PRODUCTION OF HEXAGONAL BORON NITRIDE BY CARBOTHERMIC REDUCTION OF COLEMANITE-BORIC OXIDE MIXTURES

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ABSTRACT

PRODUCTION OF HEXAGONAL BORON NITRIDE BY CARBOTHERMIC REDUCTION OF COLEMANITE-BORIC OXIDE MIXTURES

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Carbothermic production of hexagonal BN by using boric acid and ground colemanite mined from Bigadiç Region in Turkey was investigated by subjecting pellets prepared from B_2O_3, activated carbon and colemanite mixtures to nitrogen gas at 1500°C. Similar to $CaCO_3$ addition, colemanite addition to the B_2O_3-C mixtures resulted in higher amounts of h-BN in the final products. As a result of the experiments conducted with colemanite and $CaCO_3$ additions providing the same quantity of CaO to the initial mixtures, similar amounts of hexagonal BN in the reaction products were observed. As a result of the experiments conducted with different compositions of colemanite- B_2O_3- C mixtures, 5 wt % colemanite addition was determined to be the optimum composition giving the highest amount of hexagonal BN in the reaction products. Increasing duration of the experiments increased the amount and particle size of h-BN formed in the products. Optimum amount of colemanite addition resulted in higher amounts and coarser particles of h-BN in the products than the optimum amounts of $CaCO_3$ addition.

Keywords: Hexagonal boron nitride, colemanite, carbothermic formation, optimum amount, particle size

ÖZ

KOLEMANİT-BOR OKSİT KARIŞIMLARININ KARBOTERMİK İNDİRGENMESİYLE HEKZAGONAL BOR NİTRÜR ÜRETİMİ

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B_2O_3, aktive edilmiş karbon ve kolemanit karışımlarından hazırlanan peletler 1500°C sıcaklıkta azot gazına tabi tutularak, borik asit ve Türkiye'nin Bigadiç bölgesinden çıkarılmış kolemanit karışımlarından karbotermik yöntemle hekzagonal BN üretimi incelenmiştir. $CaCO_3$ ilavesine benzer şekilde, B_2O_3-C karışımlarına kolemanit ilavesi de son üründe daha yüksek miktarda hexagonal BN oluşumuna sebep olmuştur. Başlangıç karışımlarına aynı miktarda CaO sağlayan kolemanit ve $CaCO_3$ ilaveleri ile yapılan deneylerin sonuçlarında reaksiyon ürünlerinde benzer miktarlarda hekzagonal BN gözlenmiştir. Değişik kolemanit-B_2O_3-C karışımları ile yapılan deneyler sonucunda, reaksiyon ürünlerindeki en yüksek hekzagonal bor nitrür miktarını veren ağırlıkça % 5 kolemanit ilavesi, optimum kompozisyon olarak belirlenmiştir. Deney süresinin artırılması, ürünlerdeki oluşmuş hekzagonal BN'nin miktarını ve tane boyutunu artırmıştır. Optimum miktarda kolemanit ilavesi, optimum miktarda $CaCO_3$ ilavesinden daha yüksek miktarda ve daha büyük taneli hekzagonal BN oluşmasına sebep olmuştur.

Anahtar kelimeler: Hekzagonal bor nitrür, kolemanit, karbotermik oluşum, optimum miktar, tane boyutu.

To My Family

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CHAPTER 1

INTRODUCTION

Turkey owns 72 % of the world’s boron reserves. However, the export of boron products in Turkey is mainly based on raw boron ores and minerals of low prices. Therefore, some researches and investments to produce valued boron products should be done in order to be involved with decisions in the boron market [1].

Carbides and nitrides are beneficial materials due to their large application areas in industry. Furthermore, the industrial importance of these materials is growing rapidly due to their superior properties than oxides which cannot meet the whole needs of the industry. Carbides and nitrides are not only important in industry for their traditional characteristics such as strength and refractoriness, but also for their usage in electronics or opto-electronics industry [2].

Boron nitride is an important advanced ceramic with many different crystal structures and applications. Hexagonal form of boron nitride has excellent thermal, electrical and chemical properties and there is a wide range of application areas of hexagonal boron nitride due to these properties [3, 4].

There are a lot of studies on production techniques of boron nitride in the literature. Among these techniques, carbothermic production method is considered to be the most commercial method today [4]. Effect of some additions on this formation reaction was studied in previous studies. These studies have shown that addition of $CaCO_3$ to initial B_2O_3-C mixtures increased the amount and improved the crystal structure of hexagonal BN formed [5, 6].

Colemanite is a mineral consisting of both B_2O_3 and CaO. In addition, colemanite is a commercially produced boron product in Turkey and its price is low. Therefore, it is suitable for the production process to be done with this mineral instead of boron oxide and calcium carbonate separately.

In this study, carbothermic production of hexagonal boron nitride was investigated by subjecting colemanite, boron oxide and carbon mixtures to nitrogen gas at 1500°C. For this purpose, samples with colemanite concentrations in the range of 0 wt % to 50 wt % were subjected to N_2 gas at 1500°C. After the optimum composition was determined, effect of duration on h-BN amount and structure was investigated.

CHAPTER 2

LITERATURE REVIEW

Boron nitride is one of the most important ceramic materials having widespread uses due to its attractive chemical, thermal and electrical properties [3]. Among different techniques used for hexagonal boron nitride production, carbothermic reduction is the predominant commercial method used today [4]. Furthermore, addition of some oxides and carbonates such as MgO and $CaCO_3$ to the initial B_2O-C mixtures is known to catalytically affect h-BN formation [5].

Colemanite is a mineral consisting of both boron oxide and calcium oxide. Turkey owns the biggest portion of the world's boron reserves and an important percentage of boron reserves exist in the form of colemanite [7]. This study was carried out in order to investigate the production of h-BN from colemanite- boron oxide- carbon mixtures under nitrogen atmosphere.

In the following section, the crystal structures of boron nitride and properties and applications of hexagonal boron nitride will be explained. Then, production methods with emphasis on carbothermic production will be summarized. Finally, a brief description of colemanite will be given.

2.1 Crystal Structures of Boron Nitride

Boron nitride has mainly four types of crystal structures namely hexagonal BN (h-BN), cubic BN (c- BN), wurtzitic BN (w-BN) and rhombohedral BN (w-BN) [5]. Among these phases, the most important ones are hexagonal and cubic BN phases [3]. Hexagonal and cubic boron nitride phases show a strong similarity to graphite and diamond phases of carbon, respectively [8]. Hexagonal boron nitride also called white graphite crystallizes in a hexagonal sheet layered structure which is the cause of soft and lubricious nature of this phase of BN. Cubic boron nitride, on the other hand, crystallizes in a tetragonal structure like diamond giving this phase hardness and abrasiveness. In addition to these crystal structures, boron nitride also exists in amorphous and turbostratic phases [3, 8].

Hexagonal modification of BN is the most common structure. It has a unit cell with a simple layer structure. Figure 2.1 shows the layered structure of h-BN. Each layer consists of a flat or nearly flat network of B_3N_3 hexagons [8, 9]. The bonds between B and N atoms in these layers are strong covalent bonds while the bonds between these layers are weak van der Waals bonds. The π- electron is located at the nitrogen since nitrogen has high electro negativity which makes h-BN an electrical insulator and makes its color white [3].

The planes in the h-BN structure are stacked on top of one another without any horizontal displacement while close packing exists in which half of the atoms lie between the centers of hexagonal rings of neighboring layers in graphite. This is the only difference between the structures of graphite and hexagonal boron nitride. The properties of graphite and h-BN being very similar mean that the packing difference is of secondary importance. The similarity in properties of these materials is the result of the magnitudes of the interatomic forces being similar. Unit cell dimensions of h-BN and graphite are also very similar as shown in Table 2.1 [3, 8, 9].

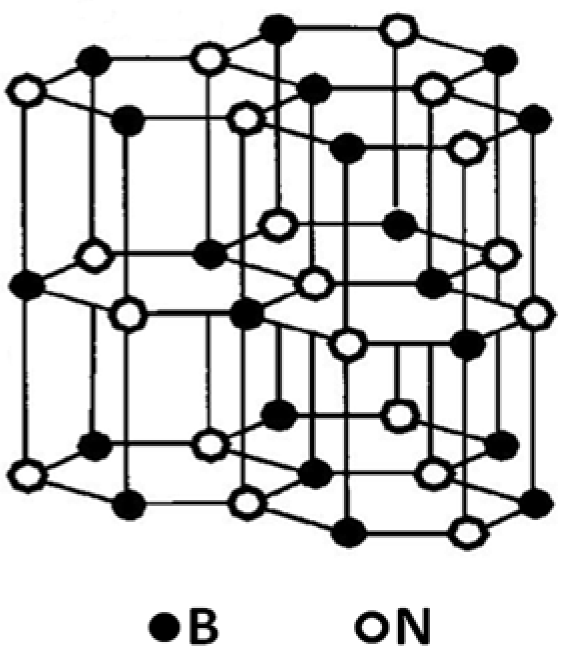


Figure 2.1 Layered hexagonal structure of boron nitride [3]

Table 2.1 Unit cell dimensions of graphite and hexagonal boron nitride (in Angstroms)

	a	c	c/a
Graphite	2.464	6.736	2.73
h- BN	2.504	6.661	2.66

2.2 Properties of Hexagonal BN

The properties of h-BN are strongly dependent on the production techniques due to crystallinity, particle size distribution and purity differences. Therefore, values given in the next part are a general average.

Three most important properties of h- BN are electrical insulation and thermal conductivity and solid lubricity. It is also white, soft and inert [2, 9].

The specific resistance of boron nitride is larger than 10^{12} ohm at room temperature and it decreases to 1900 ohm at 2000°C which is better than most refractory oxides. Similar to other covalent nitrides, the electrons are strongly and covalently bonded to the nucleus and are not available for metallic bonding which is the reason of this high electrical resistance [8, 9].

High thermal conductivity is another important property of h-BN. However, it decreases with increasing temperature. In addition, thermal expansion of h-BN is low and increases with increasing temperature. These thermal properties are responsible for this material's widespread use in fabrication of high- temperature crucibles [2, 4].

Hexagonal BN has a high solid lubricity due to strong covalent bonds between atoms on hexagonal layers different from weak van der Waals bonds between these layers. Its excellent lubrication performance is the result of easy gliding of the hexagonal layers on each other. In addition, the low friction coefficient of h-BN does not increase at high temperatures mentioned in figure 2.2 which is responsible for this material to be used in metal working processes where high temperature lubrication and cleanliness is needed [5, 10, 11].

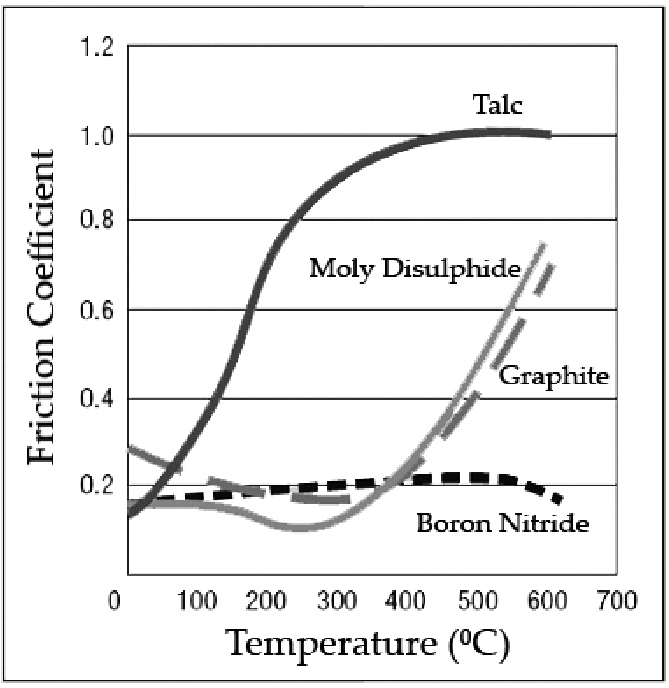


Figure 2.2 Friction coefficient variation of some important lubricants with temperature [11].

Some important properties of h-BN compared to graphite, AlN and Al_2O_3 are given in Table 2.2. Thermal expansion coefficient and thermal conductivity values are given for the direction perpendicular to C-axis.

Table 2.2 Some properties of h-BN, graphite, Al_2O_3 and AlN [2, 5, 11-14]

	h- BN	**Graphite**	**AlN**	**Al_2O_3**
Density (g/cm^3)	2.27	2.1-2.2	3.26	3.98
Melting Point (°C)	3000	3700	2015	2200
Thermal expansion coefficient (/C*10^6)	0.7	32	7.1	4.1
Thermal Conductivity at RT (W/m.K)	121	138	17-33	180-220
Dielectric Constant	4.2	-	9.7	10

Hexagonal BN powders are generally sintered by pressure- assisted sintering methods which are hot pressing or hot isostatic pressing. Small amount of B_2O_3 is used as a binder during sintering. In addition, h-BN does not form any solution during sintering different from other non- oxide ceramics. These sintered materials may also be easily machined to produce complex shapes due to weak van der Waals bonds between hexagonal layers [15].

2.3 Applications of Hexagonal BN

h- BN has a wide range of application areas due to its good chemical, thermal and electrical properties. It is found in different forms such as powders, dispersion of powder in liquid for coating, hot pressed shapes and pyrolytic shapes which is synthesized at high temperatures under vacuum. It is mainly used for four applications due to its four important properties. Firstly, it is used for lubrication purposes due to its superior lubricity. Secondly, it is used in crucibles for molten metal handling. Third application of h- BN is as additives to other ceramics or polymers. Lastly, it is used in electronic industry as coolers, insulators and heat-sinks [3, 4, 14].

Hexagonal boron nitride is a lubricious material in its powder form which gives this material a wide range of application areas where lubricity is needed. It is mainly used in high temperature applications since it does not lose its lubricity at elevated temperatures. It is added to water, oil and water oil mixtures to increase lubrication. It is also added to solid lubricants such as plastics, rubbers and resins. It is added to ceramics and alloys to reduce friction and wear [3, 4]. In his article, Kimura et al. [10] concluded that, boron nitride is a suitable additive to oil used in sliding of bearing steel. He indicated that the coefficient of friction slightly increases, but wear of this material decreases extremely when h-BN is added even at very small amounts such as 1 wt%.

Furthermore, addition of h-BN to intermetallic composites gives excellent improvement on the properties of these materials. It allows these composites to be thermally stable and chemically inert in vacuum and corrosive metal vapors. It also improves the machinability of these materials and it allows the conductivity and resistivity characteristics to be accommodated [4, 14]. Rossi [16] stated that addition of BN to some metal oxides (BeO, Al_2O_3) used in aerospace applications improves the thermal shock resistance of the material. He concluded that BN flake inclusions provide a high density in ceramic matrices blocking the crack propagation. Accordingly, these materials were able to be used for applications where thermal shock resistance is needed.

Due to its high thermal conductivity and good electrical insulation, another important application area of h- BN is electronic industry. It is used as substrate for semiconductors, as windows for microwave apparatus and insulator layers for MISFET semiconductors [3]. Various products of h-BN is given in Figure 2.3.

Figure 2.3 Various products of hexagonal boron nitride [17-19].

In addition to application areas explained above, there is a growing market for h-BN usage as listed below:

- Break rings in steel casting

- Masks for X- Ray lithography
- Radar windows and antennas
- Crucibles for aluminum evaporation and for molecular- beam epitaxy
- Vessels for Czochralski crystal growth of III-V and II- VI compounds such as gallium arsenide
- Insulating substrate in ribbon heaters in combination with a pyrolytic graphite resistance heating element
- Anti- corrosive layers and oxidation- resistant coatings with pyrolytic films

Due to dependence of properties of h-BN on the production technique, purity, particle size distribution and structure, applications also depend on these parameters as expected. For example, while high purity is needed for electronic applications and cosmetics industry, small grain size is the key property for hot pressed or hot isostatic pressed shapes.

2.4 Production Methods of Hexagonal BN

Since h- BN is not normally found in nature, it should be synthesized by various methods. Although the first production of h-BN was in 1842, the commercial production of this material could not be achieved for 100 years. There are a number of ways to produce h-BN but most of them need improvement to get desired properties because of the technical difficulties of these production methods [3, 9].

There are mainly three production methods of hexagonal BN [3, 4, 20]. The first one is the reaction of boric acid with ammonia which was considered to be the most widely used commercial method by Haubner et al [3]. The second production method is the reaction of boric acid with organic nitrogen compounds and the third one is the carbothermic production which is the concern of this study. According to Paine and Narula [4], carbothermic method is the main commercial production method of h- BN.

In the first production method, boric acid (H_3BO_3) reacts with ammonia (NH_3) at temperatures above 900°C according to reaction 2.1:

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

While this reaction occurs, some carrier substances such as calcium carbonate, calcium phosphate, calcium oxide and zinc borate should be present. In the absence of these carrier substances, formation of h-BN is very slow due to low surface area of boric oxide melt. After the reaction is complete, the product is leached in an HCl solution. However, the product of the reaction is amorphous boron nitride and it contains some oxygen impurities. Therefore a second treatment is done under nitrogen atmosphere at 1500°C in order to have hexagonal structure and less oxygen impurities [3, 5, 6].

The second production of h-BN occurs due to reaction of boric acid or boric oxide with organic nitrogen compounds such as urea, melamine, dicyanamide and guanidine under nitrogen atmosphere between 1000°C and 2100°C [3]. Boric oxide (B_2O_3) reacts with urea ($CO\,(NH_2)_2$) according to reaction 2.2:

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

After the reaction is complete, the product is leached with methanol or dilute acid solutions to get rid of the impurities. Then, the product should be heated to 1500°C under nitrogen atmosphere to remove oxygen impurities. However, the final product is boron nitride with turbostratic structure. Thereafter, turbostratic structure should be converted to hexagonal form by a thermal treatment below 1800°C [3, 9, 20].

The third production method is carbothermic production which is the concern of this study. In this reaction, a second treatment is not necessary to convert the crystal structure since the product of the reaction is hexagonal BN [5].

There have been a lot of studies conducted in order to explain the mechanism of this reaction. In his study, Pikalov [21] concluded that the formation of boron nitride from boric oxide and carbon occurs in two steps. These steps are determined to be the formation of boron carbide (B_4C) and CO from boric oxide and carbon shown in reaction 2.3; followed by formation of boron nitride and CO from boron carbide and boric oxide under nitrogen atmosphere according to reaction 2.4.

$2B_2O_3 + 7C = B_4C + 6CO$ Reaction 2.3

$3B_4C + B_2O_3 + 7N_2 = 14BN + 3CO$ Reaction 2.4

In another study, Bartnitskaya et al [22] stated that during the carbothermic reduction, boric oxide is reduced by carbon giving boron as a product according to reaction 2.5.

$2B_2O_3 + 3C = 4B + 3CO_2$ Reaction 2.5

Then, this elemental boron is considered to form boron nitride by reaction with nitrogen gas.

Yoon and Jha [23] concluded that the reacting gaseous species in the carbothermic reduction is BO. However, in the study of Aydoğdu and Sevinç[24], it was stated that the gaseous species is B_2O_3 since the equilibrium vapor pressure of BO is much lower than that of B_2O_3 at 1500°C.

Aydoğdu and Sevinç [13] has conducted some experiments subjecting pellets of boric oxide and carbon to nitrogen gas at temperatures ranging from 1100°C to

1500°C for 0.5 to 4 hours. The overall reaction of the carbothermic reduction is given in reaction 2.6.

$B_2O_3(l) + 3C(s) + N_2(g) = 2BN(s) + 3CO(g)$ Reaction 2.6

The amount of boric oxide needed was decided to be 50 % in excess of the amount calculated according to reaction 2.6 considering B_2O_3 losses due to evaporation. They conducted experiments at temperatures between 1100°C and 1500°C and they found that the amount of h-BN increases with increasing temperature. They also concluded that the products of the reactions are h- BN, unreacted B_2O_3 and unreacted carbon for experiments conducted at 1500°C for 2 hours. They also stated that some amounts of B_4C present in the samples of experiments conducted at lower temperatures or shorter durations.

Aydoğdu and Sevinç [24] conducted some experiments with different geometrical arrangements in order to understand the reaction mechanism of the carbothermic h-BN formation reaction. They suggested that the reaction proceeds through gaseous intermediates and B_2O_3 and carbon need not to be in contact for the reaction to proceed.

Aydoğdu and Sevinç [24] conducted some experiments in order to understand whether B_4C forming in the reaction products of the experiments in which BN formation is not complete is an intermediate species or not. They subjected pellets prepared from B_4C and B_2O_3 to nitrogen gas at 1500°C for 2 hours and they concluded that the amount of h-BN formed is smaller than that formed by experiments conducted with B_2O_3-C pellets. Therefore, they concluded that formation of h-BN from B_2O_3- B_4C mixtures is slower than formation from B_2O_3- C mixtures. They stated that either BN or B_4C but not both can exist in the system and B_4C is only seen in the regions where N_2 gas cannot penetrate.

In their study, Çamurlu et al [25] subjected pellets prepared from B_2O_3 and activated carbon to argon and nitrogen gases in order to investigate the role of boron carbide to carbothermic formation of h-BN. The amount of boric oxide in the mixtures was 100 % excess of the amount calculated by the stoichiometry of reaction 2.6. They concluded that formation of h- BN took place by two parallel reactions. In the regions where nitrogen gas pressure is high, reaction 2.6 takes place which is the reduction of B_2O_3 with C to BN directly under nitrogen gas. This reaction was found to be completed in 3 hours at 1500°C. In the second route, in regions where nitrogen cannot penetrate to the pellets, formed B_4C by reaction 2.3 converts to BN by reacting B_2O_3 and N_2 according to reaction 2.4.

Çamurlu et al [25] conducted experiments with subjecting B_2O_3 and activated carbon pellets to argon gas at 1500°C in order to produce B_4C. Then, produced B_4C and B_2O_3 mixture was subjected to nitrogen gas at 1500°C for 3 hours. It was seen that the B_4C was not converted to h-BN completely. Hence, they reported that formation of BN from B_4C according to reaction 2.4 is slower than direct carbothermic reduction of B_2O_3 to BN according to reaction 2.6. Therefore, it was concluded that B_4C is not a necessary intermediate compound in carbothermic formation of h-BN. They also stated that B_4C formed during reaction retards the h-BN formation reaction. Therefore, prevention of formation of B_4C was necessary in order to increase the rate of formation of h-BN and to decrease the boric oxide losses due to evaporation.

Catalytic effect of some compounds added to the initial B_2O_3- activated C mixtures on carbothermic formation of h- BN is another important subject. This importance is due to increase of the efficiency of the reaction in order to meet the growing needs for h-BN. Bartnitskaya et al [26] has conducted experiments by adding Li_2CO_3 and LiOH to initial B_2O_3-carbon mixtures to investigate the catalytic effect of these compounds on carbothermic formation reaction. They conducted experiments at 1500°C for 3 hours and they reported that addition of 12.5 wt. % Li_2CO_3 increases the amount of h-BN formed about twice of that without addition. They also concluded that Li_2CO_3 addition improves the crystal structure of boron nitride formed. They stated that a lithium borate melt forms and h-BN crystallizes from this melt increasing the rate of formation reaction [26-29].

Effect of calcium carbonate ($CaCO_3$) addition on carbothermic formation of h-BN was investigated by Çamurlu et al [5, 20]. Pellets prepared from B_2O_3- activated C and $CaCO_3$ with compositions ranging from 5-50 wt % was subjected to nitrogen gas at 1500°C. The experiments were conducted for 30 minutes since it was concluded that boron carbide forms in the first 30 minutes of the reaction, then it starts to disappear by reaction 2.4. It was stated that addition of $CaCO_3$ to the plain mixture increases the amount of h-BN formed and decreases the amount of B_4C formed. Optimum addition was found to be 10 wt % $CaCO_3$ in accord with the results shown in Figure 2.4 where amounts of h-BN and B_4C are seen to be maximum and minimum, respectively, for 10 wt % addition of $CaCO_3$. They reported that the efficiency of the reaction increases with increasing $CaCO_3$ addition up to 10 wt % then it decreases.

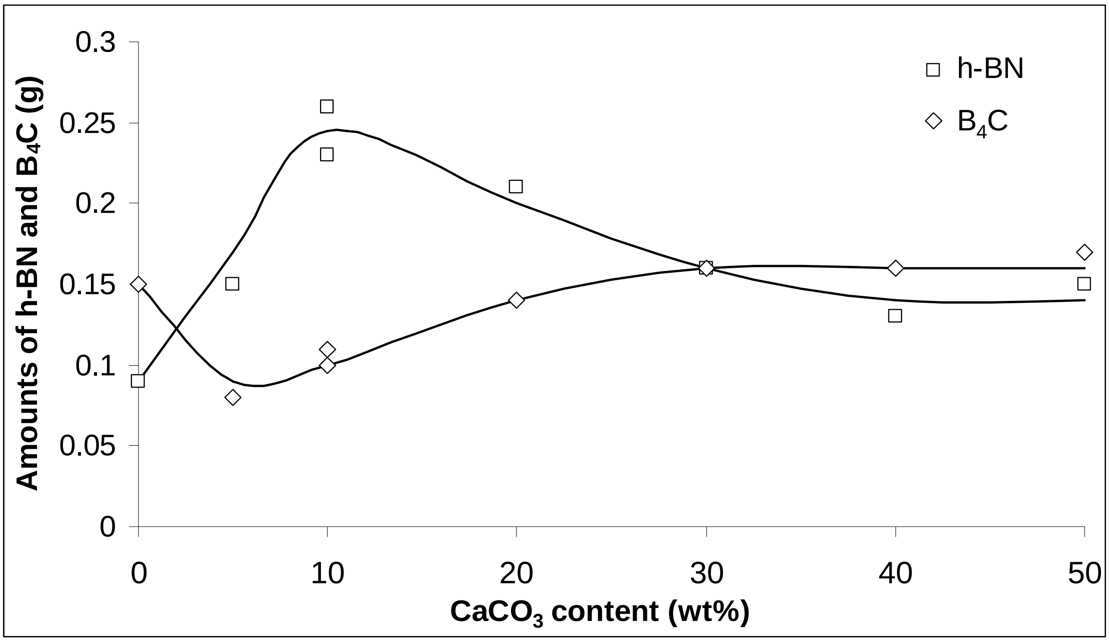


Figure 2.4 Effect of $CaCO_3$ content on the amounts of h- BN and B_4C formed during carbothermic reaction at 1500°C for 30 minutes [5].

After the optimum amount was found, the experiments with 10 wt % $CaCO_3$ added mixture were conducted for longer durations. The results of these experiments are shown in Figure 2.5.

Çamurlu [5] reported that, all B_4C formed during the first 30 minutes of the reaction was used up in 3 hours with plain mixture while it was used up in 2 hours for 10 wt % $CaCO_3$ added mixture. In addition, it was concluded that increasing duration of the experiments up to 2 hours increases the amounts of h-BN produced [5, 20].

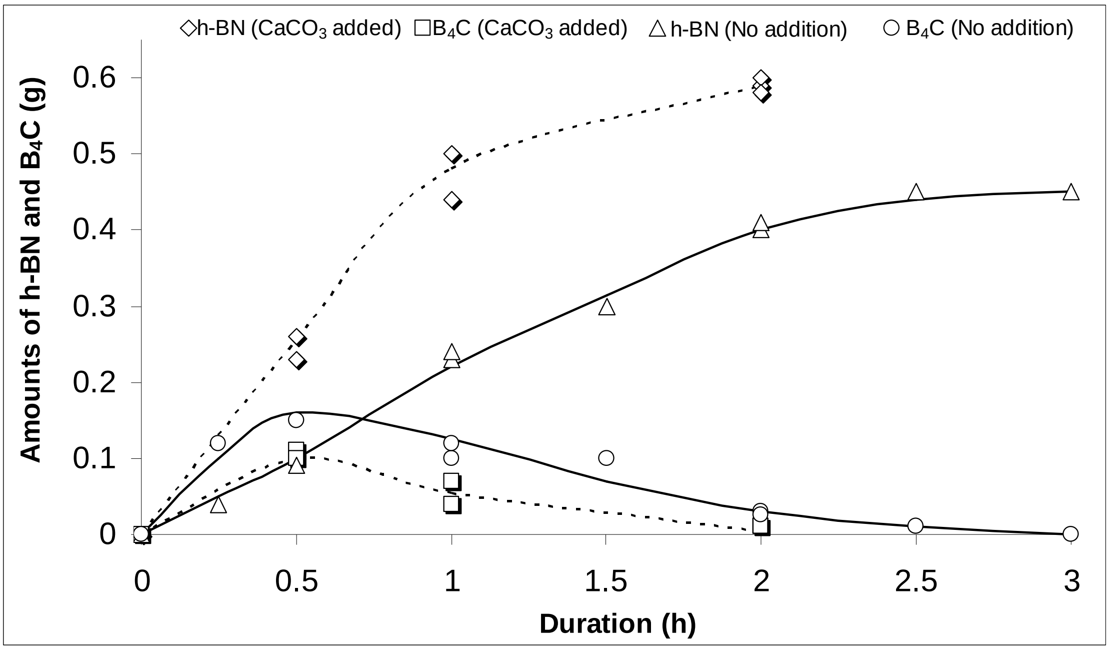


Figure 2.5 Changes of the amounts of h-BN and B_4C formed in the products of the experiments conducted at 1500°C for different durations for plain and 10 wt % $CaCO_3$ added mixtures [5]

The effect of $CaCO_3$ addition on average crystal thickness of h-BN particles formed was also studied by Çamurlu et al [5, 20]. They reported that addition of $CaCO_3$ promotes the growth of h-BN particles. In addition, by BET specific surface area measurements, they found that specific surface area of the particles decreases with $CaCO_3$ addition which means that $CaCO_3$ addition converts the merged polycrystalline structure of h-BN particles formed from initial plain mixture to separate particles with definite edges.

$CaCO_3$ addition increases the efficiency of carbothermic formation reaction in two different ways. Çamurlu et al [20] stated that addition of $CaCO_3$ up to 20 wt % increases the porosity of the reaction aggregate. This increase in the porosity permits the nitrogen gas to penetrate in to the pellets retarding the B_4C formation. Therefore, porosity increases the rate of h-BN formation. These porosities are believed to be due to calcination of $CaCO_3$ evolving CO_2 gas during the reaction.

They also stated that porosity of the pellets decreases after 20 wt % addition of $CaCO_3$ due to changes in viscosity, density etc. of the calcium borate phase.

The other mechanism promoting the h- BN formation by $CaCO_3$ addition is reported to be the formation of a calcium borate phase at 1500°C. CaO forming due to calcination of $CaCO_3$ forms a calcium borate melt with B_2O_3. Nitrogen gas was suggested to be dissolved in this melt as N^{3-} and N^{-} ions depending on the basicity of the melt. Then, these nitrogen ions react with $(BO_3)^{3-}$ ions in basic melts or $(B_2O_5)^{4-}$ ions in acidic melts to form h-BN [20]. They also stated that there are two liquid phases namely calcium borate melt with 25 wt % CaO and B_2O_3 melt. The CaO increase with addition of $CaCO_3$ decreases the rate of evaporation of B_2O_3 which retards reaction 2.6. Therefore, while $CaCO_3$ addition increases the porosity of the pellet increasing the reaction rate, it decreases the evaporation of B_2O_3 decreasing the reaction rate resulting an optimum concentration [5, 20].

In his study, Özkenter[6] conducted experiments subjecting pellets prepared from $CaCO_3$ and CaO added B_2O_3- activated carbon mixtures to N_2 gas at 1500°C in order to compare the effects of $CaCO_3$ and CaO additions on the amount and structure of h-BN formed by carbothermic reduction. It was stated that similar to $CaCO_3$ addition, CaO addition has also a catalytic effect on h-BN formation. However, it was reported that $CaCO_3$ added samples have higher h-BN amount in the product. This difference was explained to be due to CO_2 gas evolution during calcination of $CaCO_3$ giving higher porosity of the $CaCO_3$ added pellets compared to that of CaO added pellets. In addition, it was indicated that both $CaCO_3$ and CaO added samples result in larger particle size of h- BN.

Ionic mechanism was also investigated by Özkenter [6] by subjecting pellets prepared from B_2O_3 and B_2O_3-CaO mixtures in absence of carbon to N_2 gas at 1500°C. It was concluded that nitrogen does not dissolve in B_2O_3 melt. However, he reported that nitrogen dissolves in the calcium borate melt forming BN in presence of BN particles to start nucleation. Therefore, it was concluded that BN formation by ionic mechanism in calcium borate melt is possible but there is a nucleation barrier in the system. Based on these experimental results, it was proven that h-BN forms by two different and parallel ways namely by reaction 2.6 and by ionic dissolution of nitrogen in calcium borate melt forming h-BN.

Effect of addition of alkaline earth oxides other than $CaCO_3$ was also studied by Çamurlu et al [5, 30]. MgO and $BaCO_3$ were added to plain mixtures and the experiments were conducted for 30 to 120 min at 1500°C. It was found that addition of these alkaline earth oxides increases the amount and particle size of h-BN formed and decreases the amount of B_4C formed in the system. They suggested that a mechanism similar to that with $CaCO_3$ addition applies for these additions too. They also conducted some experiments with Cu addition in the form of cupric nitrate and they reported that Cu addition increases the crystallinity and particle size of the h-BN formed. However, the amount of h-BN did not change with Cu addition [5].

In his study, Akyıldız [31] investigated the effect of Na_2CO_3 addition on carbothermic formation of h-BN. In the first set of experiments, he investigated the effect of amount of Na_2CO_3 addition on the reaction by subjecting pellets prepared from different concentrations ranging from 5 to 40 wt % Na_2CO_3 additions to nitrogen gas at 1500°C for 30 minutes. He reported that Na_2CO_3 addition is increased the amount of the h-BN in the products. However, his results showed that there is not an optimum point of concentration and maximum amount of h-BN could be attained in the mixture with 40 wt % Na_2CO_3. Experiments with higher Na_2CO_3 additions were not conducted since it would not be efficient.

Akyıldız [31] also investigated the effect of time on carbothermic formation of BN in Na_2CO_3 added samples. He found that the amount of h-BN in the production aggregate is increased up to 3 hours. Amount of h-BN was found not to increase any more for longer durations. He found no B_2O_3 and Na_2CO_3 borate in the reaction products of the experiments conducted for 2 hours and longer periods and concluded the reaction to end in 2 hours. He also made some experiments using different temperatures in order to see the effect of temperature on reaction. He reported that increasing the temperature of the 40 wt % Na_2CO_3 added sample increases the amount of h- BN amount. However, he stated that the effect of temperature on the amount of h-BN formed from Na_2CO_3 added sample is smaller than that of $CaCO_3$ added sample. Therefore, he suggested that addition of Na_2CO_3 to initial B_2O_3- activated C mixtures may be an efficient way only for lower temperatures and shorter durations. In addition, he stated that addition of Na_2CO_3 to B_2O_3- carbon mixtures increases the average particle size of the h-BN formed using the SEM images. He also concluded that Na_2CO_3 added samples result in larger particle size of h-BN than $CaCO_3$ added samples.

2.5 Description of Colemanite

Colemanite is one of the most important boron minerals in Turkey with the production capacity of 300 000 tons / year. It is a mineral consisting of both Ca and B with the chemical formula $Ca_2B_6O_{11}.5H_2O$ having a monoclinic structure [7, 32, 33]. The mineral used in this study was ground colemanite which was mined from Bigadiç Exploitation Management. It also contains some other oxides as impurities such as SiO_2, MgO and SrO.

In this study, colemanite- boric oxide- activated carbon mixtures were subjected to nitrogen gas at 1500°C. Therefore, the changes in the characteristics of colemanite with increasing temperature are very important for us in order to discuss the effect of this addition to the initial mixtures. Thermal decomposition of colemanite has been investigated in many studies. In their study, Hartung and Heide [34] stated that dehydration of colemanite occurs between 60-430°C. They also concluded that the amorphous form after dehydration crystallizes at about 680°C forming a new phase. This phase was determined to melt at 1000°C.

In his study, Yıldız [35] investigated the effect of heat treatment on colemanite processing. He used the milled and unmilled colemanite from Emet ore. He stated that colemanite calcines at temperatures between 300 and 460°C losing its crystal water which is 20 wt %. In another study, Waclawska et al [36] indicated that dehydration of colemanite occurs in two steps. In the first step, H_2O forms from OH groups and in the second step, H_2O and borate chains bonds are broken followed by removal of whole water. Each steps show different DTA peaks.

Yıldız [35] also concluded that colemanite decomposes to B_2O_3 and CaO at temperatures below 600°C. The other compounds such as $CaCO_3$ and $SrSO_4$ were stated to remain in the product. In another study, Sattler[37] stated that above 800°C $CaO.B_2O_3$ and $CaO.2B_2O_3$ crystallize which melt at 930°C.

Yıldız [35] also indicated that at temperatures above 670°C, new compounds form. CaB_2O_4 and $Ca_2B_6O_{11}$ were seen in the products at 800°C. Some other experiments were conducted with colemanite and petroleum coke in air and in argon atmosphere. It was concluded that CaB_2O_4 forms at 1000°C in air and at 1400°C in water.

When all of the studies are considered, it can be concluded that colemanite dehydrates at temperatures between 300°C and 460°C giving 2 different DTA peaks. In addition, all of the studies show that calcium borates crystallize at about 800°C. Then, these calcium borates melt at temperatures between 930°C- 1000°C.

CHAPTER 3

EXPERIMENTAL SET- UP AND PROCEDURE

Main aim of this study was to investigate the mechanism of formation of hexagonal boron nitride from colemanite- boric oxide-carbon mixtures. First of all, colemanite- boric oxide- carbon mixture with the same amounts of CaO and B_2O_3 with 10 wt % $CaCO_3$ added mixture used by Çamurlu and Özkenter [5, 6] was subjected to nitrogen gas for 2 hours in order to compare the amounts and structures of h-BN formed from colemanite added and $CaCO_3$ added mixtures. Then, colemanite- boric oxide- carbon mixtures with different concentrations were subjected to nitrogen gas for 1 hour in order to determine the optimum concentration. Thereafter, the pellets prepared with this optimum concentration were subjected to nitrogen gas for different durations to see the effect of time on amount and structure of h-BN formed. All of the experiments were conducted at 1500°C and the pellets prepared from the mixtures were put in an horizontal tube furnace. In the following section, experimental set-up, materials used and experimental procedure will be given in detail.

3.1 Experimental Set-Up

The furnace used in this system is a horizontal tube furnace which has a 1000 mm long alumina tube of 50 mm inner and 60 mm outer diameters closed at both ends by silicon stopples having gas inlet and outlet tubes. Schematic representation of the furnace is given in Figure 3.1. Radiation shields which were shaped from isowool board and ceramic fibres were utilized at about 30 cm away from the hot zone of the furnace in order to save the silicon stopples from high furnace temperature.

Schematic drawing of the system is given in Figure 3.2. SiC heating elements were used to heat the furnace. Gas flow rate was adjusted to be 100 cc/min with the help of a gas flow meter and overflow gas was allowed to exit the furnace by overflow exit. Temperature was controlled by a digital temperature controller using an S type thermocouple and it was kept at a constant range of 1°C error.

The pellets prepared from the powder mixtures were placed in a graphite crucible. This graphite crucible was inserted to the furnace with help of an alumina bar and it was located in the hot zone during the experiments.

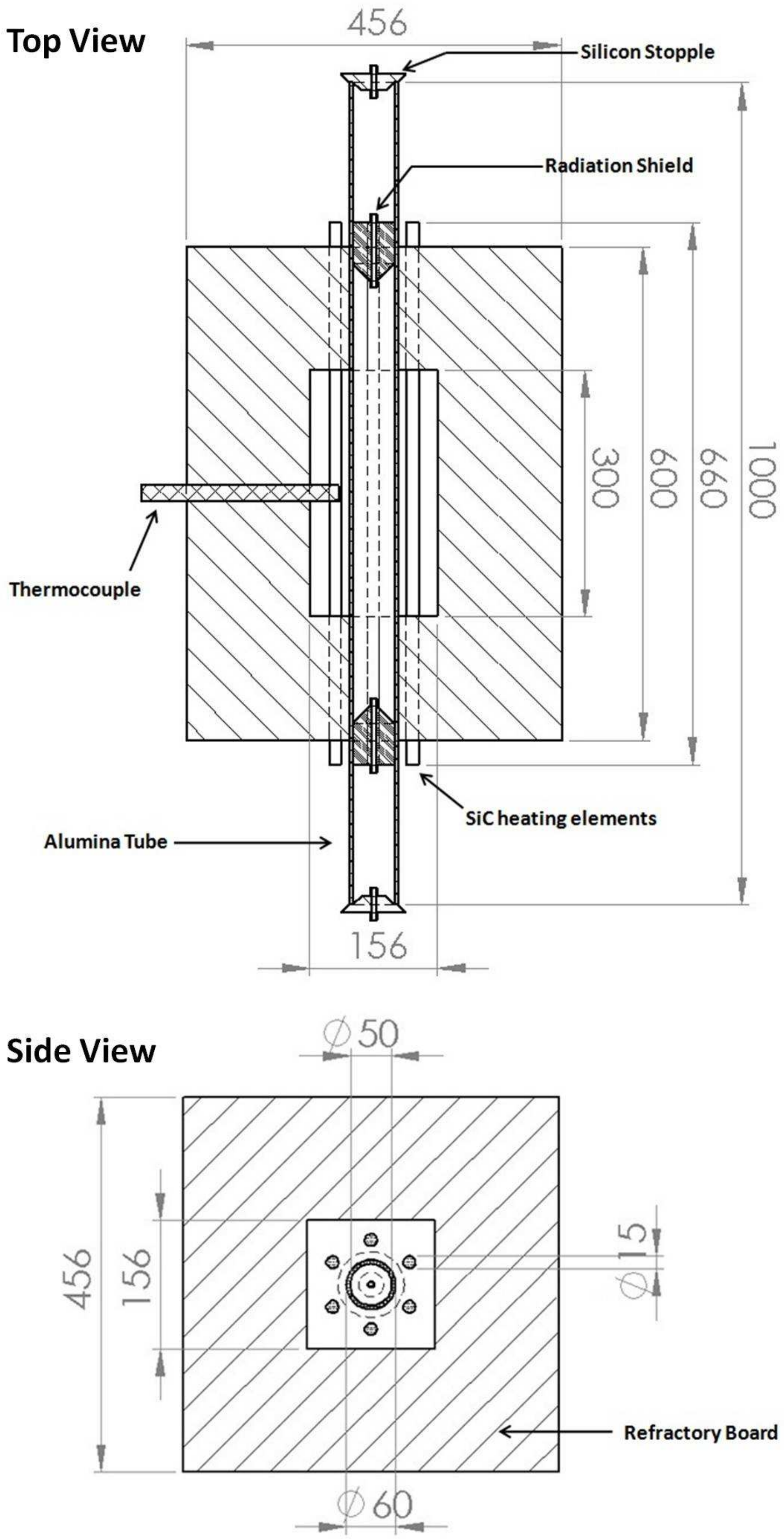


Figure 3.1 Schematic representation of the furnace

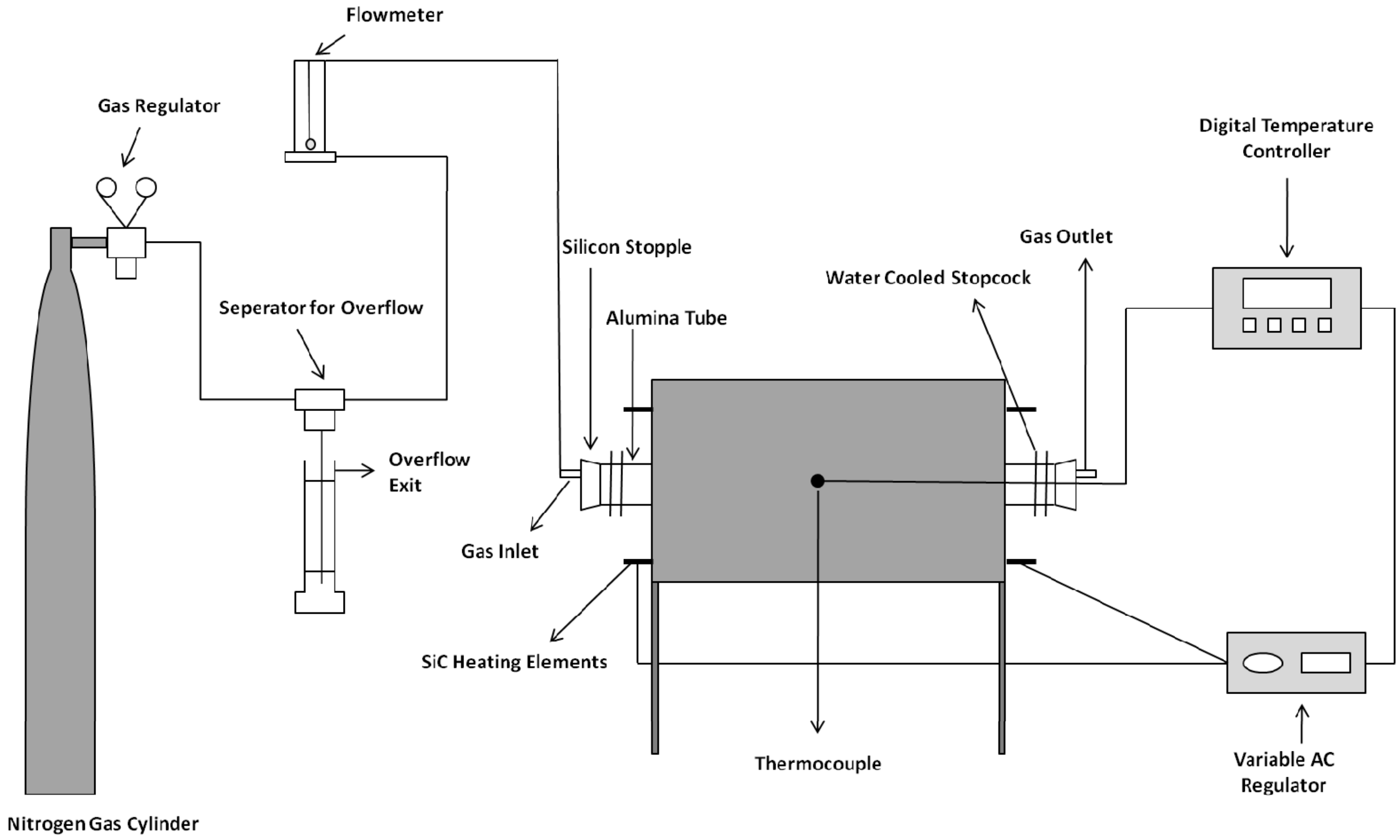


Figure 3.2 Schematic drawing of experimental set-up (reporıduced from Çamurlu [5])

3.2 Materials Used

3.2.1 Boric Oxide (B_2O_3), Activated Carbon, Calcium Carbonate ($CaCO_3$) and Hydrochloric Acid (HCl)

Boric oxide used in the experiments was calcined from the boric acid obtained from Merck Company with larger than 99.8 % purity. Boric acid was calcined in a nickel crucible at 1000°C for 2 hours according to reaction 3.1.

$2H_3BO_3 = B_2O_3 + 3H_2O$ Reaction 3.1

Nickel crucible supplied from Sigma Aldrich has a height of 60 mm and an inner diameter of 50 mm (Figure 3.3). When all of the H_2O was removed, molten B_2O_3 with a glassy structure was poured on to a stainless steel plate. After it got cold, it was ground into small pieces and put in a desiccator in order to avoid hydration.

Figure 3.3 Nickel Crucible

Activated carbon supplied from Merck Company was larger than 99 % pure. Nitrogen gas supplied from BOS A.Ş. was 99.998% pure containing moisture amount smaller than 30 vpm and oxygen amount smaller than 50 vpm.

Calcium carbonate supplied from Merck Company was larger than 99 % pure and hydrochloric acid with 37% purity was supplied from Sigma Aldrich. Supplier name, catalog number and purity values of these materials are summarized in Table 3.1

Table 3.1 Supplier name, catalog number and purity values of materials used

Chemical	**Supplier**	**Catalog number**	**Purity (%)**
H_3BO_3	Merck	100165	>99.8
Active carbon	Merck	102183	>99
$CaCO_3$	Merck	102066	>99
HCl	Sigma Aldrich	30721	Extra Pure 37- 38

Some experiments were conducted with boric acid supplied from Eti Mine Works General Management in order to compare the results of the experiments conducted by using boric acid supplied from Merck Company and Eti Mine Works General Management. Chemical specification of boric acid supplied from Eti Mine Works General Management which is 99.9 % pure is given in Table 3.2.

Table 3.2 Composition of boric acid supplied from Eti Mine Works General Management as received.

Component	**Content**
B_2O_3	56,25 wt % min.
SO_4	500 ppm max.
Cl	10 ppm max.
Fe	5 ppm max.

3.2.2 Colemanite

Colemanite used in the experiments was supplied from Eti Mine Works General Management. The mineral was mined from Bigadiç Region in Turkey and ground to small pieces. Composition of this mineral is given in table 3.3. Any further process was not applied to colemanite taken from Eti Mine Works. In other words, it was used as in the supplied form.

Table 3.3 Composition of ground colemanite taken from Eti Mine Works General Management as received.

Component	Concentration
B_2O_3	40.00+/-0.50 wt %
CaO	27.00+/-1.00 wt %
SiO_2	4.00-6.50 wt %
SO_4	0.60 wt % Max
As	35 ppm Max
Fe_2O_3	0.08 wt %
Al_2O_3	0.40 wt % Max
MgO	3.00 wt % Max
SrO	1.50 wt % Max
Na_2O	0.35 wt % Max

Particle size analysis data of colemanite mineral used is given in Table 3.4.

Table 3.4 Cumulative undersize analysis of ground colemanite taken from Eti Mine Works General Management

Particle Size (µm)	Percentage
+600	0.02 Max
+250	0.5 Max
-75	87 +/- 5
-45	75 +/- 5

DTA and TGA curves of colemanite used are given in Figure 3.4. These analyses were also obtained from Eti Mine Works General Management to specify the material. In DTA curves, peaks at temperatures of 385.1°C and 401°C show the removal of bonded water from the mineral. The second peak seen on the curve at 771.9°C shows the crystallization of a calcium borate. The mass change at 771.9 may be probably due to removal of remained water. These discussions were done on the basis of the information given in the literature review part.

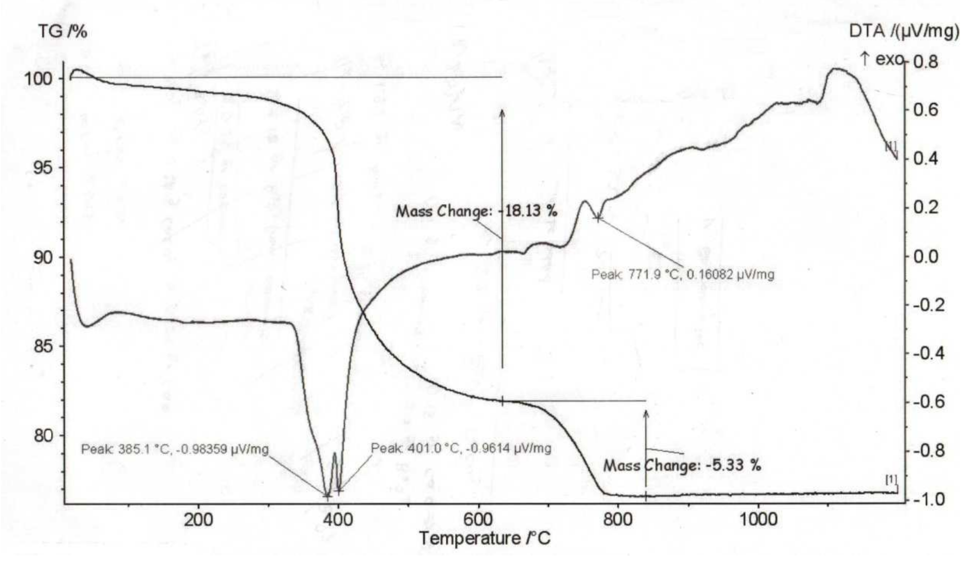


Figure 3.4 DTA and TGA curves of colemanite taken from Eti Mine Works General Management

3.3 Experimental Procedure

In the first set of experiments, colemanite- boric oxide- carbon mixtures with the same amount of CaO and total B_2O_3 with 10 wt % $CaCO_3$ added mixture (1.986 g total B_2O_3 and 0.514 g carbon) was subjected to nitrogen gas at 1500°C for 2 hours. Then, the amounts and structures of h-BN formed from $CaCO_3$ added and colemanite added mixtures were compared.

In the second set of experiments, mixtures with different colemanite concentrations were subjected to nitrogen gas at the same temperature for 1 hour. Total B_2O_3 and C amounts did not change in the experiments. In other words, mixtures were prepared using the formula providing the sum of the amounts of the B_2O_3 added and B_2O_3 coming from colemanite remained constant. Formula to calculate colemanite % is given in equation 3.1:

$$((B_2O_3 \text{ added}+0{,}514)*(0.4)*(\text{colemanite } \%)/100) + B_2O_3 \text{ added} = 1.986 \quad \text{Equation 3.1}$$

In equation 3.1, 0.4 value were used since B_2O_3 percentage in the ground colemanite taken from Eti Mine Works General Management is 40 wt %. Colemanite % shows the percentage of the sum of the added B_2O_3 and C mixture. 0.514 and 1.986 are the amounts of the C and total B_2O_3 respectively which have the same values with the mixtures used by Çamurlu, Özkenter and Akyıldız [5, 6, 31]. Same amounts of the reaction ingredients were used to make comparison in order to understand the effect of colemanite addition.

Finally mixtures with the optimum colemanite concentration were subjected to nitrogen gas at 1500°C for different durations in order to see the effect of time on the reaction.

Boric oxide used in the experiments was obtained from the calcinations of boric acid as explained above. The calcined, poured and ground boric oxide was ball milled in a Retsch PM 100 planetary ball mill (Figure 3.5). Then, it was sieved by a Tyler 80 mesh sieve with 175µm width opening in order to control and unify the particle size of the boric oxide used. The mixtures prepared from the powders were pressured in a die with 58.9 MPa to produce the pellets.

Figure 3.5 Retsch 100 PM Planetary Ball Mill [38]

The pellets prepared were charged into the tube furnace in a graphite boat with 7 cm length and 2.5 cm width. The inside of the crucible was coated with a thin (~ 0.5 mm) h-BN layer in order to avoid reaction of the pellets with crucible. Figure 3.6 shows the photograph of the graphite boat. After the experiment was finished, the graphite boat suddenly removed from the furnace and let to get cold in air. The products then weighed and cut into two similar pieces. One of these pieces was used for XRD analysis and the other piece was leached in order to find the final h-BN, remained B_2O_3, unreacted C and B_4C amounts. Leaching process used was the process developed by Aydoğdu and Sevinç[13] which will be explained in detail in results and discussion part. Leached products were also analyzed by XRD and SEM.

Figure 3.6 Graphite boat

Unleached and leached products were analyzed with a Rigaku Multiflex X- Ray diffractometer with Cu- Kα radiation with 2θ values between 20° and 80° at a rate of 2°/min. Peaks on the XRD patterns were identified using a qualitative analysis software program. Microscopic examinations were conducted with field emission scanning electron microscope (FEI Nova Nano 430). Particle size measurements were done using the images taken with this SEM.

CHAPTER 4

RESULTS AND DISCUSSION

This study was a continuation of the previous studies conducted in this department in order to investigate the mechanism of h-BN formation by carbothermic reduction. In their study, Aydoğdu and Sevinç [24] concluded that h-BN formation from B_2O_3- carbon mixtures subjected to nitrogen gas at elevated temperatures was completed in 2 hours at 1500°C and the reaction proceeds through gaseous intermediates. Thereafter, Çamurlu et al [25] stated that B_4C is not a necessary intermediate compound in formation of h-BN from B_2O_3- carbon mixtures and he concluded that formation of B_4C retards the formation reaction. He also investigated the effect of some additives and he concluded that addition of $CaCO_3$ to the initial B_2O_3- C mixtures increases the reaction rate. He stated that 10 wt % $CaCO_3$ addition provides the optimum composition [20]. In his study, Özkenter [6] investigated the role of CaO addition on the reaction and he concluded that CaO addition also catalytically affects the reaction increasing the reaction rate. However, he concluded that the amount of h-BN in $CaCO_3$ added samples is higher than CaO added samples due to the gas release causing porosities in the pellet. Özkenter [6] also concluded that h-BN formation by a second mechanism based on the dissolution of nitrogen in the calcium borate melt and formation of h-BN by reaction of nitrogen ions with borate ions in this melt is possible in CaO added samples.

Main aim of this study was to investigate the formation of hexagonal boron nitride from B_2O_3-colemanite-carbon mixtures under nitrogen gas at 1500°C. In this section, first the results of the experiments conducted with plain, $CaCO_3$ added and colemanite added samples will be compared. Then, the optimum composition of colemanite-boric oxide-carbon mixtures will be given. Lastly, the effect of time on formation reaction of h-BN with the optimum composition found will be investigated.

Quantities of the compounds in the reaction products of all of the experiments were calculated using the method developed by Aydoğdu and Sevinç [13]. The product of the experiment consisting of h-BN, calcium borate, B_2O_3, B_4C and unreacted C was weighed after removal from the furnace. This product was leached in a 50 vol. % HCl- 50 vol. % purified water solution for 3 hours. By this process, calcium borate and B_2O_3 dissolved in the solution. By weighing the product of leaching, sum of the amounts of calcium borate and unreacted B_2O_3 were calculated. After that, the residue containing BN, B_4C and unreacted C were put in to a furnace at 800°C for 15 hours. During this process, unreacted C was removed from the sample by burning. B_4C, on the other hand, was completely converted to B_2O_3 by oxidation. BN was not affected from this oxidation process. Then, the residue was leached again for 2 hours to remove B_2O_3 formed by oxidation of B_4C. The final product of this leaching-oxidation-leaching process is pure h-BN. Schematic representation of this process is given in Figure 4.1.

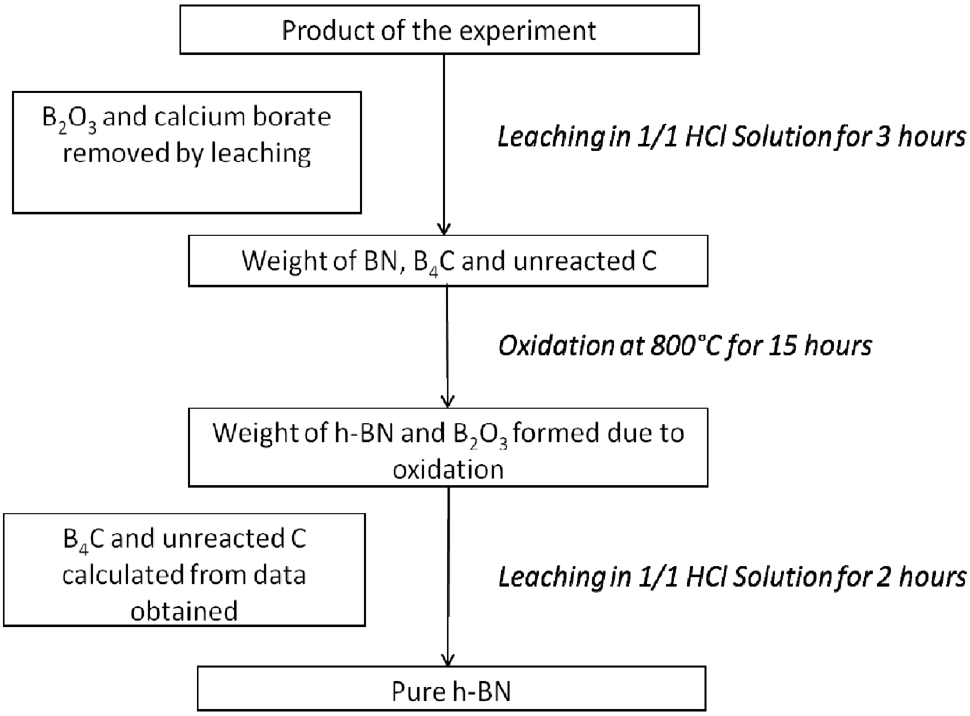


Figure 4.1 Schematic representation of leaching- oxidation- leaching process

H_3BO_3 and $CaCO_3$ used were obtained from Merck Company and as such did not contain other substances in appreciable quantities. Colemanite, on the other hand, is of commercial grade and contains several compounds in addition to CaO and B_2O_3. All of these compounds are expected to dissolve in the calcium borate melt resulting in a complex slag at 1500°C.

Before all of the experiments, 22.64 wt % colemanite added mixture without C was subjected to N_2 gas at 1500°C for 2 hours. Then, the product was leached in a 1/1 (volume) HCl solution. The reaction product dissolved in the solution completely which is an indication of the fact that the final product after leaching of the colemanite added mixtures is pure h-BN.

4.1 Experiments Conducted with Plain, $CaCO_3$ Added and Colemanite Added Samples

First set of experiments were conducted by subjecting plain, 10 wt % $CaCO_3$ added and 22.64 wt % colemanite added samples to nitrogen gas at 1500°C for 2 hours. These experiments were conducted in order to see whether h-BN formation from colemanite- boric oxide- carbon mixtures is possible or not. In addition, the results of the experiments were compared in order to see the effect of using colemanite instead of using B_2O_3 and CaO separately. The amounts of the ingredients of samples are given in Table 4.1. All of the experiments were conducted twice in order to check the reproducibility of the results.

Table 4.1 The amounts of ingredients of plain, 10 wt % $CaCO_3$ added and 22.64 wt % colemanite added samples

Weight of ingredients in grams		
Plain mixture	10 % $CaCO_3$ added mixture	22.64 % colemanite added mixture
B_2O_3: 1.986	B_2O_3: 1.986	B_2O_3: 1.778
C: 0.514	C: 0.514	C: 0.514
	$CaCO_3$: 0.25	Colemanite: 0.519

Çamurlu et al [20] studied the effect of $CaCO_3$ addition on carbothermic formation reaction of h-BN, and he stated that $CaCO_3$ addition catalytically affects the reaction and increases the reaction rate. He also concluded that the optimum amount of $CaCO_3$ addition is 10 wt %. This is the reason why 10 wt % $CaCO_3$ added mixture was used in these experiments. 10 wt % $CaCO_3$ and 22.64 wt % colemanite additions provide the same quantity of CaO to the mixture which is 5.6 wt %. Total B_2O_3 amounts for the two mixtures are same too.

In his study, Özkenter [6] conducted experiments by using pellets prepared from B_2O_3- CaO and C mixtures. He stated that similar to $CaCO_3$, CaO addition has a catalytic effect on carbothermic formation of h-BN. However, he concluded that $CaCO_3$ added samples have higher h-BN amount in the product due to CO_2 (g) release causing porosities in the pellet which let N_2 gas to enter to these porosities and increase the rate of carbothermic h-BN formation reaction. Similar to $CaCO_3$, colemanite also gets calcined during the process and gases released increase the porosity of the pellet.

Pictures of the samples are given in Figure 4.2. These images show that porosities of the pellets containing $CaCO_3$ and colemanite are larger than that of plain mixture. In addition, the colors of $CaCO_3$ and colemanite added samples show that the amount of h-BN formed is larger for these samples.

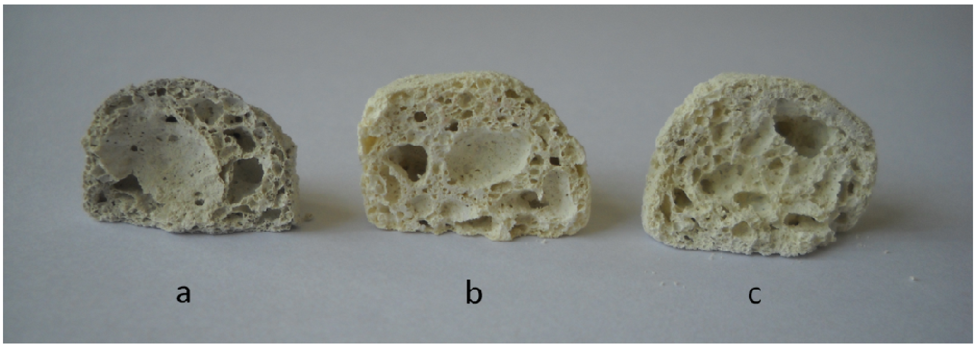


Figure 4.2 Pictures of a) plain, b) 10 wt % $CaCO_3$ added and c) 22.64 wt % colemanite added samples

The amounts of h-BN in the final products of these experiments are given in Table 4.2. They were found to be similar. These results showed that using colemanite instead of using B_2O_3 and $CaCO_3$ separately is appropriate providing the same quantity of final h-BN.

Table 4.2 The amounts of the final h-BN for plain, 10 wt % $CaCO_3$ added and 22.64 wt % colemanite added mixtures

	Plain mixture	**10 wt % $CaCO_3$ added mixture**	**22.64 wt % colemanite added mixture**
h-BN(g)	0.404	0.471	0.458
	0.401	0.447	0.447
Average	0.40	0.46	0.45

In his study, Çamurlu et al [20] concluded that B_2O_3 and CaO in the starting pellet form a calcium borate liquid at 1500°C in accord with the reaction 4.1. N_2 gas passing over the samples dissolves in this borate melt and then reacts with borate ions to give h-BN. This mechanism results in quantity of h-BN forming to increase. The same mechanism should be operative in colemanite containing samples also. That the results obtained with $CaCO_3$ addition and colemanite addition are similar may be taken as indication of this mechanism to be operative.

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

XRD patterns of these samples before leach are given in Figure 4.3. In addition to h-BN, some CaB_2O_4 is present in the samples with $CaCO_3$ and colemanite additions. These results show that one of the phases in the experimental conditions is B_2O_3 (l) and the other phase is calcium borate melt.

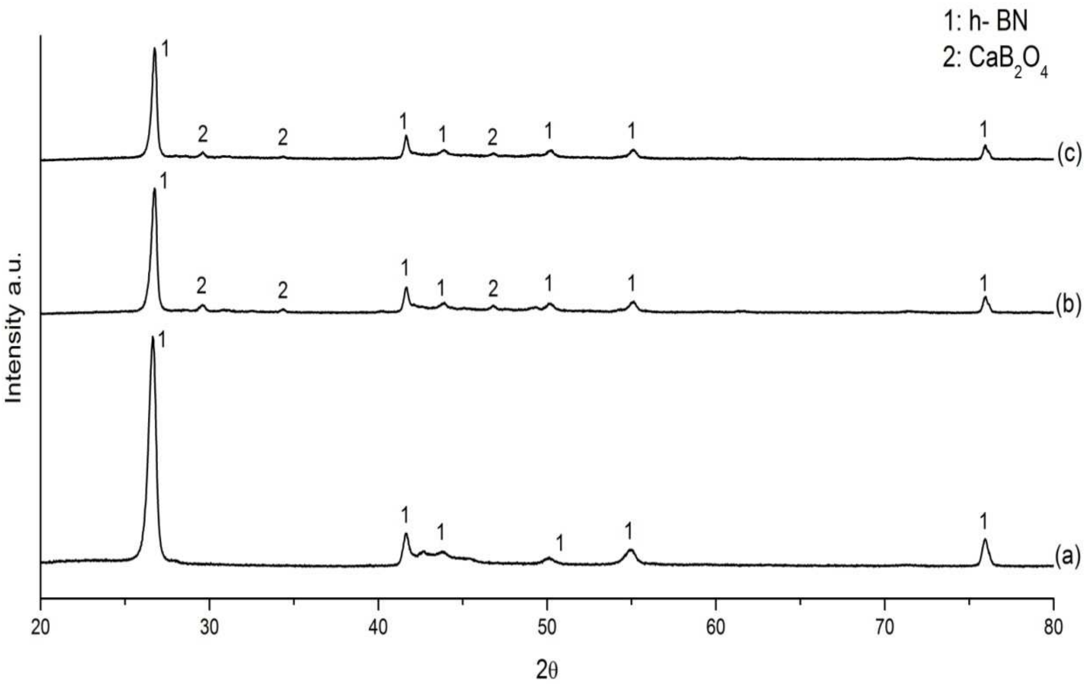


Figure 4.3 XRD patterns of a) plain mixture, b) 10 wt % $CaCO_3$ added mixture, c) 22.64 wt % colemanite added mixture before leach

As discussed above, a calcium borate melt also forms in colemanite added samples. The oxides in the colemanite dissolves in this melt forming a complex slag. XRD patterns of the samples after leach are given in Figure 4.4. All of the peaks in these patterns belong to h-BN which means that calcium borate melt formed at high temperatures in colemanite added samples may also be dissolved in 1/1 (vol) HCl solution.

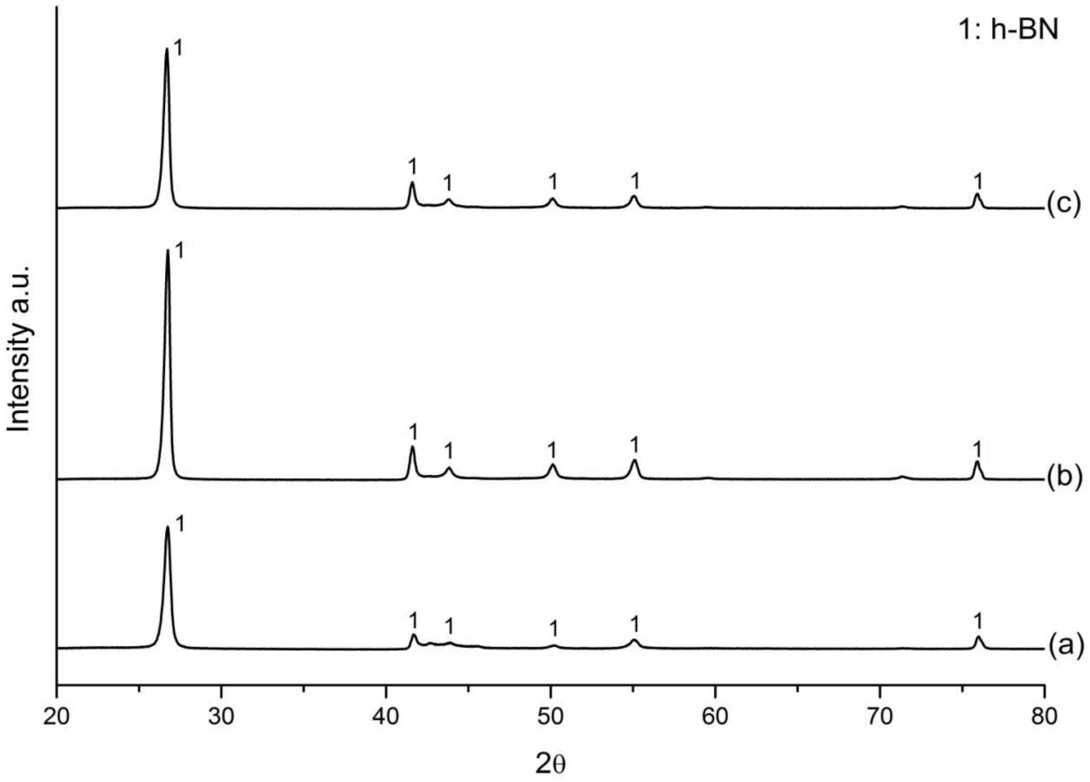


Figure 4.4 XRD patterns of a) plain mixture, b) 10 wt % $CaCO_3$ added mixture, c) 22.64 wt % colemanite added mixture after leach

Çamurlu et al [20] stated that addition of $CaCO_3$ to the initial B_2O_3-C mixtures increases the particle size of h-BN formed. SEM images of plain, 10 wt % $CaCO_3$ added and 22.64 wt % colemanite added mixtures after leach are given in Figure 4.5, 4.6 and 4.7, respectively. All of the flake like particles seen on these images are h-BN particles.

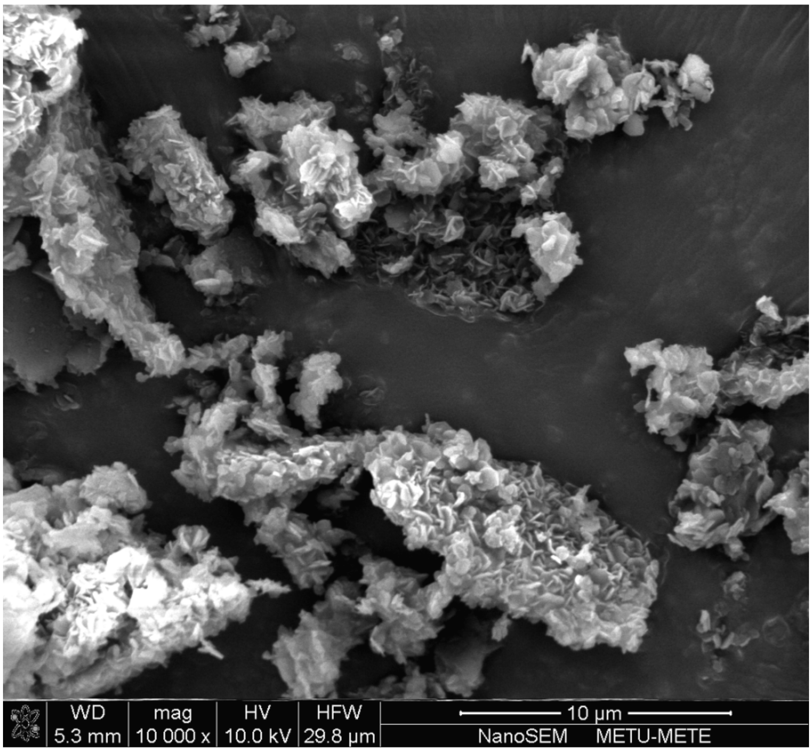


Figure 4.5 SEM image of plain mixture after leach

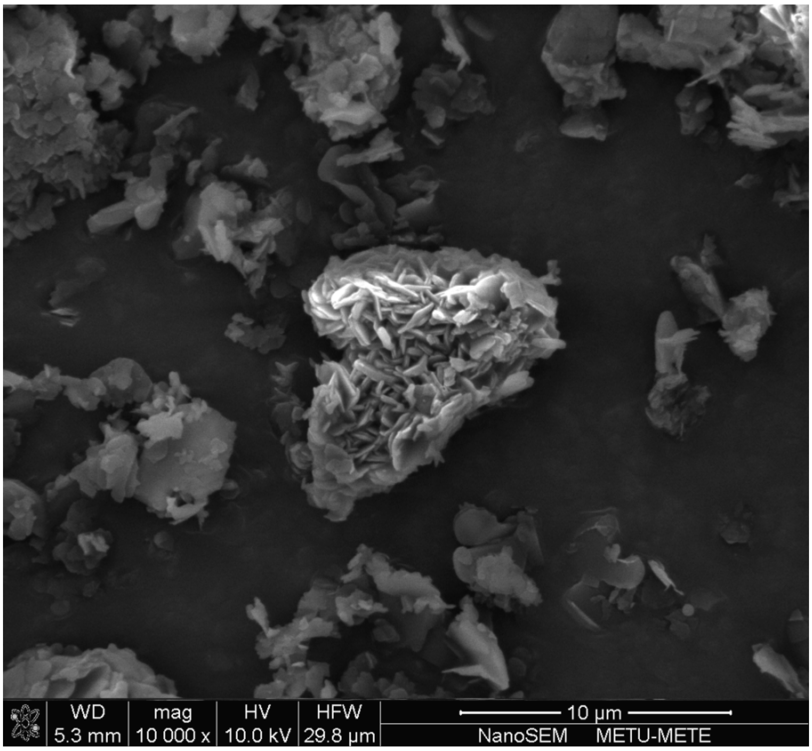


Figure 4.6 SEM image of 10 wt % $CaCO_3$ added mixture after leach

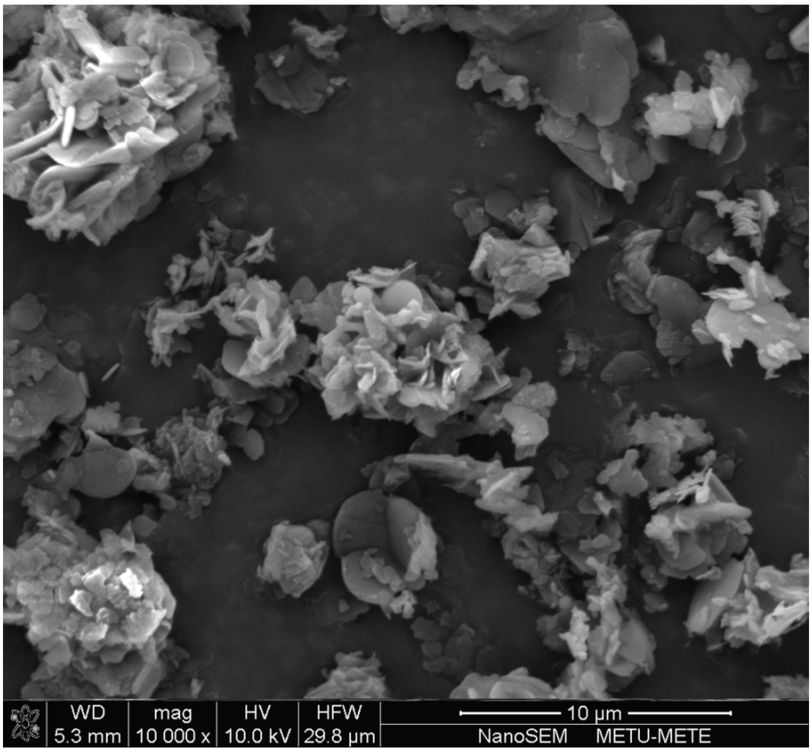


Figure 4.7 SEM image of 22.64 wt % colemanite added mixture after leach

Particle size measurements were done using the SEM images. The results of the analysis are given in Table 4.3

Table 4.3 Particle sizes of plain, 10 wt % $CaCO_3$ added and 22.64 wt % colemanite added samples

	Plain mixture	**10 wt % $CaCO_3$ added mixture**	**22.64 wt % colemanite added mixture**
Particle Size (nm)	490 ± 110	850 ± 460	1220 ± 520

Particle size analysis of the samples showed that addition of $CaCO_3$ and colemanite to the initial B_2O_3-C mixtures increases the particle sizes of h-BN formed. In addition, addition of colemanite instead of B_2O_3 and $CaCO_3$ separately results in higger particle sizes of h-BN formed.

In his study, Özkenter [6] stated that addition of CaO instead of $CaCO_3$ to the initial mixtures results in coarser particles and smaller amount of h-BN formed. Since colemanite also contains CaO, coarser particle size of h-BN with colemanite addition is an expected result. However, different from CaO addition, colemanite addition gives similar amounts of h-BN due to calcination causing the gases to be released increasing the porosity of the pellet.

4.2 Experiments Conducted with 5 wt % to 50 wt % Colemanite Additions

As discussed above, colemanite is a mineral consisting of both B_2O_3 and CaO. There are some other oxides in this mineral which may affect the carbothermic formation reaction of h-BN. Therefore, it was decided to investigate the effect of composition of the colemanite-B_2O_3-carbon mixtures to final h-BN amount and structure.

Experiments with plain and 5 wt % to 50 wt % colemanite added samples were conducted by subjecting pellets prepared from these mixtures to nitrogen gas at 1500°C for 1 hour. The amounts of the ingredients were calculated according to equation 3.1 given in the experimental procedure part. All of the experiments were conducted twice in order to control the results exactly. The amounts of the ingredients for the samples are given in Table 4.4.

Table 4.4 Amounts of the ingredients for plain and 5 wt % to 50 wt % colemanite added samples

	Weight of ingredients in grams						
	Plain	**5%**	**10%**	**15%**	**22.64%**	**35%**	**50%**
B_2O_3	1.986	1.937	1.890	1.844	1.778	1.679	1.569
C	0.514	0.514	0.514	0.514	0.514	0.514	0.514
Colemanite	0	0.123	0.240	0.354	0.519	0.768	1.042

After the samples were removed from the furnace, they were cut in to half. Pictures of the plain, 5 wt % and 15 wt % colemanite added samples are given in Figure 4.8. It is seen from these pictures that 5 wt % colemanite added sample is more porous than plain and 15 wt % colemanite added samples.

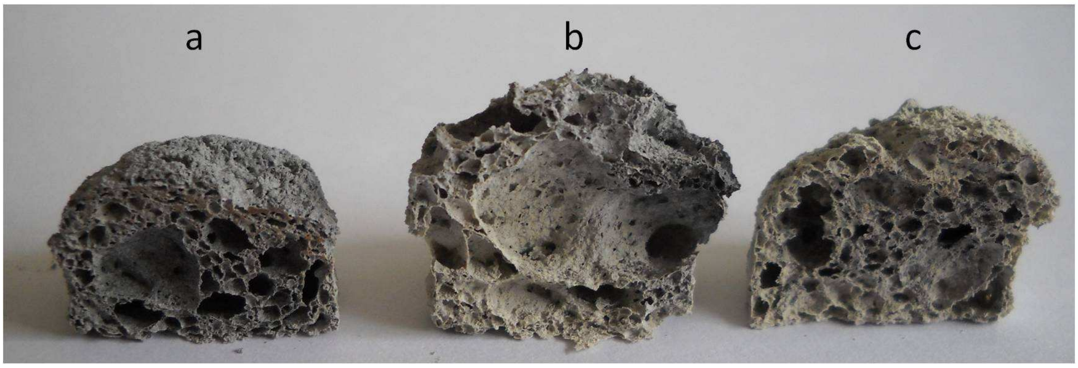


Figure 4.8 Pictures of a) plain, b) 5 wt % and c) 15 wt % colemanite containing samples

Pictures of 10 wt %, 22.64 wt %, 35 wt % and 50 wt % colemanite added samples are given in Figure 4.9. These pictures show that addition of colemanite after 10 wt % decreases the porosity of the pellet.

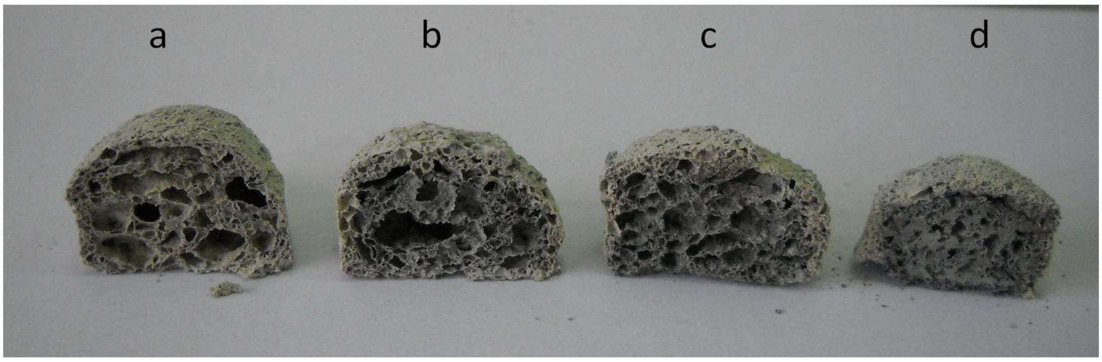


Figure 4.9 Pictures of a) 10 wt %, b) 22.64 wt % and c) 35 wt % and d) 50 wt % colemanite containing samples

After the products were removed from the furnace, leaching-oxidation-leaching process summarized in Figure 4.1 was applied to them. The amounts of final h-BN, B_2O_3 and CaO, B_4C and C calculated are given in Table 4.5.

Table 4.5 Amounts of h-BN, B_2O_3, CaO and B_4C in grams in the final products of the experiments conducted with plain and 5 wt % to 50 wt % colemanite added samples using boric acid supplied from Merck Company

Colemanite %	**h-BN**	**B_2O_3 + CaO**	**B_4C**	**Unreacted C**
0	0.360	0.60	0.02	0.07
0	0.354	0.72	0.03	0.07
5	0.428	0.77	0.01	0.04
5	0.396	0.86	0.01	0.04
10	0.405	0.68	0.01	0.04
10	0.398	0.86	0.02	0.07
15	0.378	0.99	0.02	0.06
15	0.338	0.86	0.03	0.06
22,64	0.342	0.93	0.02	0.05
22,64	0.313	0.89	0.03	0.05
35	0.258	1.13	0.03	0.06
35	0.271	1.11	0.03	0.05
50	0.227	1.26	0.04	0.07
50	0.212	1.31	0.04	0.06

This table shows that amounts of the sum of B_2O_3 and CaO are increasing with colemanite addition. This is an expected result since amounts of the ingredients are increasing with colemanite addition too. In addition, amount of h-BN formed is increasing up to 5 wt % colemanite addition and then it decreases which is an indication of the fact that the product contains larger amount of unreacted B_2O_3 and formed calcium borate phase for colemanite concentrations larger than 5 wt %. According to the phase diagram of B_2O_3- CaO given in Figure 4.12, amount of calcium borate phase increases with increasing CaO percentage up to composition a' shown on the diagram and for larger CaO contents, there are calcium borate compounds without any B_2O_3. Therefore, while increase in the $CaCO_3$ addition increases the porosity of the pellet causing h-BN formation reaction to increase, decrease in B_2O_3 content of the pellet decreases the evaporation of B_2O_3 causing the reaction rate to decrease which results in an optimum composition of the mixtures. Same mechanism is operative for colemanite added samples giving the optimum composition of the pellets as 5 wt % colemanite added samples. According to Table 4.5, B_4C amount is decreasing up to 5 wt % colemanite addition then it increases for higher colemanite percentages.

Experiments explained above were conducted with boric acid supplied from Merck Company. Then, some experiments were also done by using boric acid supplied from Eti Mine Works General Management instead of that supplied from Merck Company in order to compare the results of the experiments. The resultant h-BN, B_2O_3 and CaO and B_4C amounts are given in Table 4.6.

Table 4.6 Amounts of h-BN, B_2O_3 and CaO and B_4C in grams in the final products of the experiments conducted with plain and 5 wt % and 22.64 wt % colemanite added samples using boric acid supplied from Eti Mine Works General Management

%Colemanite	h-BN	B_2O_3 + CaO	B_4C	Unreacted C
0	0.348	0.55	0.02	0.05
0	0.336	0.62	0.03	0.07
5	0.395	0.84	0.02	0.06
22.64	0.303	0.96	0.03	0.06

Graph showing h-BN amounts changing with colemanite percentages is given in Figure 4.10. This graph was drawn according to values given in Tables 4.5 and 4.6.

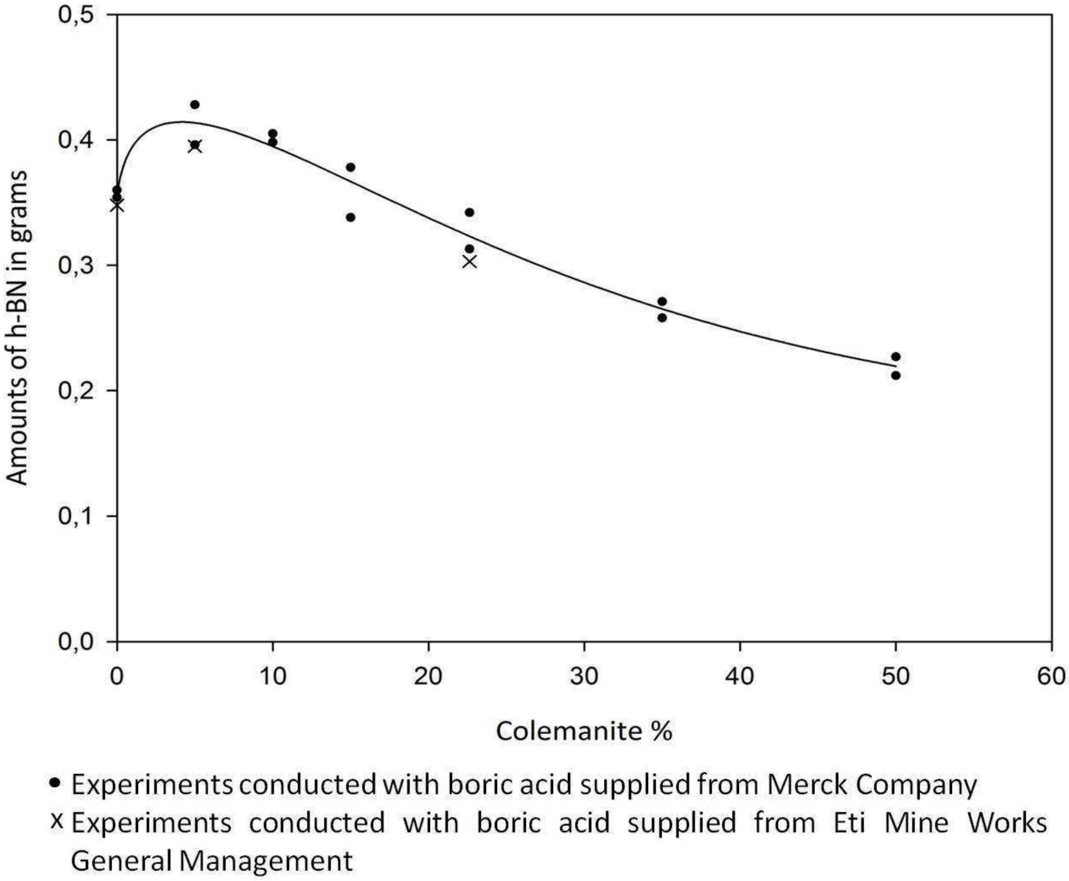


Figure 4.10 Change in the amounts of h-BN with colemanite percentages for the experiments conducted at 1500°C for 1 hour

As can be seen from Figure 4.10, the results of the ingredients of the products are similar for the experiments conducted using boric acid supplied from 2 different companies which means that h-BN formation using boric acid and colemanite supplied from a Turkish Company is possible by the carbothermic method.

The maximum amount of final boron nitride was expected to be at 22.64 wt % colemanite added sample since it is equivalent in terms of the calcium oxide and boric oxide amounts to 10 wt % calcium carbonate added sample. However 5 wt % colemanite addition which is equivalent to 2.4 wt % $CaCO_3$ addition gave the maximum amount of final h-BN. The reason for this should be related to impurity oxides in the colemanite which may also affect the carbothermic formation of h-BN.

In his study, Çamurlu [5] stated that, in addition to direct carbothermic reduction, boron nitride forms with a second mechanism in calcium carbonate added samples. Nitrogen gas passing over the samples dissolves in the calcium borate melt forming nitrogen ions at 1500°C. He stated that nitrogen dissolves in oxide melts as N^{3-} and N^{-} ions. These nitrogen ions then react with borate ions forming h-BN. Martinez et al.[39] stated that nitrogen solubility in the oxide melts depends on the basicity and temperature of the system and slag basicity depends on the relative amounts of the basic and acidic oxides in the melt

Wakasugi et al [40] has concluded that hexagonal boron nitride is also soluble in oxide melts and the solubility depends on the temperature and the composition of the oxide melts. When the solubility limit of nitrogen is exceeded, formation of h-BN from a boric oxide melt is possible.

Çamurlu [5] suggested that the reactions between nitrogen and borate ions to form BN may be the reactions 4.2 and 4.3.

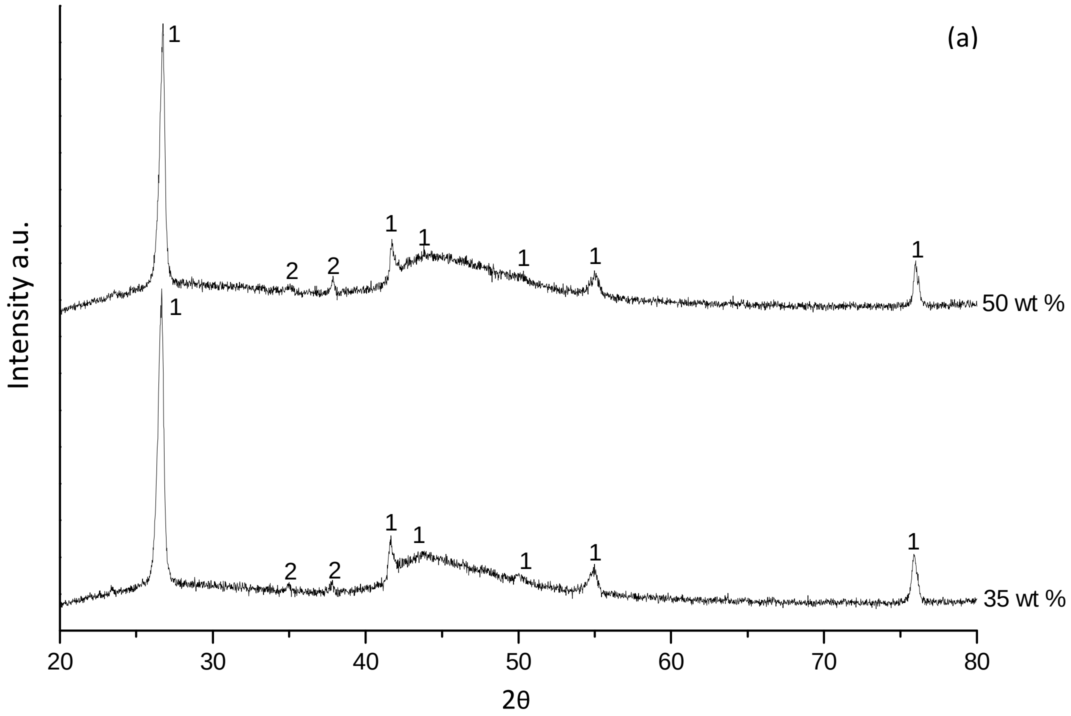
$(BO_3^{3-}) + (N^{3-}) = BN(s) + 3O^{2-}$ Reaction 4.2

$(B_2O_4N)^{5-} = BN(s) + (BO_3^{3-}) + O^{2-}$ Reaction 4.3

Colemanite consists of some other oxide impurities such as SiO_2, MgO and SrO as explained above. These impurities change the basicity of the slag resulting in the nitride capacity of the melt to change which results in quantity of h-BN forming by the ionic mechanism to change.

In the light of the foregoing, the oxide impurities in the colemanite may catalytically affect h-BN formation reaction and they may also change the nitride capacity. These two factors change the optimum amounts of colemanite added and pure calcium carbonate added samples.

XRD patterns of the samples before leach are given in Figure 4.11.



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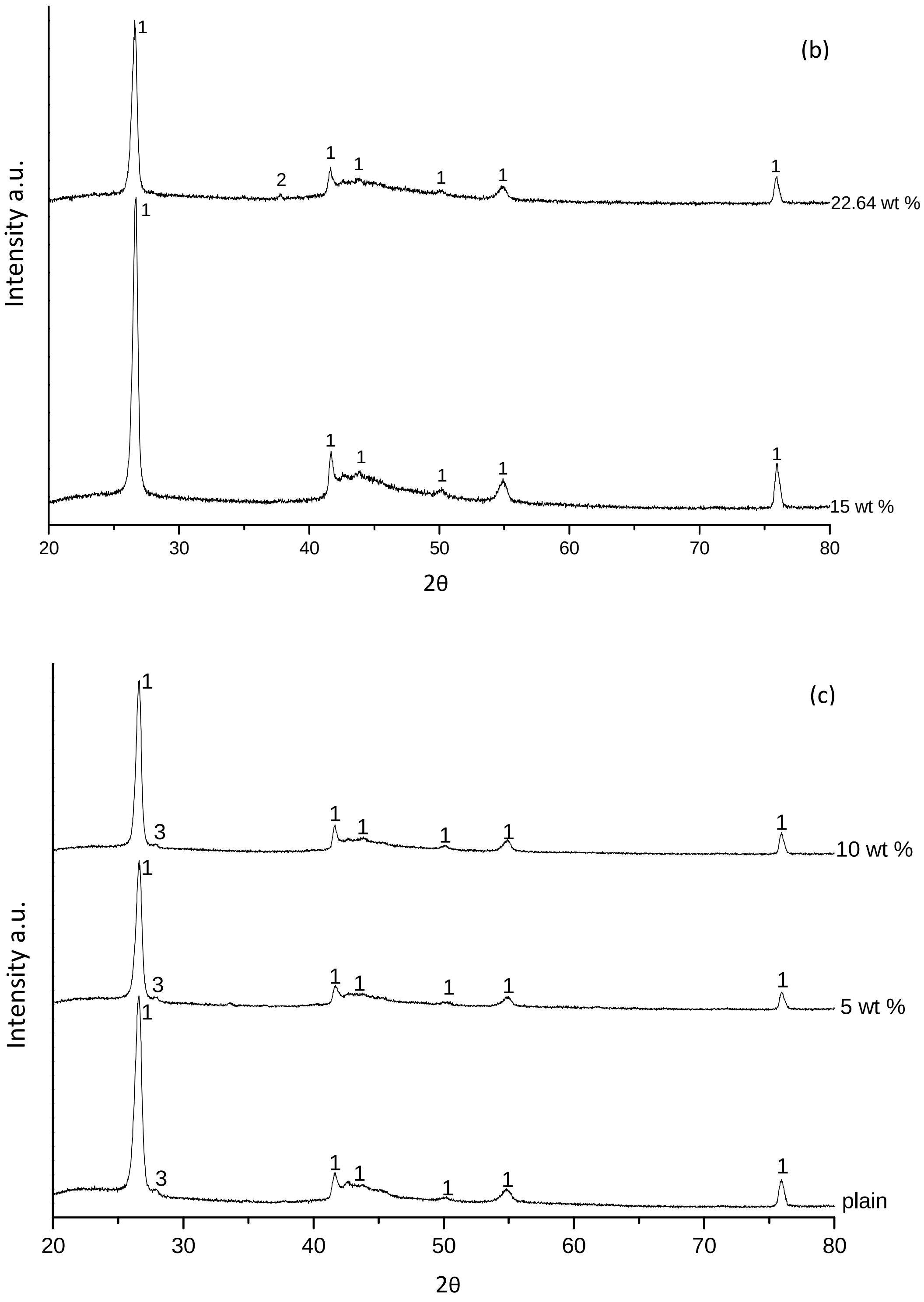


Figure 4.11 XRD patterns of; a) 50 and 35 wt % colemanite added mixtures, b) 22.64 and 15 wt % colemanite added mixtures, c) 10 wt % and 5 wt % colemanite added and plain mixtures before leach; 1: h-BN, 2: B_4C, 3: H_3BO_3

Çamurlu et al [25] reported that formation of BN from B_4C according to reaction 2.4 is slower than direct carbothermic reduction of B_2O_3 to BN according to reaction 2.6. They also stated that B_4C formed during reaction retards the h-BN formation reaction. Therefore, prevention of formation of B_4C is necessary in order to increase the rate of reaction. In these experiments, the amounts of boron carbide decrease up to 5 wt % colemanite addition and then increase with colemanite additions as shown on the previous table. Boron carbide peaks are seen in the XRD patterns of the samples containing 22.64 wt %, 35 wt % and 50 wt % colemanite.

B_2O_3 and CaO phase diagram is given in Figure 4.12. This diagram shows that B_2O_3 and CaO form four compounds during heating which are $CaO.2B_2O_3$, $CaO.B_2O_3$, $2CaO.B_2O_3$ and $3CaO.B_2O_3$ in the solid state and at 1500°C, the mixtures with CaO content smaller than 80 wt % is in the liquid form.

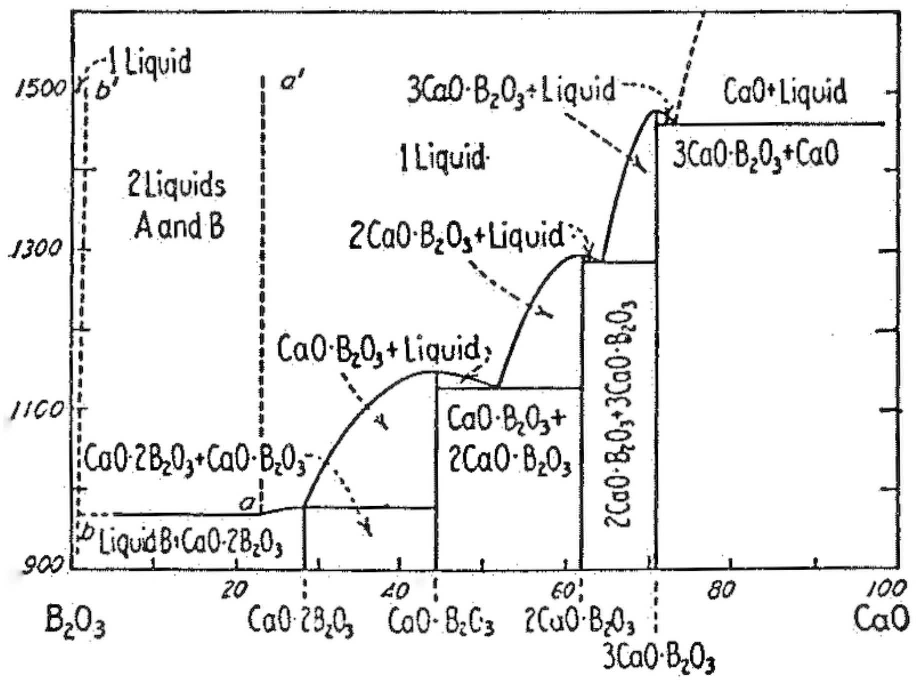


Figure 4.12 B_2O_3-CaO phase diagram [41]

At compositions to the left of a’, there are two phases in the system at 1500°C. One of these phases is B_2O_3(l) and the second phase is CaO.2B_2O_3(l). The XRD patterns of the experiments conducted with 5 wt % and 10 wt % colemanite concentrations show H_3BO_3 peaks which indicate that the compositions of these mixtures are to the left of a’. However, increasing the colemanite concentration of the mixtures which leads to higher CaO content, decreases B_2O_3 content of the mixture as expected from the phase diagram. As a result, XRD patterns of the samples with higher colemanite percentages than 10 wt % do not show any H_3BO_3 peaks. The XRD patterns of the samples do not show any calcium borate phase which may be due to solidification of these phases in to an amorphous structure.

XRD patterns of the samples after leach are given in Figure 4.13. These patterns show no other peak than h-BN as expected.

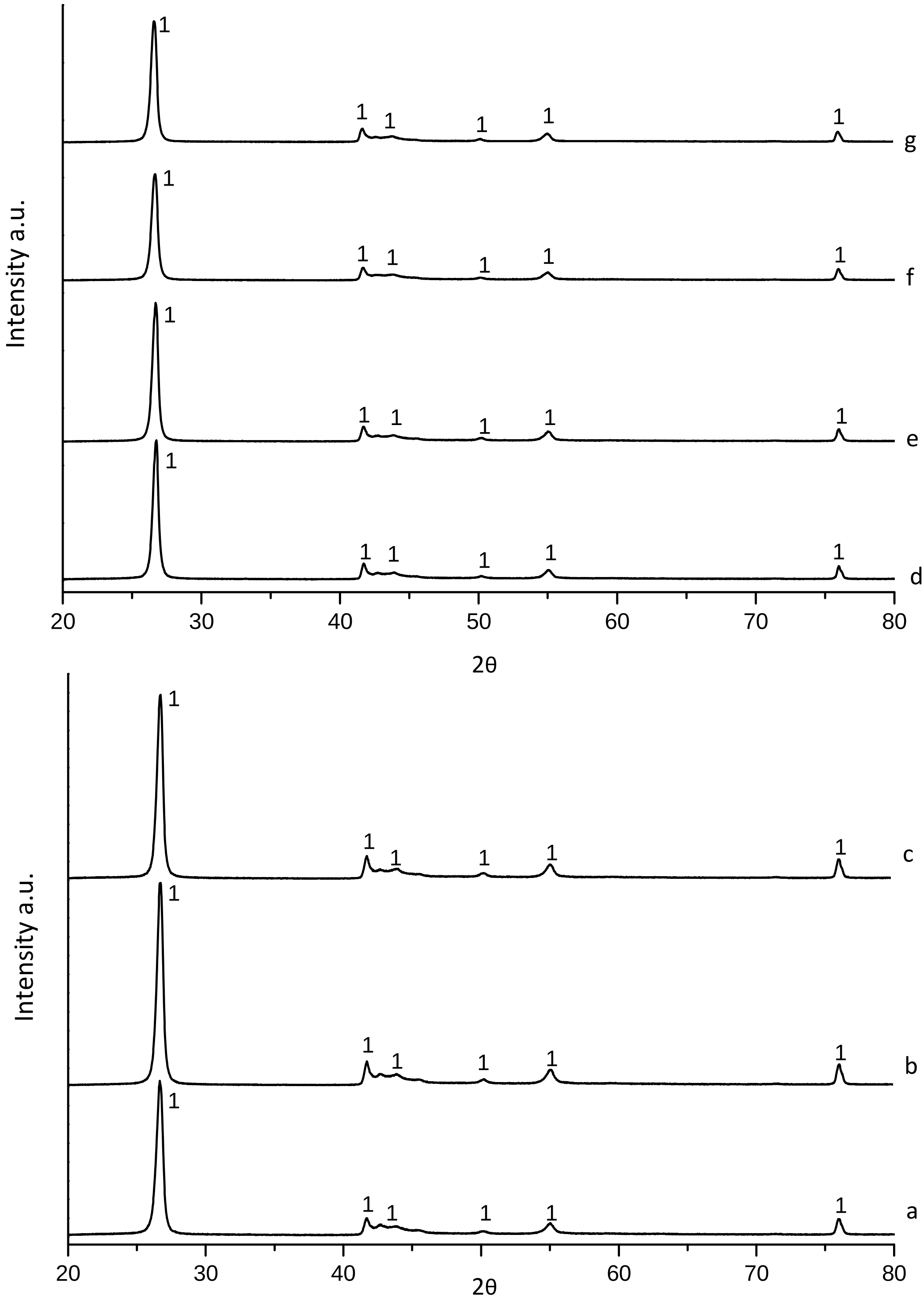


Figure 4.13 XRD patterns of; a) Plain mixture, b) 5 wt % colemanite added mixture, c) 10 wt % colemanite added mixture, d) 15 wt % colemanite added mixture, e) 22,64 wt % colemanite added mixture, f) 35 wt % colemanite added mixture,(g) 50 wt % colemanite added mixture after leach, 1: h-BN

In their study, Çamurlu et al [20] stated that addition of $CaCO_3$ to the initial mixtures increases the particle size of h-BN formed. They concluded that $CaCO_3$ addition encourages the formation of particles having separate surfaces with definite edges different from the merged polycrystalline form of particles seen in the samples without $CaCO_3$ addition. SEM images of plain and 5 wt % colemanite added samples after leaching process are given in Figures 4.14 and 4.15, respectively.

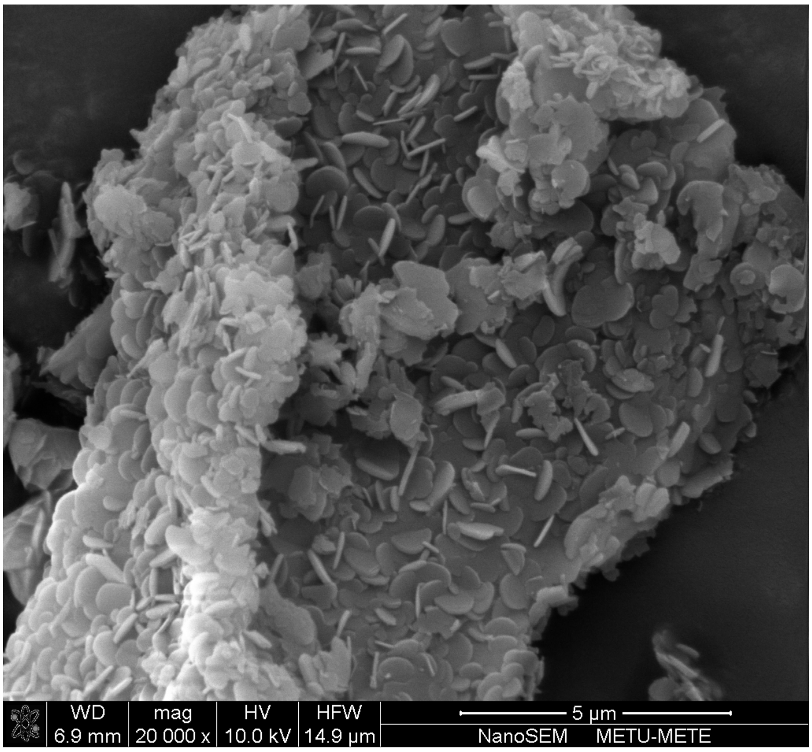


Figure 4.14 SEM image of plain mixture after leaching process

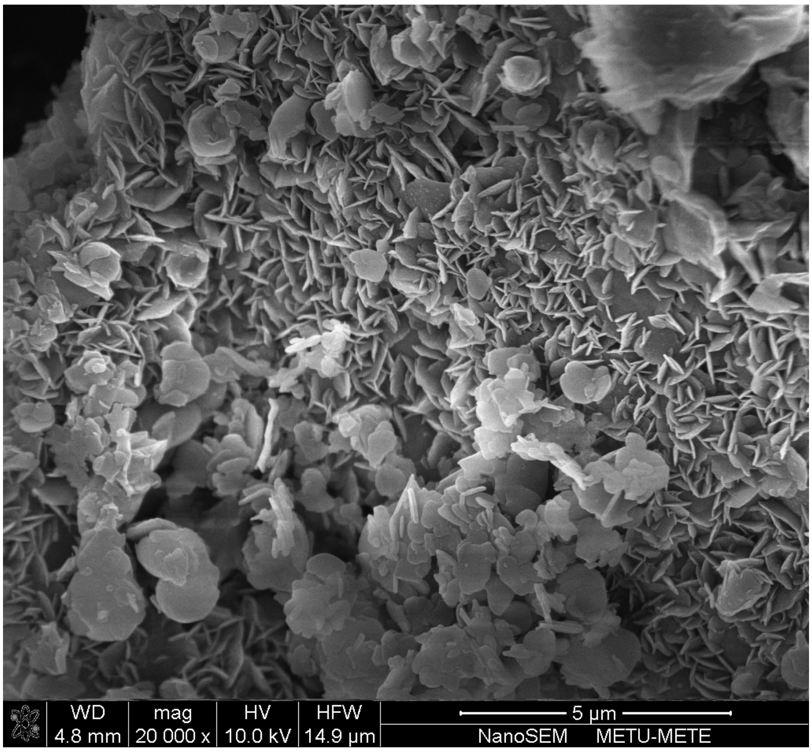


Figure 4.15 SEM image of 5 wt % colemanite added sample after leaching process

The particle size of plain mixture was measured as 490 ± 110 nm and particle size of 5 wt % colemanite containing sample was found to be 849.4 ± 144.8 nm. These results show that addition of colemanite also increases the particle sizes of h-BN. In addition, it can be seen from the images that h-BN particles have separate surfaces with definite edges in colemanite added samples similar to $CaCO_3$ added samples.

SEM image of 5 wt % colemanite added sample before leach is given in Figure 4.16. Flake like boron nitride particles in the calcium borate matrix is observed in this micrograph.

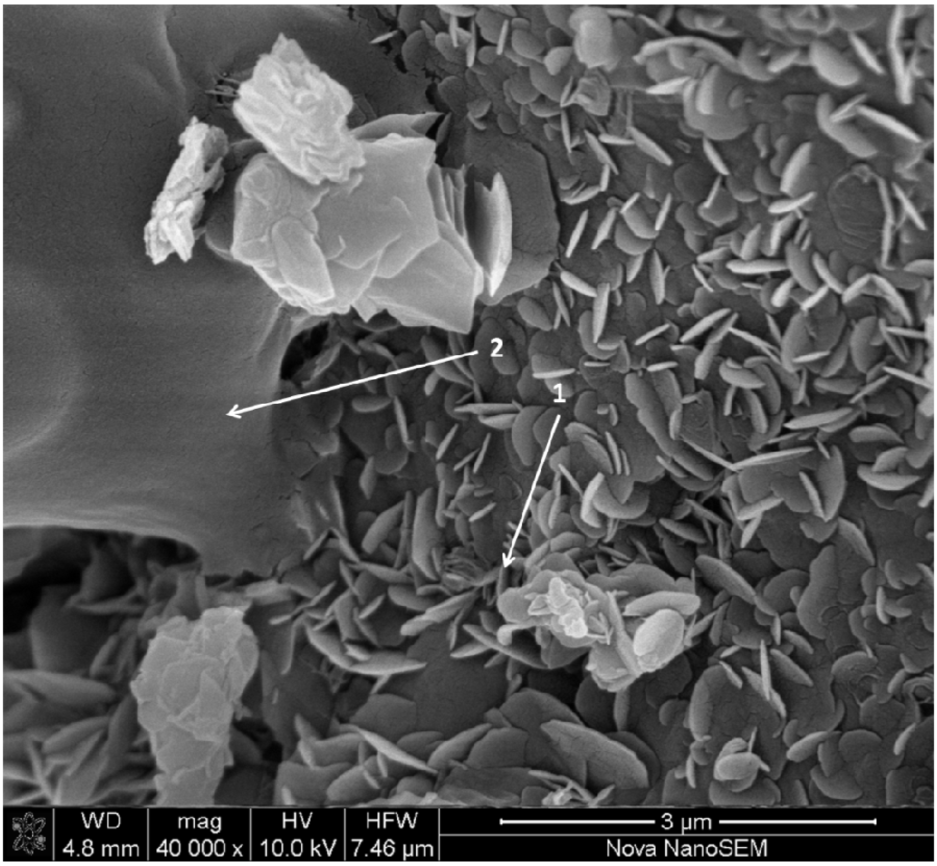


Figure 4.16 SEM image of 5 wt % colemanite added sample before leach; 1: Flake like h-BN particles, 2: Calcium borate matrix

4.3 Effect of Duration

Effect of duration to the h-BN formation reaction was investigated by subjecting 5 wt % colemanite added samples which was found to be the optimum composition to nitrogen gas at 1500°C for durations between 0.5 to 5 hours.

Çamurlu et al [25] stated that, the amount of h-BN formed is increasing with increasing reaction time and the reaction in 10 wt % $CaCO_3$ added sample is complete in 2 hours at 1500°C. He also stated that B_4C forms in the first 30 minutes of the reaction then it disappears in the reaction products. He explained this to be due to high carbon concentration in the initial stages of the reaction which decreases with time due to reaction and carbon losses. Thereafter, the formation of boron nitride from boron oxide carbon mixtures become dominant in the next stages which cause the consumption of B_4C decreasing B_4C amount in the reaction products.

Effect of time was expected to be similar for colemanite added samples and 5 wt % colemanite added sample was chosen to be used in the experiments. Pictures of the products of the experiments conducted for 0.5 to 3 hours are given in Figure 4.17. It is seen from this figure that the color of the pellets are changing with increasing duration of the reaction which is an indication of formation of boron nitride giving pellet a white color. The sizes of the pellets become smaller with increasing reaction time due to B_2O_3 consumption by reaction and evaporation.

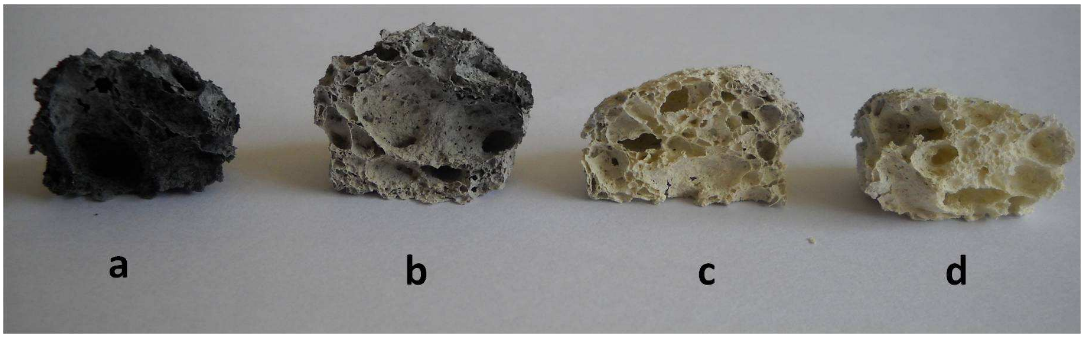


Figure 4.17 Pictures of the products of the experiments with 5 wt % colemanite added sample for a) 0.5 hours, b) 1 hours, c) 2 hours, d) 3 hours.

Amounts of h-BN formed, B_2O_3 and calcium borate and B_4C of the reaction products of the experiments conducted for 0.5 to 5 hours is given in Table 4.7.

Table 4.7 Amounts of the boron nitride formed, B_2O_3 and calcium borate and B_4C of the experiments conducted for 0.5 to 5 hours in grams.

Duration (hours)	**h-BN**	**B_2O_3 and calcium borate**	**B_4C**	**Unreacted C**
0.5	0.102	1.127	0.024	0.18
0.5	0.0998	1.029	0.05	0.17
1	0.428	0.769	0.012	0.04
1	0.396	0.859	0.012	0.04
2	0.461	0.748	0.006	0.06
2	0.521	0.682	0.006	0.05
3	0.595	0.629	0.007	0.05
3	0.57	0.334	0.005	0.05
4	0.575	0.329	0	0.05
5	0.582	0.233	0	0.04

Figure 4.18 shows the amounts of h-BN in the reaction products changing with duration of the experiments.

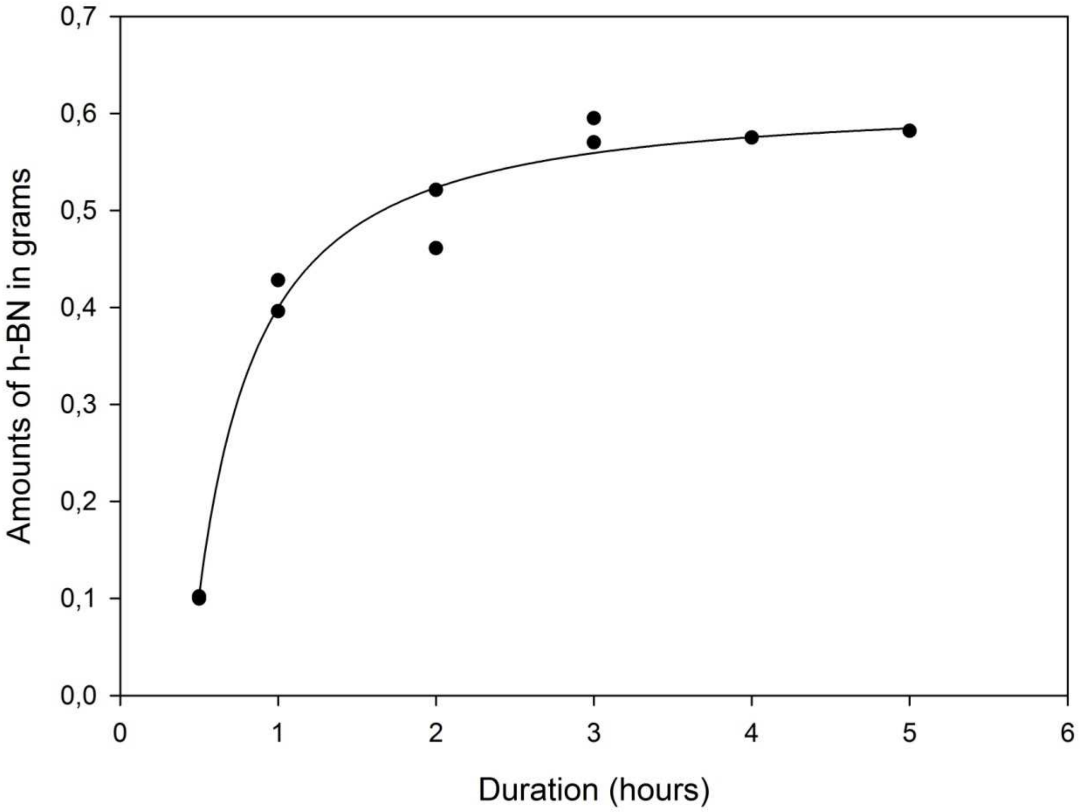


Figure 4.18 Amounts of h-BN changing with reaction duration for 5 wt % colemanite added sample

As can be seen from this figure, formation of h-BN is increasing drastically in durations increasing from 0.5 to 2 hours. In addition, amounts of h-BN are slightly increasing between 2 and 3 hours which become constant for longer durations.

XRD pattern of the sample with the experiment conducted for 3 hours is given in Figure 4.19. There is no other peak than BN and H_3BO_3 seen in the pattern of the experiment before leach. H_3BO_3 peak seen in the XRD pattern of before leach sample shows that the composition of the sample is left of A shown in B_2O_3- CaO phase diagram (Figure 4.12).

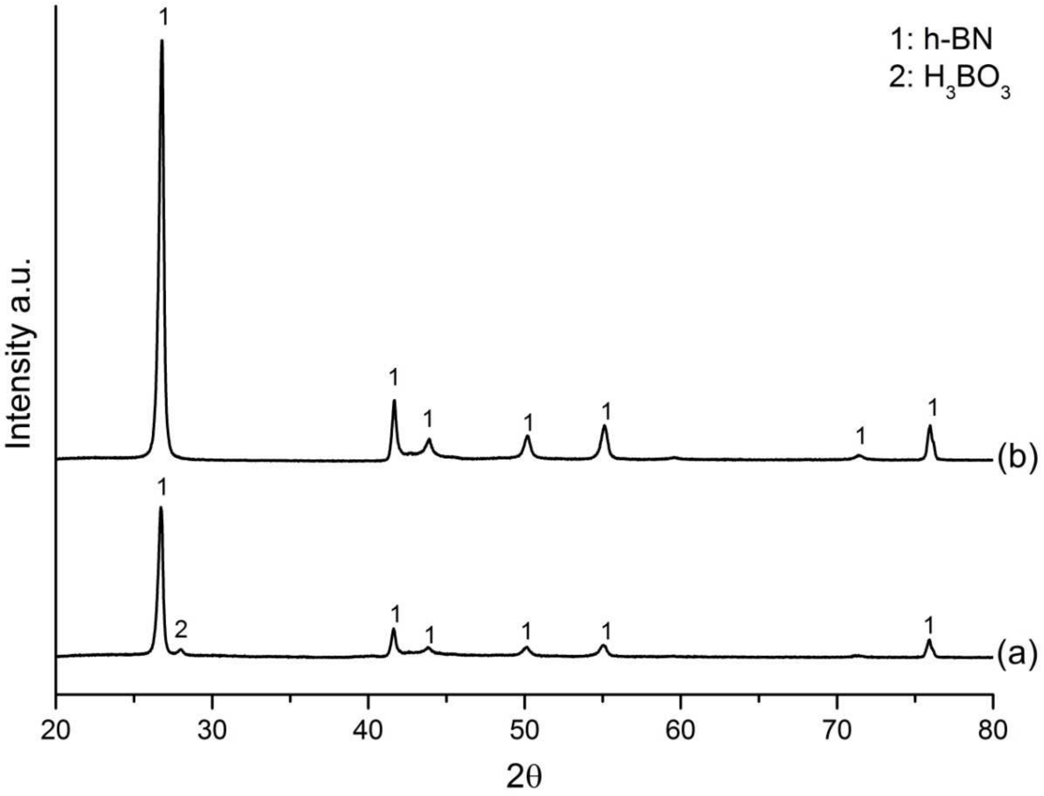


Figure 4.19 XRD patterns of the 5 wt % colemanite added sample after the experiment conducted for 3 hours a) before leach, b) after leach.

Amounts of B_4C formed in the reaction products is seen to increase in the first 30 minutes of the experiments then it decreases as can be seen from Table 4.17. This is an expected result and consistent with the results of Çamurlu et al[25]. XRD patterns of the sample of the experiment conducted for 30 minutes before and after leaching process are given in Figure 4.20.

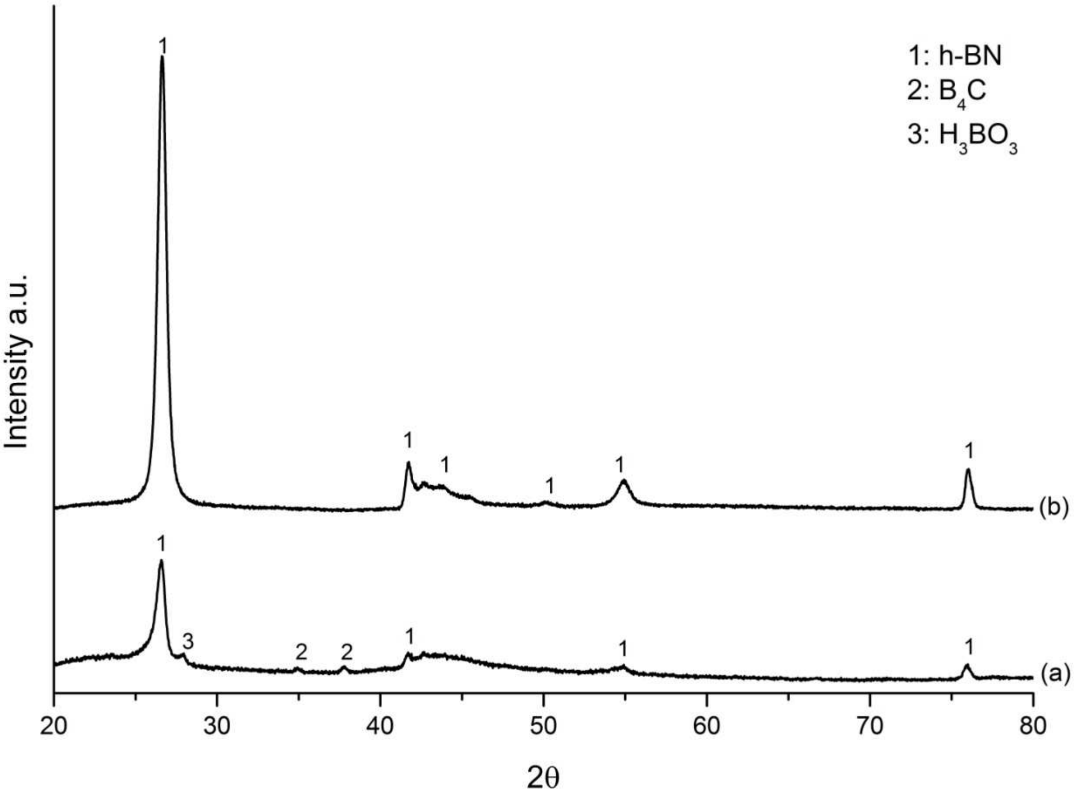


Figure 4.20 XRD patterns of the 5 wt % colemanite added sample after the experiment conducted for 0.5 hours a) before leach, b) after leach.

XRD pattern of the sample before leach shows B_4C peaks which is consistent with the resultant amounts of the ingredients in the products of the experiment conducted for 30 minutes. XRD pattern of the sample with the experiment conducted with 5 wt % colemanite addition for 1 hour before leaching process shown in Figure 4.11 shows no B_4C peaks which is an indication of the fact that B_4C is consumed in the second 30 minutes of the experiment as indicated by Çamurlu et al [25].

The amounts of C shown in Table 4.7 shows that C is not completely consumed even in 5 hours. These results may be due to measurement errors during leaching process since the amounts are very small and a small error in measurement may cause large differences in the results. Secondly, the reason of these C amounts may be the properties of the melt forming with colemanite addition. The physical properties of the melt such as density, viscosity etc. may cause C not to be consumed completely during the reaction.

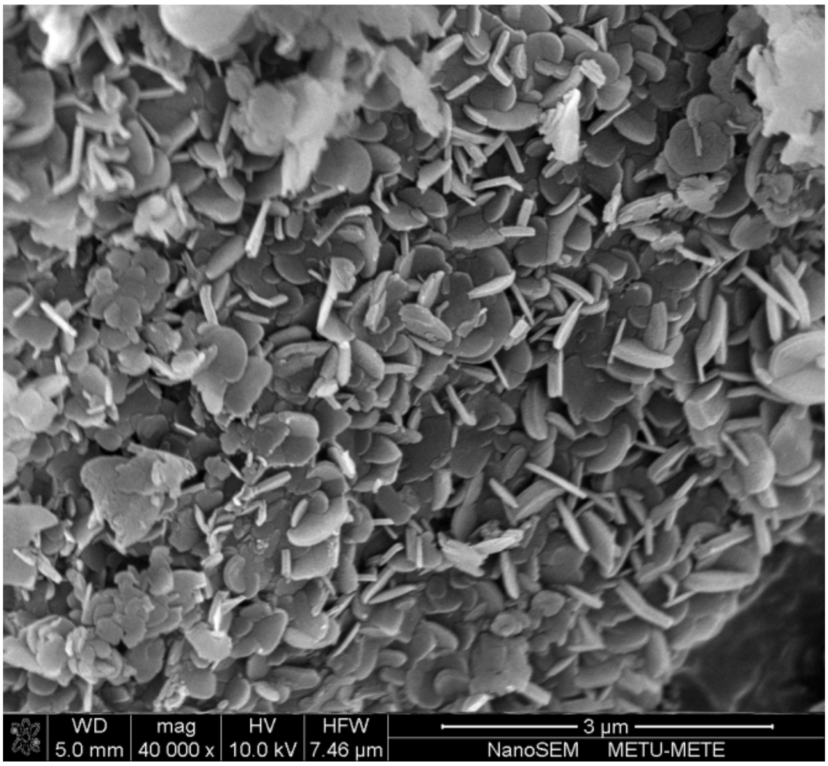
Effect of reaction time on particle sizes of h-BN formed was analyzed by using SEM micrographs of the products. SEM images of the products with experiments conducted for 0.5, 2 and 3 hours are given in Figure 4.21. Table 4.8 shows the particle size analysis changing with reaction time.

Table 4.8 Particle sizes of h-BN formed for the experiments conducted for 0.5 to 5 hours.

Duration (hours)	Particle size (nm)
0.5	438.81±100.34
1	849.41±144.75
2	913.44±222.72
3	1276.46±427.46
4	1310.37±256.42
5	1333.88±264.88

Particle size analysis shown in Table 4.8 shows that particle sizes of h-BN formed is increasing drastically in the first 3 hours of the experiment while particle sizes for 4 and 5 hours of experiments are increasing slightly.

a)



b)

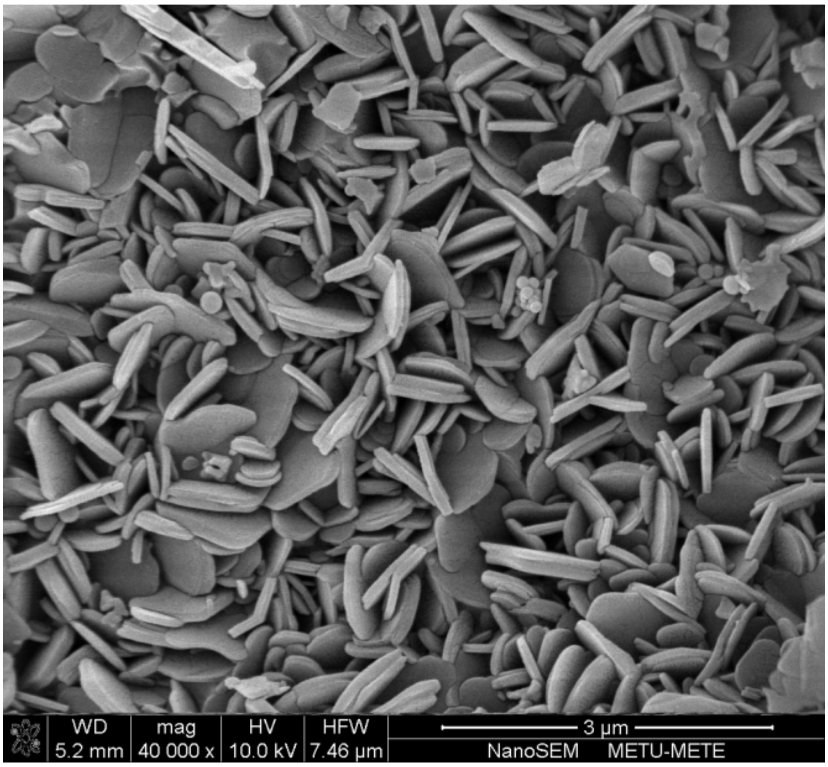


Figure 4.21 continued on the next page

c)

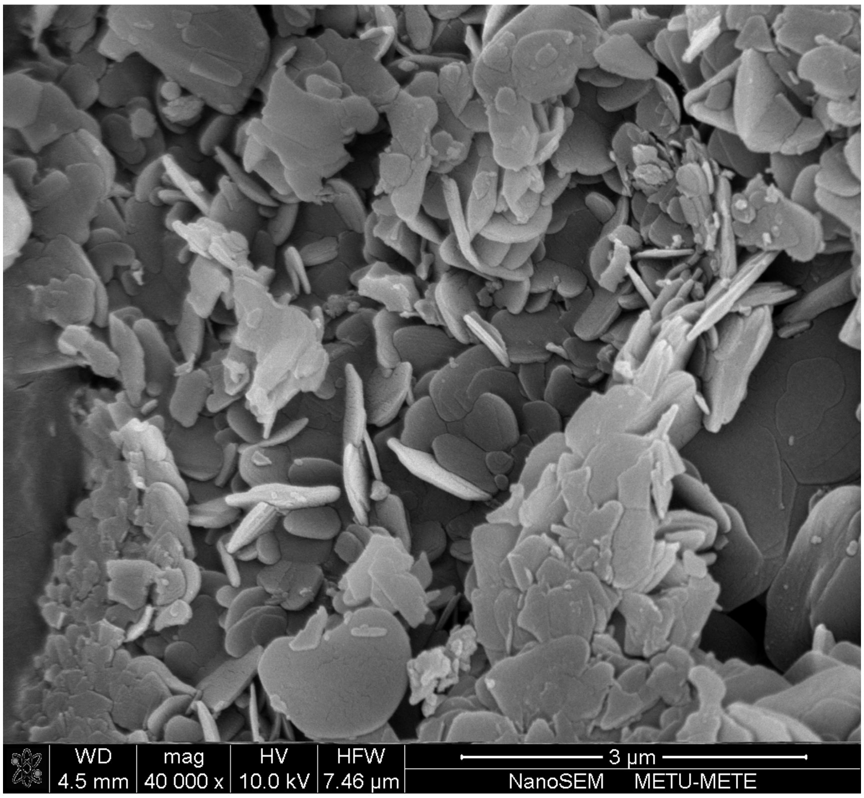


Figure 4.21 SEM images of the products of experiments conducted for a) 0.5 hours, b) 2 hours and c) 3 hours after leaching process

When the results of the experiments conducted for 2 hours with 10 wt % $CaCO_3$ added sample explained in section 4.1 and 5 wt % colemanite added sample explained in this section are compared, it can be seen that while the amount of h-BN formed with 10 wt % $CaCO_3$ addition is 0.471 grams, that with 5 wt % colemanite addition is 0.521 grams which shows that the amount of h-BN formed in 2 hours is increasing with 5 wt % colemanite addition instead of 10 wt % $CaCO_3$ addition. In addition when the particle sizes of two samples are compared; while the product of the experiment conducted for 2 hours with 10 wt % $CaCO_3$ addition has a particle size of 850 ± 460 nm, that with 5 wt % colemanite addition has a particle size of 913.44±222.72 nm. In light of the foregoing, addition of optimum amount of colemanite gives more amount and coarser particle size of h-BN formed than that of $CaCO_3$.

CHAPTER 5

CONCLUSION

This study was conducted in order to see whether h-BN formation by carbothermic reduction method using commercial boron products in Turkey namely colemanite mineral and boric acid is possible or not. In previous studies conducted in this department, carbothermic production of h-BN was studied by many researchers and it was found that addition of 10 wt % $CaCO_3$ addition to initial boric oxide-activated carbon mixtures increases the reaction rate resulting in an increase in the amount of h-BN formed [5, 6, 13, 31]. Colemanite is a mineral consisting of both CaO and B_2O_3. Therefore, it was decided to use this mineral instead of using B_2O_3 and CaO separately.

In the first set of experiments, plain, 10 wt % $CaCO_3$ added and 22.64 wt % colemanite added samples were subjected to nitrogen gas at 1500°C. 10 wt % $CaCO_3$ addition and 22.64 wt % colemanite addition gives the same amounts of CaO to the initial mixtures. Total B_2O_3 coming from B_2O_3 added and B_2O_3 coming from colemanite addition was chosen to be constant and it was decided to be the same amount used in the previous studies which is 100 % excess of the amount calculated by stoichiometry of reaction 2.6. The results of these experiments showed that addition of 10 wt % $CaCO_3$ and 22.64 wt % colemanite gives similar amounts of h-BN formed in the reaction product which is higher than plain mixture. In his study, Özkenter [6] stated that CaO addition also catalytically affect h-BN formation. However he stated that, $CaCO_3$ addition gives higher amounts of boron nitride in the final product due to CO_2 gas release causing porosities in the pellet. Nitrogen penetration to these porosities causes the reaction rate to increase. Colemanite also gets calcined during the reaction which gives porosity to the pellet similar to $CaCO_3$. Çamurlu et al[20] stated that when $CaCO_3$ is added to the initial mixtures, a calcium borate melt forms. Nitrogen gas passing over the sample dissolves in this melt which results in the formation of h-BN by a second mechanism called ionic mechanism. Same quantities of h-BN in the final products of $CaCO_3$ and colemanite added samples show that the same mechanism is operative in colemanite added samples. The leaching process applied to plain and $CaCO_3$ added samples were also applied to colemanite added samples and the product of leach was seen to be pure h-BN which is an indication of the fact that leaching process used is appropriate for colemanite added samples too. Particle size analysis of these samples showed that addition of colemanite instead of $CaCO_3$ gives higher particle sizes of h-BN formed. In addition, similar to $CaCO_3$ addition, colemanite addition results in particles having separate surfaces with definite edges.

In colemanite mineral, there are some other oxides than B_2O_3 and CaO such as SiO_2, MgO and SrO as impurities which may also affect the reaction rate. Therefore, it was decided to change the composition of colemanite added samples. During these experiments, total B_2O_3 was chosen to be constant and the amounts of the ingredients were calculated according to equation 3.1. Colemanite % was calculated to be the percentage of the sum of B_2O_3 added and activated carbon. Experiments were conducted for 1 hour at 1500°C. As a result of these experiments, 5 wt % colemanite addition was found to be the optimum amount for the maximum h-BN formation. 5 wt % colemanite addition gives the same amount of CaO to the mixture with 2.4 wt % $CaCO_3$ addition. Change in the optimum amounts were discussed to be the effect of other oxides coming from colemanite to the mixtures. These oxides may also catalytically affect h-BN formation reaction which changes the optimum amount. In addition, CaO and B_2O_3 forms a calcium borate melt at 1500°C and oxides coming from colemanite is thought to dissolve in this borate melt. Nitrogen dissolution is strongly dependent on the basicity of this melt and these oxides are thought to change the basicity of this melt resulting in the nitride capacity to increase causing h-BN formation by ionic mechanism to increase. In addition, addition of 5 wt % colemanite to plain mixture was seen to increase the particle sizes of h-BN formed. Same experiments with plain, 5 wt % and 22.64 wt % colemanite addition were conducted by using boric acid supplied from Eti Mine Works General Management instead of Merck Company. The results of the experiments were found to be similar which means that using commercial boric acid from Eti Mine Works General Management which is a Turkish company instead of Merck grade boric acid is appropriate.

Finally effect of time on amount and structure of h-BN formed in the product were investigated. Experiments were done at 1500°C for durations between 0.5 to 5 hours with 5 wt % colemanite added mixture which was determined to be the optimum composition. Results of these experiments showed that increasing reaction duration increases the amount of h-BN formed as expected. While an important increase in amount of h-BN was observed between durations of 0.5 to 2 hours, a slight increase was observed between 2 and 3 hours and this amount remained constant for longer durations. B_4C was found to form in the first 30 minutes of the experiments then it disappears. Particle sizes of the products were calculated by using SEM images of the products after leach. Particle sizes of h-BN were observed to increase considerably in the first 3 hours of the experiment. For longer durations, particle size was observed to increase slightly.

When optimum compositions of $CaCO_3$ added sample and colemanite added sample are compared in terms of final amount of h-BN for experiments conducted for 2 hours at 1500°C, it was seen that amount of h-BN formed by the optimum amount of colemanite addition gives a higher value compared to $CaCO_3$ addition. In addition, it was seen that colemanite addition results in coarser particles than $CaCO_3$ addition.

As a result of this study, it was shown that using commercial grade colemanite and boric oxide supplied from Eti Mine Works General management which is a Turkish company is appropriate to produce hexagonal boron nitride which is an advanced ceramic with important properties and widespread application areas. Turkey is rich in boron minerals and raw materials and this study is important in terms of production of h-BN which is a valuable boron product from abundant boron minerals and raw materials in Turkey.

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