EFFECT OF CALCIUM OXIDE ADDITION ON CARBOTHERMIC FORMATION OF HEXAGONAL BORON NITRIDE

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ABSTRACT

EFFECT OF CALCIUM OXIDE ADDITION ON CARBOTHERMIC FORMATION OF HEXAGONAL BORON NITRIDE

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Hexagonal boron nitride (h-BN) formation by carbothermic reduction of B_2O_3 under nitrogen atmosphere at 1500°C and effect of CaO addition into the initial B_2O_3 – active C mixture were investigated during this study. Reaction products were characterized by powder X-ray diffraction, scanning electron microscopy (SEM) and quantitative chemical analysis.

Main aim of this study was to investigate the presence of a second reaction mechanism that catalytically affects h-BN formation during CaO or $CaCO_3$ addition into the initial mixture. It was found that similar to $CaCO_3$ addition, CaO addition has a catalytic effect on carbothermic formation h-BN. In order to investigate the reaction mechanism experiments with B_2O_3 – CaO mixtures without active carbon addition into the mixture were conducted. Furthermore nucleation of h-BN from calcium borate melts had been investigated and experiments were conducted with h-BN addition into CaO – B_2O_3 mixtures. It was concluded that nucleation of h-BN in calcium borate slags under experimental conditions is not possible. Hexagonal BN should be present in the system in order to activate the second nitrogen dissolution followed by h-BN precipitation mechanism. Highest efficiency was achieved in the experiment conducted with $CaCO_3$ addition and largest particle size was observed during the experiment conducted to investigate the effect of nucleation.

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

ÖZ

KALSİYUM OKSİT İLAVESİNİN KARBOTERMİK YÖNTEMLE HEKZAGONAL BOR NİTRÜR OLUŞUMU ÜZERİNE OLAN ETKİSİ

Özkenter, Ali Arda
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Bu çalışmada B_2O_3'ün karbotermik yöntemle, 1500°C'de, azot atmosferi altında indirgenmesi ile hekzagonal bor nitrür oluşumu ve B_2O_3 – aktif C karışımına CaO ilavesinin etkisi araştırılmıştır. Reaksiyon ürünlerinin karakterize edilmesi için; X-ışınları kırınımı ile tarama elektron mikroskobu (SEM) ve reaksiyon ürünlerinin miktarı için kimyasal analiz metotları uygulanmıştır.

Bu çalışmanın ana amacı, asıl toz karışımına CaO ya da $CaCO_3$ ilave edilmesi halinde aktive olan ve h-BN oluşumunu katalitik olarak etkileyen ikinci bir reaksiyon mekanizmasının varlığının araştırılmasıdır. $CaCO_3$' e benzer olarak CaO ilavesinin de h-BN oluşumuna katalitik etkisi olduğu bulunmuştur. Reaksiyon mekanizmasının araştırılması için aktif karbon içermeyen B_2O_3 – CaO karışımı ile deneyler yapılmıştır. Ek olarak h-BN in kalsiyum borat eriyiklerinden çekirdeklenmesini araştırmak için deneyler yapılmış ve B_2O_3 - CaO karışımına h-BN eklenerek çekirdeklenme süreci incelenmiştir. Sonuç olarak h-BN in deneysel koşullar altında kalsiyum borat curuflarında çekirdeklenmediği görülmüştür. Hekzagonal BN in, azot çözünümünü takip eden h-BN çökelmesi mekanizmasının aktive olması için sistemde bulunması gerektiği anlaşılmıştır. En yüksek verimlilikteki deneyler karışıma $CaCO_3$ ilavesi yapıldığında ve en büyük tane boyutu da çekirdeklenmenin araştırıldığı deneylerde gözlemlenmiştir.

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

To My Father

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TABLE OF CONTENTS

CHAPTERS

LIST OF TABLES

TABLES

LIST OF FIGURES

FIGURES

CHAPTER 1

INTRODUCTION

Minerals and compounds of boron are being widely used for many applications all over the world. These large application fields, varying from metallurgy to nuclear industry, increase the importance of boron and its compounds [1]. Recent developments in technical ceramics technology shows that demand for advanced ceramics containing boron are going to increase significantly for the following decades.

BN has a unique place between advanced ceramics with its many different crystal structures and wide applications. Hexagonal form of boron nitride has properties of solid lubrication, refractoriness and excellent chemical, thermal and electrical properties. Hexagonal BN is analogous to the graphite form of carbon and also known as the white graphite [2, 3].

Some studies on the production of h-BN have been found in the literature and different production methods and reaction mechanisms were investigated. Between these production methods, carbothermic formation of h-BN under nitrogen atmosphere is an important one and previous studies about the topic indicate that some additives catalytically affect h-BN formation. The aim of this study was to investigate the effect of CaO addition on carbothermic formation of h-BN. Experiments were conducted in order to investigate the efficiency and reaction mechanism of the CaO addition into the boric oxide – active carbon mixture.

Turkey owns 72% of the worlds total boron reserves and importance of boron industry for Turkey is obvious [4]. Nevertheless, production of processed materials containing boron is still limited. Therefore, it is essential to investigate production methods for advanced ceramics those contain boron such as h-BN.

CHAPTER 2

LITERATURE REVIEW

Boron nitride has been known for a long time and the preparation of the material has been studied quite extensively. Nevertheless even the most recent synthetic procedures involve considerable technical difficulties and their efficiencies should be increased to meet increasing industrial demand for BN products [5].

Hexagonal boron nitride production has also been studied for a long time and different production methods had been developed in recent studies. Between these methods carbothermic production of h-BN shows promising results [3, 6]. Furthermore, addition of some compounds into the initial boric oxide - active carbon mixture was reported to catalytically effect h-BN formation [7]. This study was carried out in order to investigate the catalytic effect of CaO addition into the initial mixture of B_2O_3 – active C.

In the following section, crystal structures of BN and properties – applications of h-BN will be given. Finally production methods of h-BN will be examined while giving emphasis to the carbothermic production.

2.1 Crystal Structures of BN

Bonding characteristics of nitrogen and boron forms many different crystal structures and these structures usually show a close resemblance to the crystal structures of carbon [6]. Well defined crystal structures of BN are hexagonal BN (h-BN), rhombohedral BN (r-BN), wurtzitic BN (w-BN), and cubic BN (c-BN). Between these phases most important ones are hexagonal and cubic. Hexagonal boron nitride is soft and lubricating on the other hand, cubic boron nitride, which could be synthesized from h-BN at high temperatures and pressures, is hard and abrasive [2]. Hexagonal boron nitride is also called “white graphite” and cubic BN is analogous to diamond form of carbon. Other than these crystal structures amorphous and turbostratic (t-BN) boron nitride phases exist [5, 6].

The hexagonal form of boron nitride (h-BN) having a bimolecular unit cell with a simple layer structure similar to graphite is the most common. These layers consist of a flat network of B_3N_3 hexagons. A boron atom in one layer of these hexagons is located over a nitrogen atom in the next layer and hexagons are packed directly on top of each other. Figure 2.1 shows the layered structure of h-BN. Weak Van Der Waals bonds (π-bonds) between layers is the origin of the lubricating nature of h-BN [2, 8].

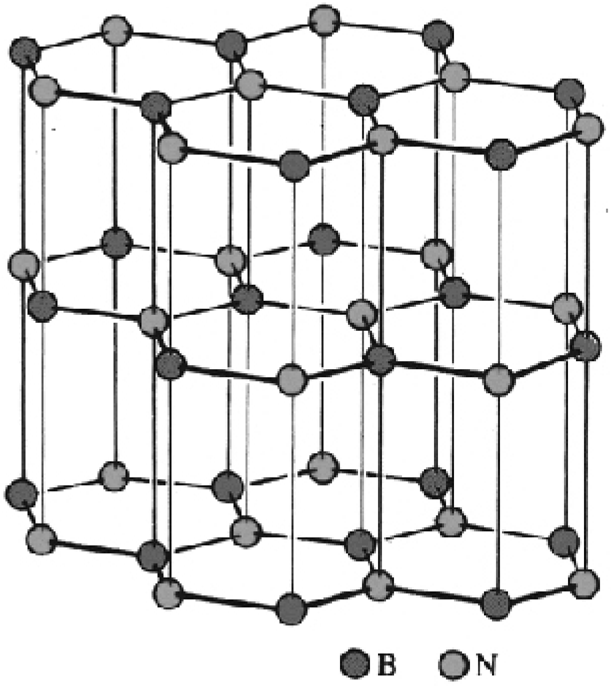

Figure 2.1 Layered hexagonal structure of BN [9].

Graphite is the only close analog of hexagonal boron nitride, but there still exists a difference in the packing structure. Unit cell dimensions of hexagonal boron nitride and graphite are compared in Table 2.1 and interlayer spacing of h-BN (3.33Å) and graphite (3.35Å) are very similar [5].

Table 2.1 Unit cell dimensions of graphite and hexagonal boron nitride in Å [5].

				Density (g/cm^3)	
	a	c	c/a	Calculated	Observed
Graphite	2.464	6.736	2.73	2.26	2.255
h-BN	2.504	6.661	2.66	2.27	2.29

Graphite is soft, lubricating, black and electrical conductor on the other hand its iso-electronic analog h-BN is soft, lubricating, white and electrical insulator. The electronic properties of hexagonal boron nitride distinguish it most strikingly from graphite. The difference in electrical conduction of graphite and h-BN can be summarized as follows; Bonding in graphite can be described in terms of localized trigonal sp^2 σ–orbitals and delocalized π-orbitals along the hexagonal planes. π-electrons are in a π-band that contains the highest valence band and the lowest conduction band. This leads to the electrical conduction observed parallel to the planes and the relative high resistance across the planes. When h-BN is taken into account, same σ-bond distribution is present in the plane but requires an ionic contribution of π-electrons from nitrogen to boron in order to generate the double bonds for the resonating π-orbitals. In this case, the π-electron band is divided into two sub-bands separated by an energy gap of about 4.6 eV, which is enough for explaining the insulating nature of h-BN [3, 5, 6].

2.2 Properties of Hexagonal Boron Nitride

Depending on the production technique, properties of h-BN show distinct differences. These differences are mainly due to the crystallinity, particle size distribution and purity of the h-BN synthesized. Because of these facts, production method of h-BN powder must be determined based on the area of utilization.

Hexagonal BN has three important properties; solid lubricity, electrical insulation and good thermal conductivity. In contrast with other materials having the property of solid lubrication, h-BN can retain its low friction coefficient up to very high temperatures [2, 3, 10]. Figure 2.2 shows the variation in coefficient of friction of some lubricants with temperature.

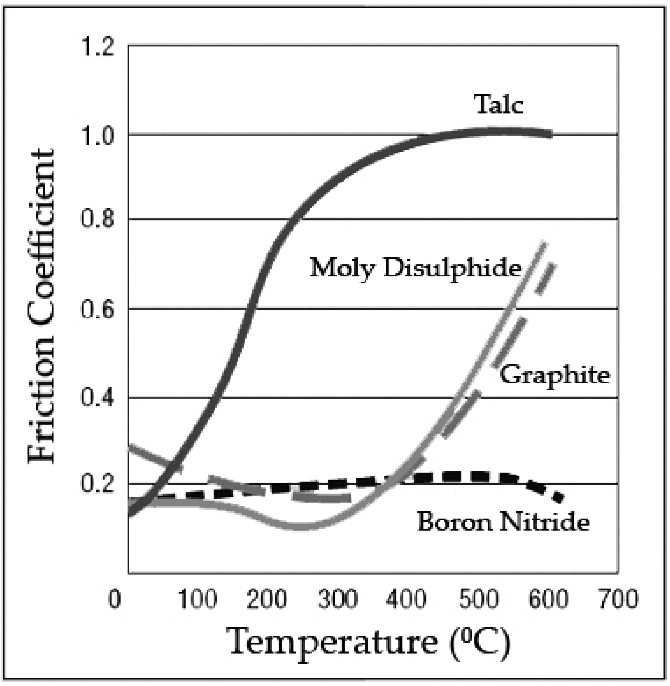

Figure 2.2 Variation in coefficient of friction of some lubricants with temperature [11].

The specific resistance of BN is about 1*10^{13} ohm cm at 25°C, which is comparable to a good insulator; at 2000°C the resistivity is decreased to the values about 1*10^{3} ohm cm, better than most refractory oxides. This decrease in resistance with temperature is characteristic of semiconductor behavior although it appears that the forbidden energy gap is rather large [5]. Thermal conductivity and dielectric constant of h-BN is very high, furthermore its thermal expansion is low and it has very good thermal shock resistance. These properties make h-BN a candidate material for insulator and cooler parts of electronic circuits.

Another important property of boron nitride is that, inertness to and non-wettability by many metallic melts such as Al, Cu, Fe, Zn and non-metallic melts such as B, Si and glasses. It is not attacked by mineral acids and in general has been found to be very resistant to other kinds of chemical attack. Oxidation of boron nitride in air begins above 1000°C, but dissociation starts in vacuum near 2700°C. In inert atmosphere h-BN is stable up to 3000°C. This high chemical and thermal stability enables one to utilize boron nitride as a crucible material [5 - 8].

Table 2.2 Some physical and chemical properties of h-BN, Graphite, Aluminum Nitride and Alumina [11 -13, 15].

	h-BN	**Graphite**	**AlN**	**Al_2O_3**
Density g/cm^3	2.27	2.2	3.26	3.98
Hardness Mohs and	2	2		9
knoop kg/mm^2	205		1200	2000
Melting Point °C	3000	3700	2200	2015
Dielectric constant	4.2	-	10	9.7

Production of dense parts made of BN is generally carried by pressure assisted sintering (hot pressing or hot isostatic pressing) [12]. Powders must be tailored prior to pressing processes and properties like particle size, particle shape and purity must be highly controlled. Free boric oxide is generally used as a binder and the supplier of the liquid phase during sintering of h-BN. The densification mechanism can be described as vitreous sintering. Machinability of pressed products is as high as the machinability of graphite products [12, 13].

2.3 Applications of Hexagonal Boron Nitride

Hexagonal boron nitride has many industrial applications because of its outstanding properties. Four main properties of h-BN determine its four main application fields. First one is the high temperature lubrication purposes, after that it could be used as crucibles in molten metal handling. Thirdly h-BN could be utilized as additives in other ceramics and polymers, and finally it has applications in electronic industry as coolers, insulators or as heat-sinks. It is possible to utilize h-BN in many forms such as hot pressed solids, powders, fibers and as dispersed powders in liquid media [10, 11].

Nowadays, between h-BN products, powders synthesized for lubrication purposes holds the biggest portion of the economic market. Hexagonal boron nitride is used as a lubricant and mold release agent in casting, forging, rolling, pressing and extrusion processes. Also, in their study, Kimura et al. [10] reported that h-BN is effective in reducing wear if used as a lubricant oil additive. They claimed that h-BN addition into some lubricant oils slightly increases coefficient of friction but, due to presence of h-BN particles on wear scars, wear of material decreased drastically.

Growing market of h-BN on the world results with wide applications such as;

- Solid lubricants (powder form)
- Gas seals for oxygen sensors
- Composite materials production including ceramic, polymer or metal matrix with h-BN as the reinforcement.
- Break rings in steel casting
- Insulators for high-frequency electrical equipment
- Due to its high stability in molten metal and glass environment, it could be used as highly effective refractive coatings
- Masks for x-ray lithography
- High temperature furnace hardware and boats for molten metal, glasses and ceramic processing
- Crucibles for aluminum evaporation and for molecular beam epitaxy
- Radar windows and antennas
- Vessels for Czochralski crystal growth of III-V and II-VI compounds (as gallium arsenide)
- Release agents
- Filler for plastics
- Cubic BN production at high temperatures and pressures [5, 6, 10-12].

Properties of hexagonal boron nitride could vary drastically depending on processing parameters. Particle size, crystallinity and purity of the product should be carefully determined during process design in order to produce the hexagonal boron nitride needed for specific applications. Coarse particle sized h-BN is suitable for applications such as solid phase lubrication and high temperature requirements. On the other hand finer h-BN powder particles have better sintering performance [11].

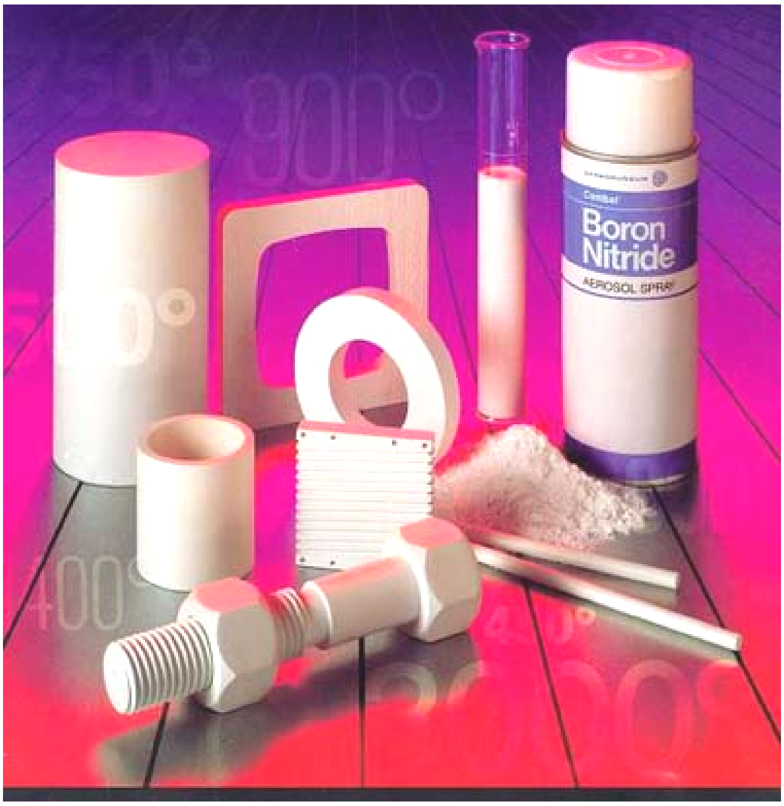

Figure 2.3 Photograph of h-BN products [14].

2.4 Production Methods of h-BN

Although h-BN was first synthesized in middle of 19th century, it became a commercial material after 1950s. Growing demand for h-BN products enforces researchers to develop processes with low costs and high efficiencies [5 - 6, 9]. In the following section production methods of h-BN will be discussed.

Three main methods are utilized for production of h-BN in industrial scale [2, 3, 7]. First one is the reaction of boric acid or boron oxide with ammonia. Overall reaction of the process is given in reaction 2.1;

$H_3BO_3 + NH_3 = BN + 3H_2O$ Reaction (2.1)

An inert carrier substance is necessary for increasing the rate of reaction between boric acid and ammonia. Calcium phosphate or calcium carbonate is used as the carrier substance and reaction takes place at temperatures above 900°C. Product obtained has an amorphous structure and containing oxygen as impurity. In order to overcome these problems a second treatment under N_2 atmosphere and above 1500°C is needed [2, 3, 7].

Second process designed for h-BN production is reaction of boric acid or boron oxide with nitrogen containing organic materials.[2, 16] Reaction of boron oxide with urea is given in reaction 2.2;

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

Reaction product is turbostratic boron nitride and similar to previous method secondary processes are needed for crystallization and purification of h-BN formed [2, 3, 7, 16].

Third main method of h-BN production, which is also concern of this study, is the carbothermic method. According to Paine and Narula [3], carbothermic method should become the most suitable method for industrial production of h-BN. An important advantage of h-BN production by carbothermic method is that product obtained does not need secondary heat treatments for converting crystal structure into hexagonal form. Information existing in literature on carbothermic method of h-BN production is summarized below.

In their study Aydoğdu and Sevinç [17] investigated formation of h-BN by subjecting pellets prepared from boric oxide – carbon mixtures to nitrogen gas in a horizontal tube furnace. During carbothermic reduction of B_2O_3, nitridation can be applied in order to produce h-BN from mixture under N_2 atmosphere. Formation of BN in the system consisting of boric oxide, carbon and nitrogen gas proceeds according to the overall reaction 2.3.

$$B_2O_3(l) + 3C(s) + N_2(g) = 2BN(s) + 3CO(g) \qquad \text{Reaction (2.3)}$$

They conducted experiments for 0.5 to 4 hours and from 1100°C to 1500°C. It was found that h-BN formation was observed for temperatures above 1100°C and as temperature increases amount of h-BN in the reaction products increases. Furthermore, they concluded that reaction 2.3 was completed in 2 hours, at 1500°C and B_4C, unreacted B_2O_3, unreacted C and h-BN formed to exist in reaction products for experiments with shorter durations [17, 18].

In order to investigate the reaction mechanism of carbothermic production of hexagonal boron nitride, Aydoğdu and Sevinç [17] conducted experiments employing different geometries. They concluded that liquid boric oxide and carbon need not to be in contact for formation of solid BN and reaction proceeds through gaseous intermediates. Boric oxide gas formed due to evaporation reacts with nitrogen gas and carbon on solid carbon particles. B_4C phase was observed in the portions of product where $N_2(g)$ pressure was too low to form BN. B_4C was formed by reaction of B_2O_3 and C. Gibbs phase rule dictates that either BN or B_4C but not both can exist in the system at equilibrium. Thermodynamic analysis based on the reaction 2.4 shows that B_4C was unstable in the system. Finally boron carbide reacts with B_2O_3 (liquid or gas) and $N_2(g)$, forming BN [17, 18].

$$3B_4C(s) + B_2O_3(l) + 7N_2(g) = 14BN(s) + 3CO(g) \qquad \text{Reaction (2.4)}$$

Reaction mechanism had also been investigated in other studies. One of them which was conducted by Bartnitskaya et al. [19] suggested that B_2O_3 first gets reduced to elemental B by carbothermic reduction and followed by nitridation of elemental boron, while Yoon and Jha [20] considered h-BN formation to proceed through gaseous BO. On the other hand in the study conducted by Pikalov [21], it was presumed that formation of h-BN proceeds in two consecutive steps with B_4C forming by reaction of B_2O_3 and C in the first step and h-BN forming by reaction of B_4C with B_2O_3 and $N_2(g)$ in the second step. Formation of boron carbide takes place as the reduction product by reaction 2.5, followed by h-BN formation with reaction 2.4.

$$2B_2O_3(l) + 7C(s) = B_4C(s) + 6CO(g) \qquad \text{Reaction (2.5)}$$

In their study Çamurlu et al. [22] investigated the role of boron carbide in carbothermic formation of hexagonal boron nitride. They conducted experiments by subjecting B_2O_3 – activated C mixtures to nitrogen and argon atmospheres at 1500°C. Boric oxide quantity in the mixtures was 100 mole% excess of the stoichiometric amount calculated with respect to reaction 2.3. They found that reaction 2.3 reached completion in 3 hours. They produced B_4C by keeping B_2O_3 – C mixtures at 1500°C under argon atmosphere and studied formation of h-BN with reaction 2.4, by subjecting B_4C (produced by them) and B_2O_3 mixtures to $N_2(g)$ at 1500°C. It was reported that boron carbide charged into the furnace was not completely converted to h-BN in 3 hours. Therefore, they concluded that formation of h-BN from boron carbide by reaction 2.4 is slower than formation of h-BN by reaction 2.3. These results may be taken as an indication that boron carbide is not a necessary intermediate product in formation of hexagonal boron nitride and that formation of B_4C retards h-BN formation [22, 23].

One other important subject of carbothermic formation of h-BN is the catalytic effect of some compounds added to the system. The increase in demand of h-BN results in further research for more efficient methods. Bartnitskaya et al. [24], investigated the catalytic effect of lithium compounds such as Li_2CO_3 and LiOH on yield and crystallographic ordering of h-BN production. They reported from experiments conducted at 1500°C for 3 hours in nitrogen atmosphere that addition of 12 wt.% Li_2CO_3 to the initial carbon–boric acid mixture, the amount of h-BN formed was about twice more than the amount formed in the experiment without Li_2CO_3 addition. The crystal structure of the formed h-BN was also seen to be improved by the addition of Li_2CO_3. They believe that a catalyst-solvent mechanism is present for the role of Li_2CO_3, in which Li_2CO_3 reacts with B_2O_3 resulting in a lithium borate melt. Then, h-BN forms and crystallizes from the formed melt [24 - 28].

Other than lithium compounds, catalytic effect of $CaCO_3$ was investigated by Çamurlu et al. [7, 23]. In their study, they added $CaCO_3$ into the initial plain B_2O_3 – activated C mixture in various amounts ranging in 5 – 50 wt.% of the mixture. First of all they determined the optimum amount of $CaCO_3$ addition by carrying experiments with different compositions. They found 10 wt.% $CaCO_3$ addition to be the optimum value to keep the amount of B_4C as low as possible and h-BN as high as possible in the reaction products. Results of their experiments conducted for 30 min at 1500°C are shown in Figure 2.4 [7, 23].

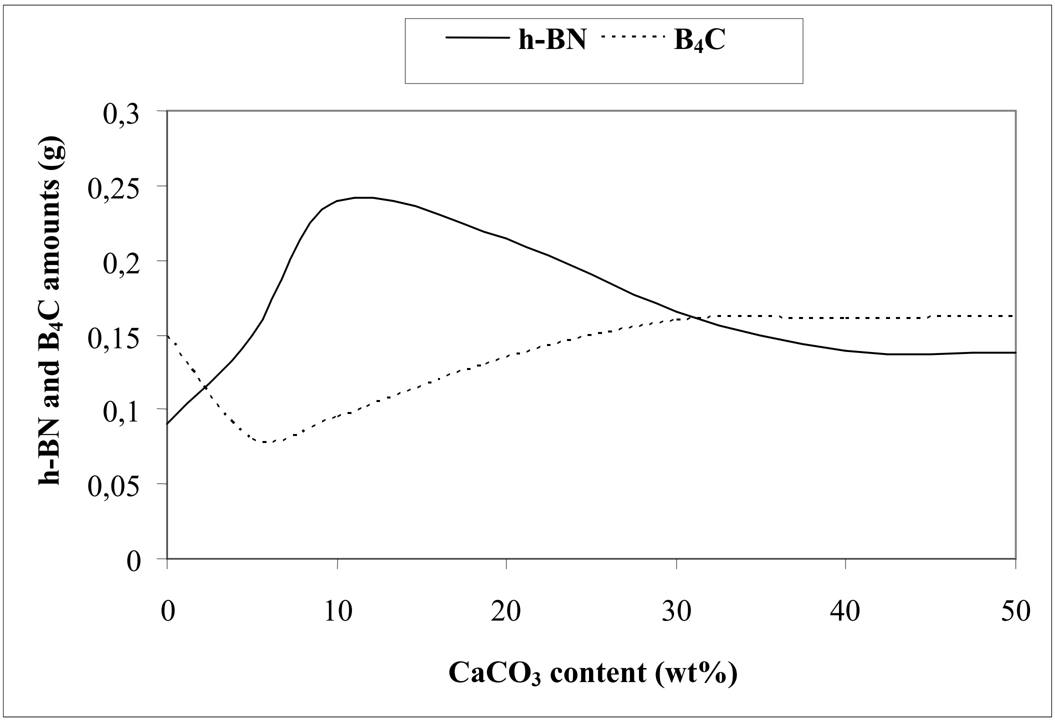

Figure 2.4 Variation in the amounts of h-BN and B_4C at 1500°C and 30 min [7].

10 wt.% $CaCO_3$ addition into B_2O_3 – activated C mixture was reported to be the optimum amount with experiments of 30 min by Çamurlu et al [7]. After

that they conducted experiments with 10 wt.% $CaCO_3$ – added mixture for longer durations in order to determine the completion time for h-BN formation. It was found that h-BN formation was completed in 2 hours with 10 wt.% $CaCO_3$ addition at 1500°C and amount of h-BN in the reaction products was reported to be significantly larger compared to the amount in plain mixture. Boron nitride amount in the reaction products of plain mixture was reported to be 0.40 g, which was increased to 0.60 g during the experiment conducted with 10 wt.% $CaCO_3$ addition [23].

Aydoğdu and Sevinç [17] reported that boron carbide was formed in the first 30 min of the experiments and as reaction proceeded, it was used up by reaction 2.4. Çamurlu et al. [7] reported that all boron carbide formed in 30 min of experiment was used up in 3 h with plain mixture. They found that $CaCO_3$ addition decreases the amount of boron carbide formed in the first 30 min of the experiments. Furthermore, they reported that all boron carbide in the system was used up in 2 hours during the experiments with 10 wt.% $CaCO_3$ addition. Amounts of h-BN and B_4C for different experimental durations are shown on figure 2.5 [7, 22 - 23].

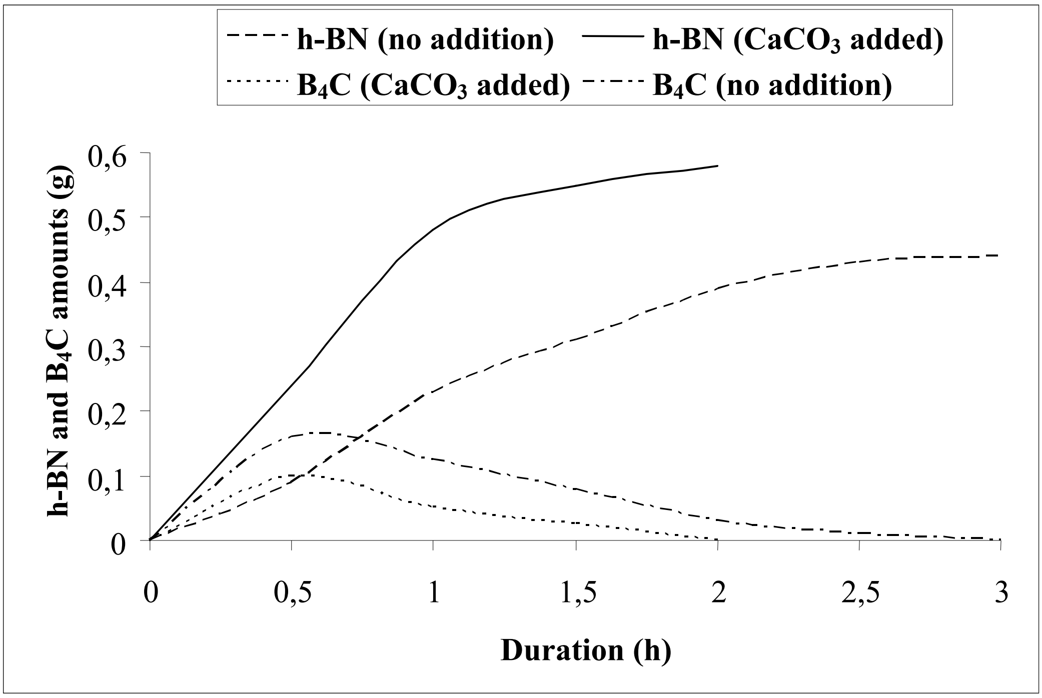

Figure 2.5 Amounts of h-BN and B_4C in the reaction products [7].

Çamurlu et al. [7, 23] calculated the average particle size of the products with $CaCO_3$ addition and plain mixture with aid of the SEM micrographs. They reported that average particle size of the product without any addition was 0.36 ± 0.08 μm and $CaCO_3$ addition increased the average particle diameter to 0.70 ± 0.14 μm. Structure of h-BN particles was reported to be merged polycrystalline when there were no additions, on the other hand $CaCO_3$ addition converted this structure into separate particles, having definite edges. Also BET specific surface area measurements were in accord with SEM micrographs. Specific surface area of the powder obtained from plain mixture was reported as 31.7 m^2/g whereas the specific surface area of the sample obtained from $CaCO_3$ addition was 21 m^2/g. These results indicate that $CaCO_3$ addition has a positive effect on growth of hexagonal boron nitride phase formed during carbothermic production [7, 23].

Reaction mechanism and catalytic effect of $CaCO_3$ addition had been observed by Çamurlu et al. [7] and they proposed that if the reaction mechanism described by Aydoğdu and Sevinç [17] in previous section is not changed during $CaCO_3$ addition, there should be another mechanism present for h-BN formation. They found that $CaCO_3$ addition up to 20 wt.% increased the porosity of the reaction aggregate, but porosity was decreased by higher additions of $CaCO_3$. This increase in porosity increases the efficiency of reaction by permitting the diffusion of N_2 gas into the pellet easier. Increased porosity of the pellet was stated to arise probably by calcination of $CaCO_3$. Decrease in porosity of the B_2O_3 – C – $CaCO_3$ pellets containing more than 20 % $CaCO_3$ was suggested to be due to changes in viscosity, density etc. of the calcium borate.

$CaCO_3$ addition results in formation of calcium – borate in the system. According to the phase diagram of B_2O_3 and CaO (Figure 4.10), two liquids are present in the system at 1500°C with 10 wt.% $CaCO_3$ addition. One of the phases is essentially pure B_2O_3 and the other one is 25 wt.% CaO – B_2O_3 melt. CaO amount in the system increases as wt.% $CaCO_3$ in the mixture increases. This results in a decrease in the rate of evaporation of $B_2O_3(l)$ in the system which decreases the rate of the reaction 2.3. Çamurlu et al.[23] considered, increase in porosity of the pellet with increase in $CaCO_3$ addition to favorably affect BN formation and decrease in rate of evaporation of B_2O_3 with increase in $CaCO_3$ addition to decrease the rate of h-BN formation. These opposing two factors determine the rate of formation of h-BN and they reported that 10 wt.% $CaCO_3$ addition is the optimum value to increase the reaction rate as much as possible [7, 23].

Çamurlu et al. [7] proposed that increase in the h-BN amount during experiments conducted with $CaCO_3$ addition is probably based on a second mechanism that consist of dissolution of $N_2(g)$ in calcium-borate melts followed by h-BN crystallization from the melt. Nitrogen dissolves in slags as N^{3-} or as N^- depending on the basicity of the melt. Hexagonal boron nitride is also soluble in oxide melts and if solubility product of h-BN is exceeded h-BN formation could become possible. They suggested that h-BN formation may take place with reactions 2.5 and 2.6 depending on the basicity of the melt [7, 23].

$(BO_3^{3-}) + (N^{3-}) = BN(s) + 3O^{2-}$ Reaction 2.5

$(B_2O_4N)^{5-} = BN(s) + (BO_3)^{3-} + O^{2-}$ Reaction 2.6

Most important thing about reactions 2.5 and 2.6 is that they do not use carbon for h-BN formation. It may be concluded that h-BN may be produced from calcium-borate slags under nitrogen atmosphere at low O_2 pressures. Low O_2 pressures could be obtained in the system with aid of carbon addition at elevated temperatures and carbon presence in the system may be necessary for h-BN formation from slags containing $B_2O_3(l)$ and dissolved nitrogen [23].

Other than $CaCO_3$ addition, Çamurlu et al. [23, 29], separately, investigated the catalytic effect of alkaline earth oxide additions such as MgO and BaO. In their study MgO was used as an oxide and BaO was added into mixture in the form of carbonate ($BaCO_3$). They reported that a mechanism similar to catalytic effect of $CaCO_3$ addition is present in MgO and BaO additions.

Amount of hexagonal boron nitride formed during the experiments and particle size of h-BN flakes was found to be increased compared to the plain mixture in the reaction products. After that they investigated the effect of Cu addition, in the form of cupric nitrate, into boric oxide – active carbon mixture. They reported that addition of Cu increases the particle size and crystallinity of h-BN formed similar to $CaCO_3$ addition. Furthermore Cu was reported to be inert in the system and did not form secondary compounds such as its carbides or borides, but Cu addition did not increase the amount of h-BN formed in reaction products.

CHAPTER 3

EXPERIMENTAL PROCEDURE AND SET-UP

The main aim of this study was to investigate the catalytic effect of CaO in carbothermic formation of h-BN. Experiments were conducted in order to investigate the reaction mechanism and yield of different compositions. First of all, pellets produced from boric oxide – active carbon mixtures were subjected to nitrogen gas at 1500°C. Then experiments were conducted with B_2O_3 – C – $CaCO_3$ and B_2O_3 – C – CaO mixtures. By these experiments reference values were achieved. After that experiments with CaO – B_2O_3 (no active C) mixtures were conducted. Finally h-BN had been added into B_2O_3 – CaO mixture in order to investigate nucleation of h-BN from calcium borate melts under nitrogen atmosphere. In the following chapter the experimental set-up, materials used and experimental procedure will be given.

3.1 Experimental Set-Up

Experiments were conducted in a horizontal tube furnace which was an 800 mm long alumina tube of 50 mm inner and 60 mm outer diameters. The alumina tube was closed at both ends by silicon stopcocks having thermocouple insertion, gas inlet and outlet tubes. Gas flow was adjusted

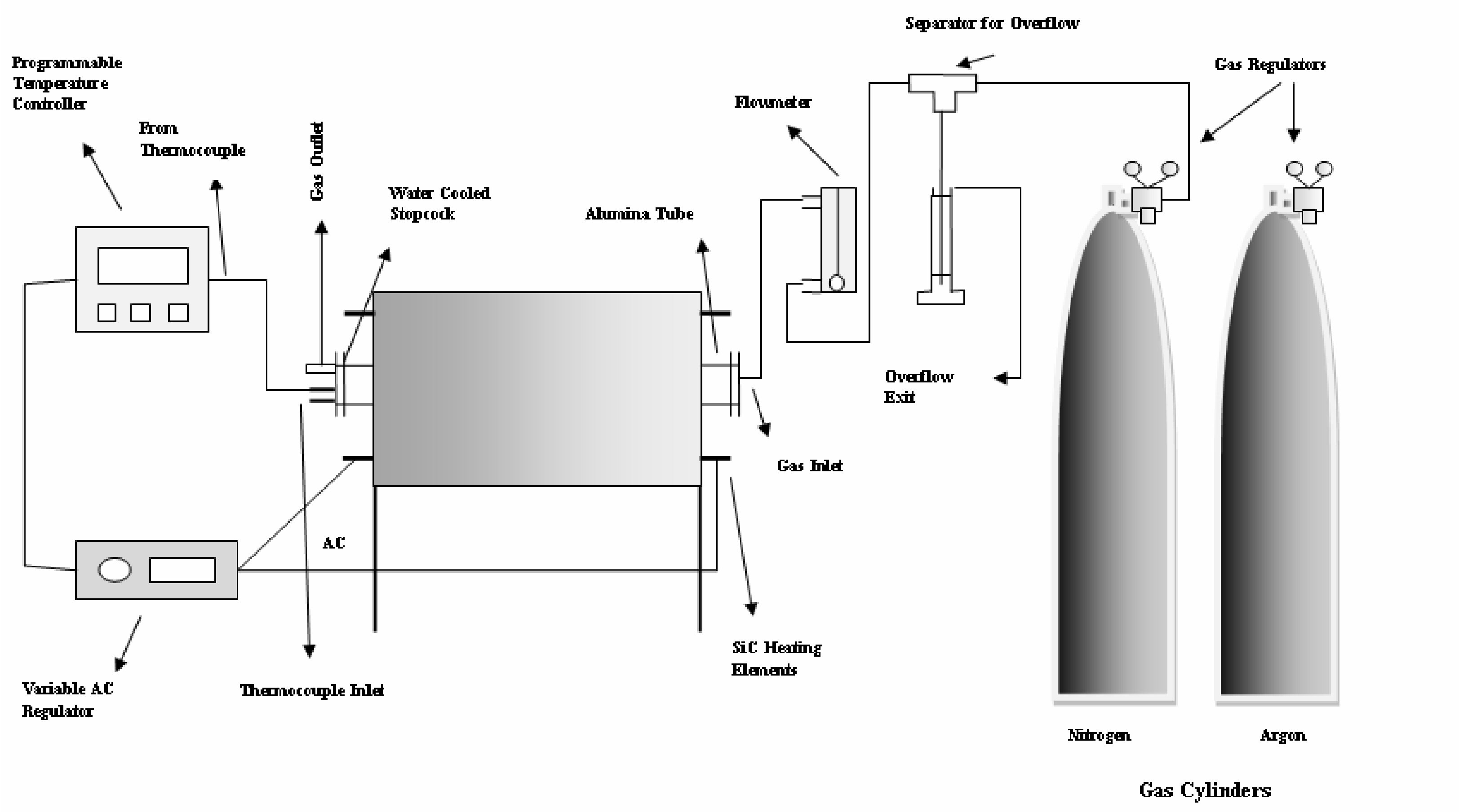

Figure 3.1 Schematic drawing of the experimental set-up

by a flowmeter before entering into the furnace and overflow gas was permitted to exit from the system by overflow exit. Temperature of the furnace was kept at constant in range of 1°C error by a digital temperature controller. Schematic drawing of the experimental setup is given in figure 3.1. An S type thermocouple was used to measure temperature.

Pellets were placed in a graphite boat, inside of which was lined with a 0.5 mm thick layer of h-BN in order to prevent reaction with its contents. Graphite boat was charged into the furnace with help of a thin alumina bar. Radiated heat from the hot zone of the furnace causes overheating of furnace components at both ends. Radiation shields made of refractory fiber board were utilized at about 30 cm away from the hot zone of the furnace in order to overcome this problem.

3.2 Materials Used

3.2.1 Boric Oxide (B_2O_3)

Boric oxide used in the mixtures was prepared by calcination of boric acid (H_3BO_3) at 1000°C for 1 h in a pot furnace. Boric acid used was obtained from Merck was 99.8% pure. Overall calcination reaction is given in reaction 3.1.

$2H_3BO_3 = B_2O_3 + 3H_2O$ Reaction (3.1)

Calcination of boric acid takes place in two steps; firstly boric acid decomposes into metaboric acid (HBO_2) and water. After that metaboric acid decomposes into boric oxide and water vapor. Reactions of metaboric acid formation step (reaction 3.2) and boric oxide formation step (reaction 3.3) are as follows;

$H_3BO_3 = HBO_2 + H_2O$ Reaction (3.2)

$HBO_2 = \frac{1}{2} B_2O_3 + \frac{1}{2} H_2O$ Reaction (3.3)

Calcination of boric acid was performed in a nickel crucible which has a height of 60 mm and an inner diameter of 50 mm. Figure 3.2 shows the nickel crucible used during calcination. The calcination of H_3BO_3 process was started with placing nickel crucible including 45 g boric acid into pot furnace at 1000°C. When $H_2O(g)$ removal was finished, molten B_2O_3 was poured onto a stainless steel plate. After solidification of B_2O_3, it was ground into small pieces and placed in a desiccator in order to prevent rehydration.

Figure 3.2 Nickel crucible used for calcination.

3.2.2 Calcium Carbonate ($CaCO_3$) and Calcium Oxide (CaO)

Experiments including both $CaCO_3$ and CaO addition were conducted. $CaCO_3$ used during experiments was supplied from Merck. Purities and catalog numbers of all chemicals used in experiments are given on Table 3.1. Calcium oxide used in experiments was produced by calcination of $CaCO_3$ in a nickel crucible at 1000°C for 15 hours. To check whether the calcination is complete, weight loss determinations were used. Calcination reaction of calcium carbonate is given in reaction 3.4.

$CaCO_3(s) = CaO(s) + CO_2(g)$ Reaction (3.4)

Table 3.1 Identifications and purities of chemicals used in experiments.

Chemical Name	Brand	Catalog Number	Purity (%)
Active Carbon	Merck	102186	>99
$CaCO_3$	Merck	102066	>99
H_3BO_3	Merck	100165	>99.8
HCl (fuming)	Merck	100314	Extra pure 37-38

3.2.3 Active Carbon and Gases Used (N_2 – Ar)

Activated carbon, which was supplied from Merck Chamicals, was over 99% purity. In order to determine the ash content of carbon it was combusted at 800°C for 24 hours in a muffle furnace. Ash content of the carbon was found to be 0.25%. The active carbon was determined to be amorphous.

High purity nitrogen gas supplied from BOS A.Ş. was used in the experiments. Nitrogen gas was of 99.998% purity and containing <30 vpm moisture and <50 vpm oxygen. Argon gas was supplied from Habaş A.Ş. and it was 99.998% pure, containing <0.9 vpm moisture, <2.8 vpm nitrogen and <1.7 vpm oxygen.

3.3 Experimental Procedure

Firstly experiments with plain and $CaCO_3$–added boric oxide – activated carbon mixtures were conducted in order to compare the results of the later experiments with these reference results. After that experiments were conducted with CaO–added B_2O_3 – C mixtures. Thirdly experiments with CaO – B_2O_3 mixture (no activated C) were conducted in order to study whether BN formation takes place by the mechanism of nitrogen dissolution in and crystallization from the calcium borate melt. Finally experiments with CaO – B_2O_3 mixtures into which h-BN has been added were conducted to study the effect of nucleation in BN formation.

Activated carbon (Merck, 99% purity) – boric oxide mixtures, each having a weight of 2.5 g were prepared with 100 mole% excess boric oxide than the stoichiometric amount required for reaction 2.3. Excess boric oxide was necessary due to evaporation loss. Plain mixtures consisting of 0.514 g active C and 1.986 g B_2O_3 was prepared.

All materials used in experiments were mixed in an agate mortar and cylindrical pellets were produced by pressing mixtures in a die with a pressure of 58.9 MPa (6 kg/mm^2). Boric oxide used during the experiments was ball milled in a Retsch PM 100 planetary ball mill (Figure 3.3) in order to produce homogeneous mixtures for high reproducibility. Ball milled B_2O_3 powder was sieved by a Tyler 80 mesh (width of opening: 175 μm) sieve in order to control particle size variation of powder.

Figure 3.3 Retsch PM 100 high – energy planetary ball mill [36].

Boats made of graphite were used to charge samples into the furnace. They had a length of 8 cm and Figure 3.4 shows the photograph of the graphite boat. Before placing graphite boat into the hot zone, flushing of the furnace was carried out for 5 minutes with nitrogen gas. After that, graphite boat was placed into the furnace and experiment time started when temperature of the hot zone regained its stable state at 1500°C. When the experiment was completed, sample was quickly removed from the furnace and cooled down to room temperature under flowing argon gas. Products obtained from experiments were weighed and then cut horizontally into two pieces. One half of the sample was used for scanning electron microscopy (SEM) examinations and the other half was first ground in an agate mortar and pestle, then used for XRD analysis and chemical analysis.

Figure 3.4 Photograph of the graphite boat

Nitrogen gas flow rate was set to 200 cc/min with help of a flowmeter. Different flow rates between 50 cc/min and 200 cc/min were tested in experiments and no difference had been encountered during the results conducted with flow rates higher than 100 cc/min. While samples were placing in the hot zone of the furnace, gas flow rate was increased to 1000 cc/min in order to prevent oxygen entrance to the system from the open end of the furnace.

Effect of $CaCO_3$ and CaO additions were investigated by mixing them with the B_2O_3 – active C mixture. The emphasis was on CaO and experiments including CaO – B_2O_3 mixture (without active C) were conducted to investigate the reaction mechanism. h-BN formed during carbothermic reduction experiments was added into CaO – B_2O_3 mixture in order to investigate the effect of nucleation in calcium – borate melts.

Rigaku Multiflex Powder X-Ray diffractometer with Cu-Kα radiation in the range of 20° to 80° with 0.02° steps at a rate of 2°/min was used to analyze reaction products (Figure 3.5). Software including qualitative analysis program was utilized during operations performed on XRD patterns. After indication of reaction products by qualitative analysis software program raw data obtained, without smoothing of the curve - Kα elimination etc, was reported in the following chapters. Morphology examinations and particle size calculations were conducted with aid of a Joel JSM 6400 (Figure 3.6) scanning electron microscope (SEM).

Each experiment related to one topic was repeated at least for twice and average of the results obtained from chemical analysis was reported. Method developed by Aydoğdu and Sevinç [17], which includes successive leaching and oxidation steps, was used for chemical analysis in order to determine the amounts of constituents in the reaction products. Details of method will be given in Results and Discussion part.

Figure 3.5 Rigaku Multiflex Powder X-Ray diffractometer.

Figure 3.6 JSM – 6400 scanning electron microscope.

CHAPTER 4

RESULTS AND DISCUSSION

This study was a continuation of studies conducted on carbothermic formation of BN in this department. In their study Aydoğdu and Sevinç [17] investigated carbothermic formation of h-BN by subjecting pellets composed of B_2O_3 – active C mixtures to nitrogen gas at elevated temperatures. They concluded that h-BN formation was completed in 2 hours at 1500°C and reaction proceeds through gaseous intermediates. After that Çamurlu et al. [22] conducted experiments in order to investigate the role of boron carbide in the reaction mechanism and they reported that B_4C is not a necessary intermediate during h-BN formation. Finally Çamurlu et al. [7, 23] investigated the catalytic effect of various additives into the initial plain mixture and they found that addition of $CaCO_3$ significantly increases the amount of h-BN formed in the reaction products. Also they reported that a second reaction mechanism could be present simultaneously with carbothermic reduction during $CaCO_3$ addition. In literature, some other studies also suggest the possibility of this second reaction mechanism [24 - 27].

The main aim during this study was to investigate the second reaction mechanism that catalytically affects carbothermic production of hexagonal boron nitride. This second mechanism consists of nitrogen dissolution in calcium borate slags, followed by h-BN precipitation from the formed melt. Experiments with CaO–added B_2O_3 – active C mixtures and carbon free CaO – B_2O_3 mixtures were done in order to investigate this second mechanism. For clear comparison of results with previous studies, experiments including plain mixture and $CaCO_3$ addition were also conducted. Finally effect of hexagonal boron nitride nucleation from calcium borate melts was investigated by h-BN addition into the mixture. In this chapter, results of experiments and their discussion will be given.

4.1 Experiments Conducted with Plain B_2O_3 – active C Mixture

Experiments with plain B_2O_3 – active C mixtures were conducted in order to investigate h-BN formation and to compare the results with the following CaO–added B_2O_3 – C mixture. Pellets produced from plain mixture were subjected to nitrogen gas at 1500°C for 2, 3 and 4 hours.

Quantities of the constituents of the reaction products were determined by the method developed by Aydoğdu and Sevinç [17]. Sample obtained form each experiment was ground in an agate mortar and pestle. After that product was dissolved in 1/1 (v/v) HCl solution. Boric oxide and ash of the carbon were soluble in the solution and after filtration all boric oxide and ash were removed. Solid to liquid ratio in the leaching operations was 1/100 in weight. Amount of unreacted boric oxide was determined by weighing the residue after drying the filtrate. The residue containing unreacted carbon, boron carbide and hexagonal boron nitride was placed in an alumina boat and oxidized at 800°C in a muffle furnace for 15 hours. During this process unreacted carbon was completely burned and removed from the system. Boron carbide was completely converted into boric oxide and h-BN was not affected from this oxidation process. Boric oxide, formed due to oxidation of boron carbide, was removed by second leaching with HCl solution. Pure h-BN was obtained after these leaching-oxidation-leaching processes. Amounts of constituents in the reaction products determined by the method should be regarded as approximate, due to the fact that small errors in successive weighing, leaching and filtering steps may lead to magnified errors in the relative amounts of the constituents in the reaction products.

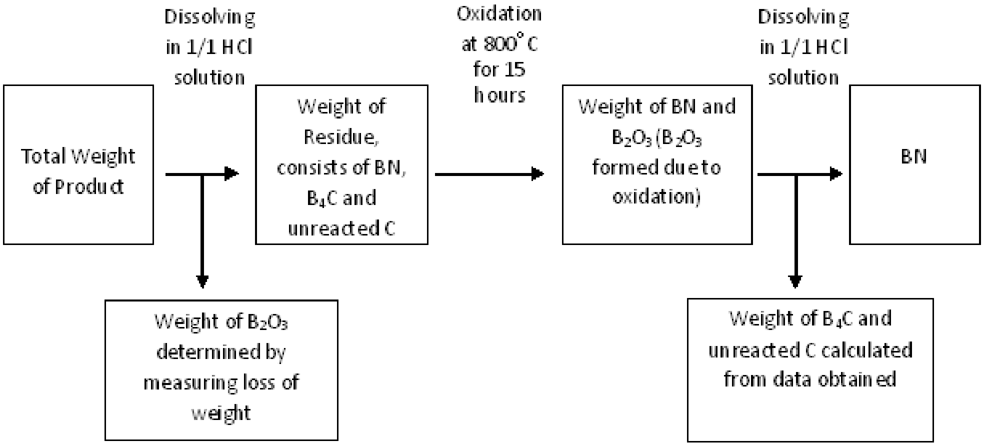

Figure 4.1 Schematic representation of successive leaching-oxidation-leaching process for purification of h-BN [17].

In the study conducted by Aydoğdu and Sevinç [17], it was found that reaction 2.3 is completed in 2 hours and all B_4C and C was used up. Çamurlu et al. [23] completed experiments with plain mixtures in 3 hours and similar experiments conducted in this study was completed in 4 hours. These differences in the results were due to the geometrical changes in furnace design. Çamurlu et al. [23] used a vertical tube furnace on the other hand a horizontal tube furnace was utilized by Aydoğdu and Sevinç [17].

$B_2O_3(l) + 3C(s) + N_2(g) = 2BN(s) + 3CO(g)$ Reaction (2.3)

For the experiment with 2 hours duration B_4C, unreacted C and unreacted boric oxide quantities were determined to be very high as shown on Table 4.1. This indicates that experiments with longer durations were needed to complete reaction 2.3. Unreacted B_2O_3 phase can not be identified on XRD analysis because of its amorphous structure. B_2O_3 is hydrated when left on moisturizing atmosphere and converted into boric acid (H_3BO_3), which can be examined on XRD analysis.

Table 4.1 Comparison of experimental result with plain mixture and different durations.

Duration	**2 Hours**	**3 Hours**	**4 Hours**
h-BN	0.37g	0.48g	0.49g
B_4C	0.10g	0.03g	-
C	0.11g	0.05g	-
B_2O_3	0.40g	0.34g	0.32g

XRD pattern of sample obtained from plain mixture with 2 hours duration is given on Figure 4.2 and XRD patterns before and after purification processes are shown. Hexagonal boron nitride peaks are originating from (002) planes. This XRD pattern shows that h-BN (ICDD card number 34-0421), B_4C (ICDD card number 35-0798) and H_3BO_3 (ICDD card number 23-1034) phases were present in the products of the experiment conducted for 2 hours. XRD patterns of experiments conducted for 2, 3, and 4 hours before purification processes are given on Figure 4.3. Relative heights of peaks shown on the XRD pattern indicate that B_4C amount was highest during the experiment conducted for 2 h and as time passes it was used up. No peaks belonging to B_4C had been observed during the experiment conducted for 4 hours.

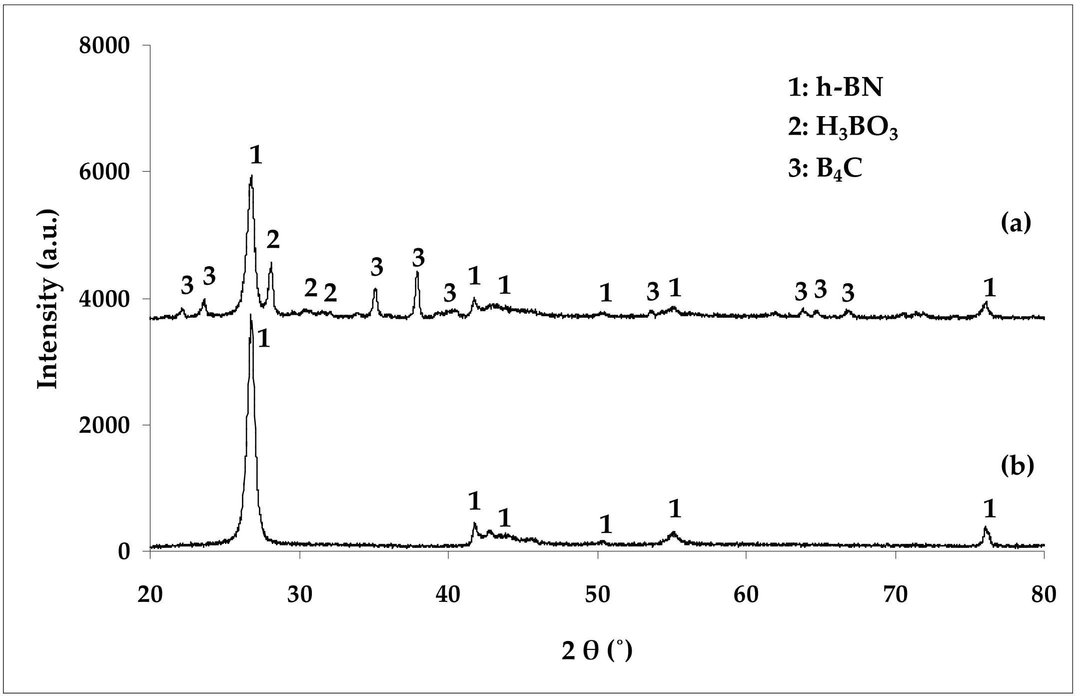

Figure 4.2 XRD pattern of sample with plain mixture (B_2O_3 – active C) and 2 h. a) Sample before leaching operations, b) Pure h-BN formed during the experiment.

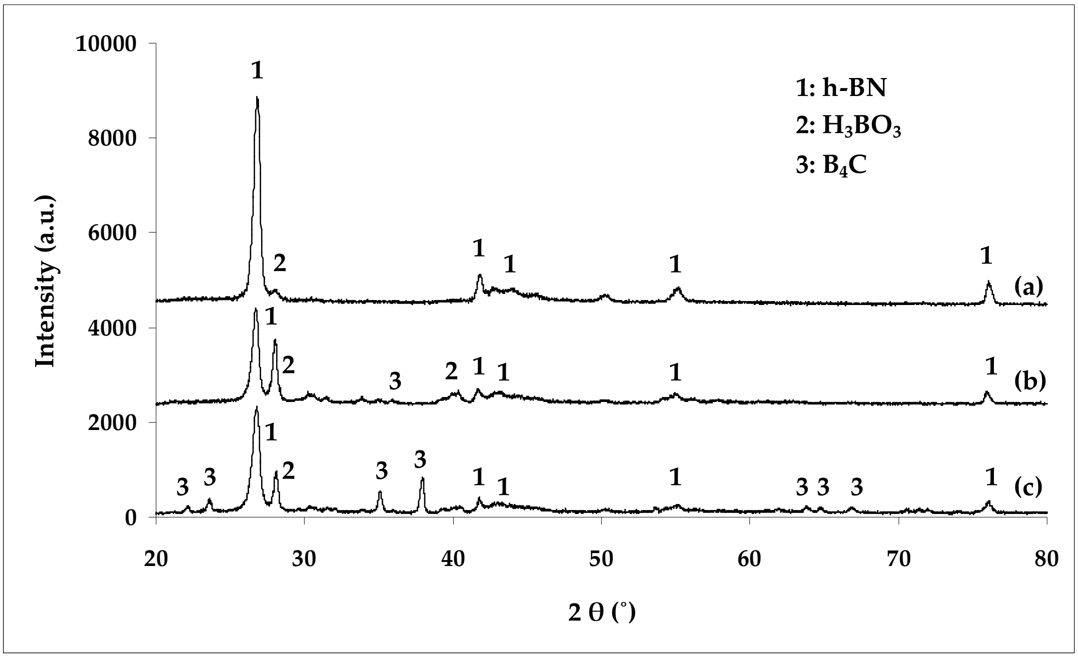

Figure 4.3 XRD patterns of experiments conducted for 2, 3, and 4 hours with plain mixture before leaching processes. a) experiment conducted for 4 h, b) experiment conducted for 3 h, c) experiment conducted for 2 h.

SEM micrographs of the experiment conducted for three hours with plain mixture before and after leaching operations are given in Figures 4.4 and 4.5 respectively. Boron carbide, hexagonal boron nitride and glassy boric oxide phases can be observed on Figure 4.4. Pure h-BN phase on Figure 4.5 shows the structure with very fine particle size. Figure 4.6 is pure h-BN formed during the experiment conducted for 3 hours with plain mixture and fine flake like structure can be observed on the micrograph with higher magnification. Average particle size formed from plain mixture had been calculated to be 0.49 ± 0.11 μm from SEM micrographs.

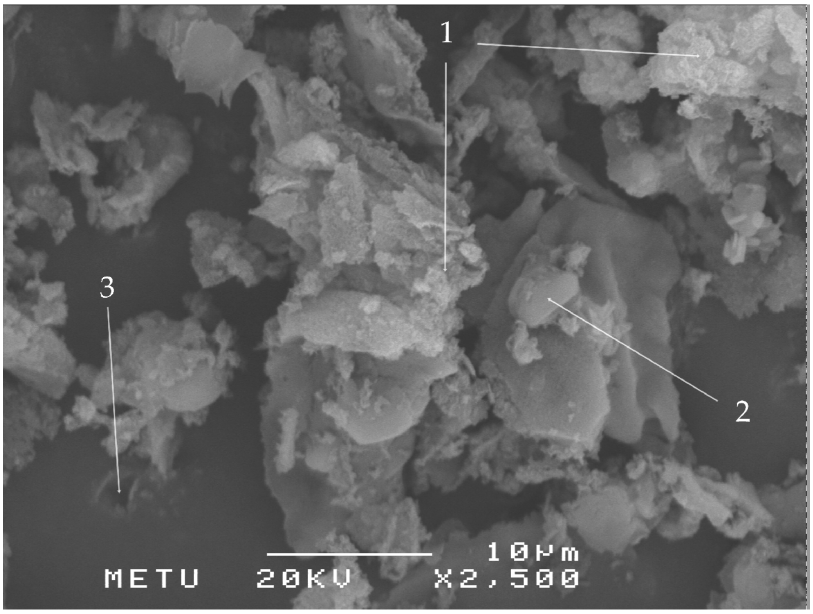

Figure 4.4 SEM micrograph of the experiment conducted for 3 h and plain mixture before leaching. 1) h-BN, 2) glassy B_2O_3, 3) B_4C.

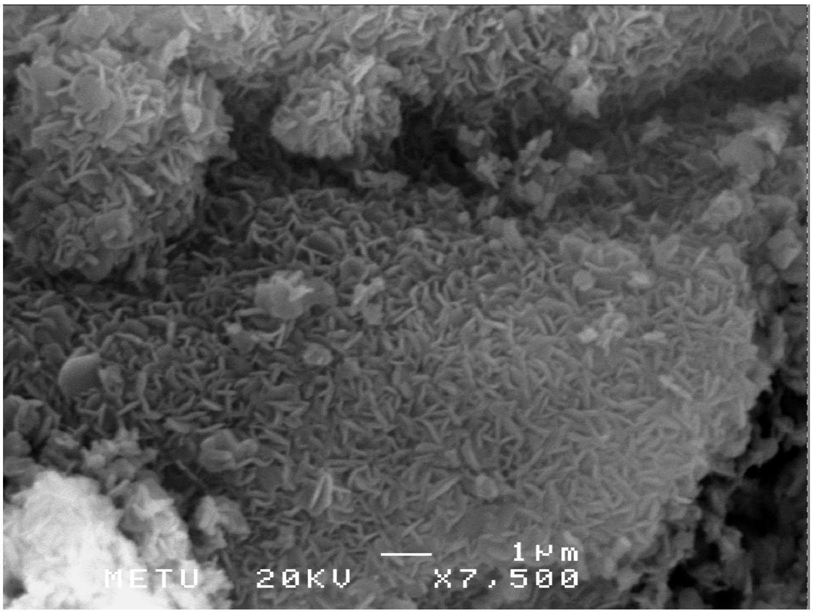

Figure 4.5 SEM micrograph of h-BN produced from plain mixture at 3 hours.

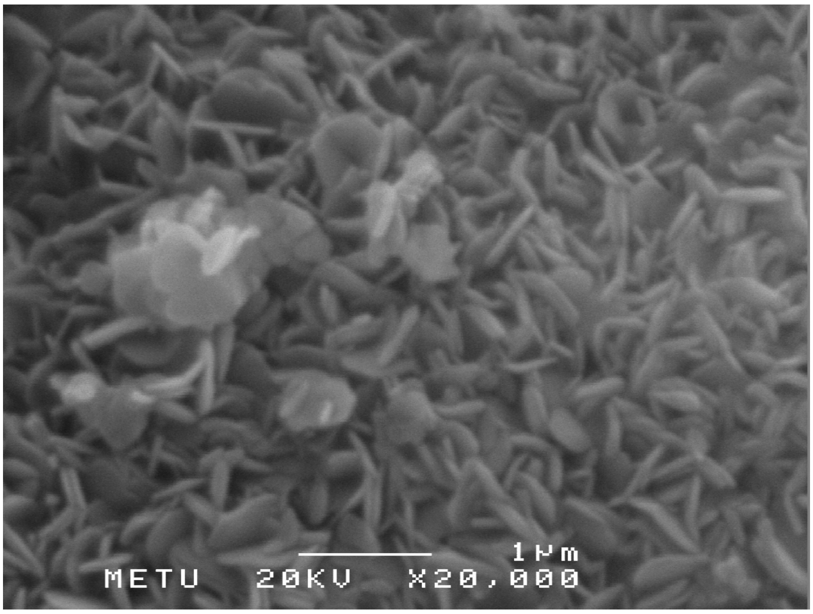

Figure 4.6 SEM micrograph of h-BN produced from plain mixture at 3 hours. (higher magnification)

4.2 Experiments Conducted with $CaCO_3$ - B_2O_3 - Active C and CaO - B_2O_3 - Active C Mixtures

Effect of $CaCO_3$ addition had been studied by Çamurlu et al.[7] and they reported that $CaCO_3$ addition catalytically affects h-BN formation. Not only the amount of h-BN formed in the reaction products was increased, but also the rate of B_4C formation was decreased during experiments. Addition of $CaCO_3$ into the plain mixture results in formation of a calcium borate liquid at 1500°C and reaction mechanism of h-BN formation could be altered. For clear understanding of the catalytic effect of $CaCO_3$ addition, experiments with both $CaCO_3$ and CaO additions were conducted in this study.

In their study Çamurlu et al.[7] investigated the possible reactions that could take place in the experiments conducted with $CaCO_3$–added B_2O_3 – C mixtures. They made necessary thermodynamic calculations and reported that CaO reduction by carbon and formation of elemental Ca or CaC_2 is not possible in the system. This is due to the fact that formation of elemental Ca or CaC_2 necessitates very low pressures and very high temperatures and is not expected under experimental conditions. They found that formation of a calcium borate in accord with the reaction 4.1 took place in the furnace.

$mB_2O_3(l) + nCaO(s) = nCaO.mB_2O_3(l)$ Reaction (4.1)

Çamurlu et al. [7] have found the optimum $CaCO_3$ weight to be 10 wt.% of the 100 mole% excess B_2O_3 – C mixture. Due to this fact it was decided to conduct the experiments with respect to their study. Mixtures containing $CaCO_3$ – B_2O_3 – active C powders were prepared in an agate mortar and pestle and pressed into pellets as in the previous experiments. 10 wt.% $CaCO_3$-added mixture is in the two immiscible liquids region shown on the phase diagram of CaO – B_2O_3 (Figure 4.10). H_3BO_3 and CaB_2O_4 peaks were seen in the XRD pattern (Figure 4.7) of the experiment conducted with 10 wt.% $CaCO_3$ addition with 3 hours, indicating that one of the phases was $B_2O_3(l)$ and the other one was calcium borate in experimental conditions at 1500°C.

Experiments with $CaCO_3$ added mixtures were conducted for 2 and 3 hours. Results of the experiments indicate that amounts of h-BN produced were significantly larger in experiments conducted for 2 and 3 hours with 10 wt.% $CaCO_3$ addition. Results also indicate that B_4C and unreacted C amount in the reaction products were significantly decreased in experiments with shorter durations compared to the plain mixture. Reaction

2.3 was completed in 4 hours with plain mixture as stated in the previous section; on the other hand $CaCO_3$ addition decreased the completion time to 3 hours. Quantitative chemical analysis indicates that 0.43 g h-BN, 0.04 g B_4C, 0.05 g unreacted C and 0.96 g calcium borate formed to exist in the reaction products in experiment conducted for 2 hours. On the other hand, 0.60 g h-BN, 0.61 g calcium borate and no B_4C or unreacted carbon found in the sample obtained from experiment with 3 hours. XRD pattern of the sample with $CaCO_3$ addition before and after leaching operations is given in Figure 4.7.

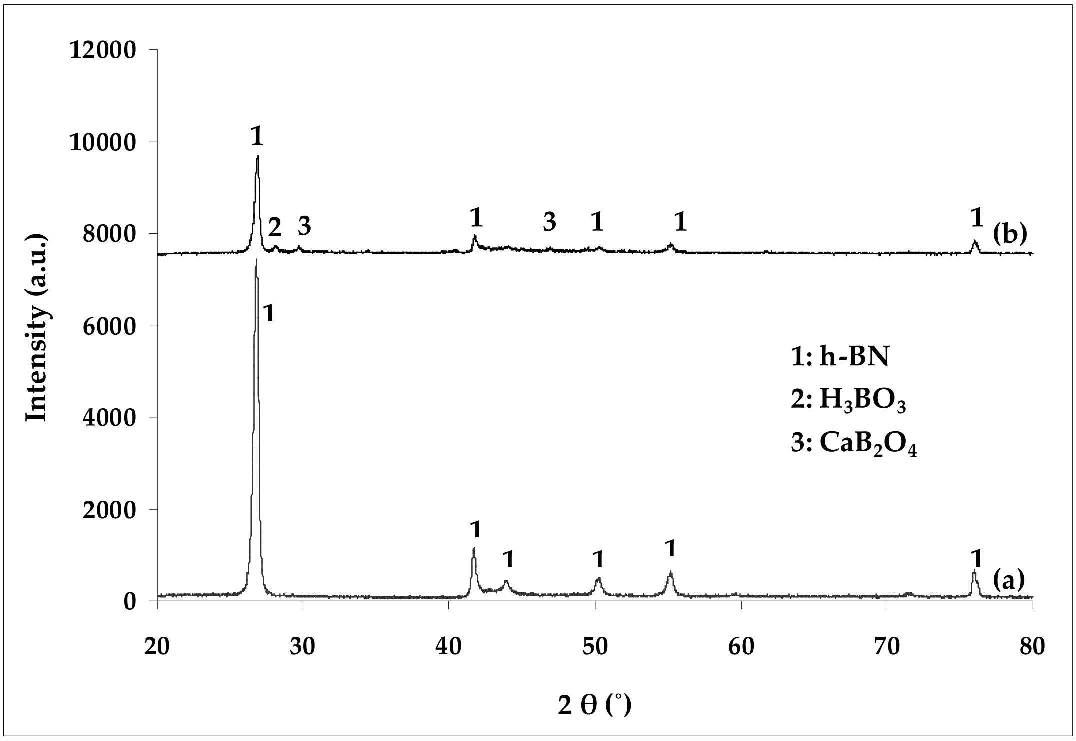

Figure 4.7 XRD pattern of the sample with $CaCO_3$ addition before and after leaching processes. a) After leaching, b) Before leaching, Duration for experiment was 3 hours.

SEM micrograph of $CaCO_3$ added sample shows marked differences from plain mixture. Hexagonal boron nitride synthesized with $CaCO_3$ addition is observed to have larger grains compared to h-BN synthesized with plain mixture and average particle size had been calculated to be 1.19 ± 0.37 μm (Figure 4.9). Furthermore h-BN grains have definite edges and flake like structure had been observed at all portions of sample. Glassy calcium borate phase with h-BN rich parts can be observed on Figure 4.8. Furthermore, a marked improvement in XRD pattern of the samples obtained from experiments with $CaCO_3$ addition compared to plain mixture in 3 hours. Higher XRD peak intensities and increased definability of peaks on difractogram in $CaCO_3$ addition can be taken as an indication of increased crystal thickness - ordering and particle size of sample.

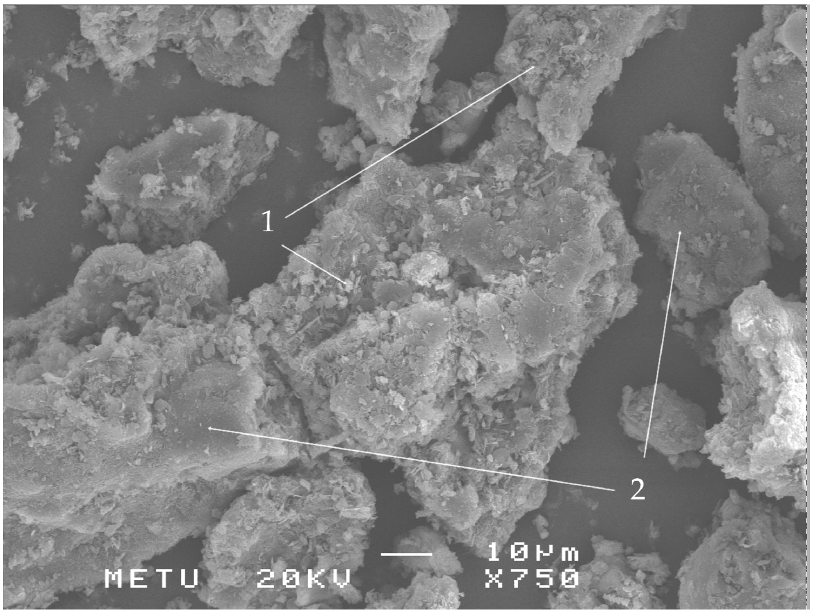

Figure 4.8 SEM micrograph of sample with $CaCO_3$ addition before leaching operations. 1) h-BN, 2) glassy calcium borate phase.

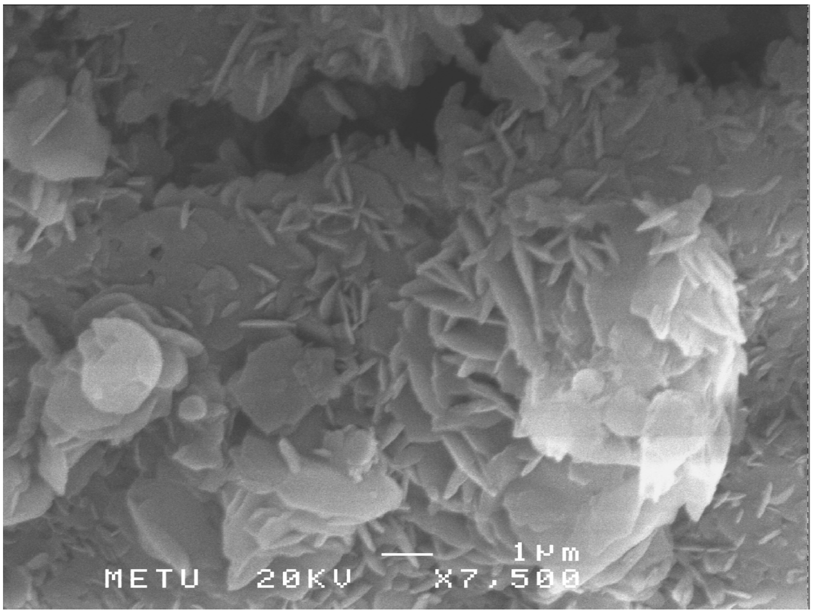

Figure 4.9 SEM micrograph of h-BN formed during $CaCO_3$ addition after purification processes.

In their study Çamurlu et al.[7, 23] have suggested one reason for the effect of $CaCO_3$ in favorably affecting h-BN formation by reaction (2.3) to be increased porosity of the pellet, probably resulting from calcination of the added $CaCO_3$, which eases the access of N_2(g) into the pellet and thereby increases the rate of h-BN formation. In order to eliminate porosity factor and investigate the mechanism of nitrogen dissolution followed by h-BN precipitation from oxide melts, experiments with CaO addition were conducted.

During the experiments conducted with $CaCO_3$ addition it was observed that $CaCO_3$ was quickly calcined at 1500°C and CaO formed. This CaO formed was expected to form a calcium borate liquid. Molecular weight of $CaCO_3$ is 100 g/mole and that of CaO is 56 g/mole. Amount of CaO in the mixture after calcination will be 5.6 wt.% of the initial mixture. Due to this fact it was decided to add 5.6 wt.% CaO, equivalent to 10 wt.% $CaCO_3$ addition, for experiments with CaO addition.

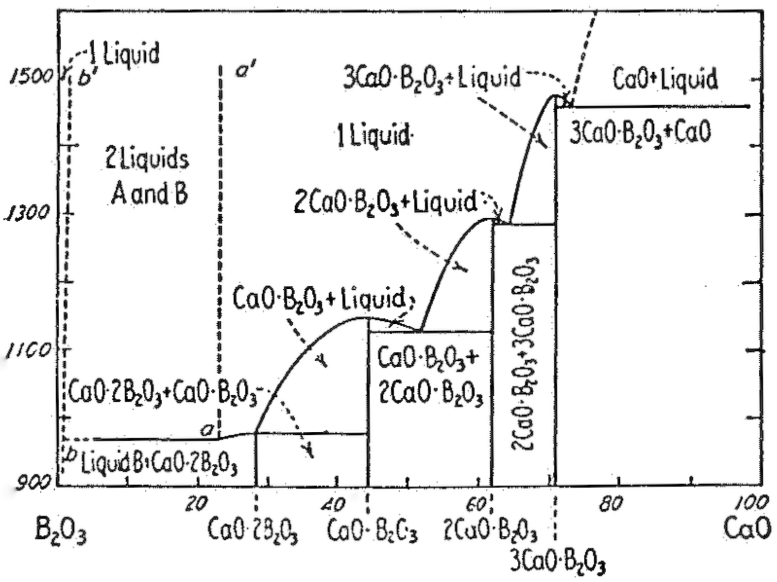

Figure 4.10 B_2O_3 – CaO phase diagram [30].

Calcium oxide used in these experiments was obtained from calcination of $CaCO_3$ at 1000°C for 20 hours. Completeness of calcination was confirmed by weight loss measurements. Similar to previous experiments, CaO–added B_2O_3 – active C mixture was mixed in an agate mortar and pestle and pressed at 58.9 MPa (6 kg/mm^2) into pellets. Pellets were charged into the furnace at 1500°C under nitrogen atmosphere. For clear comparison of results with $CaCO_3$ addition, experiments with 2 and 3 hours were conducted. After purification processes, similar to $CaCO_3$ addition, it was found that CaO addition has a catalytic effect on carbothermic formation of h-BN.

Constituents of reaction products conducted with CaO addition were found to be 0.55 g h-BN, 0.64 g CaO-B_2O_3 and no B_4C or unreacted C in 3 hours. While those of the experiment conducted for 2 hours were 0.41 g h-BN, 0.05 g B_4C, 0.05 g unreacted C and 1.02 g CaO-B_2O_3.

During experiments conducted with CaO and $CaCO_3$ additions, it was found that h-BN formation reaction was completed in 3 hours. Hexagonal boron nitride amount was calculated to be 0.48 g for experiments conducted with plain B_2O_3 – C mixture for 3 h. Calcium carbonate addition increases amount of h-BN in the reaction products to 0.60 g and calcium oxide addition increases it to 0.55 g. Comparison of experimental results with 3 hours as reference duration is given on Table 4.2 where in addition to h-BN, B_4C, unreacted carbon and unreacted B_2O_3 quantities in samples are shown. Overall composition of CaO and B_2O_3 could not be determined in the final products of the experiments conducted with CaO or $CaCO_3$ additions due to the fact that assumptions like only B_2O_3 evaporates during experiments or no CaO is lost from the system could be misleading. Also in their study Wakasugi et al.[31] proposed that calcium borate melts probably evaporate in a molecular forms of CaB_2O_4 or CaB_4O_7, which makes calculation of exact quantities of B_2O_3 and CaO in the reaction products very hard.

$CaCO_3$ addition was found to increase the efficiency of reaction more than CaO addition. This difference may be present due to the fact that CO_2 gas, formed during calcination of $CaCO_3$, increases the porosity of the sample and this increase in porosity increases the efficiency of process by enabling N_2(g) diffusion into system easier. Increased porosity of the pellet favorably affects h-BN formation by increasing the efficiency of carbothermic formation mechanism described by Aydoğdu and Sevinç [17]. XRD pattern of sample with CaO addition is given in Figure 4.11.

Table 4.2 Comparison of results with plain mixture, $CaCO_3$ addition and CaO addition. All experiments were conducted for 3 hours.

	Plain Mixture	**%10 $CaCO_3$ addition**	**%5.6 CaO addition**
h-BN	0.48 g	0.60 g	0.55 g
B_4C	0.03 g	-	-
C	0.05 g	-	-
B_2O_3	0.34g	B_2O_3 – CaO (0.61 g)	B_2O_3 – CaO(0.64 g)

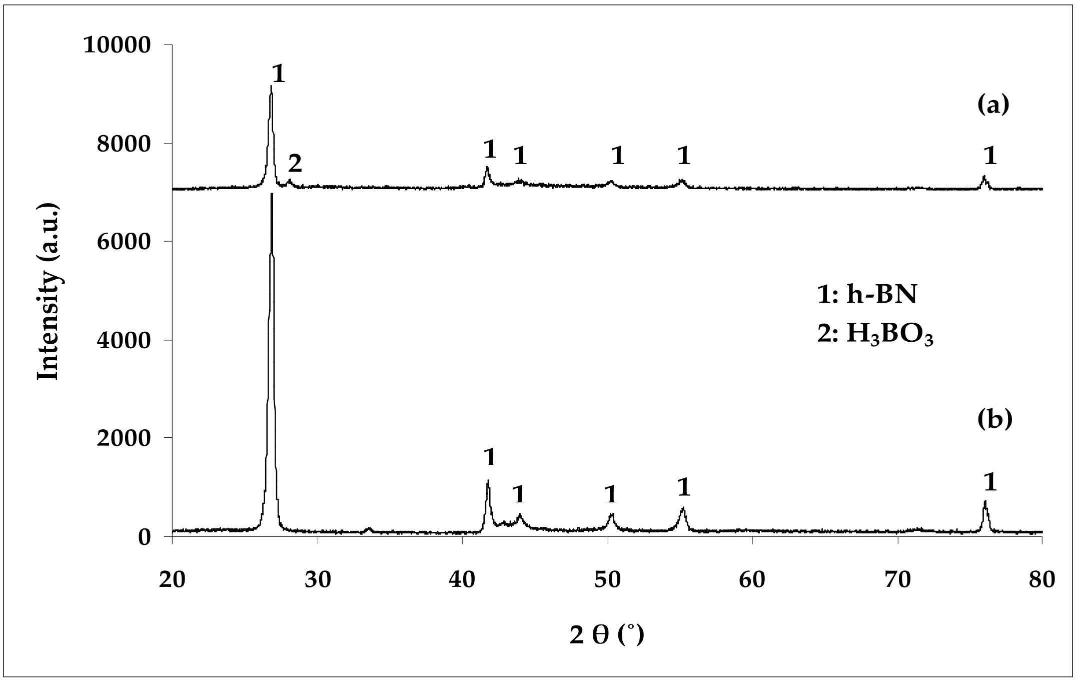

Figure 4.11 XRD pattern of sample with CaO addition (3 h) before and after leaching. a) sample before leaching, b) sample after leaching.

Similar to $CaCO_3$ addition, CaO addition has a marked effect on particle shape and size of the formed h-BN. Glassy calcium borate phase and h-BN rich portions before purification processes can be observed on Figure 4.12. Flake like structure and growth of h-BN grains by CaO addition can be observed on Figure 4.13. Figure 4.14 shows the flake like structure of the h-BN formed during CaO addition and average particle size was calculated to be 1.30 ± 0.45 μm from the micrograph. Comparison between microstructures of h-BN formed by CaO addition (Figure 4.14) and by the plain mixture (Figure 4.6) clearly indicates that CaO addition has a positive effect on particle growth. BN particles synthesized from CaO–added mixture were seen to be coarser than $CaCO_3$–added mixture, on the other hand amount of h-BN formed was higher in the $CaCO_3$-added experiment. This difference seems to arise due to the fact that rate of formation of BN by the overall reaction (2.3) appears to be related to access of N_2 into the reaction aggregate. Rate of formation of BN by the overall reaction (2.3) is expected to be higher in $CaCO_3$-added mixtures, in view of their porosity, than that in CaO-added mixtures which should result in more BN formation by the overall reaction (2.3) in a given time before carbon is completely used in $CaCO_3$-added B_2O_3 – C mixtures compared to that in CaO-added B_2O_3 – C mixtures.

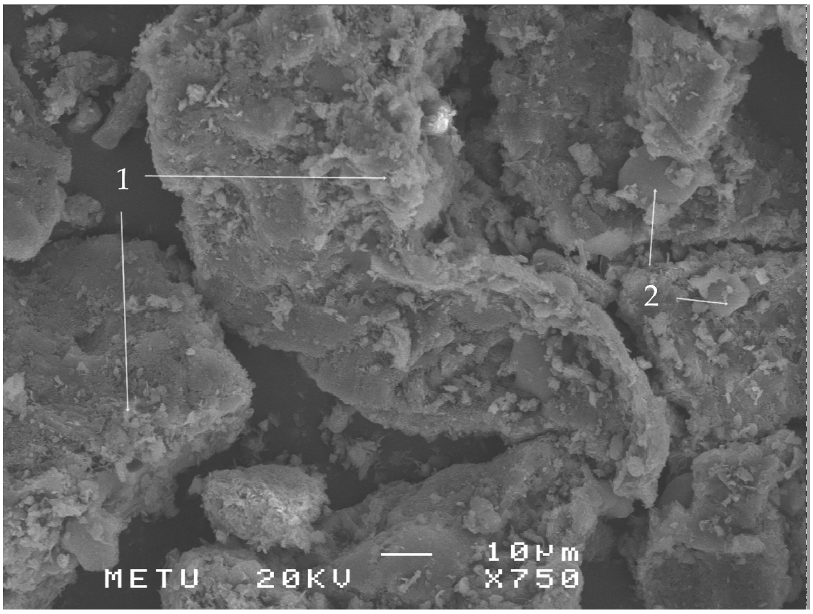

Figure 4.12 SEM micrograph of sample with CaO addition before leaching operations. 1) h-BN, 2) glassy calcium borate phase.

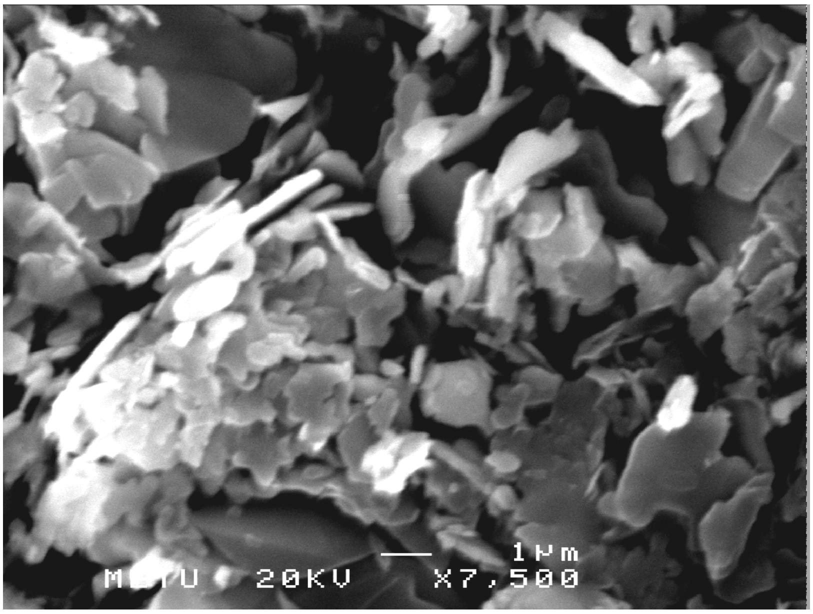

Figure 4.13 SEM micrograph of h-BN formed during CaO addition after purification processes.

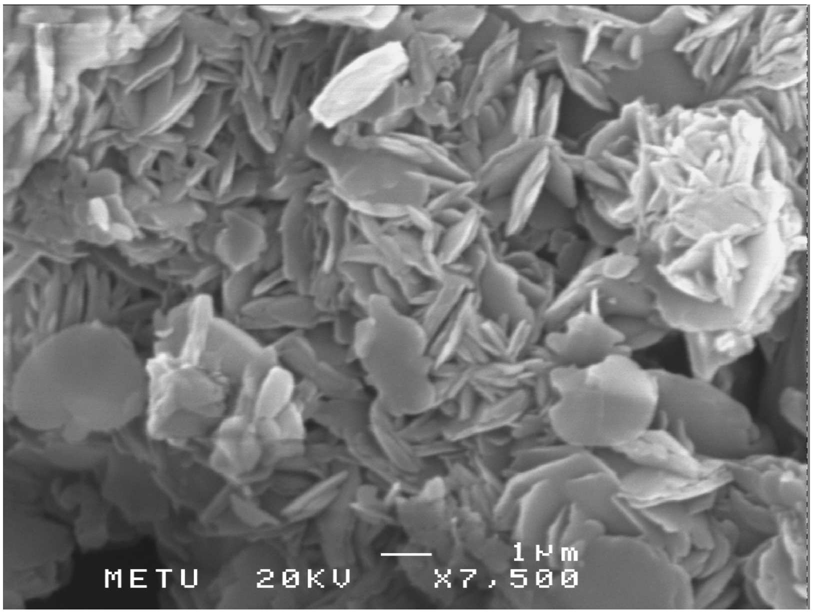

Figure 4.14 SEM micrograph of h-BN formed during CaO addition after purification processes. (Micrograph showing flake like structure better)

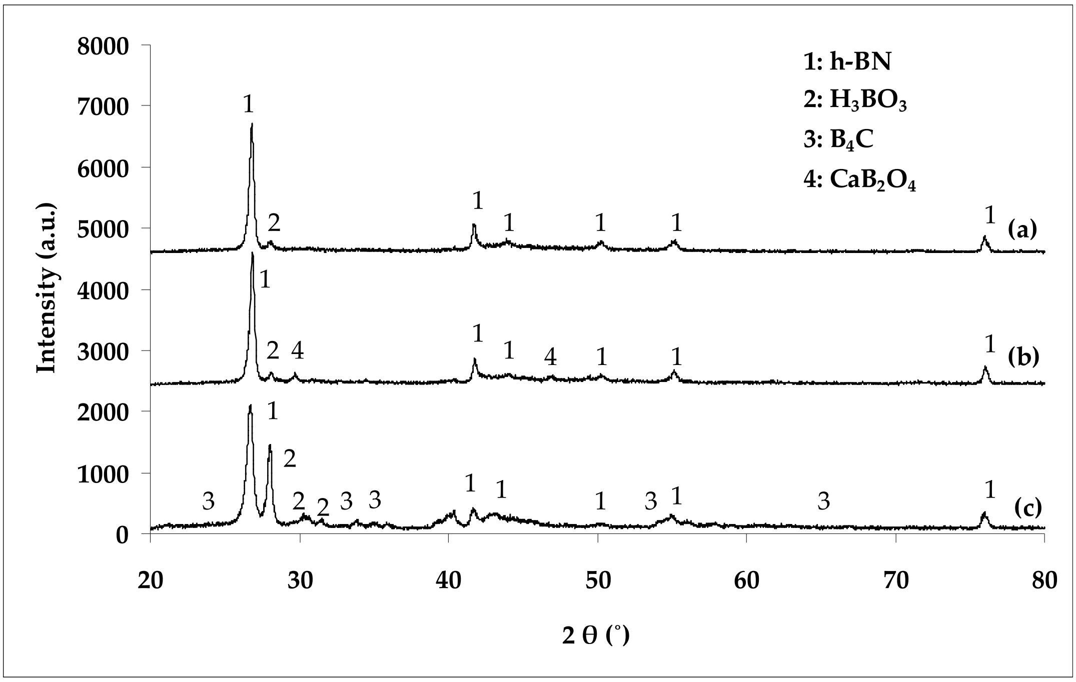

Figure 4.15 Comparison of XRD patterns before purification processes experimental duration 3 h. a) CaO addition, b) $CaCO_3$ addition, c) plain mixture.

4.3 Experiments Conducted with CaO – B_2O_3 Mixture (no active C)

In their study Çamurlu et al.[7] reported that two main factors increase the amount of h-BN formed during $CaCO_3$ addition. First one is the increase in porosity due to CO_2 evolution and the other one may be the presence of a second reaction mechanism. Previous experiments showed that both $CaCO_3$ and CaO additions catalytically affected h-BN formation. Presence of a second reaction mechanism was investigated during this study and experiments were conducted by keeping CaO – B_2O_3 mixture containing no active C under N_2 atmosphere at 1500°C.

It was expected that in accord with the phase diagram of CaO – B_2O_3 shown in Figure 4.10, prepared mixture would melt and form a calcium borate liquid at 1500°C. In accord with the suggestion of Çamurlu et al [7] nitrogen is expected to dissolve in the calcium borate melt and h-BN precipitation is expected to take place when the solubility limit of BN is exceeded. Most important aspect of this mechanism is that carbon is not used for h-BN formation.

This second reaction mechanism for h-BN formation can be summarized as follows;

CaO originating from addition or calcination of $CaCO_3$ forms a calcium borate liquid in which N_2 (g) dissolves as N^{3-} or as N^{-} depending on the basicity of the calcium borate phase. Then, h-BN forms and crystallizes from the formed melt [7].

Nitrogen is soluble in oxide melts (slags) and nitrogen solubility depends on slag basicity, oxygen pressure, nitrogen pressure and temperature of the system. Proportions of acidic and basic oxides in the slag determine basicity of the melt. During dissolution of an acidic oxide O^{2-} ion is consumed in the melt, on the other hand during dissolution of a basic oxide O^{2-} ion is provided to the system. Reaction (4.2) shows dissolution of an acidic oxide and reaction (4.3) shows dissolution of a basic oxide. When O^{2-} provided by basic oxides exceeds O^{2-} needed for acidic oxides then slag becomes basic and there will remain free O^{2-} in the system. On the other hand when the slag is acidic, oxides like B_2O_3 forms more complicated anions like $(B_2O_5)^{4-}$ or $(B_3O_7)^{5-}$ by polymerization reactions like reactions (4.4) and (4.5) [32];

$$B_2O_3 + 3O^{2-} = 2(BO_3)^{3-} \qquad \text{Reaction (4.2)}$$

$$CaO = Ca^{+2} + O^{2-} \qquad \text{Reaction (4.3)}$$

$$2(BO_3)^{3-} = (B_2O_5)^{4-} + O^{2-} \qquad \text{Reaction (4.4)}$$

$$(BO_3)^{3-} + (B_2O_5)^{4-} = (B_3O_7)^{5-} + O^{2-} \qquad \text{Reaction (4.5)}$$

Nitrogen dissolution in basic slags is governed by reaction (4.6). Nitrogen dissolution in acidic slags is more complicated as nitrogen has been observed to combine to the acidic oxide ions. Min and Fruehan [33] has suggested nitrogen dissolution in acidic slags to be governed by the reaction (4.7). O^- and N^- shown on the reactions are non-bridging oxygen and non-bridging nitrogen, respectively.

$1/2N_2(g) + 3/2O^{2-} = N^{3-} + 3/4O_2(g)$ Reaction (4.6)

$1/2N_2(g) + 2O^{-} = N^{-} + 1/2O^{2-} + 3/4O_2(g)$ Reaction (4.7)

Equilibrium constant of reaction (4.6) is:

$$K_{4.6} = \frac{a_{N^{3-}} \times P_{O_2}^{3/4}}{P_{N_2}^{1/2} \times a_{O^{2-}}^{3/2}} = \frac{\gamma_{N^{3-}} \times (\%N) \times P_{O_2}^{3/4}}{P_{N_2}^{1/2} \times a_{O^{2-}}^{3/2}} \qquad \text{Equation (4.1)}$$

Rearranging equation (4.1) gives equation (4.2) with the right hand side, containing measurable quantities, called the nitride capacity $C_{N^{3-}}$.

$$C_{N^{3-}} = K_{4.6} \times \frac{a_{O^{2-}}^{3/2}}{\gamma_{N^{3-}}} = (\%N) \times \frac{P_{O_2}^{3/4}}{P_{N_2}^{1/2}} \qquad \text{Equation (4.2)}$$

Equilibrium constant of reaction (4.7) is:

$$K_{4.7} = \frac{a_{N^{-}} \times a_{O^{2-}}^{1/2} \times P_{O_2}^{3/4}}{P_{N_2}^{1/2} \times a_{O^{-}}^{2}} = \frac{\gamma_{N^{-}} \times (\%N) \times a_{O^{2-}}^{1/2} \times P_{O_2}^{3/4}}{P_{N_2}^{1/2} \times a_{O^{-}}^{2}} \qquad \text{Equation (4.3)}$$

And rearranging equation (4.3) yields:

$$C_{N^{-}} = K_{4.7} \times \frac{a_{O^{-}}^{2}}{\gamma_{N^{-}} \times a_{O^{2-}}^{1/2}} = (\%N) \times \frac{P_{O_2}^{3/4}}{P_{N_2}^{1/2}} \qquad \text{Equation (4.4)}$$

The right hand side of equation (4.4) also contains measurable quantities and is called as the incorporated nitride capacity. The right hand side of equations (4.4) and (4.2) is the definitions of $C_{N^{3-}}$ and $C_{N^{-}}$ are identical and is called the nitride capacity. Both definitions of nitride capacity are seen to depend on the composition of the oxide melt at a given temperature. If $a_{O^{2-}}$ is considered to be a measure of the basicity of the slag, with the increase in slag basicity, $C_{N^{3-}}$ is seen to increase while $C_{N^{-}}$ is seen to decrease. So nitride capacity of any slag is defined as:

$$C_N = (\%N) \times \frac{P_{O_2}^{3/4}}{P_{N_2}^{1/2}} \qquad \text{Equation (4.5)}$$

Nitride capacity is expected to decrease with increase in slag basicity in acidic slags and to increase with the increase in slag basicity in basic slags. Nitride capacity of a given slag with definite composition should be constant at a given temperature.

Hexagonal boron nitride is soluble in oxide melts and its solubility depends on composition [34]. For a given slag composition h-BN solubility should become a constant at a given temperature. Nitrogen dissolved in boric oxide containing slags may result in formation of h-BN when the solubility limit of the h-BN in the melt exceeded.

Possible reactions for formation of h-BN from nitrogen and B_2O_3 containing oxide melts should be given as the reactions (2.5) and (2.6), again depending on the basicity of the melt. Main aim of this study was to investigate the reaction mechanism described above and shown by reactions (2.5) and (2.6).

$$(BO_3^{3-}) + (N^{3-}) = BN(s) + 3O^{2-} \qquad \text{Reaction (2.5)}$$

$(B_2O_4N)^{5-} = BN(s) + (BO_3)^{3-} + O^{2-}$ Reaction (2.6)

Reactions (2.5) and (2.6) indicate that h-BN may form by the reaction mechanism described above, without active carbon addition into the mixture. In order to investigate the mechanism, a second graphite boat containing active C was placed in experimental setup to make sure that oxygen pressure in the system was low. Active carbon in second graphite boat was not in contact with the sample and it was close to the gas inlet part of the furnace. By this way it could be assumed that most of the oxygen in nitrogen gas was removed from the system as CO(g) by reaction with active carbon. Schematic drawing of graphite boat locations at hot zone of furnace is given in Figure 4.16.

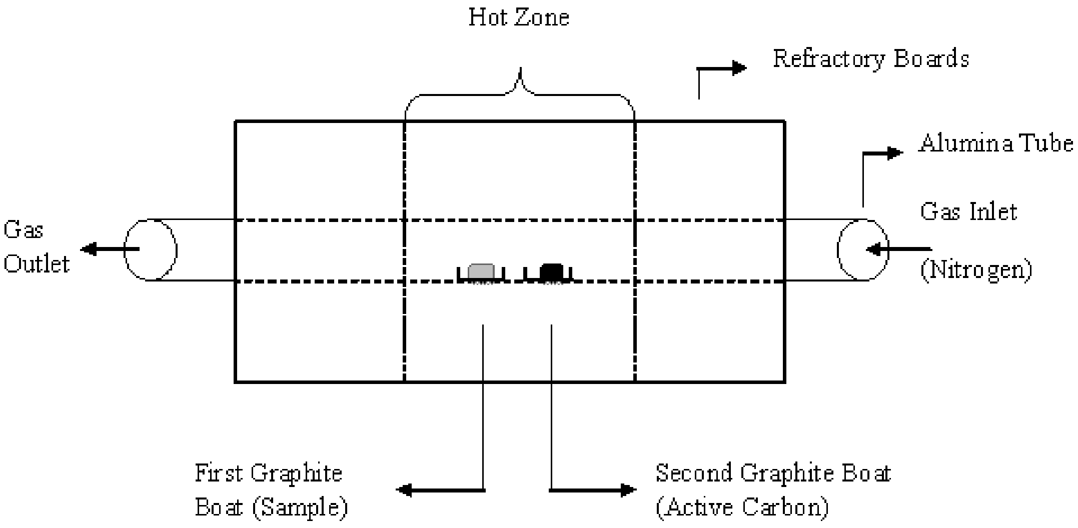

Figure 4.16 Schematic drawing that shows locations of graphite boats during plain calcium borate melt experiments.

Similar to previous experiments C–free 5.6 wt.% CaO – B_2O_3 mixture was pressed and pellets charged into the furnace at 1500°C under nitrogen atmosphere. Total weight of charge was increased from 2.5 g to 4 g because of the fact that in absence of active carbon volume of the pellet becomes very small for easy handling. Moreover due to evaporation loss, product obtained became very small to divide it into pieces for chemical analysis, SEM examinations and XRD analysis.

Sample formed from the experiment containing 5.6 wt.% CaO was a two layered immiscible glassy phase and final weight of the product was decreased to 3.10 g. The two layers should therefore be essentially pure B_2O_3 and a calcium borate melt of composition "a" shown on the phase diagram (Figure 4.10). Both of the glassy phases have no peaks in XRD analysis. The upper layer could be completely taken into solution after grinding by water leaching. This layer was concluded to be B_2O_3. The lower layer did not dissolve in water but could completely be taken into solution with 1:1 HCl leaching and was concluded to be calcium borate. No h-BN has been found to have formed as no solid phase remained after leaching.

5.6 wt.% CaO – B_2O_3 mixture is in the two immiscible liquids gap region shown on the phase diagram. One of the phases is calcium borate mixture and the other one is basically B_2O_3. B_2O_3 phase is approximately 3 times more in amount compared to the calcium borate phase. Due to density differences B_2O_3 phase was placed over calcium borate phase and prevented it from contact with nitrogen gas in furnace. This experiment did not bring enough information about calcium rich melt due to absence of contact of this phase with N_2(g) in furnace.

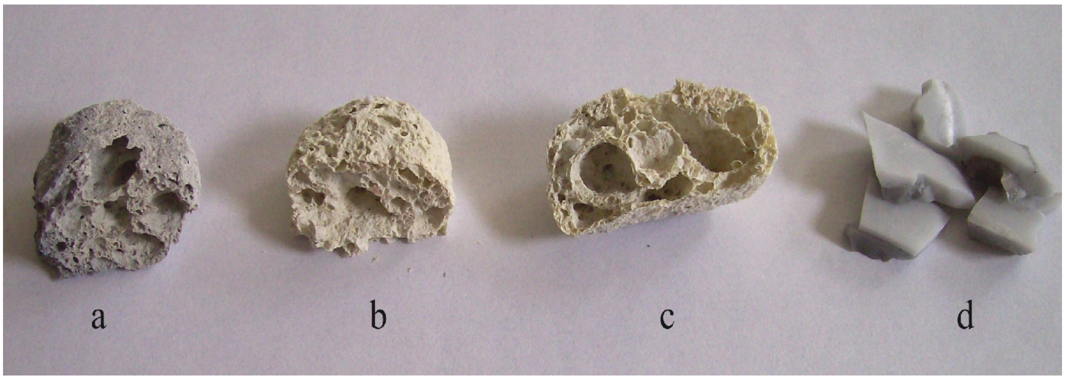

Figure 4.17 Products obtained from experiments as they come out of furnace. a) Plain B_2O_3 – active C mixture, b) 5.6 wt.% CaO addition, c) 10 wt.% $CaCO_3$ addition, d) 5.6 wt.% CaO – B_2O_3 mixture (without active C).

During the experiments conducted with $CaCO_3$ and CaO addition, as time passes concentration of CaO increases in the melt due to consumption of B_2O_3 in the reactants. This results with a shift of composition on the phase diagram towards the CaO rich part as reaction proceeds. Reaction mechanism involving nitrogen solution in calcium borate melts may be operative in CaO rich solutions. In order to investigate this fact experiments with carbon free 25 wt.% CaO – B_2O_3 mixture, single phase at 1500°C, were conducted.

In order to bring the composition into one phase liquid region shown on the phase diagram, CaO wt.% added in the mixture was increased from 5.6 to 25. Using the same experimental conditions, results indicate that homogeneous calcium-borate melt achieved in the furnace and product of the experiment comes out to be a single glassy phase with 3.45 g. CaO rich lower layer of 5.6 wt.% CaO mixture and 25 wt.% CaO mixture were found to be very similar in composition, in accord with the phase diagram by 1:1 HCl leaching and XRD patterns. XRD patterns of glassy products obtained from 5.6 and 25 wt.% CaO – B_2O_3 glasses are shown in Figure 4.18. Similar to experiments conducted with 5.6 wt.% CaO addition, h-BN formation was not observed.

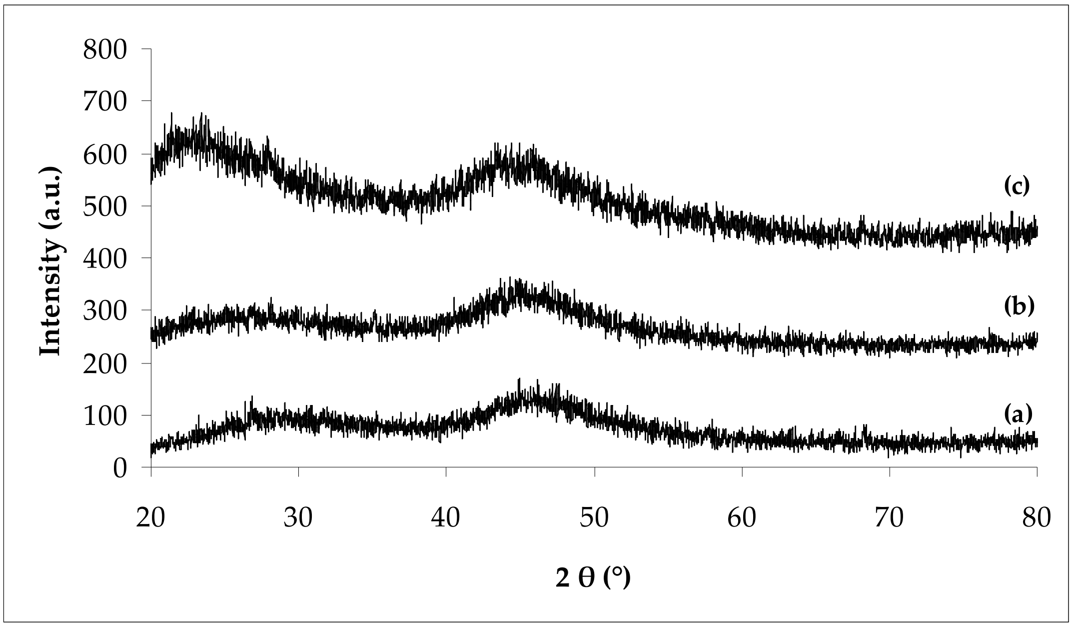

Figure 4.18 XRD patterns of glassy phases formed during CaO – B_2O_3 melts. a) 25 wt.% CaO - B_2O_3 mixture single glassy phase, b) 5.6 wt.% CaO – B_2O_3 mixture lower CaO rich part, c) 5.6 wt.% CaO – B_2O_3 mixture upper, essentially B_2O_3 part.

CaO and $CaCO_3$ addition into B_2O_3 – active carbon mixture increases h-BN amount in the reaction products, on the other hand when active carbon is not present in the mixture h-BN formation was not observed. There could be two reasons for explaining this situation. First one is that reaction mechanism described above may not be correct or secondly nucleation of h-BN from calcium borate liquids may not be possible under experimental conditions. In order to investigate effect of nucleation, experiments including h-BN addition into 25 wt.% CaO – B_2O_3 mixture were conducted.

Hexagonal boron nitride formation was not observed during both carbon free 25 wt.% CaO – B_2O_3 and 5.6 wt.% CaO – B_2O_3 mixtures and it was considered that nucleation might be a barrier to BN formation. Before h-BN addition into the mixture as a nucleation site, slow cooling of the 25 wt.% CaO – B_2O_3 mixture under flowing nitrogen had been investigated. Sample was cooled down at a rate of 5°C/min with help of a digital controller after being kept at 1500°C for 3 hours in the furnace. It was observed that slow cooling of the melt did not initiate nucleation of the h-BN and similar to the experiments conducted with carbon free mixtures of CaO – B_2O_3, product came out to be a single glassy phase. XRD pattern of the product is given on Figure 4.20 indicating that no h-BN formation took place and CaB_2O_4 phase was formed according to the phase diagram during slow cooling. SEM micrograph of the glassy sample with slow cooling is given on Figure 4.19. Final product weight was decreased to 2.19 g from 4.0 g which indicates a huge weight loss during experiment due to extended exposure time to high temperatures.

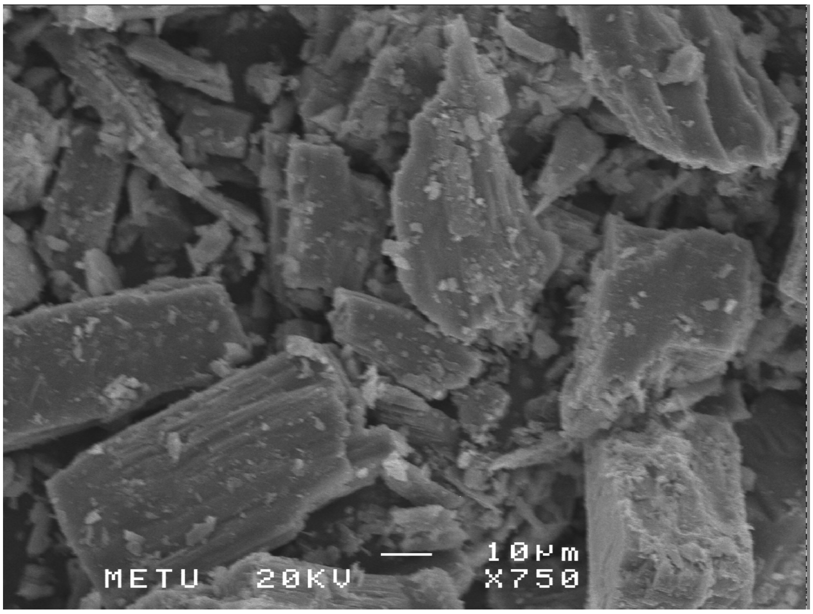

Figure 4.19 SEM micrograph of sample obtained from experiment with slow cooling after grinding glassy product into powder form.

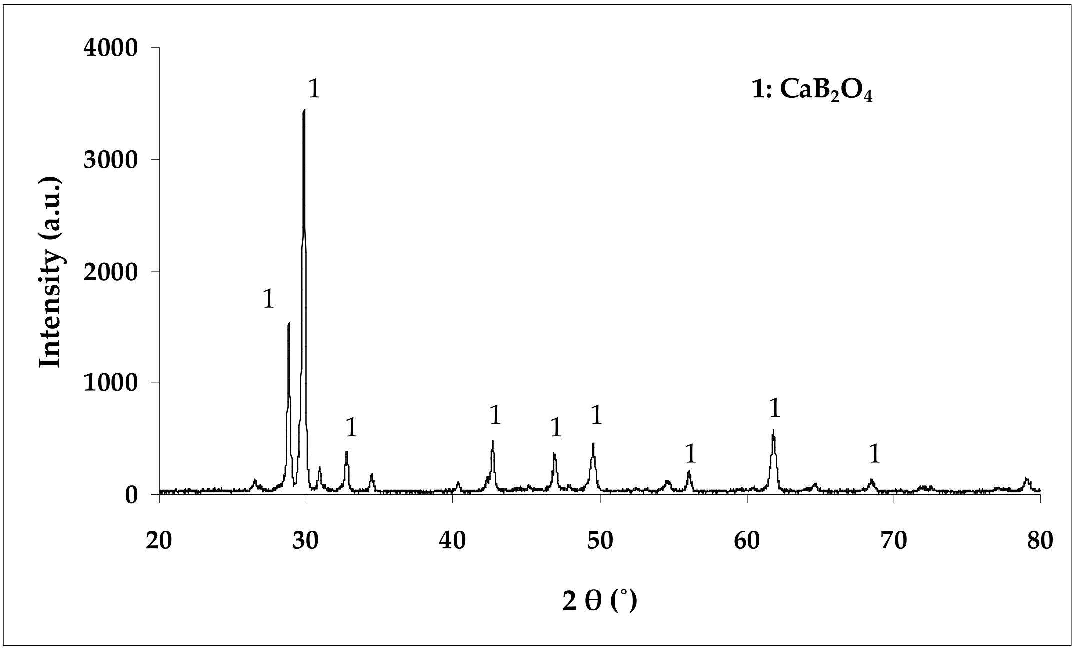

Figure 4.20 XRD Pattern of the sample obtained from experiment conducted with slow cooling of calcium borate melt.

4.4 Experiments Conducted with h-BN Addition to Investigate Nucleation

After conducting experiments with slow cooling, it was considered that nucleation barrier could be avoided by presence of h-BN in the B_2O_3 – CaO system and experiments were done with pellets prepared from h-BN-added 25 wt.% CaO – B_2O_3 mixture (0.25 g h-BN + 1 g CaO + 3 g B_2O_3). Two experiments were conducted under same conditions with previous ones and after leaching operations results indicate that amount of h-BN was increased. Hexagonal boron nitride amount in the final product was increased from 0.25 g to 0.30 g during experiment conducted under nitrogen atmosphere and when experiment was repeated it was increased to 0.31 g indicating a 0.05 – 0.06 g increase in h-BN amount. BN added in previous nucleation experiments was originating from the experiments conducted with 10 wt.% $CaCO_3$ addition. Experiment with h-BN addition, BN of which was originating from plain mixture, into calcium borate was conducted and similarly h-BN amount in the final product was increased from 0.25 g to 0.32 g. It could be concluded there is BN formation in calcium borate melts subjected to N_2 gas without use of carbon by dissolution of nitrogen in the calcium borate melt followed by BN formation by ionic reactions like those suggested above. The results also indicate that there is nucleation barrier to BN formation by this mechanism and that presence of BN in the calcium borate is necessary for the mechanism to be operative. This mechanism should be operative in formation of BN by carbothermic method in which B_2O_3 – C – CaO or B_2O_3 – C – $CaCO_3$ mixtures are subjected to N_2 gas as there is some BN formation in this method by overall reaction 2.3 which could act as nucleation site.

Morphology of the products was totally changed into a porous structure and weight loss due to evaporation was significantly decreased, showing a final product weight of 3.82 g for the experiment conducted with h-BN addition. h-BN was originating from $CaCO_3$-added experiments and at the bottom of the sample small islands of glassy phase were observed with the same structure as the sample obtained from the experiment with C free 25 wt.% CaO – B_2O_3 mixture. Figure 4.21 shows samples as they come out of the furnace.

Figure 4.21 Samples as they come out of the furnace. a) C free 25 wt.% CaO – B_2O_3 mixture, b) C free 25 wt.% CaO – B_2O_3 and h-BN addition for nucleation.

In order to check the effect of nucleation, same mixture (0.25 g h-BN + 1 g CaO + 3 g B_2O_3) was exposed to argon gas at 1500°C for 3 h then quickly removed out from the furnace as usual. Results of the experiment showed that weight loss due to evaporation was highest in this experiment and after leaching processes it was proven that amount of h-BN added for nucleation was not increased, showing a final value of 0.24 g. Also morphology of the product consists of glassy phase at the bottom and on top of it h-BN phase, added to investigate nucleation, was present. One important thing about the experiment under argon atmosphere was that microstructure and particle size of h-BN added was improved as shown on Figure 4.26 which indicates the importance of calcium borate melt in growth step of h-BN formation.

Morphology of the two products with the same compositions, one of the experiments conducted under N_2 and the other under Ar atmosphere, show marked differences. Nitrogen dissolution and h-BN growth results in formation of branches and foam like structure in the sample exposed to nitrogen gas. Figure 4.22 shows the cross section of samples as they come out of the furnace.

Figure 4.22 Products obtained from experiments as they come out of the furnace. a) 0.25 g h-BN + 1 g CaO + 3 g B_2O_3 mixture, experiment conducted under Nitrogen gas, b) 0.25 g h-BN + 1 g CaO + 3 g B_2O_3 mixture, experiment conducted under Argon gas.

Figures 4.23, 4.24, 4.25 and 4.26 are SEM micrographs of h-BN formed during nucleation experiments. Flake like structure of the h-BN shows significant differences from other experimental results and average particle size was determined to be 2.37 ± 0.61 µm for the experiment conducted with h-BN (originating from $CaCO_3$-added experiment) added 25 wt.% CaO – B_2O_3 mixture. Furthermore XRD pattern of the sample (Figure 4.27) shows peaks with highest intensities between all other h-BN samples and a very significant improvement on XRD pattern was achieved. High intensities of X-ray peaks could be taken as an indication of larger particles with high purity and crystallinity [35]. Average particle size of h-BN, originating from plain mixture, formed in nucleation under N_2 was calculated to be 1.58 ± 1.04 µm from SEM micrograph (Figure 2.25). High standard deviation value (± 1.04 µm) of this experiment indicates that both fine and coarse sized particles are formed during the experiment. Together with the SEM micrographs and XRD patterns it could be concluded that crystal thickness and particle size of the h-BN formed was significantly increased during the experiments. Growth of h-BN particles was also observed during the experiment conducted under argon atmosphere with average particle size of 1.94 ± 0.51 µm (figure 4.26) but, amount of h-BN added was not increased. It could be concluded that presence of h-BN in calcium borate melts results with formation of coarser, flake like h-BN particles with higher crystal thickness. Comparison of experimental results is given in Table 4.3.

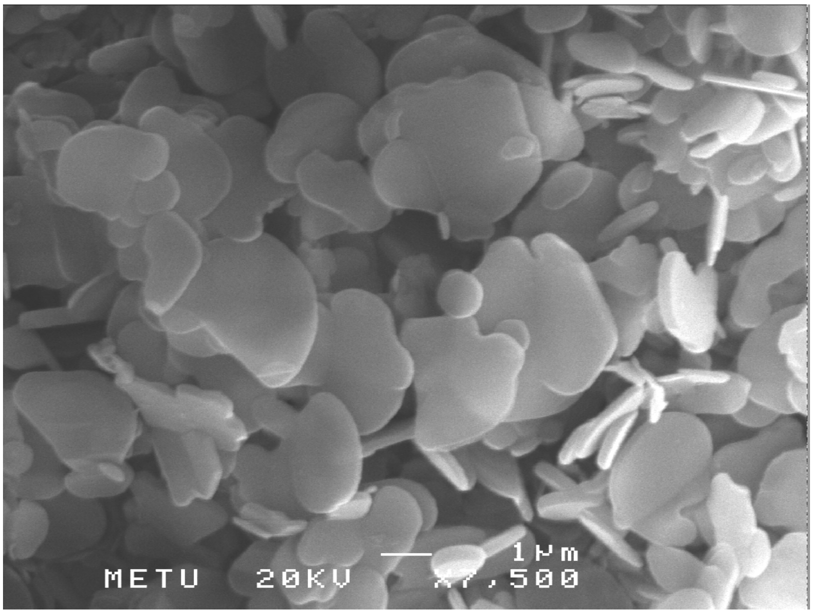

Figure 4.23 h-BN formed in experiment for investigation of nucleation under nitrogen gas. Flake like h-BN particles can clearly be observed.

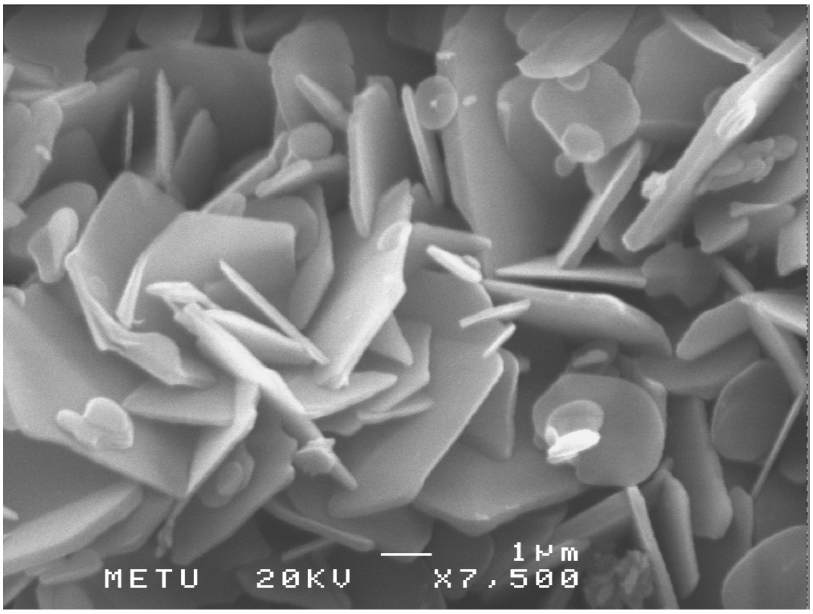

Figure 4.24 h-BN formed in experiment for investigation of nucleation under nitrogen gas. Flake like h-BN particles can clearly be observed. (Different portion of sample)

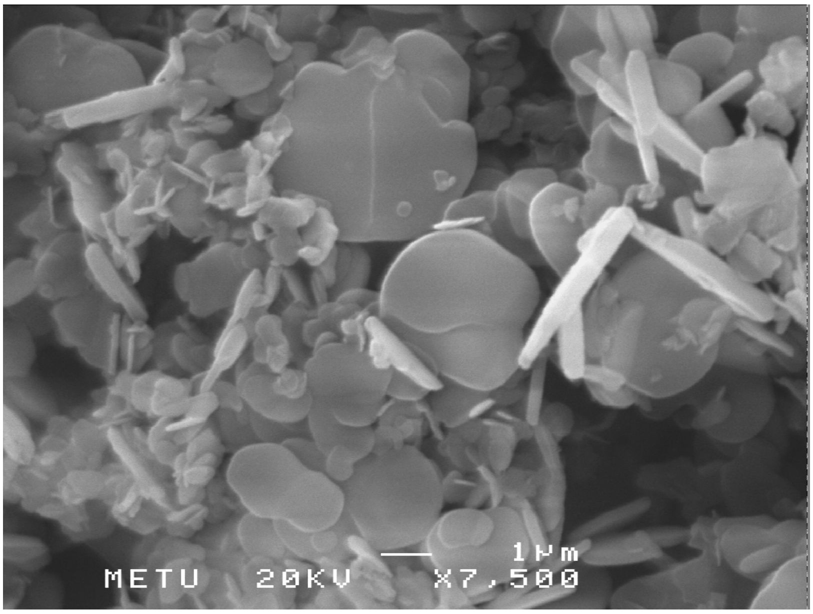

Figure 4.25 h-BN formed in experiment for investigation of nucleation under nitrogen gas. h-BN used was originating from plain mixture.

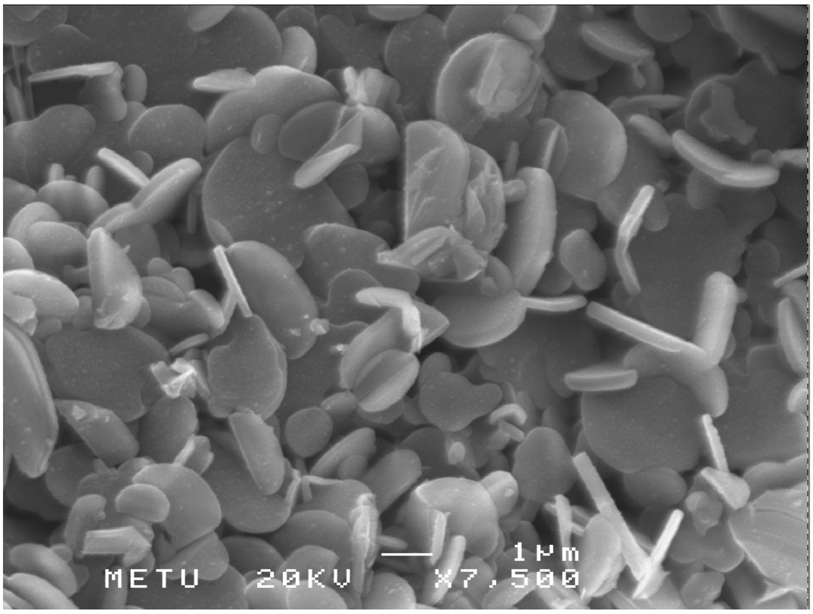

Figure 4.26 h-BN obtained from experiment for investigation of nucleation under Ar atmosphere. Flake like h-BN particles can clearly be observed.

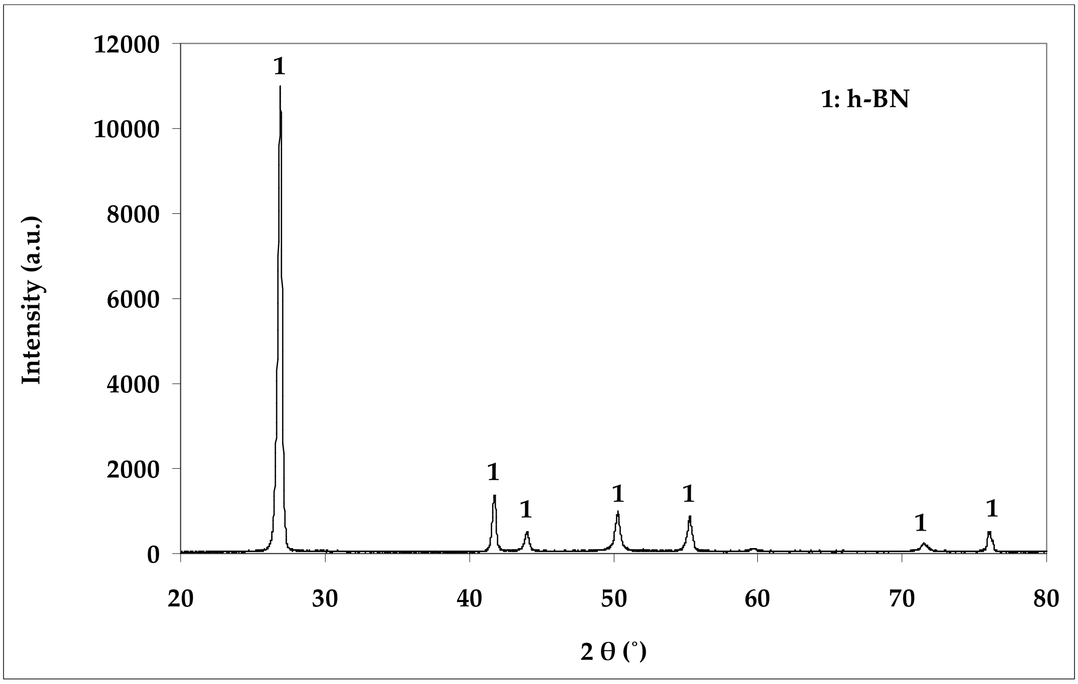

Figure 4.27 XRD pattern of the sample with h-BN (h-BN originating from $CaCO_3$ added experiments) addition for nucleation.

Newly forming BN should form on already existing BN particles with consequent increase in particle size. So increase in particle size of BN particles in previous experiments should be an expected result. 0.05 – 0.07 g of newly forming BN may not be sufficient for the growth seen in Figures 4.23 and 4.25. Growth of h-BN flakes during the experiment conducted under argon atmosphere also indicates that BN particles grow in calcium borate melt even when there is no new BN forming.

When only high temperature under nitrogen atmosphere was applied to previously synthesized h-BN originating from plain mixture, the kind of coarsening stated previously was not observed. Average particle size of the h-BN was slightly increased to 0.53 ± 0.13 μm from 0.49 ± 0.13 μm. Experiment conducted with pure h-BN from plain mixture at 1500°C and under N_2 atmosphere for 3 h indicates that a solid state coarsening mechanism was not taking place during the experiments (Figure 4.28).

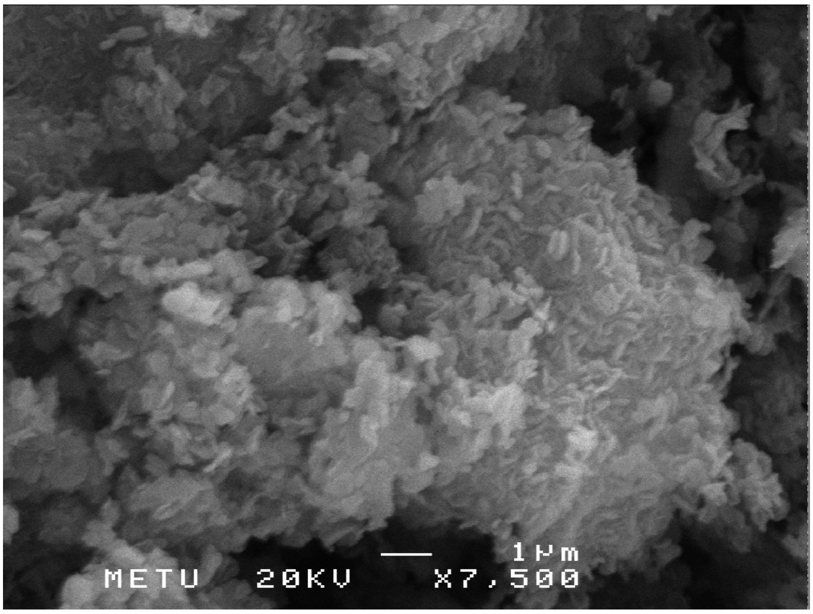

Figure 4.28 SEM micrograph of h-BN originating from plain mixture kept at 1500°C under flowing N_2 for 3 hours.

In order to check the results, experiments were conducted with B_2O_3 without any addition. B_2O_3 was placed in the furnace under N_2 atm, at 1500°C for 3 hours. Hexagonal BN formation did not take place during the experiment. After that effect of nucleation was analyzed with 0.25 g h-BN addition (h-BN originating from experiments conducted with plain mixture) into 4 g B_2O_3. Product with partial porosity with large glass islands was achieved but, amount of h-BN remained after leaching was determined to be 0.24 g (some loss of BN should not be an unexpected result considering processes like leaching, filtration etc that the reaction product is subjected to) indicating that there is no BN formation in liquid B_2O_3 by the mechanism

Table 4.3 Comparison of the experimental results

Composition	**Additives**	**Atm.**	**Wt. of Final Product**	**h-BN formed**	**Av. Particle Size**
B_2O_3 – C (2.5 g charge)	-	N_2	0.90 g	0.48 g	0.49 ± 0.11 μm
B_2O_3 – C (2.5 g charge)	10 wt% $CaCO_3$	N_2	1.21 g	0.60 g	1.19 ± 0.37 μm
B_2O_3 – C (2.5 g charge)	5.6 wt.% CaO	N_2	1.19 g	0.55 g	1.30 ± 0.45 μm
25 wt.% CaO - B_2O_3 (4.0 g charge)	0.25 g h-BN (from $CaCO_3$)	N_2	3.82 g	0.31 g	2.37 ± 0.61 μm
25 wt.% CaO - B_2O_3 (4.0 g charge)	0.25 g h-BN (from $CaCO_3$)	Ar	2.06 g	0.24 g	1.94 ± 0.54 μm
25 wt.% CaO - B_2O_3 (4.0 g charge)	0.25 g h-BN (from plain)	N_2	3.57 g	0.32 g	1.58 ± 1.04 μm
B_2O_3 (4.0 g charge)	0.25 g h-BN (from plain)	N_2	3.21 g	0.24 g	0.65 ± 0.16 μm

of nitrogen dissolution in and formation of BN from the melt. Figure 4.29 show the SEM micrograph of the pure h-BN after purification operations and a small increase in particle size of h-BN flakes are observed with 0.65 ± 0.16 μm average size distribution.

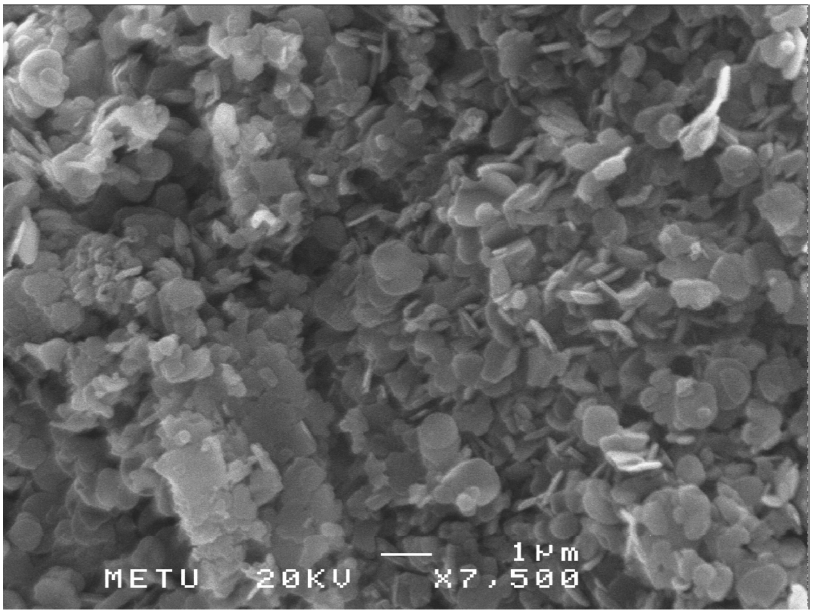

Figure 4.29 SEM micrograph of h-BN originating from plain mixture, added into B_2O_3 and kept at 1500°C under flowing N_2 for 3 hours.

In their study Çamurlu et al. [7] found that $CaCO_3$ addition increases particle size of the h-BN formed during the experiment. Results in accord with this study were reported and they calculated average particle diameter of h-BN phase formed in 2 h from plain mixture as 0.36 ± 0.08 μm and 10 wt.% $CaCO_3$ addition increases grain diameter to 0.70 ± 0.14 μm. Calculation of grain size in the study conducted by Çamurlu et al. was based on SEM micrographs of the samples and can be taken as an indication of increased grain growth rate during h-BN formation by $CaCO_3$ addition.

Average particle size calculations based on SEM micrographs were carried during this study and average particle size of the h-BN formed in 3 h during plain B_2O_3 - active C mixture was determined to be 0.49 ± 0.11 μm. That of $CaCO_3$ addition was determined to be 1.19 ± 0.37 μm and CaO addition was determined to be 1.30 ± 0.45 μm. Furthermore, average particle size was increased up to 2.37 ± 0.61 μm during the experiment conducted in order to investigate nucleation from calcium borate melts under nitrogen atmosphere and 1.94 ± 0.51 μm under argon atmosphere. These data obtained from SEM micrographs indicates significant effect of the second reaction mechanism on particle size growth and comparison of XRD patterns of boron nitrides formed during experiments clearly indicates the improvement on particle size, crystal thickness and ordering (Figure 4.30).

SEM micrographs and XRD patterns of the h-BN produced during the nucleation experiments was compared with the SEM and XRD of high quality commercial h-BN. It was observed that produced h-BN has higher XRD intensity and similar particle size distribution, indicating that crystal thickness and particle size of the product formed is comparable with its high quality commercial counterparts. Presence of a mechanism as stated above could also be utilized as a secondary treatment for producing high quality h-BN powders for advanced applications. This study also indicates that flake like h-BN powders with average particle size ranging in 0.20 to 2.5 μm could be synthesized by methods described above.

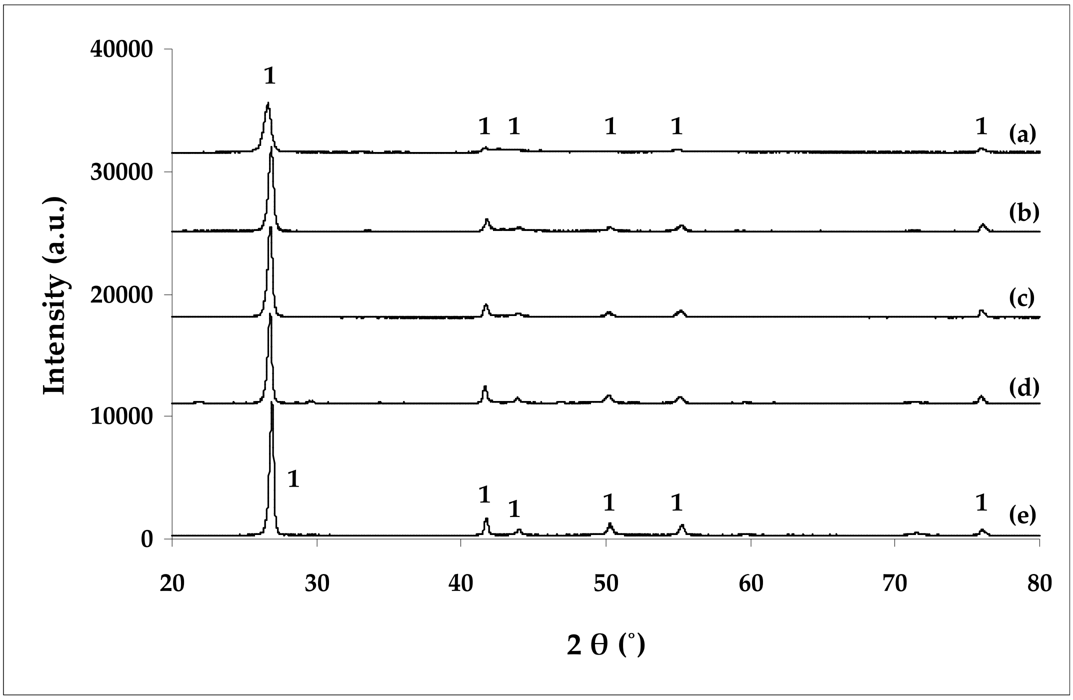

Figure 4.30 XRD Pattern of the h-BN obtained from a) plain mixture, b) CaO added, c) $CaCO_3$ added, d) nucleation under Ar(g), e) nucleation under N_2(g)

CHAPTER 5

CONCLUSION

Effect of calcium oxide addition on carbothermic formation of hexagonal boron nitride has been investigated during this study and it was found that similar to $CaCO_3$ addition CaO addition has a catalytic effect on carbothermic formation of h-BN.

The results presented above, combined with those obtained in previous studies conducted in this department [7, 17, 29], indicates that carbothermic formation of h-BN proceeds by two different mechanisms, formation of BN by the overall reaction 2.3 and by dissolution of nitrogen in and precipitation of BN from calcium borate melt, when CaO or $CaCO_3$ containing B_2O_3 – activated C mixtures are subjected to N_2 gas.

Hexagonal boron nitride amount in the reaction products was the highest in experiments conducted with 10 wt.% $CaCO_3$ addition into the B_2O_3 – active C mixture. Higher efficiency attained by $CaCO_3$ addition compared to CaO addition was observed due to the fact that CO_2(g) evolution, originating from calcination of $CaCO_3$, increases the porosity of the sample. Rate of formation of BN by the overall reaction 2.3 appears to be related to access of N_2 into the reaction aggregate and depend on porosity of the aggregate, by this way efficiency of carbothermic mechanism increases simultaneously with solution precipitation mechanism.

CaO – B_2O_3 mixtures with two different compositions (%5.6 CaO and %25 CaO) were subjected to nitrogen atmosphere, ensuring low oxygen pressures in the furnace. Glassy products, without h-BN, had been formed and it was concluded that nucleation of h-BN is not possible in calcium – borate melts under experimental conditions.

In order to investigate nucleation of h-BN from calcium borates, h-BN formed during carbothermic reduction experiments was added into the %25 CaO – B_2O_3 mixture. Nitrogen dissolved in the melt and formation of h-BN was observed over previously formed h-BN grains. Morphology of the sample was drastically changed when compared with the glassy phase synthesized from plain CaO – B_2O_3 mixtures. Effect of nitrogen had been investigated by conducting an experiment with same composition but under argon gas. Hexagonal boron nitride formation was not observed under argon gas and morphology of product was observed to be markedly different from the same experiment conducted under nitrogen gas. Furthermore weight loss due to evaporation was significantly increased under argon atmosphere. Slow cooling of the 25 wt.% CaO – B_2O_3 mixture was done in order to investigate nucleation and it was found that CaB_2O_4 phase, with no h-BN, formed during the experiment.

It could be concluded that growth rate of h-BN phase formed during carbothermic reduction is increased when calcium – borate liquid is present. CaO or $CaCO_3$ addition into the system results with; firstly normal carbothermic reduction mechanism forms fine h-BN particles. After that as time passes concentration of CaO in the system increases by consumption of B_2O_3 and with help of the presence of h-BN in the system, solution – precipitation mechanism is activated. Growth rate of formed h-BN particles increases with the help of the second mechanism. It could be reported that h-BN should be present in the system for formation of h-BN by the reaction mechanism described above.

Another indication of increased growth rate during CaO or $CaCO_3$ addition is that the particle size of the h-BN formed by CaO and $CaCO_3$ additions was significantly increased compared to the experiments without additives. Average particle size calculations were carried with aid of SEM micrographs and average particle size of the h-BN formed during plain B_2O_3 - active C mixture was determined to be 0.49 ± 0.11 μm. That of $CaCO_3$ addition was determined to be 1.19 ± 0.37 μm and CaO addition was determined to be 1.30 ± 0.45 μm. Average particle size was increased up to 2.37 ± 0.61 μm during the experiment conducted in order to investigate nucleation from calcium borate melts under nitrogen atmosphere.

Results of this study indicate that additives like CaO and $CaCO_3$ were useful for increasing the formation rate and the quality of the product in carbothermic formation of h-BN. Moreover, production methods by solution – precipitation mechanism, those do not contain carbon, should become possible. Not only new production methods, but also secondary treatments for higher quality h-BN formation could be accomplished by the mechanism described in this study.

As the future work it can be suggested that investigation of other catalysts such as Na_2O will be beneficial for production of h-BN economically in larger quantities by carbothermic reduction. Similar to CaO, Na_2O is a basic oxide and presence of a similar reaction mechanism should be operative in sodium borate melts. Furthermore, investigation of using boric acid as the starting material instead of boric oxide may be useful for economic and industrial production of h-BN by eliminating initial calcination processes.

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