss in the previous studies conducted in this Department [14]. A higher amount of loss of B_2O_3 and also some loss of Na_2O from the system due to evaporation was expected from the system at the beginning of the study in view of the results of Cole who found B_2O_3, Na_2O and sodium borates like $Na_2B_4O_7$ to evaporate from liquid Na_2O-B_2O_3 system at high temperatures [38, 39]. The possibility of loss of Na_2O from the system due to reaction

$$Na_2O(l) + C(s) = 2\,Na(g) + CO(g) \qquad \text{Reaction 4.1}$$

was also considered but these losses were not expected to reach to the point where there would remain no Na_2O and B_2O_3 in the system as shown in Figure 4.6 where the weights of (B_2O_3 + Na_2O) or B_2O_3 in the reaction products are plotted against time.

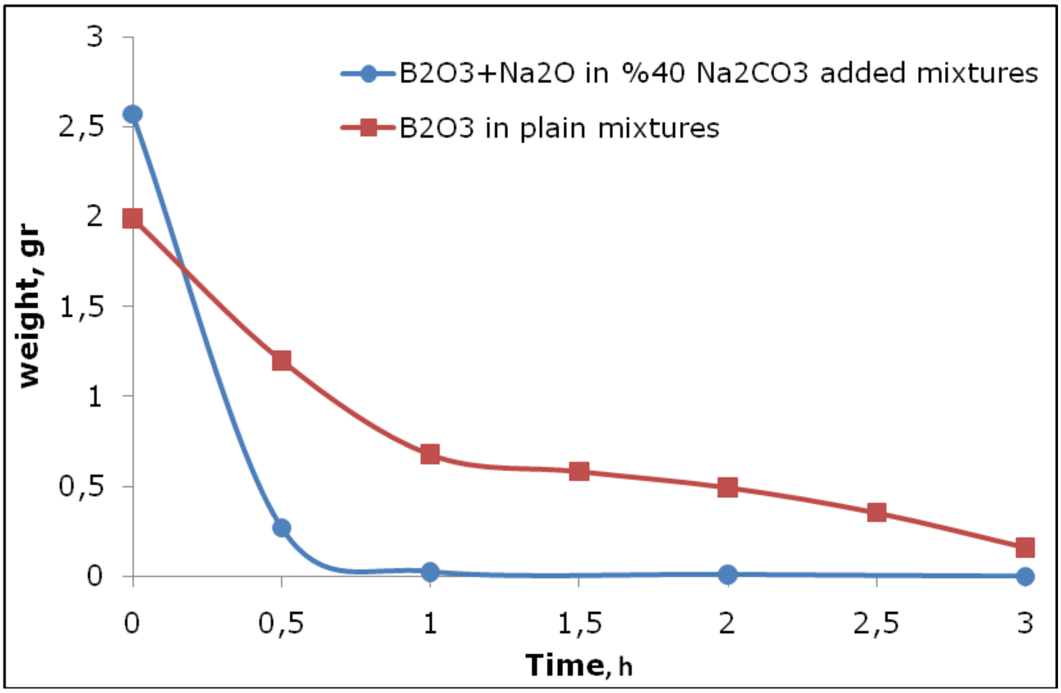

Figure 4.6 Amounts of B_2O_3 in plain and B_2O_3-Na_2O in 40 wt.% Na_2CO_3 added plain mixtures with time.

These results indicate that Na_2CO_3 significantly increases the rate of carbothermic formation of h-BN but loss of Na2O and B2O3 is severe which makes its use to be impractical at 1500°C. Possibility of use of Na_2CO_3 as a catalytic additive into B2O3 + C mixtures at lower temperatures was decided to be studied and experiments were made with again 40%Na_2CO_3 addition at 1300 and 1400°C. Amounts of the constituents of the reaction products of these experiments together with that at 1500oC are given in Table 4.4 and Figure 4.7. The only study, to the knowledge of the authors, on the effect of temperature on carbothermic formation of h-BN is that done by Aydoğdu and Sevinç with plain B_2O_3–C mixtures [25]. Direct comparison of their results with those of this study is not possible because the quantities of B2O3 and C in the two studies are different but while the quantity of h-BN that has formed at 1500°C 0.64 gr in the study of Aydoğdu and Sevinç is about 2.8 times as large as that at 1300°C, the quantity of h-BN that has formed at 1500°C in the present study is about 30%

more than that at 1300°C. This may be taken as an indication that Na_2CO_3 may be used as an additive to produce h-BN at lower temperatures which may be of practical interest.

Table 4.4 Amounts of constituents in the reaction product with 40 wt.% Na_2CO_3 added mixtures plain mixtures conducted at 1300-1500°C for 3 hours.

Temperature (°C)	B_2O_3+ Na_2O (gr)	B_4C (gr)	Carbon (gr)	BN (gr)
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

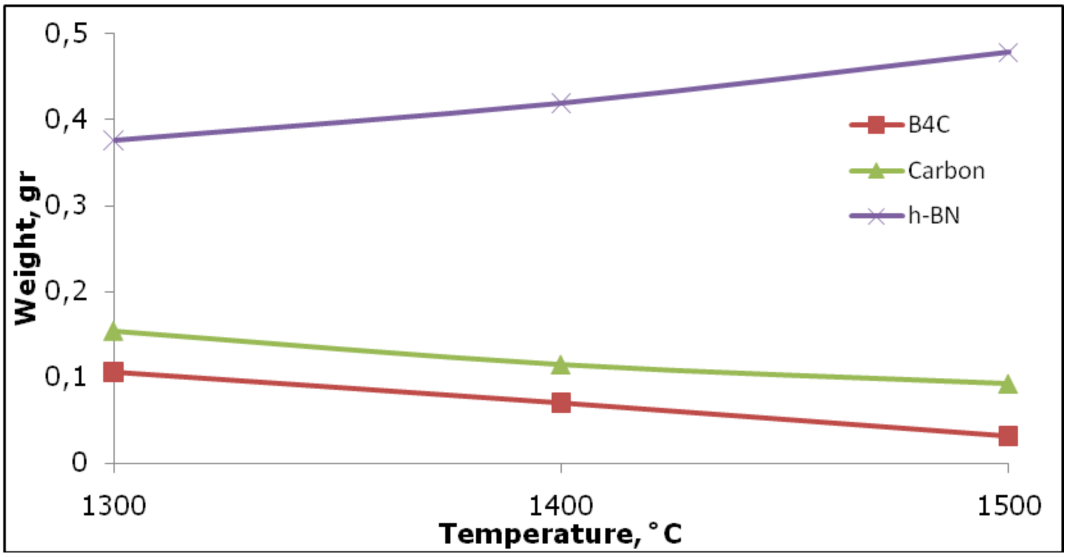

Figure 4.7 Variation of B_2O_3, B_4C and h-BN in 40 wt.% Na_2CO_3 added plain mixtures with time.

4.3 Experiments Conducted with Sodium Carbonate and Calcium Carbonate added B_2O_3–C Mixtures

Use of Na_2CO_3 at 1500°C was found to be impractical as stated above. $CaCO_3$ is known to catalytically affect h-BN formation and obtimum CaCO3 addition was found to be 10 wt.% [34]. Use of both Na_2CO_3 and $CaCO_3$ as additives to B_2O_3–C mixtures was studied by conducting experiments with B_2O_3–C mixtures containing 10 wt.% $CaCO_3$ and 10 wt.% Na_2CO_3 at 1500°C for 1 and 2 hours. Results are given in Table 4.5. Amount of h-BN in the products indicate that simultaneous addition of Na_2CO_3 and $CaCO_3$ does not improve yield of h-BN.

Table 4.5 Experiments conducted with 10wt.% $CaCO_3$ and 10wt.% Na_2CO_3 added plain mixture at 1500°C for 1 and 2 hours[34].

	10 wt.% $CaCO_3$ 10 wt.% Na_2CO_3	40 wt.% Na_2CO_3	10 wt.% $CaCO_3$
hour	h-BN	h-BN	h-BN
1.0000	0.3811	0.371	0.57
2.0000	0.3959	0.445	0.6

4.4 Effect of Na_2CO_3 addition on particle size of h-BN

Samples taken from all of the reaction products in the as removed from the furnace form as well as after the leaching-oxidation-leaching process were subjected to XRD analysis.

XRD patterns of samples obtained from the experiments carried out for 30 minutes, 1, 2 and 3 hours with 40 wt.% Na_2CO_3 added B_2O_3-C mixtures before and after leaching-oxidation-leaching process are shown in Figures 4.8 and 4.9 respectively. No boric oxide peak is observed since it is in amorphous form Instead, H_3BO_3 peaks, which originates from the hydration of B_2O_3 are seen in figures. It can be seen from the relative heights of the peaks in Figure 4.8 that H_3BO_3 was in highest amount for 30 minute and it was consumed with time. In Figure 4.9, all of the peaks belong to h-BN.

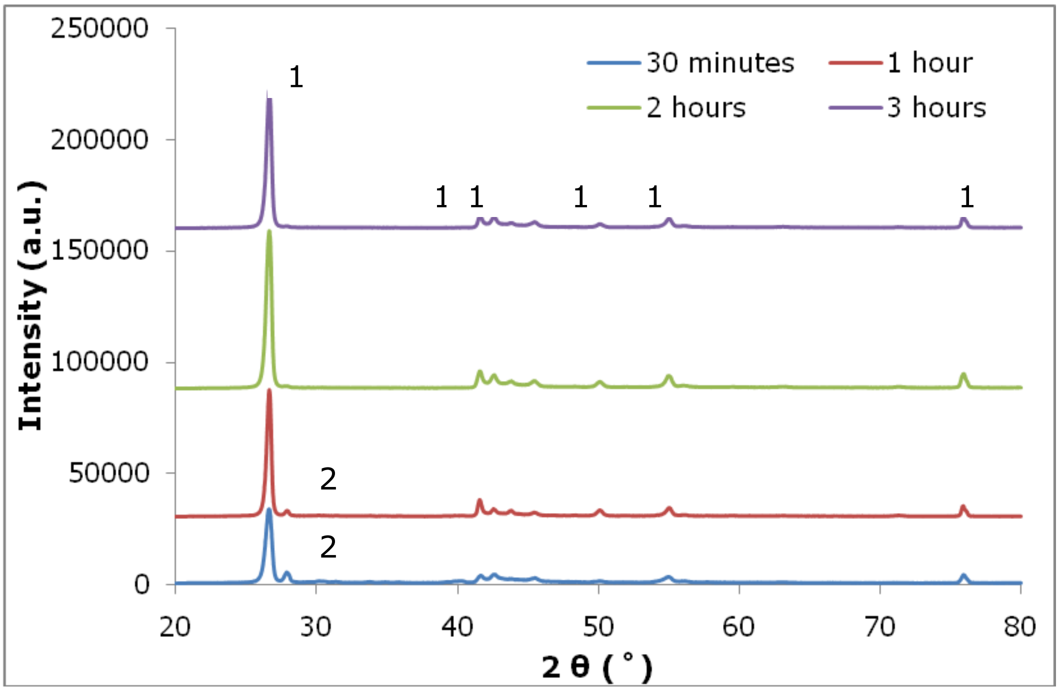

Figure 4.8 XRD patterns of the experiments with 40 wt.% Na_2CO_3 addition for 30 minutes, 1, 2 and 3 hours before leaching-oxidation-leaching process. (1) H_3BO_3, (2) h-BN.

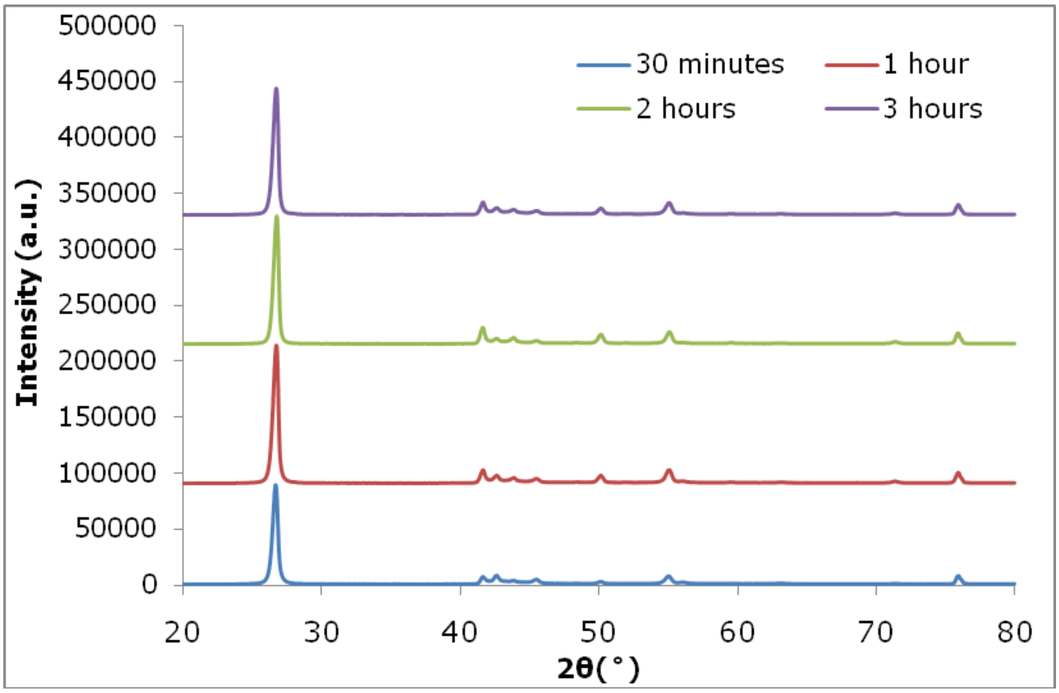

Figure 4.9 XRD patterns of the experiments with 40 wt.% Na2CO3 addition for 30 minutes, 1, 2 and 3 hours after leaching-oxidation-leaching process.

XRD patterns before and after purification of the samples obtained from experiments conducted with 40 wt.% Na_2CO_3 added B_2O_3-C mixtures at 1300, 1400 and 1500°C for 3 hours are given in Figure 4.10 and 4.11 respectively. There are no peaks other than those of h-BN in both figures.

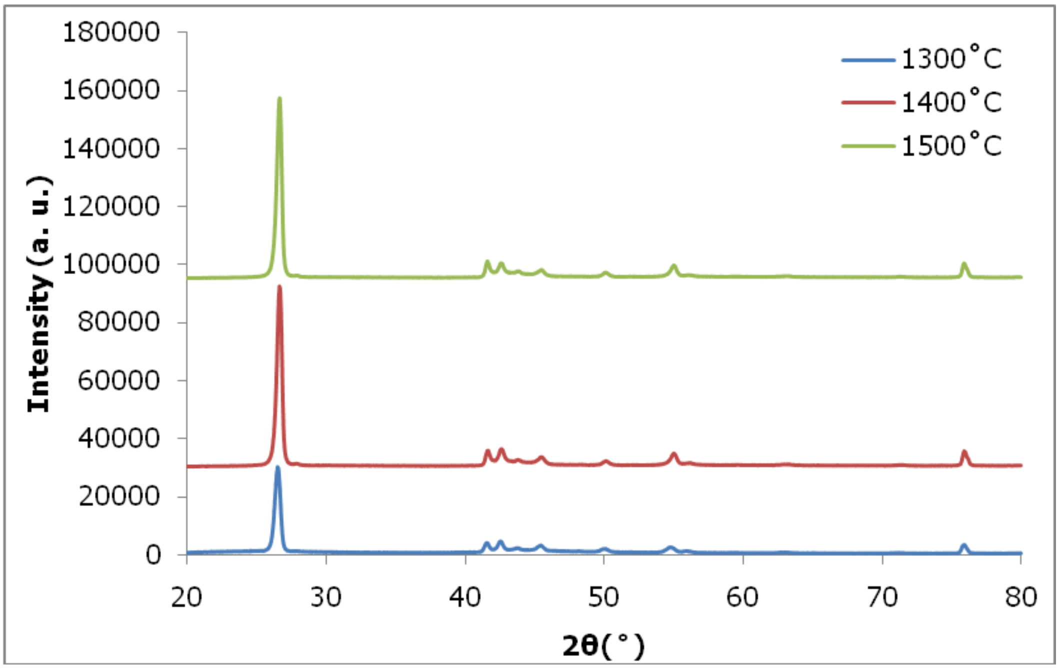

Figure 4.10 XRD patterns of the experiments with 40 wt.% Na_2CO_3 addition at 1300, 1400 and 1500°C for 3 hours before leaching-oxidation-leaching process.

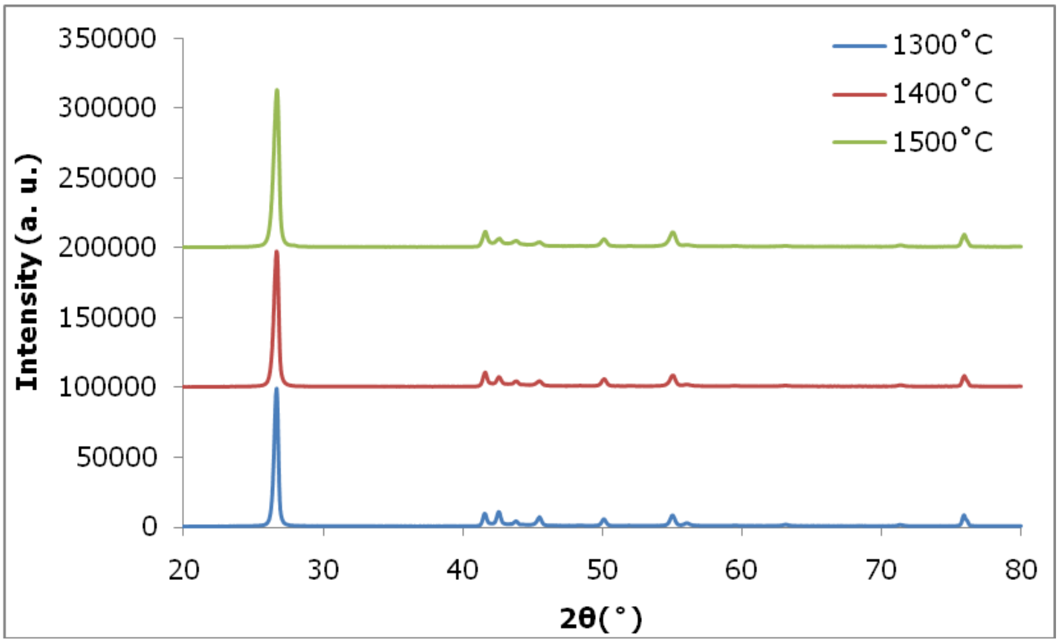

Figure 4.11 XRD patterns of the experiments with 40 wt.% Na_2CO_3 addition at 1300, 1400 and 1500°C for 3 hours after leaching-oxidation-leaching process.

XRD patterns of experiments carried out at 1500°C for 1 hour with 10 wt.% $CaCO_3$ and 10 wt.% Na_2CO_3 added B_2O_3-C mixtures before and after leaching-oxidation-leaching process are shown in Figure 4.12. All the peaks belong to h-BN also in these patterns.

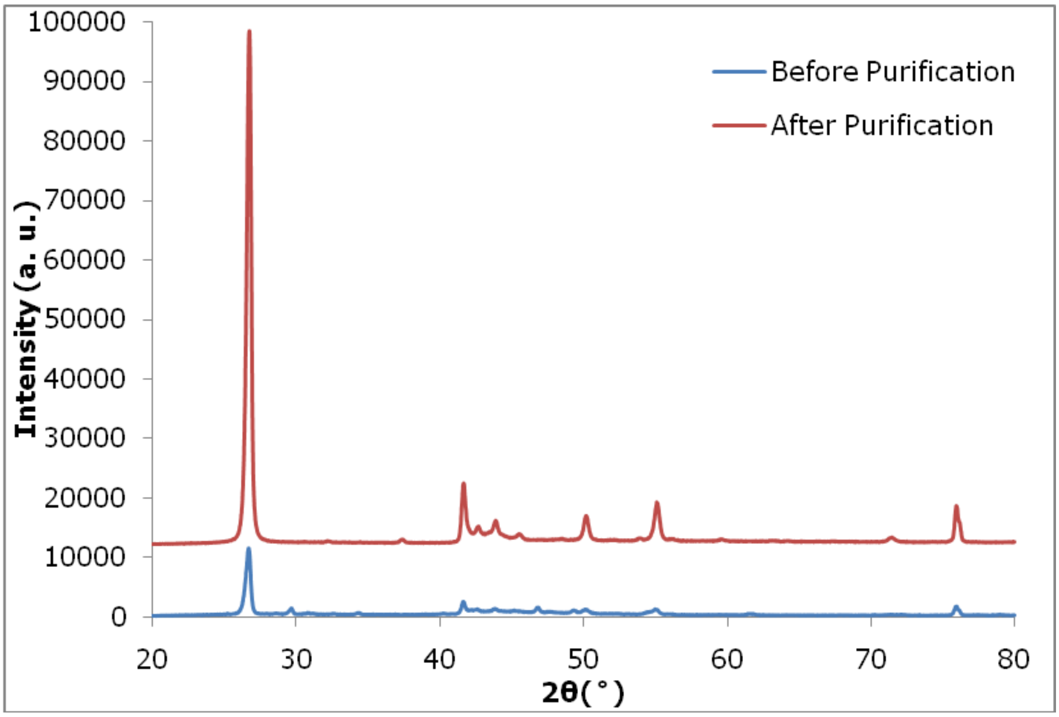

Figure 4.12 XRD patterns of the experiments conducted with 10wt.% $CaCO_3$ and 10wt.% Na_2CO_3 added plain mixture at 1500°C for 1 hour.

Samples after the leaching-oxidation-leaching process were examined by SEM also and particle sizes of the samples were calculated.

SEM micrographs of samples obtained after subjecting the reaction products of the experiments conducted with plain B_2O_3–C mixture at 1500°C for 3 hours, 40 wt.% Na_2CO_3 added mixtures at 1500°C for ½, 1, 2 and 3 hours, 40 wt.% Na_2CO_3 added mixtures at 1300°C and 1400° for 3 hours and 10 wt.% Na_2CO_3 and 10 wt.% $CaCO_3$ added mixtures for 1 and 2 hours to the leaching-oxidation-leaching process are shown in Figure 4.13 to 4.24 . SEM micrographs of the samples from plain and $CaCO_3$ added mixtures taken from Çamurlu et al. and Özkenter are also shown in the same figure [33, 34].

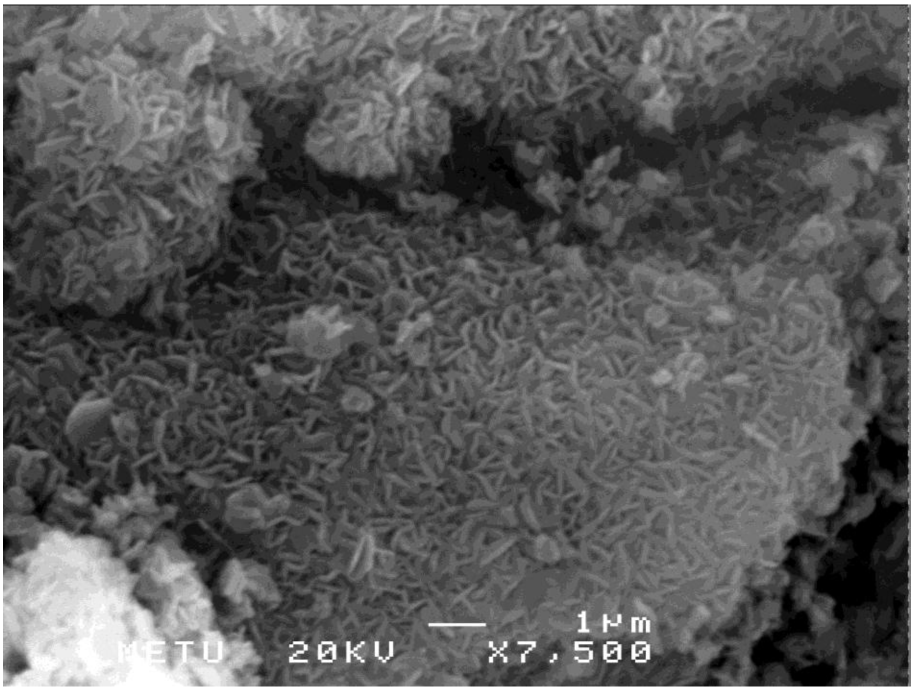

Figure 4.13 SEM micrograph of the experiment conducted for 3 hours with plain mixture at 1500°C [33].

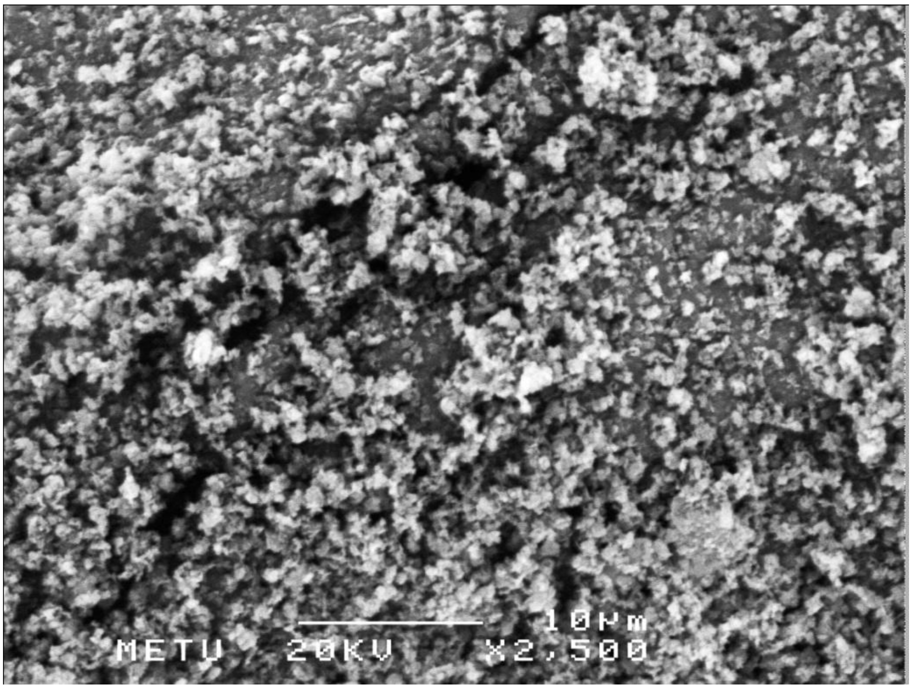

Figure 4.14 SEM micrograph of the experiment conducted for 30 minutes with 40 wt.% Na_2CO_3 added plain mixture at 1500°C.

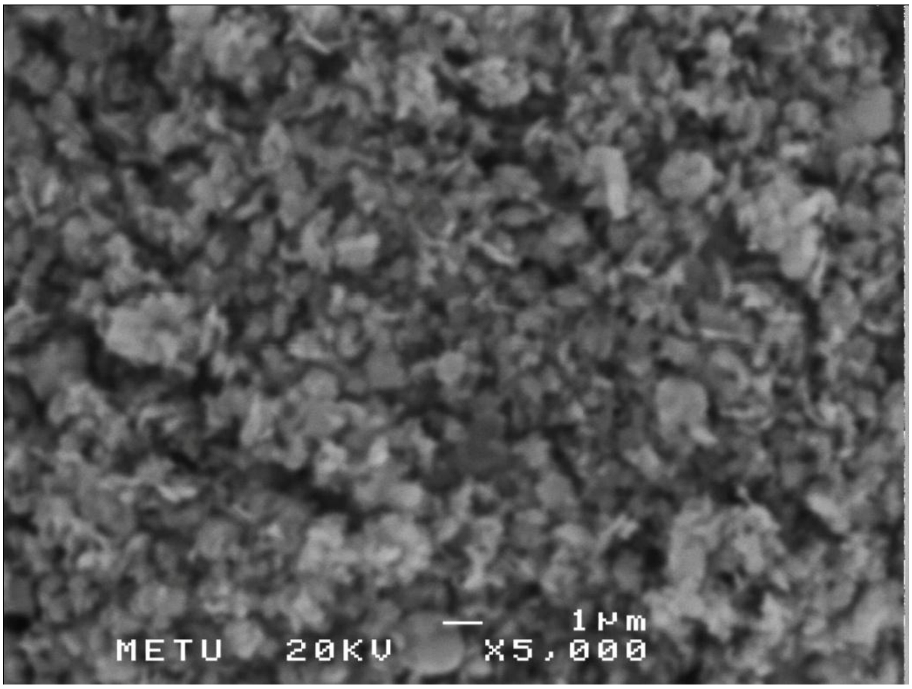

Figure 4.15 SEM micrograph of the experiment conducted for 1 hour with 40 wt.% Na_2CO_3 added plain mixture at 1500°C.

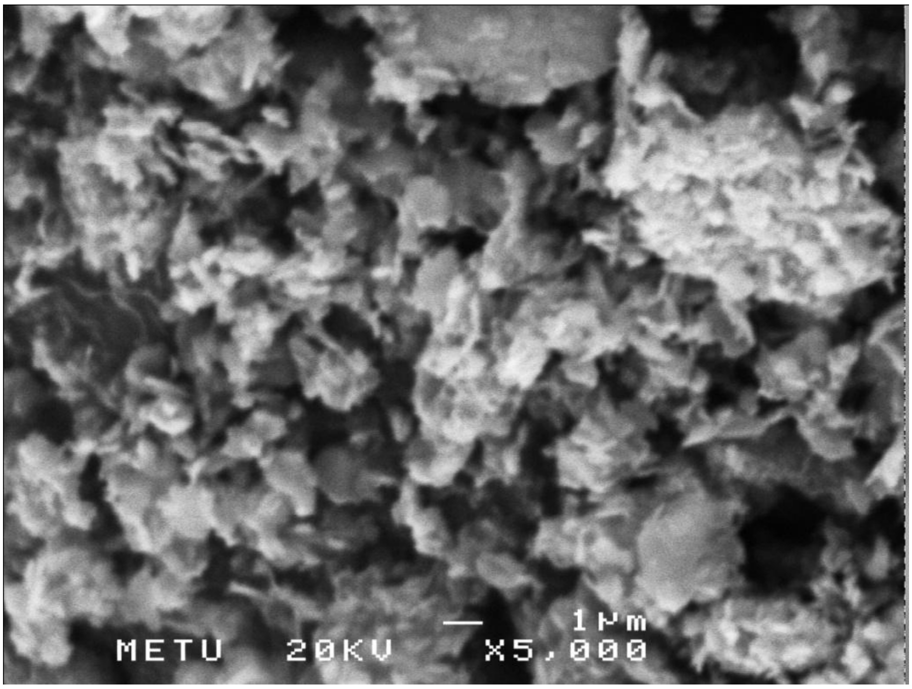

Figure 4.16 SEM micrograph of the experiment conducted for 2 hour with 40 wt.% Na_2CO_3 added plain mixture at 1500°C.

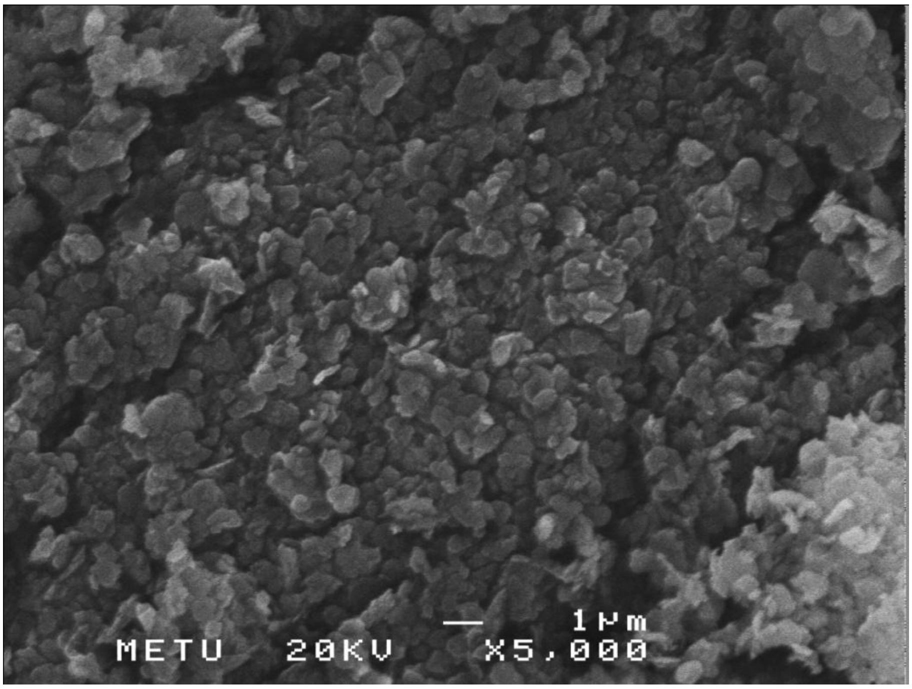

Figure 4.17 SEM micrograph of the experiment conducted for 3 hour with 40 wt.% Na_2CO_3 added plain mixture at 1500°C.

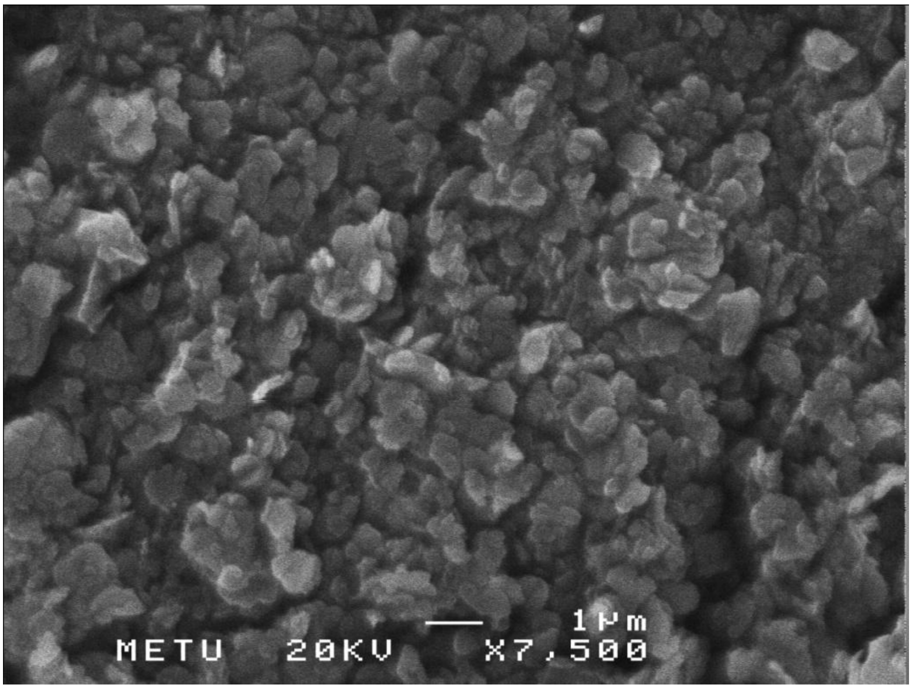

Figure 4.18 SEM micrograph of the experiment conducted for 3 hour with 40 wt.% Na_2CO_3 added plain mixture at 1500°C. (Higher magnification)

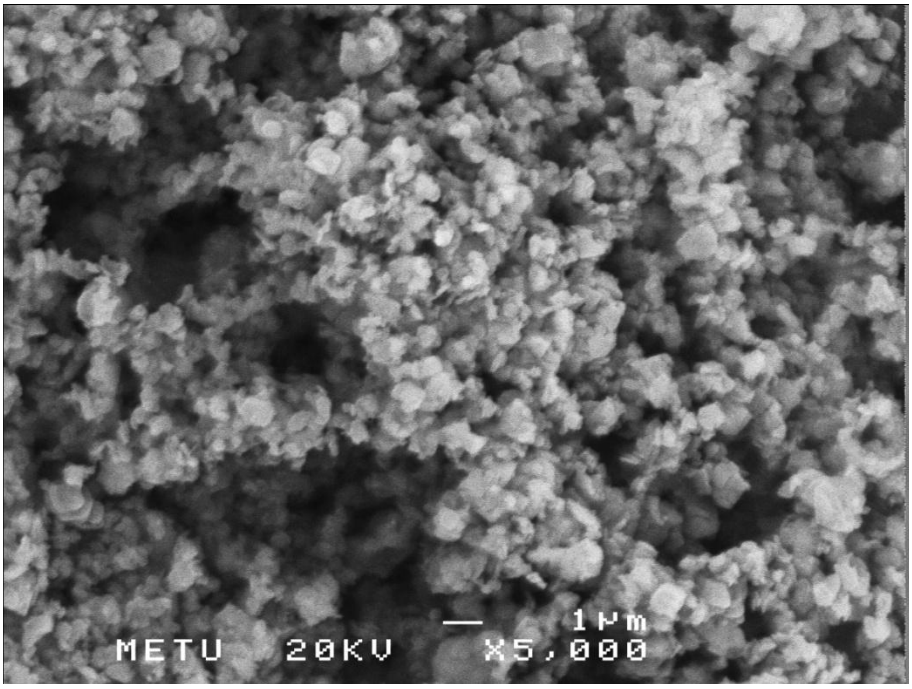

Figure 4.19 SEM micrograph of the experiment conducted for 3 hour with 40 wt.% Na_2CO_3 added plain mixture at 1300°C.

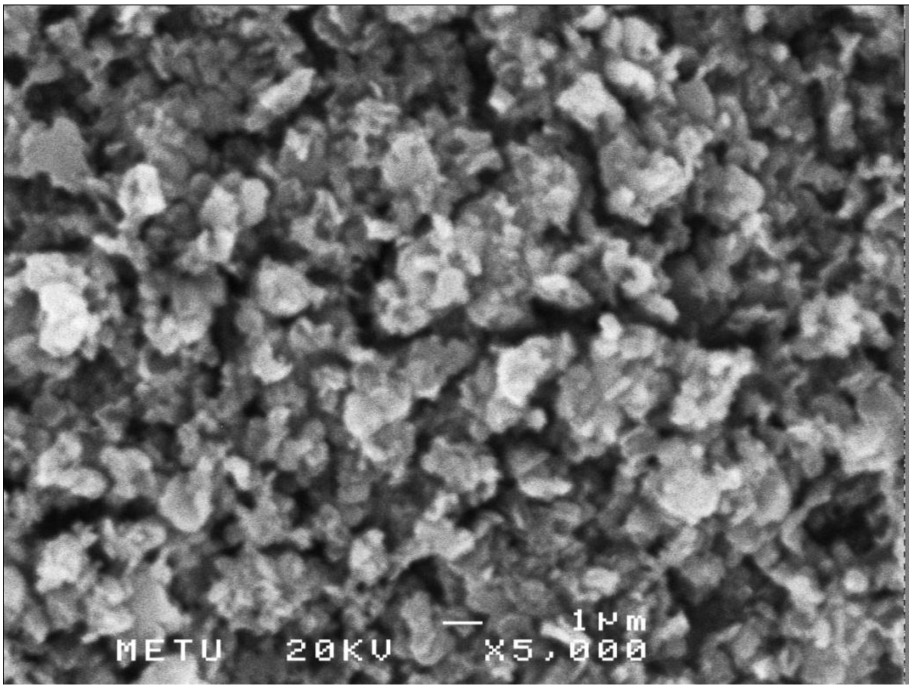

Figure 4.20 SEM micrograph of the experiment conducted for 3 hour with 40 wt.% Na_2CO_3 added plain mixture at 1400°C.

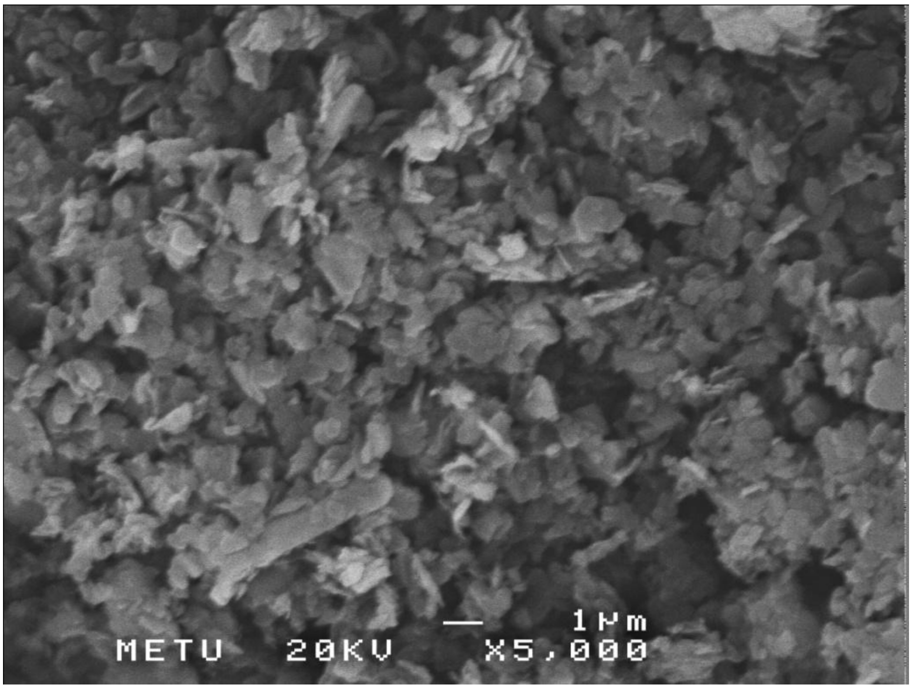

Figure 4.21 SEM micrograph of the experiment conducted for 1 hour with 10 wt.% Na_2CO_3 and 10 wt.% $CaCO_3$ added plain mixture at 1500°C.

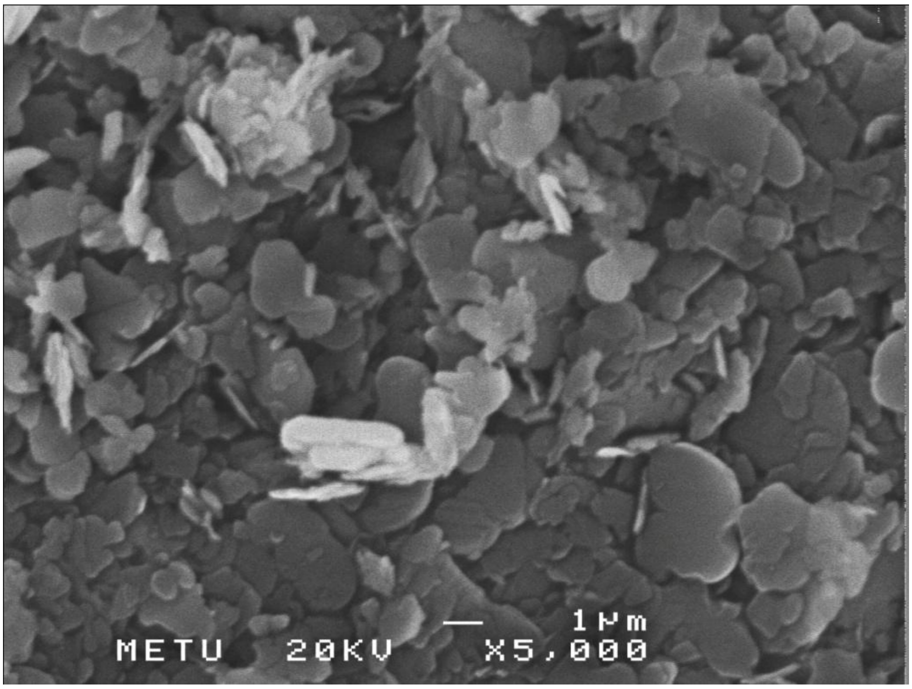

Figure 4.22 SEM micrograph of the experiment conducted for 2 hour with 10 wt.% Na_2CO_3 and 10 wt.% $CaCO_3$ added plain mixture at 1500°C.

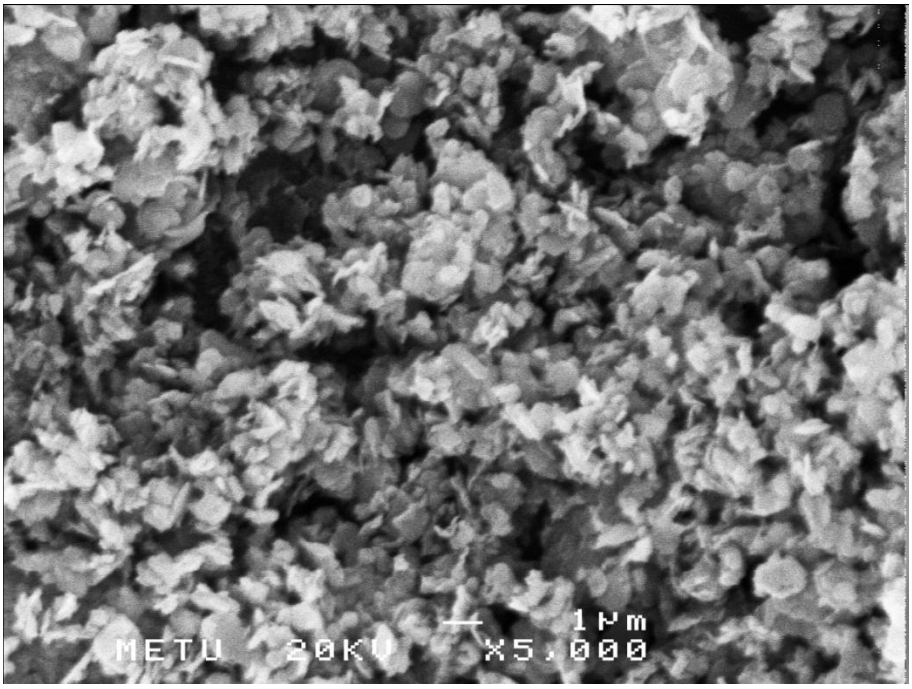

Figure 4.23 SEM micrograph of the experiment conducted for 3 hour with 40 wt.% Na_2CO_3 added plain mixture at 1500°C.

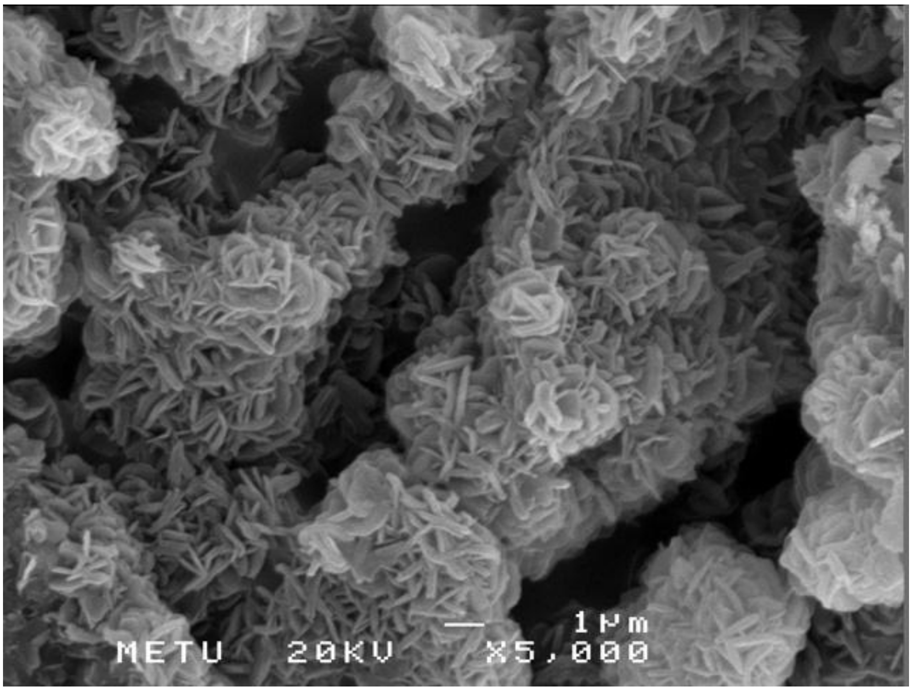

Figure 4.24 SEM micrograph of the experiment conducted for 2 hour with 10 wt.% $CaCO_3$ added plain mixture at 1500°C[34].

Average particle sizes of h-BN appearing in the figures are tabulated in Table 4.6. Particle size of h-BN obtained from B_2O_3 – C mixtures containing Na_2CO_3 or $CaCO_3$ are larger than that obtained from plain B_2O_3–C mixture at any temperature and for any time. Average particle sizes of h-BN obtained from Na_2CO_3-added mixture at 1500°C for 2 hours is not different from that for 3 hours which is expected in view of the fact that no B_2O_3 was found to exist in the system at the end of 2 hours as stated above. Comparison of the particle size of h-BN obtained from Na_2CO_3-added mixture at 1500°C for 2 hours with that from $CaCO_3$-added indicates Na_2CO_3 to much more effective than $CaCO_3$ in increasing the particle size of h-BN. When Na_2CO_3 is used with $CaCO_3$, its effectiveness on improving particle size of h-BN enhances drastically, compared to $CaCO_3$ addition or Na_2CO_3 addition alone.

Table 4.6 Particle sizes of the samples obtained from each experiment after leaching-oxidation-leaching process, and from CaCO3 added experiments acquired from Çamurlu and Özkenter [33, 34].

Addition, Temperature, Duration	avarage particle size, µm
%40 Na2CO3 at 1500C 1/2h	0.63±0.16
%40 Na2CO3 at 1500C 1h	0.85±0.24
%40 Na2CO3 at 1500C 2h	1.17±0.27
%40 Na2CO3 at 1500C 3h	1.20±0.41
%40 Na2CO3 at 1400C 3h	0.99±0.23
%40 Na2CO3 at 1300C 3h	0.77±0.23
%10 Na2CO3-%10 CaCO3 at 1500C 1h	1.01±0.36
%10 Na2CO3-%10 CaCO3 at 1500C 2h	1.80±0.66
%10 CaCO3 at 1500C 2h [34]	0.70±0.14
%10 CaCO3 at 1500C 3h [33]	1.19±0.37
Plain at 1500C 3h	0.49±0.11

CHAPTER 5

CONCLUSION

Effect of sodium oxide addition on carbothermic formation of hexagonal boron nitride was investigated by subjecting B_2O_3-C and Na_2CO_3 added B2O3-C mixtures to nitrogen gas. Amount of h-BN in the reaction products was found to increase with increase in the amount of Na_2CO_3 added.

Experiments were conducted with 0-40 wt.% Na_2CO_3 addition for 30 minutes and it was found that all of the reaction products obtained from Na_2CO_3 – added pellets contained higher amounts of h-BN than that obtained from plain mixture. It was seen that amount of h-BN increases steadily with increase in the amount of Na_2CO_3 added to the activated carbon-boric oxide mixtures while the amount of B_4C increases with increase in the amount of Na_2CO_3 up to 10 wt.% but decreases beyond 10%. The results showed that an optimum of Na_2CO_3, similar to $CaCO_3$, does not exist in the 0-40 wt.% range and that the highest amount of BN amount was obtained at 40% addition. Quantity of activated carbon-boric oxide was kept constant at 2.5 g (1.986 g B_2O_3 and 0.514 g C) in these experiments and addition of Na_2CO_3 into this mixture resulted in increase in the weight and dimensions of the pellet prepared from it. Difficulty was encountered in keeping the pellet containing 40% Na_2CO_3 in the graphite boat and modification of the system would be necessary to conduct experiments for Na_2CO_3 additions above 40%. Because of this and also because use of Na_2CO_3 in amounts higher than 40% was considered to be impractical, to it was decided to conduct experiments aiming the investigation of the catalytic effect of Na_2CO_3 for longer durations at 1500°C with 40 wt.% addition.

Experiments were continued by varying duration in the range of 0-3 hours. The effect of Na_2CO_3 in increasing the amount of h-BN forming was seen to be very pronounced for short times but less so for longer times. It was seen that the amount of B_2O_3-Na_2O mixture in the reaction products decreased rapidly after 30 minutes. Loss of B_2O_3 and Na_2O from the system was concluded to be due to the following simultaneous reactions; evaporation of Na_2O, reduction of Na_2O with carbon, evaporation of B_2O_3, reduction of B_2O_3 with carbon, and evaporation of the sodium borate melt. h-BN formation stopped after 2 hours due to absence of B_2O_3 in the system. B_4C was not entirely consumed and its amount did not change after 2 hours again due to absence of B_2O_3 in the system.

Experiments were alsoconducted with 40 wt.% Na_2CO_3 addition for 3 hours at 1300 and 1400°C. The quantity of h-BN that formed at 1500°C was about 30% more than that at 1300°C. This may be taken as an indication that Na_2CO_3 may be used as an additive to produce h-BN at lower temperatures which may be of practical interest.

Another effect of Na_2CO_3 addition was on the particle size of the h-BN forming. It was observed from SEM micrographs of the samples that Na_2CO_3 addition was very effective in increasing the amount as well as the particle size of h-BN forming.

Na_2CO_3 and $CaCO_3$ were used as additives together to see the effect on the yield and particle size of h-BN forming. Amount of h-BN in the products indicates Na_2CO_3 and $CaCO_3$ addition was not suitable to improve yield of h-BN compared to 40 wt.% Na_2CO_3 and optimum

$CaCO_3$ addition. On the other hand, particle size of h-BN obtained from B_2O_3-C mixtures containing both $CaCO_3$ and Na_2CO_3 was 50% larger than that obtained from B_2O_3-C mixtures containing only Na_2CO_3.

To conclude, Na_2CO_3 is even more effective than $CaCO_3$ in increasing the amount as well as the particle size of h-BN forming but there is significant loss of B_2O_3 and Na_2O from the system which should make use of Na_2O_3 impractical unless ways of decreasing this loss can be found.

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