ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

SYNTHESIS OF THE BN-AlN COMPOSITES BY CARBOTHERMAL REDUCTION AND NITRIDITION OF B_4C-Al_2O_3 MIXTURES

MSc. THESIS

Engineer Cem ÇELİKER

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Supervisor	:	**Prof. Dr. Adnan TEKİN**
Member	:	**Prof. Dr. Okan ADDEMİR**
Member	:	**Doç. Dr. Onuralp YÜCEL**

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AlN-BN KOMPOZİTLERİNİN REAKSİYON SİNTERLENMESİ YÖNTEMİYLE ÜRETİMİ

YÜKSEK LİSANS TEZİ

Met. Müh. Cem ÇELİKER

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Tez Danışmanı : Prof. Dr. Adnan TEKİN

Diğer Jüri Üyeleri : Prof. Dr. Okan ADDEMİR

Doç. Dr. Onuralp YÜCEL

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JANUARY, 1997 **Cem ÇELİKER, B.Sc.**

CONTENTS

SYMBOL LIST

Kp : Equilibrium Constant
P : Pressure
ΔG : Standard Free Energy
T : Temperature
A : Activation
E : Activation Energy
eV : Electron Volt
R : Particle Size
Hv : Vickers Hardness
K_{1c} : Fracture Toughness
ε : Dielectric Constant

FIGURE LIST

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SYNTHESIS OF THE BN-AIN COMPOSITES BY CARBOTHERMAL REDUCTION AND NITRIDITION OF B4C-AI2O3 MIXTURES

SUMMARY

Aluminum nitride-boron nitride both have interesting properties such as high thermal conductivity, chemically inert to various molten metals, good electrical insulation. Boron nitride has excellent lubrication properties at relatively high temperatures up the 1000°C in air. Because of these unique properties, Boron nitride-aluminum nitride composites were recently attracted interest. There are several methods for the preparation of these composites. Reaction sintering is one of the most economical process.

The objective of this research was to produce BN-AIN composites from blended Al_2O_3-B_4C powders and to characterize the kinetics of sintering these compacts. This study covers the investigation of the mass transport mechanism, the effect of sintering variables on consolidation and homogenization, and the microstructural characterization of the sintered compact. Preforms contains different percentage of Al_2O_3 and B_4C were prepared using ceramic ball mill. In order to explain the effect of B_4C to sintering, preforms contains different percentage of B_4C (30, 50, 70 wt %) were prepared. The mixtures were dry pressed then sintered at 1750-1950°C for times ranging from 1/2 hour to 5 hour, under nitrogen flow in an graphite element resistance furnace.

Each sample was weighed before and after every sintering experiment to determine weight change. Sintered samples were cut and polished for SEM. Phase analysis of the sintered samples were analyzed by XRD.

The reaction sintering of Al_2O_3 and B_4C in N_2 atmosphere and densification of the composite in N_2 atmosphere at 1850-1950 °C were achieved by using Al_2O_3-B_4C powders as the starting materials. Sintering time does not have an appreciable effects at temperatures extended soak times result BN formation increased. X-ray diffraction analysis showed that the reaction was quite nearly achieved for all compositions. Better reaction sintering results have been obtained by using I.T.U. product B_4C powders containing higher level of free C remaining from charbothermal reduction of boric acid by petroleum coke in a arc-typed graphite resistance furnace. This effect occurred because natural reduction character of C.

B_4C-Al_2O_3 BAŞLANGIÇ TOZ KARIŞIMININ KARBOTERMAL REDÜKSİYONU VE NİTRİDASYONU İLE BN-AlN KOMPOZİTLERİNİN ÜRETİMİ

ÖZET

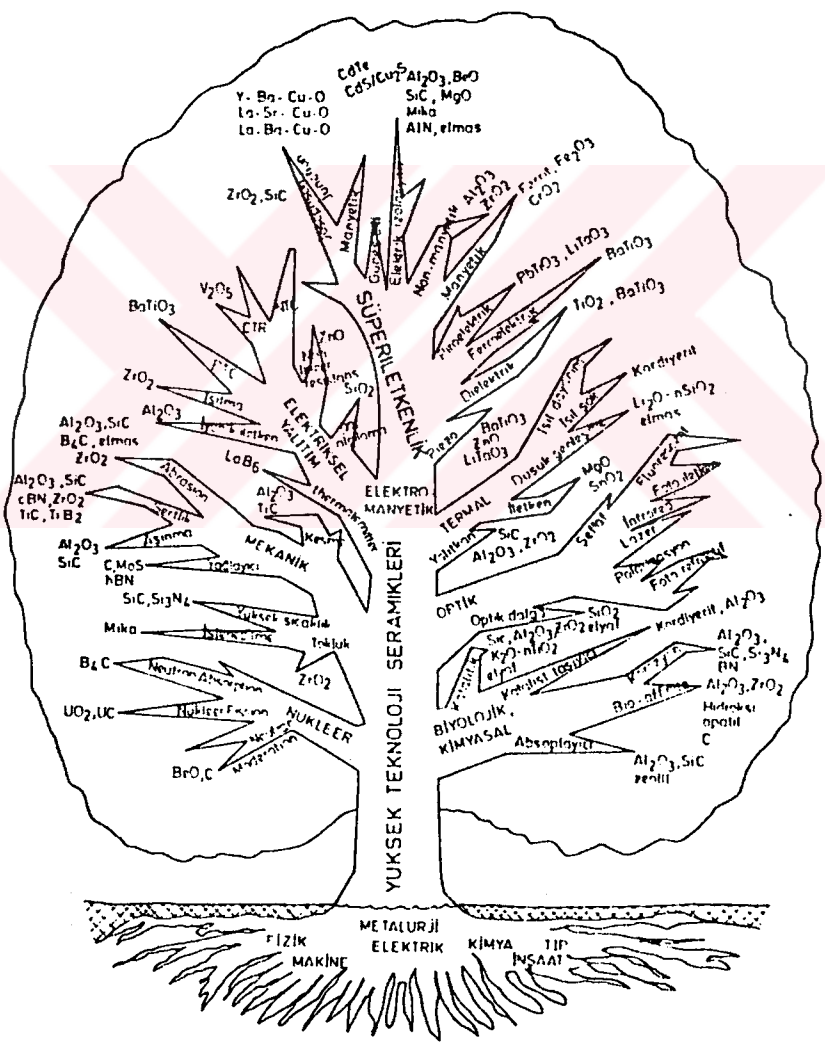
Son yıllarda teknolojide hızlı ilerleme sonucu, kullanılacak malzemelerden istenen ve beklenen özellik ve performanslar da artış olmuştur. Her yeni gelişme ve yeni uygulama, çok özel kabiliyetleri olan malzemelere ihtiyaç duymaktadır. Malzeme bilim ve mühendisliği bu gelişmelere paralel olarak hızla gelişmekte olup, hem gelişen teknolojilerin ihtiyacı olan malzemeler üretilmekte hemde geliştirilen yeni malzemeler sayesinde teknolojik alanda bazı yeni gelişmeler olmaktadır.

Günümüzde seramik endüstrisi dünya ekonomisinin büyük bir kısmına hitap etmektedir. Elektronik, uzay havacılık, nükleer enerji çalışmalarında seramik malzemelerin kullanımı günden güne artmaktadır. Seramik malzemelerin geliştirilmesi performanslarının arttırılması ve üretimi yapılan malzemenin maliyet fiyatının düşürülmesiyle sağlanmaktadır. Teknolojinin hızla gelişmesine paralel olarak malzemelerin servis ortamlarında maruz kaldıkları şartlar da değişmektedir.

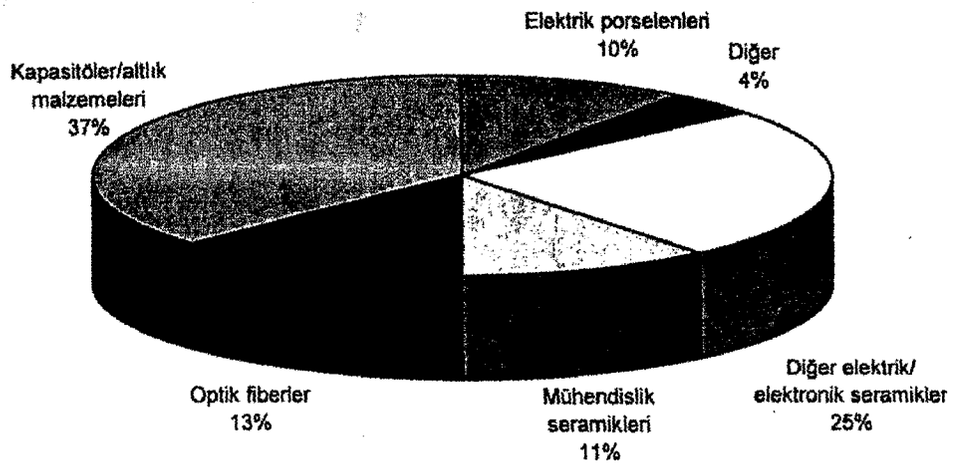
Seramik malzemeler kullanım sıcaklıkları, kimyasal dayanımları, sertlikleri, aşınma dirençleri göz önüne alındığında çok iyi mühendislik malzemeleri oldukları halde tokluk değerlerinin düşük olmalarından dolayı çok az kullanım alanı bulabilmişlerdir. Seramik malzemelerde tokluğu arttırmanın en uygun yolu kompozit malzeme anlayışıdır.

Potansiyel matriks malzemelerinin yoğunluklar ve kullanım sıcaklıkları baz alınarak yapılan kıyaslamalar sonucunda seramik malzemelerde yoğunluklar, özellikle metal matrikslere kıyasla oldukça düşük kullanım sıcaklıkları ise metal ve polimer matrikslere oranla oldukça yüksektir ve bu özellik nedeniyle tüm dünyada seramik matriksli kompozit malzemeler üzerinde çok yoğun çalışmalar sürdürülmektedir. Seramik malzemeler alanında kullanılan başlangıç tozlarının ince, saf, reaktif ve düşük sıcaklıklarda sinterlenebilir olması istenmektedir. Ayrıca klasik şekillendirme yöntemleriyle şekillendirilmeleri mümkün olmayan seramik malzemelere olan ihtiyacın artması ile bunların üretimini mümkün kılacak olan üretim yöntemlerine ihtiyaç artmaktadır.

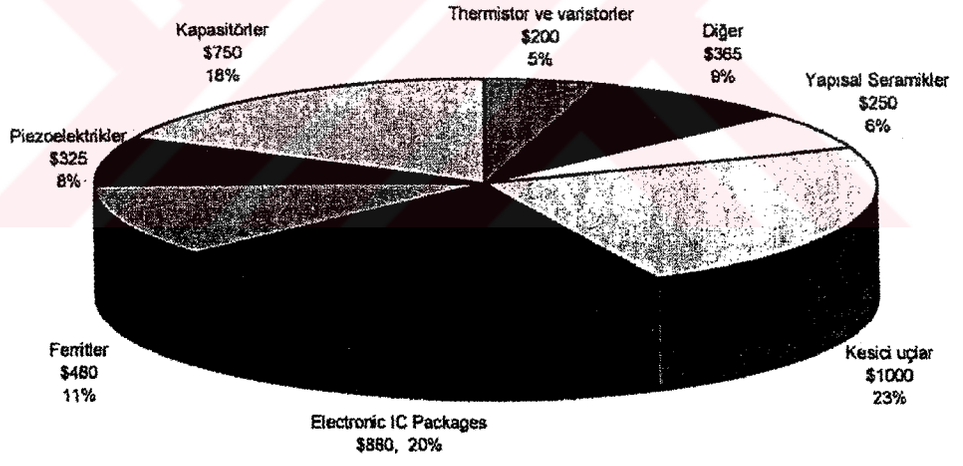
Tüm bunların yanında elektronik seramik malzemeler endüstrisi, bütün seramik pazarında büyük öneme sahiptir. Bu alanın maliyeti yaklaşık 15 milyon Amerikan Dolarıdır ki, bu da tüm seramik pazarının %30'unu teşkil etmektedir. Elektronik seramiklerin prensiplerini anlamak sadece heyecan verici bir bilimsel deneyim değil, aynı zamanda ticari bir husustur. Şekil 1., 1980, 1985 yıllarındaki dünya elektronik seramik pazar payını ve 2000 yıllarında oluşacak pazar payını göstermektedir.



Şekil 1. Yüksek Teknoloji Seramiklerinin Kullanım Alanları



Şekil 2. **Yüksek Teknoloji Malzemelerin Pazar Payları [4].**



Şekil 3. **Yüksek Teknoloji Seramikler Pazar Oranları. Üretim ve dünya Pazar Payı (milyon dolar). Toplam Pazar Payı 1980 yılında , 4.250 milyon dolar; 1985 yılında 5.500 milyon dolar, 2000 yılında, 15.000 milyon dolar [3].**

Reaksiyon sinterlemesi sistemi iki sınıfta incelenebilir;
1) Çok kristalli tek-faz katı oluşumu
2) Kompozit oluşumu

Çok kristalli tek-faz katı oluşumu
Sinterleme sırasında iki farklı başlangıç malzemesinin karışımından oluşan numunede reaksiyon ile birlikte yoğunluk kazanımıda meydana gelir ve 1 nolu eşitlikte ve şekil 4 de şematik olarak gösterildiği gibi çok kristalli, tek-faz katı oluşur.

A (toz) + B (toz) = C (çok kristalli katı) Eşitlik (1.)

Şekil 4. İki bileşenli toz (A+B) karışımından reaksiyon sinterlemesi sonucu tek fazlı katı (C) oluşumunun şematik gösterimi.

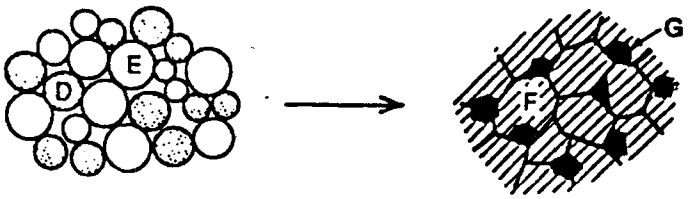
Reaksiyon sinterlenmesiyle endüstriyel olarak tek fazlı seramik üretimi, mikro yapı kontrolünün zor olmasından dolayı pek mümkün değildir.

Çok Fazlı Katı veya Kompozit Oluşumu

Reaksiyon Sinterlemesi sırasında, çok fazlı iki katı veya kompozit oluşumu eşitlik 3 ve şekil 5 de şematik olarak gösterilmektedir.

D (toz)+ E (toz) = F (katı) + G (katı) Eşitlik (3.)

Üretim maliyeti yönünden bakılacak olursa, reaksiyon sinterlemesi karmaşık katı kompozisyonların üretimi esnasında kalsinasyon aşamasını ortadan kaldırdığından iyi bir seçimdir. Normalde reaksiyon sonunda üründe bir aglomerasyon oluşumu gözlenir, bu yüzden de malzemeye istenilen şeklin verilmesinden önce öğütme işlemi kaçınılmaz olmaktadır. Reaksiyon sinterlemesinde ise, reaksiyon ve sinterleme işlemi aynı kademede gerçekleştiğinden, kalsinasyon ve öğütme gibi konvansiyonel proses kademeleri elimine edilebilir [8,9].



Şekil 5. D ve E olarak gösterilen toz karışımının reaksiyon sinterlemesi sonucu F (matriks) ve G (inklüzyon) içeren bir kompozit şeklinde gösterimi.

Uygulamada, reaksiyon sinterlemesinin birkaç dezavantajı vardır. Bunlar;

a) Tamamlanmıyan reaksiyondan dolayı kimyasal açıdan homojen olmayan üretim riski.
b) Reaksiyon esnasında mikroyapıdaki değişimlerden dolayı densifikasyonda düşüş.
c) Reaksiyonun özelillikle başlangıçtaki karmaşık yapısından dolayı mikroyapının kontrolündeki zorluklar.

Kontrollü bir mikroyapı gerektiği zaman, tek-faz saf tozların sinterlenmesi kompleks bir işlemide beraberinde getirir. Katı durum kimyasal reaksiyonlar için gerekli itici güç genelde sinterleme için gerekli itici güçten daha fazladır. Ayrıca katı-faz kimyasal reaksiyon, reaktanların kimyasına bağlı olduğu gibi bir sistemden diğerine değişiklik gösterebilir.

Reaksiyon sinterlemesi için en önemli proses parametreleri ise;
a) Tozların özellikleri, aktiviteleri, şekilleri ve boyutları gibi
b) Pişirme sıcaklığı ve
c) Uygulanan basınçdır.

Reaksiyon sinterlemesi işlemi yüksek sıcaklık senteziyle kendi kendine oluşum işlemi yerine kullanılır. Çünkü toz bileşiminin tümü ısıtılarak aynı anda yüksek sıcaklık sinterlemesiyle kendi kendine oluşum reaksiyonunun malzemenin her tarafında meydan gelmesi ile elde edilebilir. Hot-press ile reaksiyon sinterlemesi sırasında malzemenin istenilen bileşikte ve kompozisyonda üretilmesiyle beraber, uygulanan basınçla belirli şekilli parçaların aynı anda üretilmesi de sağlanır.

Reaksiyon ile birlikte sinterlenme sağlandığından üretim maliyetinin düşürülmesi yanında topaklanma oluşumu engellenerek homojen bir yapı elde edilir. Reaksiyon sinterlenmesinin çeşitli avantajları vardır. Bu avantajlar; ucuz hammadde kullanma olanağı, (örneğin yerel kaynaklardan

üretilen bor-karbür ve alüminadan başlayarak BN-AlN üretimi), ürün bileşiminin kontrolü ve homojen mikro yapı üretim olanağı olarak sıralanabilir.
AlN-BN, yüksek ısıl iletkenlik, çeşitli eriyik metallerde kimyasal olarak inert, iyi elektrik yalıtkanlığı gibi özelliklere sahiptir. BN-AlN seramik kompozitlerin üstün yüksek özelliklerinden dolayı bu malzeme son yıllarda ilgi odağı olmaya aday bir malzemedir. Başlangıç malzemesi olarak Al_2O_3 ve B_4C tozları kullanarak AlN-BN seramik kompozit üretimi, bu malzemenin direkt üretimlerinden ekonomik olarak daha ucuzdur. Özellikle ülkemizin dünya bor yataklarının büyük bir kısmına sahip olması ve İTÜ de hammaddesi çok ucuz olan bor-oksit kullanılarak B_4C üretiminin yapılması bununla beraber Al_2O_3'nın kolaylıkla ve ucuza bulunabilmesi, AlN-BN seramik kompozitlerinin reaksiyon sinterlemesiyle üretimini cazip kılmaktadır.

B_4C ve Al_2O_3 nın reaksiyonuna ait termodinamik veriler ve bu reaksiyona ait yapılan çalışmalar bu tür bir reaksiyon sinterlemesinin mümkün olduğunu bize gösteriyor. Tüm bu verilerden yola çıkarak, ticari olarak piyasada bulunan CERAC firmasına ait B_4C, İstanbul Teknik Üniversitesi, Yüksek Teknolojik Seramikler Laboratuarında üretilen B_4C tozları ve CERALOX firmasından sağlanan Al_2O_3 tozları kullanılarak dört farklı kompozisyon, değişik sıcaklık ve sürelerde azot gazı atmosferinde reaksiyon sinterlemesine tabii tutuldu. Oluşan fazlar X-Işınları Difraktometresi analizleriyle değerlendirildikten sonra uygun sıcaklık ve süre rejimi seçilerek BN-AlN seramik kompozit üretimine geçildi. Reaksiyon sinterlemesinin malzemeye olan etkisini anlamak için çeşitli karakterizasyon methodları kullanıldı. Sinterleme sonrası ağırlık kayıpları ve bulk yoğunluklar hesaplandı. Sinterlenmiş numunelerin yoğunlukları isoprophile alkol içine daldırma yöntemiyle hesaplandı. Başlangıç tozlarının ve reaksiyon sinterlemesinin sonucu olarak elde edilen numunelerin karakterizasyon işlemi için Taramalı Elektron Mikroskobu (SEM) kullanıldı. Rigaku-Rint X-Işınları Difraktometresi kullanılarak oluşan fazlar tanımlandı ve değişik sinterleme sıcaklıkları ve sinterleme süresinin bileşime ve homojenizasyon davranışına etkisi incelendi.

CHAPTER 1. INTRODUCTION

The ceramic industry is a fascinating and integral part of our world economy. Rapid changes in technology exemplified by the aerospace, electronic, and nuclear power industries have made many people aware of the versatility of ceramic materials. There are two important requirement for developing new materials; these are improved performance and a reduction in material cost [1].

The word ceramic is most often used to describe dishes, pottery and figurines. But wall tile, building brick, high voltage insulators, and glass products are also ceramics. Further, as engineers know, ceramics are widely used in a host of other specialized applications: nuclear reactors, space vehicles, electronic modules, computers, pumps, valves, metal processing furnace and ladles, optical equipment, lasers, and protective coatings [1,2].

The basis of the usefulness ceramics in their wide range of particular properties. The tailoring of these properties by careful processing makes ceramics a better alternative than either metals or organics for specific applications. Ceramic can be produced with densities as high as lead or so low that they will float on water. Ceramics are by nature brittle materials, but their strength is very, and they are therefore commonly used as construction materials. The strong chemical bonding in most ceramics makes them very hard and very stable. This stability leads to high melting temperatures and helps protect them from attack by high-temperature corrosive gases and liquid metals. It also makes many ceramics inert to attack by most strong acids. Some ceramics store electrical charges

(capacitors); others are electric insulators with truly amazing resistance to voltage breakdown; still others are electrical conductors. These properties and other have carved out a most important place for ceramics in our complex modern technology [1,2]. Key factors affecting production costs are: shape fabrication techniques, near net shape capabilities the need to machine, nondestructive evaluation techniques and overall process yields [3].

On the other hand , electronic ceramic industry have great importance in the overall ceramic market. The total cost of this field is about 15 million USD which 30% of overall ceramic market. Figure 1 shows the size of the market for High Technology Materials [2,4].

Understanding the principles of electronic ceramics is not only an exciting scientific challenge but is also an important commercial objective. Figure 1 shows the enormous size of the market for these important high technology materials in 1980, 1985, and the 300 % projected growth by the year 2000. The projected growth rate is one of the largest of any field of technology. The projected growth of the photonic materials market, which is largely ceramics and glasses, is even larger, investigate new electronic and photonic materials to take advantage of this growth potential [3,4].

The processing of AlN-BN composites by using Al_2O_3 and B_4C powders as a starting materials are economically cheaper then the direct synthesis of such composites.

If the densification can be achieved together with the reaction, not only is the manufacturing cost lowered, but the possible formation of aggregates is avoided. Several advantages can also result from reaction sintering. These advantages are the possible usage of cheap raw materials, for example, to start with boron-carbide (originally produced by domestic sources) and alumina but to end with BN-AlN, the possibility of control of the

stoichiometry of the products and the possibility of producing complex microstructures [5].

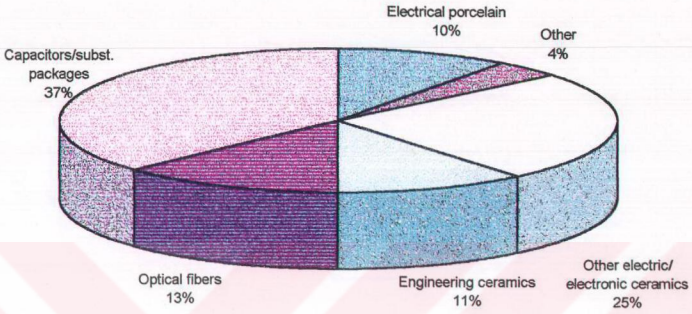


Figure 1.1. Size of the market for High Technology Materials [4].

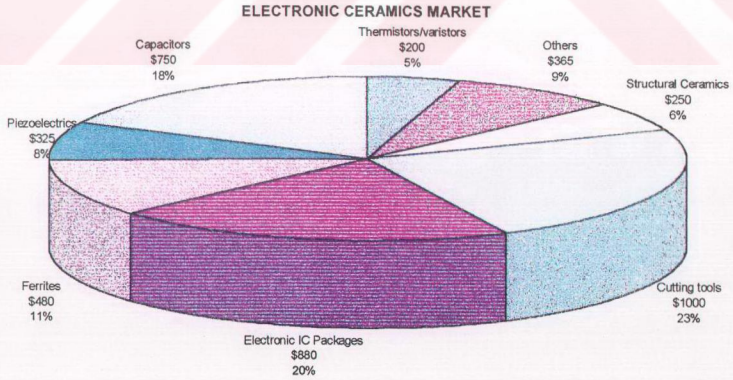


Figure 1.2. High technology ceramics market. Products and world sales(millions $). Total market in 1980, $4250 million; 1985, $5500 million; 2000, $15,000 million [3].

The term "reactive sintering" is used instead of self propagating high temperatures synthesis because the entire powder compact was heated up so that the self propagating high temperature synthesis reaction occurs throughout the sample of the same time. The pressure applied during the reactive sintering , i.e. the hot-pressing, was used to produce a nearly fully dense net-shape product [6].

Aluminum nitride-boron nitride both have interesting properties such as high thermal conductivity, chemically inert to various molten metals, good electrical insulation. Boron nitride has excellent lubrication properties at relatively high temperatures up the 1000°C in air. Because of these unique properties, Boron nitride-aluminum nitride composites were recently attracted interest [1].

The objective of this research was to produce BN-AlN composites from blended Al_2O_3-B_4C powders then to characterize the kinetics of sintering these compacts. This study included investigation of the mass transport mechanism, the effect of sintering variables on consolidation and homogenization, and the microstructural characterization of the sintered compact.

CHAPTER 2. LITERATURE SURVEY

2.1. Reactive Sintering

Reactive sintering sometimes referred to as reaction sintering , is a firing process in which the chemical reaction of the starting materials (the reactants) and the densification of the powder compact are both achieved in a single heat treatment step [7].

In reaction sintering, depending on the processing conditions such as particle size, temperature, heating rate, and applied pressure, reaction and densification can occur in sequence or concurrently or in some combination of two. An understanding of the influence of the process variables on the rate of reaction and densification is essential for the control of the microstructure of the product [7,8].

2.1.1 Reaction Sintering Systems

Systems that undergo reaction sintering can be divided into two main classes, depending on whether single-phase solids or composites are produced [7].

2.1.1.1 Production of Single-Phase Solids

For a powder compacts consisting of a mixture of reactant powders, the simplest example of reaction sintering is shown in Eq. (1) and Figure 3 [7]. During firing, reaction between two starting materials (A and B) and densification occur to produce a polycrystalline, single-phase solid (C):

A (powder) + B (powder) = C (solid polycrystal) Eq. (1.1.)

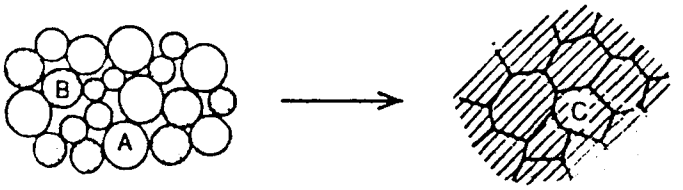


Fig 1.3. Schematic diagram illustrating the production of a single-phase solid (C) by reaction sintering of a compacted mixture of two powders (A and B) [7].

In most cases, A and B are themselves compounds. An example of the process described by Eq. (1) is the formation of zinc ferrite from a compacted powder mixture consisting of eqimolar quantities of zinc oxide and ferric oxide:

$$ZnO + Fe_2O_3 = ZnFe_2O_4 \qquad \text{Eq. (1.2.)}$$

The reaction sintering process is not used industrially to produce single-phase ceramics because of difficulties in controlling the microstructure [7,8].

2.1.1.2 Production Multiphase Solids or Composites

A more complex example of reaction sintering in a compacted mixture of reactant powders is shown in Eq. (3) and Fig. 4. During firing, reaction between two starting materials (D and E) and densification occur to produce a polycrystalline solid consisting of two phases (F and G):

D (powder) + E (powder) = F (solid) + G (solid) Eq: (1.3.)

An example of this equations is the reaction between alumina and boron carbide to produce boron nitride-aluminum nitride composites which we made [8].

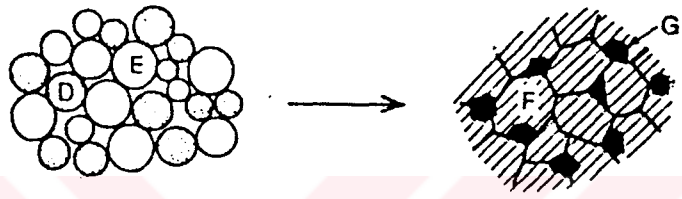


Fig. 1.4. Schematic diagram illustrating the production of a composite solid, consisting of a matrix (F) and inclusions (G), by reaction sintering of a compacted mixture of two powders (D and E).

2.1.2 General Features of Reaction Sintering

From the point of view of fabrication costs, reaction sintering has the benefit of eliminating the prereaction (or calcination) step in the formation of solids with complex composition. The reaction normally leads to agglomeration of the product, so a milling step is also necessary prior to compaction. The compacted powder is finally sintered to produce a dense solid. In reaction sintering, the reaction and densification occur in the same heating cycle, so the calcination and associated milling steps in the conventional route are eliminated [8,9].

In practice, reaction sintering has several shortcomings. As a result, it finds little use in the production of single-phase solids. The shortcomings include;

a. the risk of producing chemically inhomogeneous materials due to incomplete reaction,

b. significantly reduced densification rates caused by microstructural changes accompanying the reaction and,

c. difficulties in controlling the microstructure as a result of the added complexity introduced by the reaction.

The sintering of a pure single-phase powder can be a complex process, particularly when a carefully controlled microstructure is required. The addition of a powder reaction, which itself can be fairly complex; leads to further difficulties in understanding the reaction sintering process. Powder reactions are considerably more complicated than the idealized reactions between single crystals of the reactants. Another factor is that the driving force for a solid-state chemical reaction is normally much greater than the driving force for sintering. Furthermore, the mechanism of a solid state chemical reaction depends on the chemistry of the reactants and will differ from one system to another.

2.1.3 Effects of Processing Parameters

2.1.3.1 Powders Parameters

Powder parameters such as activity, shape, size all effect sintering behavior. The activity of the powder is influenced by particle shape, surface to volume ratio, internal grain boundaries, dislocations, internal stresses, impurities or other lattice defects. Higher activity powders require less sintering temperature and time to achieve the same degree of sintering than with lower activity powders. Eylon and Fros et al. reported that powders could be "strain energized" by passing them through a rolling mill to induce internal stresses thereby increasing their activity [8,9].

2.1.3.1.1 Particle Size of Reactants

Particle size can influence the sintering rate because the surface free energy contribution increases, the number of particle contacts increase, and the diffusion path size decreases as the particle size decreases.
Macarski and Hall found that as the particle shapes become more irregular the initial contact area increased and during sintering, the more complex shaped powders increased the rate of porosity spherodization [8].

Herring`s scaling laws predict the effect of change of scale (particle size) on the rate of matter transport during sintering. Depending on the mechanism, the densification rate varies with particle size R according to
Densification rate ~ $1/R^4$ grain boundary diffusion
Densification rate ~ $1/R^3$ lattice diffusion
For the reaction, if the product forms coherently on the surface of the particles, the reaction rate varies as $1/R^2$. If the product does not form coherently, then the rate is expected to vary as 1/R. The dependence of the densification rate and the reaction rate on the particle size is sketched in Fig. 3. Both the densification rate and the reaction rate increase with decreasing particle size. However, because of the stronger size dependence, the densification mechanism is more strongly influenced than the reaction mechanism. A reduction in the particle size increases the densification rate relative to the reaction rate.

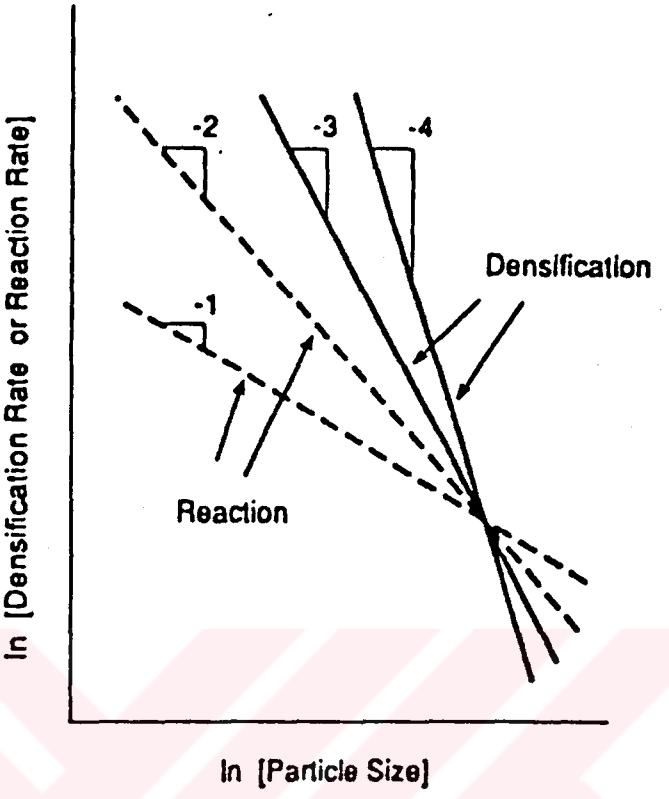


Figure 2.5. Predicted effect of particle size on the rates of densification and reaction during reaction sintering of a powder mixture. Smaller particle size enhances the rate of densification relative to the rate of reaction..

2.1.3.2 Firing Temperature

Although densification and reaction will most likely occur by different mechanism, they both involve diffusion and are therefore expected to be thermally activated; that is the rayes have an Arrhenius dependence on temperature. The dependence of the densification rate and the reaction rate on the temperature is sketched in Fig. 6. for the more typical situation in which the activation energy for densification, Qd, is greater than that for the reaction, Qr. In this case, increasing the temperature leads to an increase in the densification rate relative to the reaction rate [10].

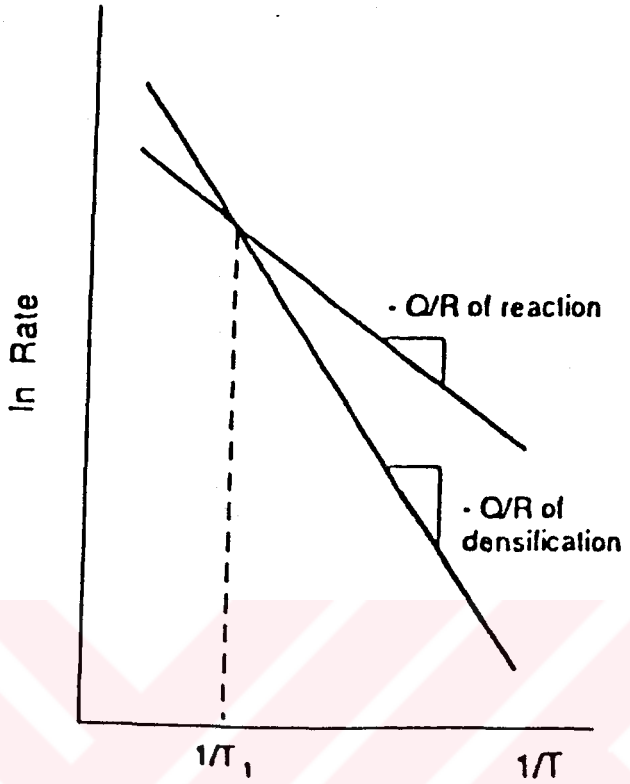


Figure 2.6. Predicted effect of sintering temperature on the rates of densification and reaction during reaction sintering of a powder mixture. When the activation energy for densification is greater than that for the reaction. higher sintering temperature enhances the densification rate relative to the reaction rate [8].

2.1.3.3 Applied Pressure

Higher compaction pressures increase the green density, the number of particle contacts, and particle contact size, which enhances homogenization and grain growth. Higher compacting pressures can also reduce the amount of internal free surface and the particle curvature, thereby reducing the associated driving forces. Closed porosity containing entrapped gases is formed with higher compaction pressures. The application of an external pressure increases the driving force for densification [10].

2.1.4 Processing Steps in Reaction Sintering

Three different trajectories in reaction sintering are sketched in Fig.7. When the reaction rate is much faster than the densification rate (curve A), the reaction occurs predominantly before any significant densification. Densification must be achieved for a microstructure consisting of the fully reacted powder. Curve C shows the trajectory when the reaction rate is much slower than the densification rate. In this case, densification occurs without any significant reaction. The reaction process must be carried out in a full dense microstructure. Curve B represents the trajectory for a system in which the reaction rate is comparable to the densification rate [8].

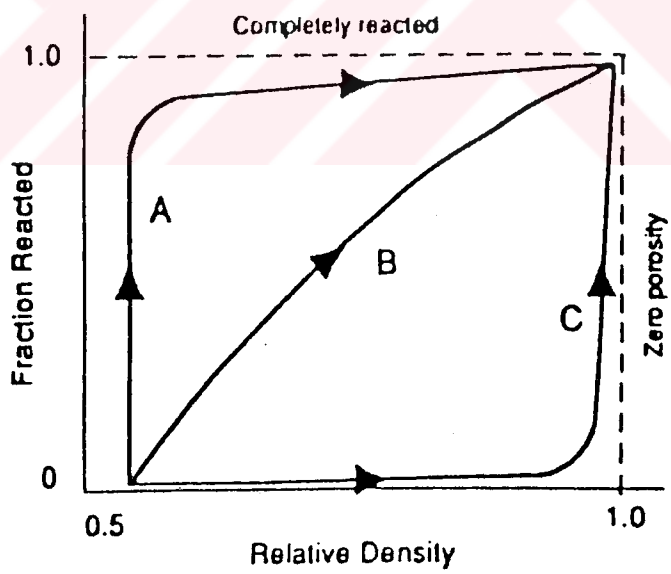


Figure 2.7. Sketch showing three different processing trajectories in reaction sintering. Curve A is the trajectory for a system in which the reaction rate is much higher than the densification rate; curve B is for a system where the reaction rate and densification rate are of roughly the same magnitude; for the system following trajectory C, the densification rate is much higher than the reaction rate [8].

The principal processing parameters, control the relative rates of densification and reaction, which in turn determine the processing trajectory. Faced with the problem of achieving a desired microstructure by reaction sintering, a useful approach is to determine the most appreciate processing trajectory and than choose the processing conditions that favor this trajectory. However, its likely that many systems will not be amenable to such process control. For such systems where favorable conditions are difficult to achieve, we would have to determine whether reaction sintering can still be exploited [8].

2.2. Raw Material

2.2.1 Alumina (Al_2O_3)

A material appearing in several crystalline forms, of which alpha-Al_2O_3 is the densest and most stable. At least four hydroxides and hydrates are known. alpha-Al_2O_3 belongs to the trigonal system, refractive index 1.765. It is insoluble in water and only slowly soluble in alkalies and strong mineral acids, but is attracted by hydrofluoric acid and potassium bisulfate. The alpha form of alumina melts at 2040°C (3704°F). In sintering, this permits the discrete crystallites to react with each other to form to large crystals making up the sintered mass. Mineralizes of fluxes permit sintering at lower temperatures. The sintered bodies take on the properties of the basic material. In 100% Al_2O_3 bodies, mechanical failure will occur through the alumina grains as readily as at grain boundaries [11].

Al_2O_3 also termed alumina, is produced by heating hydrates of alumina. A number of transitional Al_2O_3 structures can form initially with increasing temperatures but all structures are transformed irreversibly to α-Al_2O_3 with a corundum structure of a hexagonal system. α-Al_2O_3 is the only stable form above 1200°C is generally used for structural and electrical applications except for γ-Al_2O_3 which is used for catalytic application [11,12].

Because of a strong chemical bond strength between the Al and O ion, Al_2O_3 has outstanding physical stability such as a high melting point (2050°C), the highest hardness among oxides and high mechanical strength. Table.2.1. shows the physical, mechanical and electrical properties of Al_2O_3 [11].

Table 2.1. Engineering properties of α-Al_2O_3 [11].

PROPERTY	VALUE
Density (g/cm^3)	3.99
Modulus of elasticity (GPa)	393
Flexural Strength (MPa, at 25°C)	282
Tensile Strength (MPa, at 25°C)	206
Thermal Conductivity (W/cm.K at 20°C)	0.39
Dielectric Constant (at 25°C and at 1kHz)	10.1

Of all the new ceramics materials, alumina probably has the widest diversity of uses and the greatest potentialities. For electronic and aerospace applications, its outstanding mechanical strength, excellent thermal shock resistance, excellent electrical properties (high dielectric strength, low power factor, etc.) and its chemical and abrasion resistance make it well suited in this field [11,12].

Uses for high-alumina ceramics include electronic tube parts, ceramic-to-metal seals, semiconductors and IC substrates, high frequency insulators, holders and spacers for printed circuits, radomes, missile nose cones and spark plug insulators. Mechanical uses for high-alumina bodies include seal surfaces for mechanical rotary seals for pumps and similar equipment, plungers or liners in reciprocating pumps, nozzles, rock bits, cutting tools, non lubricated high-temperature roller bearings, and a wide variety of other mechanical parts [4,10,13]. As compared with other ceramic materials, alumina ceramics are superior mainly in regard to strength, impact resistance and hardness, as illustrated in Table 2.2 [11].

Table 2.2. Mechanical Properties of Different Ceramic Materials [11]

MATERIAL	TENSILE STRENGTH, 10^3 PSI	CHARPY IMPACT ENERGY IN.-LB.	MOHS' HARDNESS
Alumina	13-38	5.8-7.5	9
Zircon	10-16	5.5	8.0
Silimanite	11-14	5.5	7.5-8.0
Steatite	5-15	4.0-5.0	7.5
Forsterite	10	4.0	7.5
Electrical porcelain	2.4-8.0	4.0	6.5-7.0

The hardness of aluminum oxide compositions, which make them suitable for abrasion-resistant applications, cutting tools, etc., is greater than many materials normally considered hard as illustrated in Table 2.3. [14].

Mechanical strength is high at room temperature but is lowered largely above 1100°C . Thermal conductivity is relatively large among oxides. However, because the coefficient of thermal expansion is large, thermal shock resistance is smaller than the values for Si_3N_4 and SiC which are the representative high strength materials. Al_2O_3 is a typical electrically insulating material. The volume resistivity of high purity ceramics with a low alkali concentration is more than 10^{15} Ω.cm at room temperature. The

Table 2.3. Different Hardness Scales Values of Different Ceramic Materials.

MATERIAL	KNOOP HARD. FACTOR	MOHS` SCALE
Diamond	6000-6500	10
Boron Carbide	2300-2800	---
Silicon Carbide	2000-2500	---
Sapphire (pure corundum)	1800-2000	9
Alumina ceramics	1450-1750	---
Tungsten carbide	1050-1900	---
Topaz	1250	8
High-speed steel	650-900	---
Quartz	710-790	7

electrical conductivity of single crystal and polycrystal Al_2O_3 at high temperature. Values of elasticity, thermal conductivity and electrical resistivity largely increase as purity decreases. Mechanical strength and dielectric strength also increase with increasing purity but are more dependent on density and ceramic microstructure. Al_2O_3 has a refractive index of 1.760. Dense Al_2O_3 ceramic prepared with high purity, fine, and uniform powders shows good translucency. Both MgO and Y_2O_3 are often used as additives and effectively eliminate pores and protect against abnormal grain growth. Al_2O_3 is also chemically very stable and has high corrosion resistance. It is insoluble in water and very slightly soluble in strong acid and alkaline solution [11,13].

2.2.2 Boron Carbide (B_4C)

Boron carbide is the third hardest material known after diamond and cubic boron nitride. Above 1300°C, boron carbide is even harder than diamond and CBN. Boron carbide (B_4C) ceramic material is one of the important

group of hard nonmetallic materials, including SiC, Si_3N_4 and diamond. B_4C has several attractive properties; its refractory nature (melting point, 2450°C), its low specific weight (theoretical density, 2.52 g/cm^3) and its high neutron absorption cross section. Because of high temperature stability, recently boron rich borides have received attention for use as high temperature semiconductors. Also, a B_4C rod connected to a graphite tube by a conical fitting, because of its high thermoelectric power has been used as a high temperature thermocouple [15].

This light ceramic materials is very strong, with a 4-point flexural strength of 50,000-70,000 psi and a compressive strength of 414,000 psi. The high strength-weight ratio makes B_4C especially attractive for armor and aerospace applications. Low thermal conductivity (29-67 W/mK) combined with a large Seebeck coefficient (200-300 μmV/K) makes B_4C an efficient p-type thermoelectric, especially at elevated temperatures. electrical resistivity ranges from 0.1-10 ohm-cm, and is sensitive to hydrostatic pressure [15,16].

Boron carbide is chemically inert, although it reacts with oxygen at elevated temperatures and with white hot or molten metals of the iron group, and certain transition metals. B_4C reacts with halogens to form boron halides-precursors for the manufacture of most nonoxide boron chemicals. Boron carbide also is used in some reaction schemes to produce transition metal borides [15].

Boron carbide has a low thermal conductivity and is very susceptible to thermal shock failure. Its outstanding hardness, however is exceeded only by diamond and cubic boron nitride. Mechanical strength can be influenced by processing. Despite the problems with stoichiometry and the presence of a free graphite phase, dense boron carbide is one of the hardest material mass produced on a commercial scale. Its hardness is significantly is significantly greater than that of silicon carbide, tungsten carbide and sapphire. However, in spite of its extreme hardness, boron

carbide is not useful as a bonded abrasive (grinding wheels, sharpening tools). The material is extremely brittle and fractures into rounded fragments which are not effective in stock removal [11,15]. Typical mechanical and physical properties of boron carbide are listed in Table 2.4.

Boron carbide is a semiconductor, but it is not produced in a sufficiently pure form for its semiconductor properties to be studied in detail. Its resistivity has been reported to be 0.3 to 0.8 Ω.cm. Because of it has a good thermal neutron capture cross-section of 3960 barns, one of the major applications for boron carbide is as a neutron absorber and shielding material. It is used in nuclear reactor control rods. Absorption of a thermal neutron liberates a low energy particle [11,15].

Table 2.4. Typical properties of boron carbide

PROPERTY	VALUE
Density (g/cm^3)	2.51
Boron content (%)	78.28
Carbon content (%)	21.72
Structure	Rhombohedral
Melting point (°C)	2450
Boiling point (°C)	3500
Thermal Conductivity W/mK at 27°C	28
Young' modulus (GPa)	445
Shear Modulus (GPa)	186.5

Boron carbide is generally produced by reacting and fusing a mixture of boric oxide and carbon in an electric furnace. The product in the arc

furnace consists essentially of a partially fused "slush" having the composition approximating that of B_4C. Boron carbide does not melt congruently. Therefore, the liquid in contact with solid boron carbide does not have the same composition as the solid. The liquid in the arc furnace is solidified at a rate that the solid and the liquid do not reach an equilibrium. The material left in the molten state becomes increasingly richer in carbon than in solid until, as the last liquid solidifies its composition consists of that of a eutectic corresponding to a mixture of boron carbide and graphite. Therefore, no matter how carefully boron carbide is prepared in practice all arc furnace product will contain a quantity of free graphite [11,15,17]

All commercial boron carbide parts are produced by hot pressing or by sintering followed by hot isostatic pressing. Typical hot pressing conditions of powder (< 10μm) are 2100°C at 35 MPa for 30 min. Typical sintering and hot isostatic pressing of powder (<1μm, 1 to 3 wt % C) consists of sintering at 2200°C to 2250°C for 30 min. at low pressure (10 Pa or 0.075 torr) followed by hot isostatic pressing at 2000°C and 200 MPa in argon for 120 min. Hot pressing limits the size and complexity of shapes that can be produced. Simple cylinders, blocks, flat plates axially symmetrical nozzles and similar simple shapes can be formed directly by hot pressing [11,15,16].

Shaping these simple shapes requires very expensive diamond grinding. However, diamond grinding creates a multitude of microscopic flaws below the ground surface. These frequently are the source of strength-limiting defects within the machined parts [15].

Boron carbide is used in only a few applications, none of which utilize mechanical strength in the usual sense. It is used as a thermal neutron absorber and as a loose abrasive. In hot pressed form it is used in nozzles for abrasive slurries and in wear applications in which the load is either compressive or sliding [15].

2.3 General Properties of AlN-BN Composites

Ceramic materials are distinguished from metals and organic materials for their unique characteristics, but their use is limited because of difficulty in machining as they are generally too hard and brittle. Recently, some kinds of machinable ceramics have been developed for better machinability and they have attracted special interest. Although they have high machinability, yet they are not applicable in the engineering purpose because of low bending strength as low as 10 kg/mm^2 [18,19].

AlN-BN ceramic composites is a new type of machinable ceramic materials with high mechanical strength and thermal conductivity. Its characteristics;

a. Excellent machinability; BN-AlN ceramic composites can be machined by a broad range of methods such as drilling, lathing, milling, etc., to form complex shapes with high precision.
b. High mechanical strength; 30 kg/mm^2 comparable to bending strength of alumina ceramic.
c. High reliability as structural material.
d. High thermal conductivity; 100 W/m.K, approximately five times as much thermal conductivity as that of alumina ceramic.
e. Excellent electric insulation.
f. Low dielectric loss.
g. Low thermal expansion.
h. High thermal resistance.
I. Excellent sealing ability to vacuum..
j. High modulus of elasticity [18,19,20].

2.3.1. Applications;

a. Various electrical parts where electric insulation and heat dissipation are required.
b. Insulator or heat sink materials for high power electronic field.
c. Insulators, and special refractory parts such as protective pipe.
d. Crucibles for vacuum deposition or molten metals.
e. Engineering components such as bearing.
f. Mold materials for fabrication of plastic and metal components.
g. Applications in a wide range of industrial fields of structural material.

Table: 2.5. Physical Properties of AlN-BN Ceramic Composites [18-24]

Property	Test Conditions	AlN-BN	Machinable glass-ceramic	Units
GENERAL				
Density	Corrected to 4°C	2.95	2.52	g/cm^3
Porosity	25°C	0	0	%
ELECTRICAL				
Volume Resistivity	25°C, DC	1.8×10^{13}	10^{14}	Ω cm
Dissipation factor (tan δ)	25°C, 1 MHz	0.0004	0.003 (10kHz) 0.007 (8.6ghz)	
Dielectric Constant (ε)	25°C, 1 MHz	7.3	5.92 (10kHz) 5.68 (8.6ghz)	
Dielectric Strength	25°C, sample thickness 1mm, AC	40	40 (thickness 10 mil)	kV/mm
THERMAL				
Thermal Expansion Coefficient	RT to 400°C	4.4×10^{-6}	9.4×10^{-6}	/°C
	RT to 600°C	4.8×10^{-6}	11.0×10^{-6}	/°C
	RT to 800°C	5.1×10^{-6}	12.3×10^{-6}	/°C
Thermal Conductivity	25°C	100	1.7	W/m.K
Maximum Use Temperature	in air	1000		
	in nonoxidizing Atm	1900	1000 (unstressed)	°C
Thermal Shock Resistance ΔT	water quench	400	—	°C
MECHANICAL				
Bending Strength	25°C	30	10	kg/mm^2
Compressive Strength	25°C	110	35	kg/mm^2
Modulus of Elasticity	25°C	1.63×10^4	6.7×10^3	kg/mm^2
Poisson's Ratio	25°C	0.31	0.27	kg/mm^2
Vickers Hardness (Hv)	25°C, 300 g	560	230	kg/mm^2
Fracture Toughness (K_{1C})	25°C chevron knotched	3.5	—	$MNm^{-3/2}$
CHEMICAL DURABILITY				
Resistance to acid	5% Hcl 24hrs, 95°C	36	87	mg/cm^2 wt.loss
Resistance to Base	5%NaOH 24hrs, 95°C	100	8.5	mg/cm^2 wt.loss

CHAPTER 3. EXPERIMENTAL PROCEDURE

3.1 Identification of Raw Materials

Scanning electron microscopy image of Al_2O_3 powders can be seen from figure 3.1. These powders has a specific surface area of $3m^2/g$ and containing little quantity of impurity. XRD analysis result of these powder has shown in figure 3.2. SEM image of B_4C powders has shown in figure 3.3. which have a specific area of 4,25 m^2/g XRD analysis results of these powders also shown in figure 3.4. In experimental studies two different compositions of B_4C powders were used originally from CERAC Inc. and ITU product by domestic sources. The main difference in between these two powders were carbon content. SEM picture and XRD analysis results of ITU product boron-carbide powders have been shown in figure 3.5. and 3.6. respectively.

3. 2. Consolidation of Powders

Boron carbide and alumina powders used were -325 mesh Boron carbide, 99,5 % pure supplied by CERAC Inc. and Alumina with an average particle size of 0,5 micron, supplied by CERALOX. Table 3.1. shows the physical properties of Al_2O_3 and B_4C powders used in this study.

These powders were weighed and mixed well with a ball mill in polyethylene jars for 15 hour, so that mixed powders containing 10-90%, 30-70%, 50-50% of boron carbide-alumina were obtained. An analytical balance with an accuracy of +/- 0,001 g. was used for weighing.

Figure 3.1. SEM Image of Al_2O_3 Powders (Ceralox Inc.)

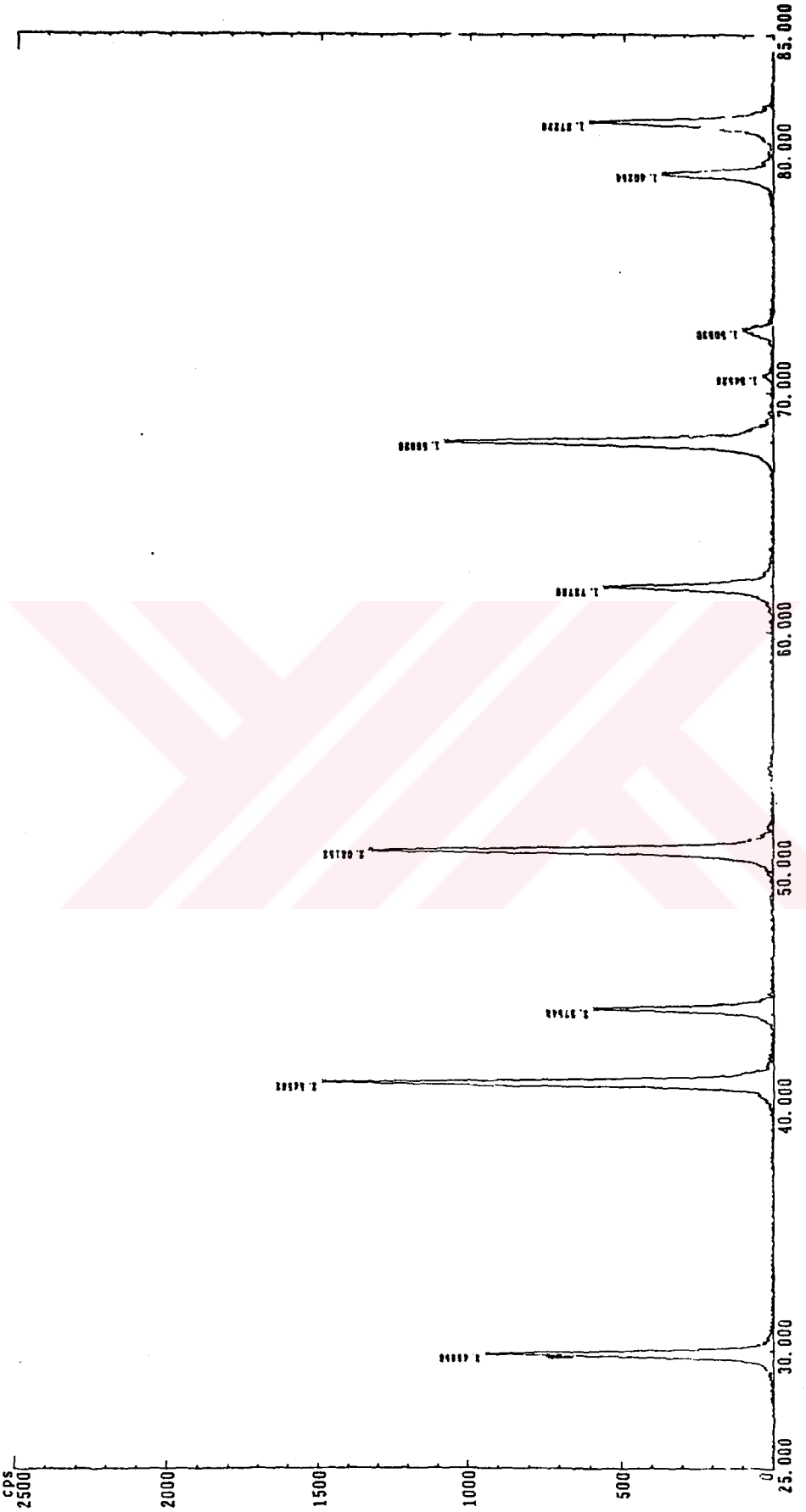


Figure 3.2 XRD analysis result of Al_2O_3 (supplied by Ceralox) powders.

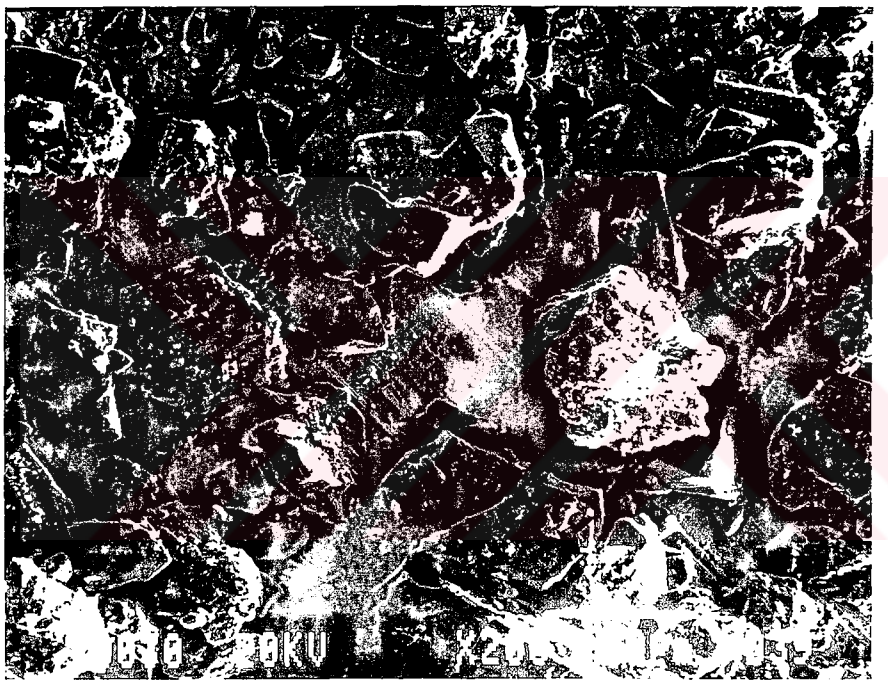


Figure 3.3. SEM Image of B_4C Powders (Cerac Inc.)

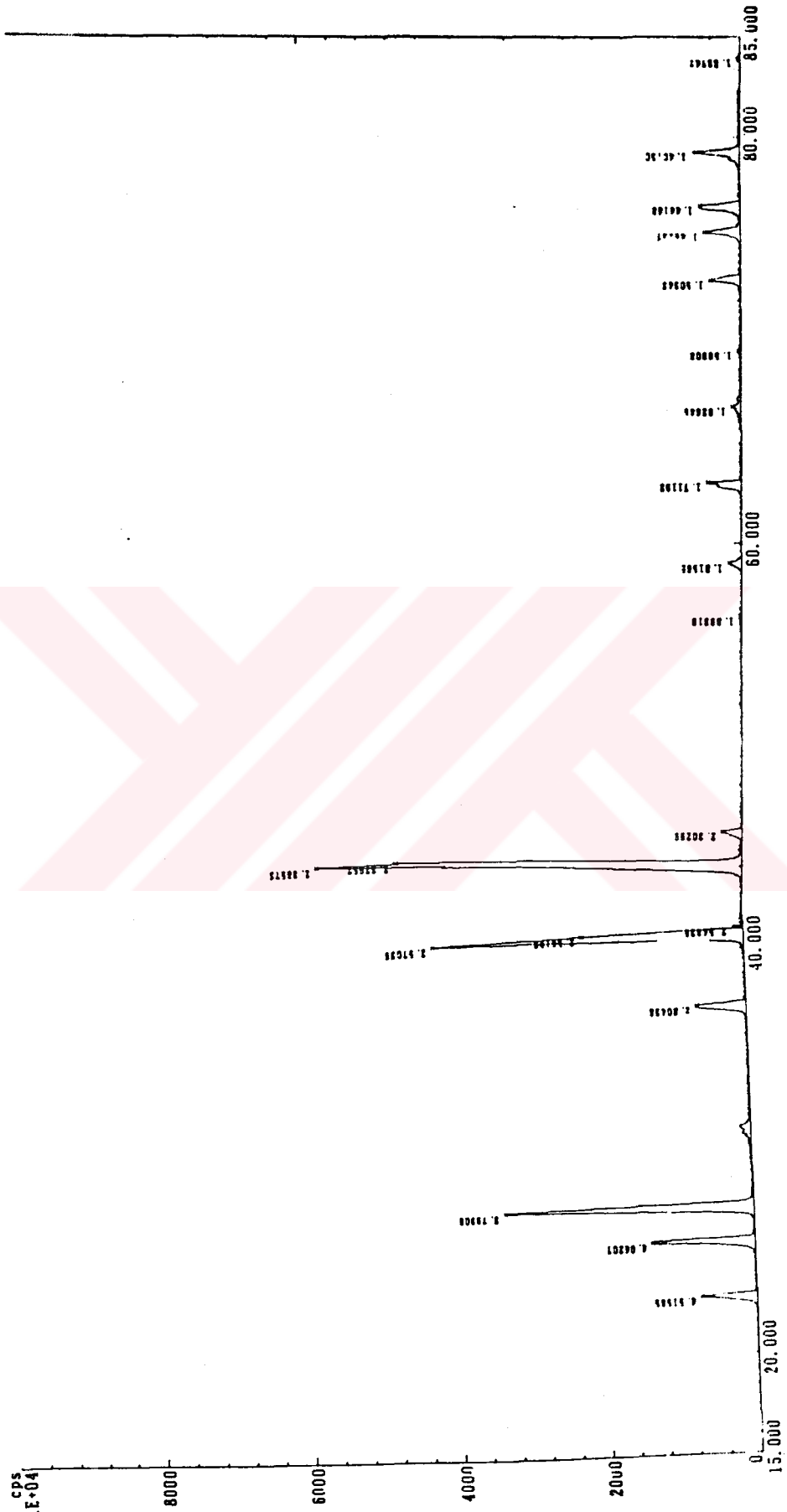


Figure 3.4 XRD analysis result of B_4C (supplied by Cerac) powders.

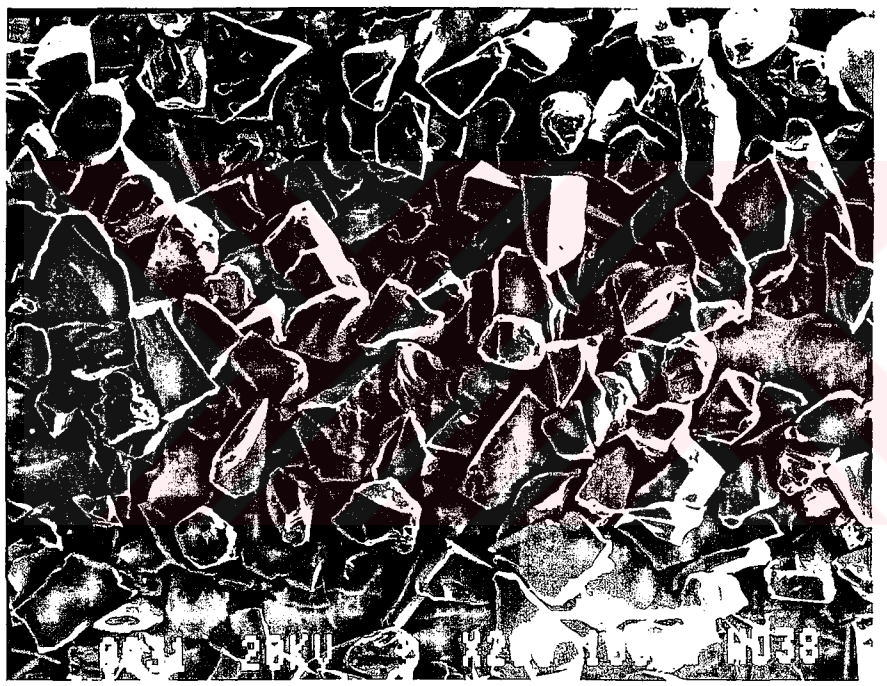


Figure 3.5. SEM Image of ITU Product B_4C Powders

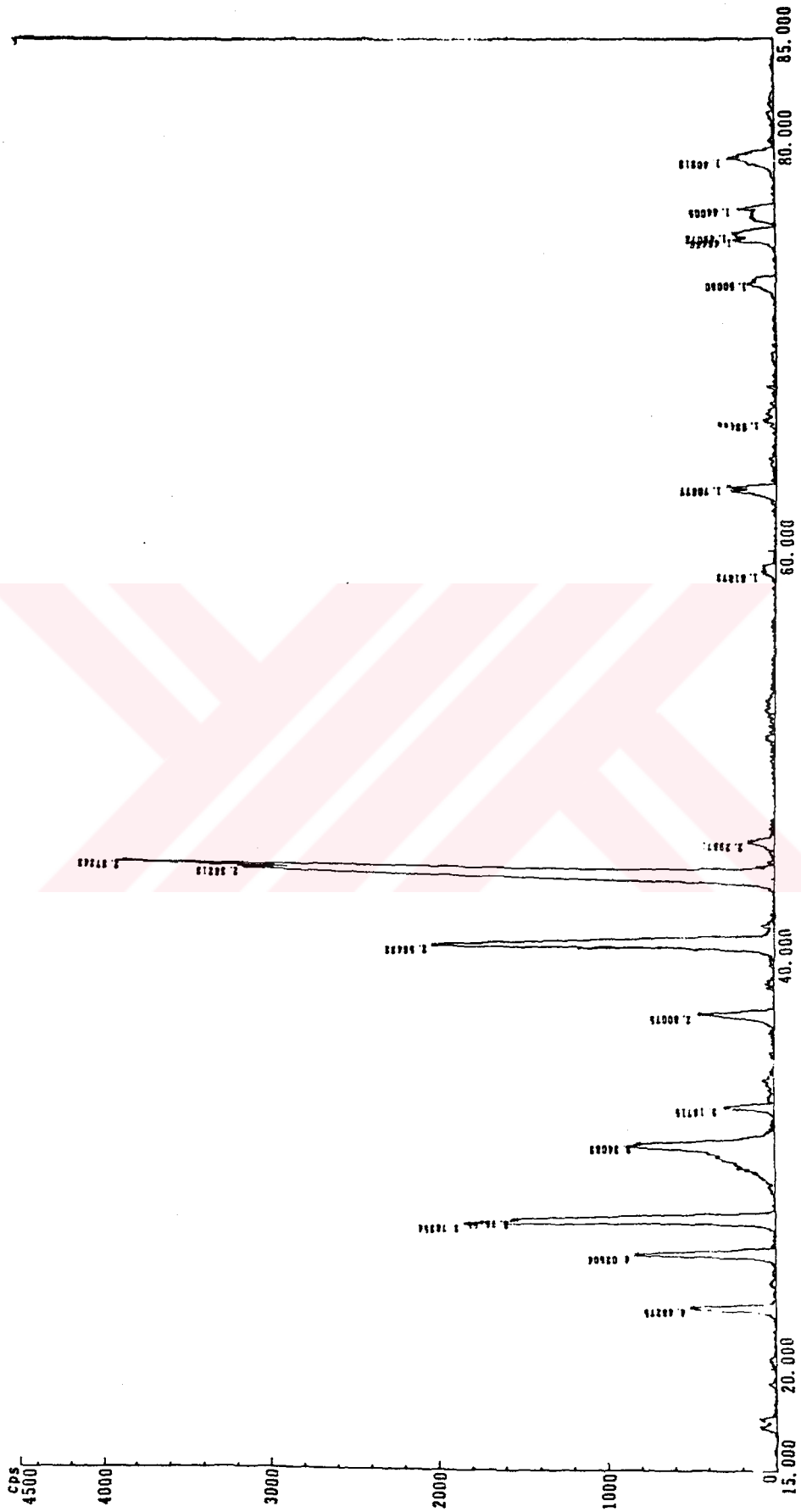


Figure 3.6 XRD analysis result of B_4C (ITU product) powders.

Table 3.1. Physical Properties of Al_2O_3 and B_4C

Powder		Average Particle Size (μm)	Surface Area (m^2g^{-1})	Purity (%)	Melting Point °C
ITU	B_4C	25-30	1.053	80	2350 °C
Cerac	B_4C	65-70	0.22	99.5	2350 °C
Ceralox	Al_2O_3	0.5	10.02	99.99	2080 °C

Microstructural investigation of powders showed a uniform powder composition and were no contamination from mechanical blending. About 1,2 g. of the powder from each composition was compressed using a hydraulic press and under 2,5 metric ton in a steel die 16,6 mm in diameter. The pressure was applied and held as constant as possible for a fifteen second period. After compaction, the compacts were ejected from the molds, identified and measured. A Schematic diagram of sample preparation is shown in Figure 3.7.

3.3. Sintering the Compact

Two processing routes were used; pressureless sintering and Hot-pressing in a nitrogen atmosphere. To prepare for sintering, four sampler from each composition were stacked and placed in a boron nitride mold. Boron nitride mold and samples were placed into the center of a vacuum furnace as seen in Fig. 3.8.

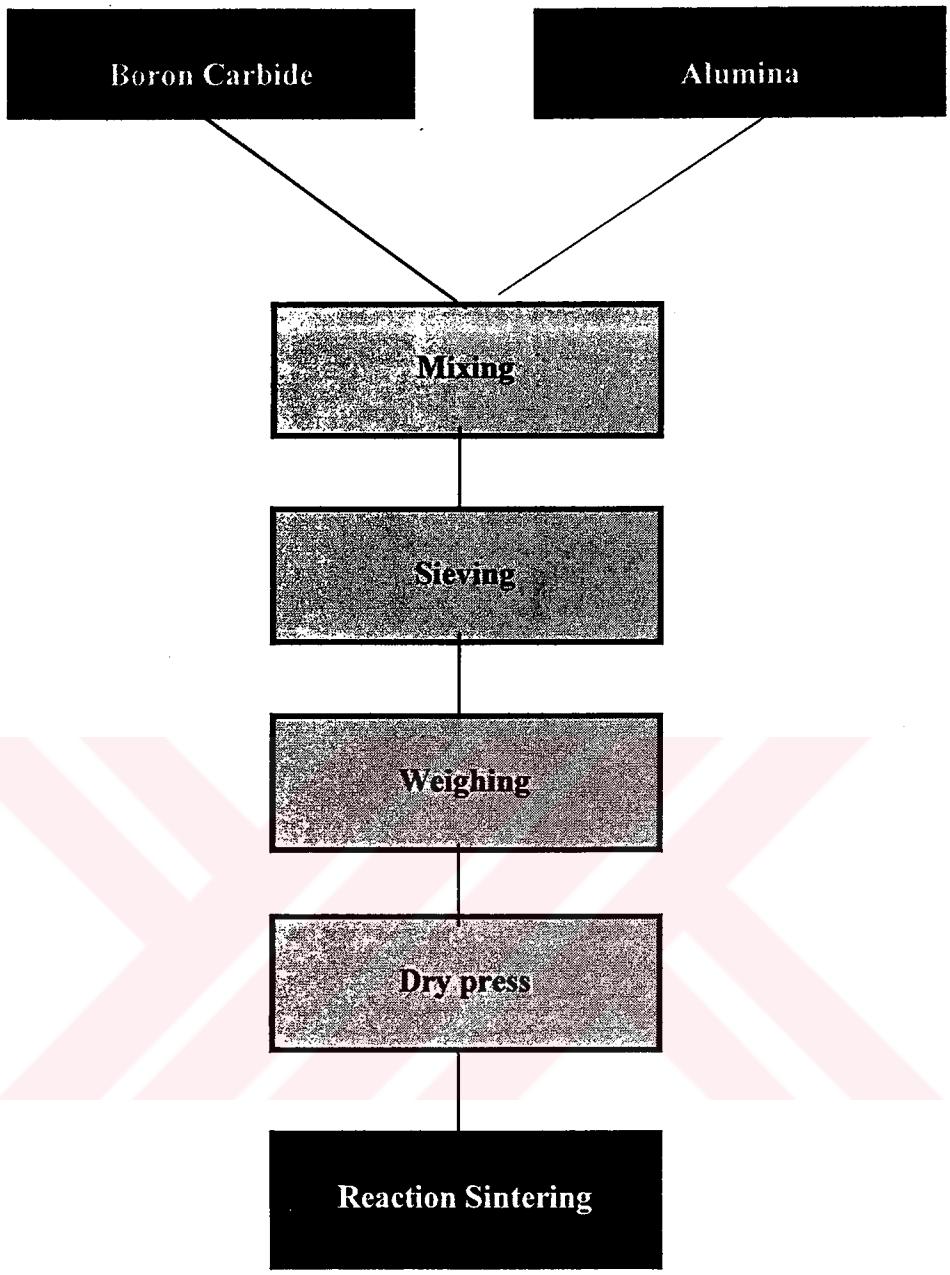


Figure 3.7. Schematic diagram of sample preparation of reaction sintering BN-AlN

Although vacuum of 10^{-3} torr was achieved within 10 minutes, using a mechanical pump, the chamber was filled with nitrogen and then evacuated two times for the removal of as much oxygen as possible in preparation for sintering.

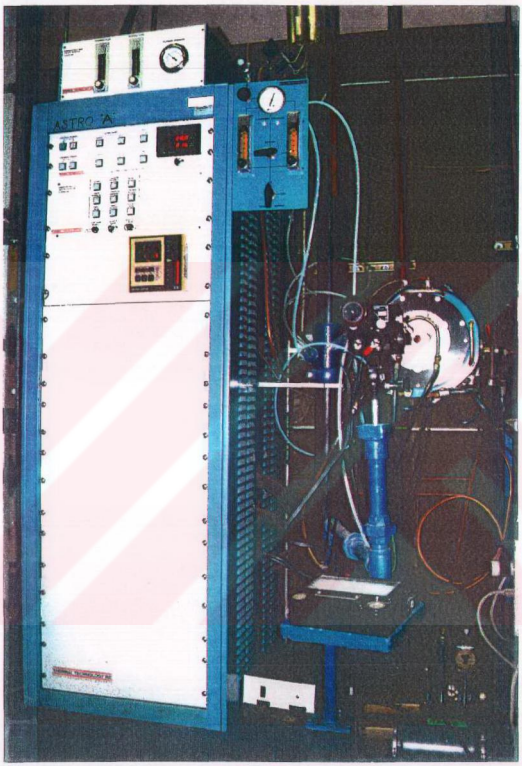


Figure 3.8. Picture of Vacuum Furnace, (Thermal Technology Inc., Astro Furnace)

The detailed patterns of applied temperature and atmosphere during reaction sintering are shown in Figure 3.9.

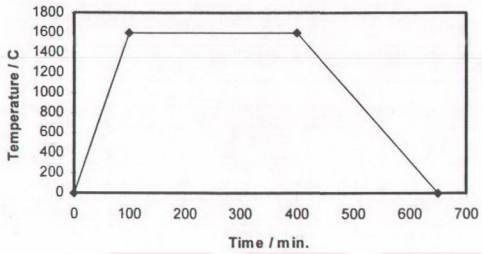


Figure 3.9. Typical Time-Temperature Plot For a Reaction Sintering Run

Sintering was performed at 1750 °C, 1850 °C and 1950 °C for times ranging from 1/2 hour to 5 hour. The furnace was controlled to +/- 5 °C. The furnace would come to sintering temperature in about 2 hours. Heating the sample slowly to the sintering temperature did have its advantages. The sample could be degassed and contaminants burned off prior to reaching the sintering temperature. Time was monitored after reaching the sintering temperature and the furnace was turned off after the appropriate sintering period, but the samples had to remain stationary until they were cooled sufficiently to avoid any substantial oxidation before they could be remove from the surface.

3.4. Hot-pressing

After the mixing the powders were than poured into graphite dies for hot-pressing. The hot-pressing was conducted in a vacuum (10^{-3}-10^{-4} torr; 1 torr = 1,333 x 10^2 Pa) induction furnace. The temperature was monitored using an optical pyrometer. Maximum hot-press temperature was approximately 1900°C. Each sample was sintered for various time, temperature, pressure in nitrogen gas atmosphere. Compaction of the powder was monitored by movement of the loading of the die plunger. The flow chart of the hot-press process is shown in Figure 3.10. After hot-pressing, the samples were removed from the graphite dies and machined to remove any products that may have resulted from surface reaction with the graphite die.

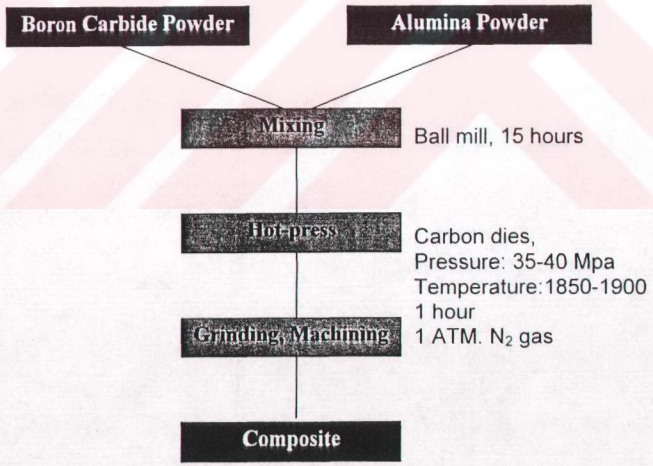


Figure 3.10. Flow chart of the hot-press process for BN-AlN Composites

Figure 3.11. Picture of Hot Press, (Centorr Vacumm Industries, USA)

3.5. Characterization Methods

Several techniques were employed to characterize the effects of sintering structure of AlN-BN ceramic composites.

After sintering, weigh loss was measured. Bulk density was calculated from the weigh and size of the specimen. The sintered pellets densities were established by isoprophile alcohol immersion in a vacuum with at least five samples per composition.

The scanning electron microscope (SEM) was used for characterization of powders and sintered compacts. In order to determine temperature, time and compaction effects during sintering, the compacts were notched and fractured to expose the sintered interior of the compact. Compacts were then mounted and examined in the SEM.

X-Ray Diffraction (XRD) utilizing a RIGAKU-RINT X-Ray diffractometer was used for phase identification, this technique was also useful for comparing the constitution and homogenization behavior of samples sintered at 1750-1950^{o}C for various time ranging from 0.5 to 5 hours.

CHAPTER 4. RESULT AND DISCUSSION

Sintering capability of Al_2O_3-B_4C composites were appeared to be strongly dependent on the properties of the Al_2O_3 powder and B_4C powder.

The pressed ceramic preforms were weighed before and after sintering to determine weigh change. Results have indicated that, the preforms which have lower B_4C and C content causes weigh loss at all sintering temperatures. The percentage of weigh change has increased with increasing sintering temperature.

Some weigh loss takes place simultaneously upon sintering due to the vaporization of oxides on the surface of BN particles and some reaction products. The weigh loss of samples depending on temperature and soaking time can be seen from Table 4.1.

Sintering time does not have an appreciable effects at temperatures of 1750°C or below. At higher temperatures extended soak times result BN formation increased. Boron carbide is unstable at high temperatures in the presence of nitrogen. Boron nitride is more stable than the carbide at all temperatures. Time appear to be significant variable in the sintering of these composites. Some loss in density was noted with extended sintering times at temperature of 1950°C.

Table 4.1. The weigh loss of samples depending on temperature and soaking time.

SAMPLE				
	1750 °C			
	0,5 hrs	1 hrs	2 hrs	5 hrs
Composition 1	2,87	2,18	4,50	3,80
Composition 2	4,20	1,39	2,20	4,76
Composition 3	2,45	4,84	1,49	3,67
Composition 4	3,93	1,97	5,24	4,49
	1850 °C			
	0,5 hrs	1 hrs	2 hrs	5 hrs
Composition 1	5,51	0,79	1,84	1,69
Composition 2	5,54	3,86	6,33	3,06
Composition 3	6,65	0,95	2,14	5,47
Composition 4	8,46	5,49	6,05	5,26
	1950 °C			
	0,5 hrs	1 hrs	2 hrs	5 hrs
Composition 1	17,90	8,82	12,73	22,05
Composition 2	19,09	40,20	17,40	40,66
Composition 3	24,18	15,50	12,84	16,49
Composition 4	18,78	19,46	16,89	20,84

The reaction used for the synthesis of composites and thermodynamics are given by equations (4.1.) and (4.2.).

$$1.5\ B_4C + Al_2O_3 + 4\ N_2 \longrightarrow 6\ BN + 2\ AlN + 1.5\ CO_2 \qquad (4.1.)$$

T °C	delta H kcal	delta S cal	delta G kcal	K
0,00	-231,695	-96,592	-205,310	1,925E+164
100,00	**-232,637**	**-99,571**	**-195,483**	**3,173E+114**
200,00	-233,193	-100,906	-185,450	4,645E+085
300,00	**-233,468**	**-101,440**	**-175,328**	**7,249E+066**
400,00	-233,533	-101,548	-165,176	4,282E+053
500,00	**-233,460**	**-101,450**	**-155,025**	**6,686E+043**
600,00	-233,292	-101,246	-144,889	1,857E+036
700,00	**-233,040**	**-100,973**	**-134,778**	**1,866E+030**
800,00	-232,726	-100,667	-124,696	2,493E+025
900,00	**-232,378**	**-100,356**	**-114,645**	**2,287E+021**
1000,00	-232,009	-100,055	-104,624	9,148E+017
1100,00	**-231,634**	**-99,771**	**-94,633**	**1,156E+015**
1200,00	-231,266	-99,512	-84,669	3,649E+012
1300,00	**-230,919**	**-99,284**	**-74,730**	**2,414E+010**
1400,00	-230,606	-99,092	-64,811	2,927E+008
1500,00	**-230,349**	**-98,942**	**-54,910**	**5,868E+006**
1600,00	-230,162	-98,839	-45,021	1,792E+005
1700,00	**-230,062**	**-98,787**	**-35,140**	**7,808E+003**
1800,00	-230,066	-98,789	-25,262	4,606E+002
1900,00	**-230,191**	**-98,848**	**-15,381**	**3,523E+001**
2000,00	-230,455	-98,966	-5,490	3,372E+000

AlN Extrapolated from 2000°K

Formula	FW g/mol	Conc. wt%	Amount mol	Amount g	Volume l or ml
B_4C	55,251	27,915	1,500	82,876	32,887ml
Al_2O_3	101,961	34,343	1,000	101,961	25,715ml
$N_2(g)$	28,013	37,742	4,000	112,054	89,654 l
BN	24,817	50,153	6,000	148,900	66,178
AlN	40,988	27,612	2,000	81,976	25,146
CO_2	44,010	22,235	1,500	66,015	33,620

$$3\,B_4C + Al_2O_3 + 7\,N_2 \longrightarrow 12\,BN + 2\,AlN + 3\,CO \qquad (4.2.)$$

T °C	delta H kcal	delta S cal	delta G kcal	K
0,00	-509,066	-156,982	-466,186	1,000E+308
100,00	**-510,415**	**-161,237**	**-450,249**	**5,343E+263**
200,00	-511,239	-163,216	-434,013	3,083E+200
300,00	**-511,654**	**-164,023**	**-417,644**	**1,848E+159**
400,00	-511,754	-164,189	-401,230	1,893E+130
500,00	**-511,628**	**-164,018**	**-384,817**	**6,125E+108**
600,00	-511,332	-163,660	-368,432	1,684E+092
700,00	**-510,891**	**-163,183**	**-352,089**	**1,199E+079**
800,00	-510,342	-162,647	-355,798	2,465E+068
900,00	**-509,723**	**-162,095**	**-319,560**	**3,442E+059**
1000,00	-509,060	-161,554	-303,378	1,209E+052
1100,00	**-508,382**	**-161,041**	**-287,249**	**5,274E+045**
1200,00	-507,713	-160,571	-271,169	1,709E+040
1300,00	**-507,080**	**-160,154**	**-255,133**	**2,801E+035**
1400,00	-506,508	-159,802	-239,136	1,733E+031
1500,00	**-506,036**	**-159,527**	**-223,170**	**3,229E+027**
1600,00	-505,694	-159,339	-207,227	1,514E+024
1700,00	**-505,512**	**-159,245**	**-191,299**	**1,550E+021**
1800,00	-505,524	-159,250	-175,375	3,086E+018
1900,00	**-505,761**	**-159,361**	**-159,445**	**1,088E+016**
2000,00	-506,257	-159,584	-143,499	6,277E+013

AlN Extrapolated from 2000°K

Formula	FW g/mol	Conc. wt%	Amount mol	Amount g	Volume l or ml
B_4C	55,251	35,737	3,000	165,753	65,775 ml
Al_2O_3	101,961	21,984	1,000	101,961	25,715 ml
$N_2(g)$	28,013	42,279	7,000	196,094	156,895 l
BN	24,817	64,208	12,000	297,800	132,356 ml
AlN	40,988	17,675	2,000	81,976	25,146 ml
CO(g)	28,010	18,118	3,000	84,031	67,241 l

Although both reactions are thermodynamically feasible, the reaction (4.2.) is more likely to occur due to the stability of CO at higher temperatures. The standard free energy of this reaction indicates that, it is possible to convert Al_2O_3 to AlN and BN. The result show that both reaction should progress toward right side. The quantity of boron nitride and aluminum nitride formation depending on temperature have been shown from figure 4.1 to 4.4 based on thermodynamic calculations considering mol fractions of powder mixing.

Mol fractions of reaction products have been calculated depending on alumina and boron carbide quantity based on thermodynamic principles were shown from figure 4.4 to 4.8.

When the effect of temperature and soaking time are considered, the result of XRD investigation can be evaluated as follows. XRD Analysis showed that reasonably good conversion were maintained for all composition.

All samples changed in color from gray to white up to the inner part of the sintered body upon sintering due to BN formation. Unreacted B_4C was detected by X-ray diffraction measurement for all sintered samples. But unreacted Al_2O_3 was not detected for all samples after heating up to 1950°C. Increasing of temperature, increases the reduction effect, so reaction sintering progresses intensively in figure 4.9.

Increasing of sintering temperature increases the amount of expected reaction products according to equation (4.1.) and (4.2.). For example XRD results of compacts which have same composition the one used in sintering at 1750°C were showed existence of AlN, AlON and BN phases respectively. Increasing 100°C in sintering temperature were resulted in complete formation of AlN, BN, AlON phases. It was observed that peak intensities of these phases increases with the increasing sintering temperature.

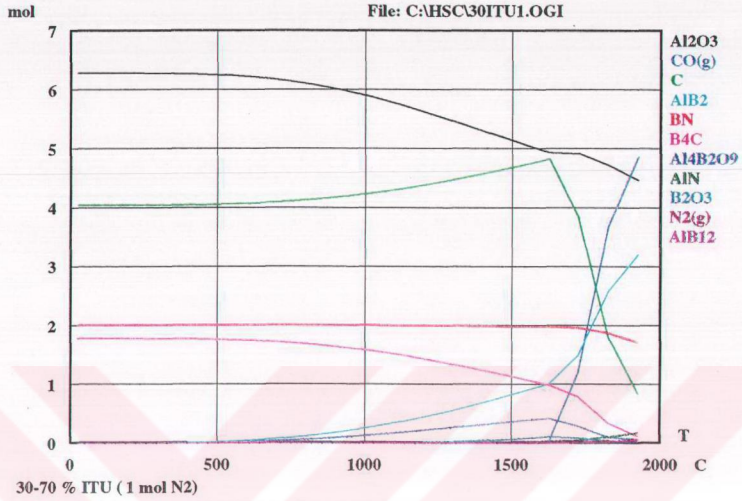


Figure 4.5 Identification of possible phase formation depending on temperature for the sample containing % 30 B_4C (ITU), % 70 Al_2O_3 (Ceralox) by using thermodynamic data.

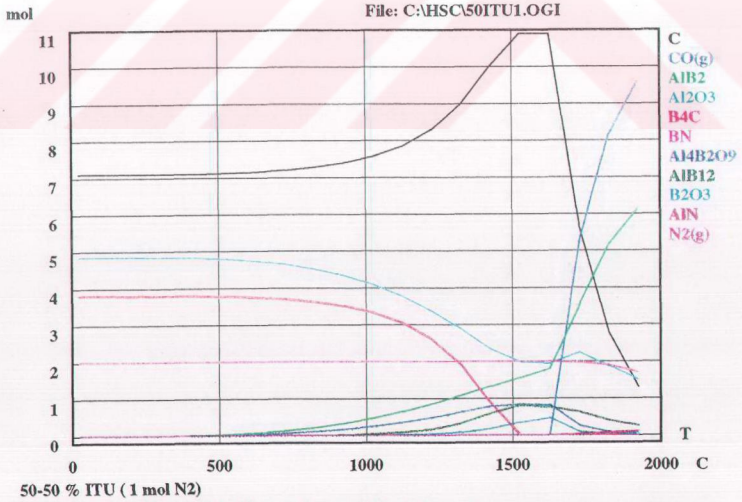


Figure 4.6 Identification of possible phase formation depending on temperature for the sample containing % 50 B_4C (ITU), % 50 Al_2O_3 (Ceralox) by using thermodynamic data.

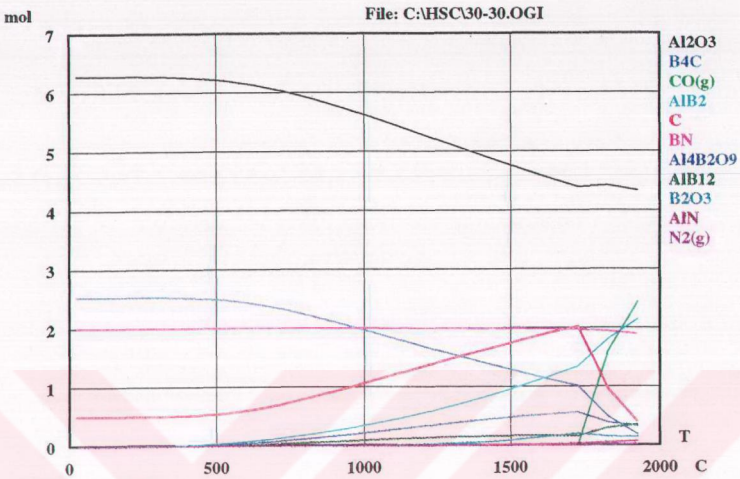


Figure 4.7 Identification of possible phase formation depending on temperature for the sample containing % 30 B_4C (Cerac), % 70 Al_2O_3 (Ceralox) by using thermodynamic data.

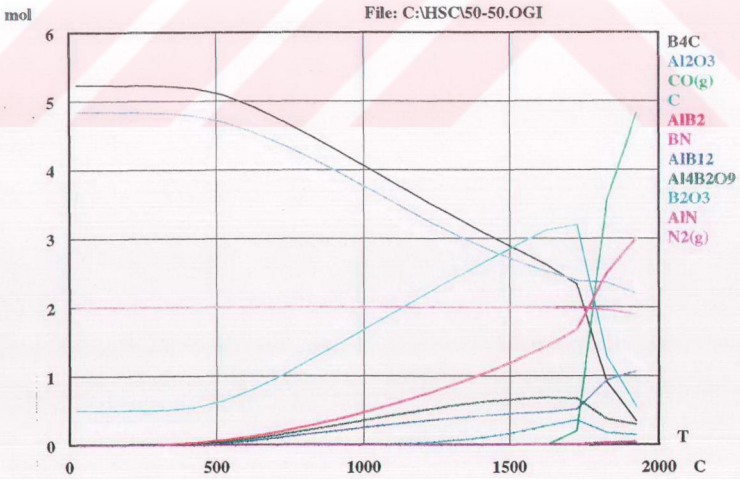


Figure 4.8 Identification of possible phase formation depending on temperature for the sample containing % 50 B_4C (Cerac), % 50 Al_2O_3 (Ceralox) by using thermodynamic data.

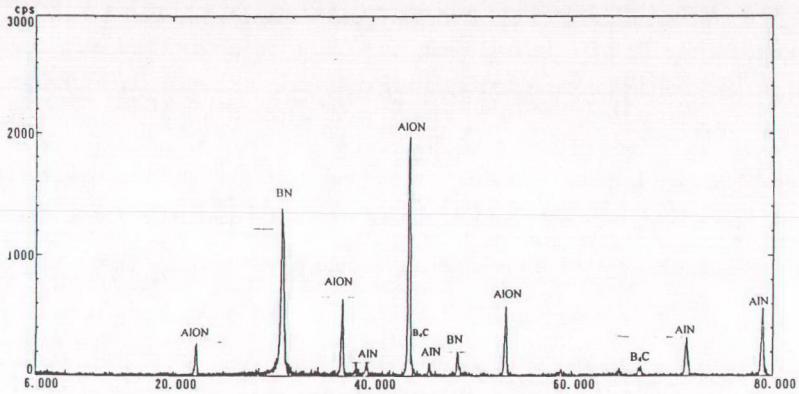


Figure 4.9. XRD Analysis Results of 1950 °C and 2 Hour Soaking Time

XRD analysis results of 30% Al_2O_3-70% B_4C powders sintered from 0,5 to 5 h showed that initially AlON formation were occurred at 1750°C, formation of AlON, AlN, BN phases were started to be visible for 1850°C and total conversion to AlN, AlON and BN were maintained by sintering at 1950°C respectively. The effect of free carbon content in B_4C powders on reaction sintering were determined by using two different commercial grade B_4C, the one were produced at ITU by domestic sources and the other from Cerac Inc..

Sintering of 50% Al2O3-50% B4C (ITU) powders at 1850 °C were showed no existence of Al_2O_3 phases. This results were suggesting that all oxygen content of Al_2O_3 have been used for formation of AlN, AlON and BN phases by means of reduction effect of C. Sintering at 1950 °C were encouraged BN formation increased and also AlN, AlON, BN phases were detected.

Volume ratio of phases formed at the end of reaction depending on temperature for the range of 1750-1950°C and from 0.5 to 5 hours time period by the calculation of XRD analysis result of peak areas were shown from figure 4.10 to 4.22.

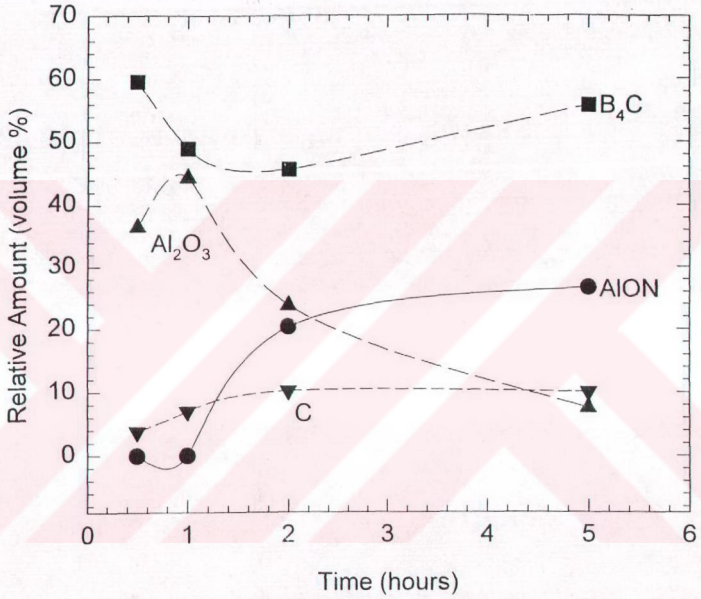


Figure: 4.10 Volume percentage of phases calculated by using peak areas of XRD analysis results for the samples containing *% 50 B_4C (Cerac) and % 50 Al_2O_3 (Ceralox)* which were exposed to sintering from 0,5 hour to 5 hour at *1850 °C*

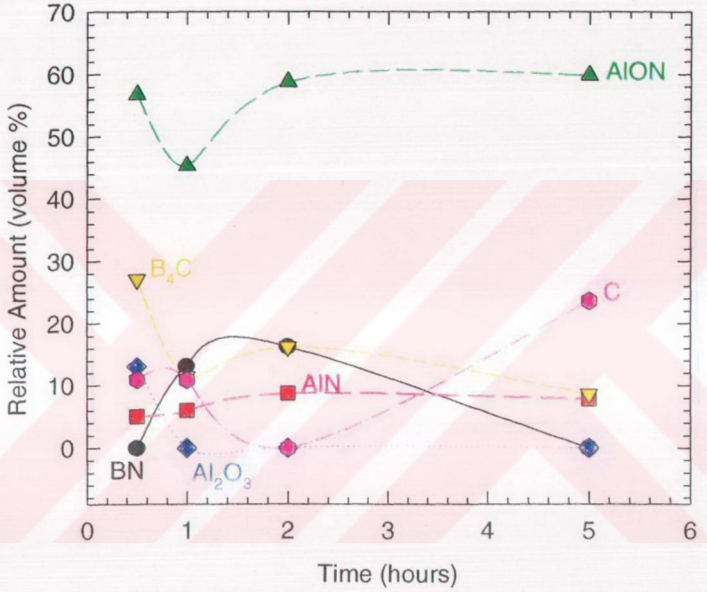


Figure 4.11 Volume percentage of phases calculated by using peak areas of XRD analysis results for the samples containing *% 30 B_4C (Cerac) and % 70 Al_2O_3 (Ceralox)* which were exposed to sintering from 0,5 hour to 5 hour at *1850 °C*

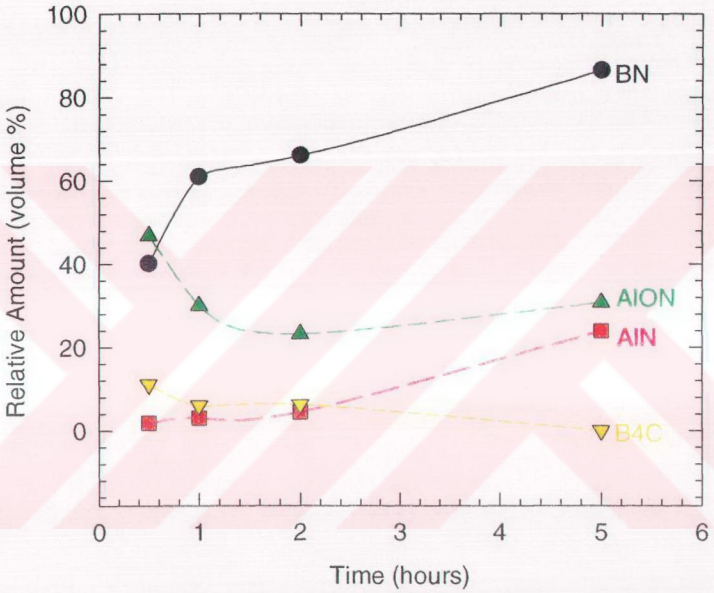


Figure 4.12 Volume percentage of phases calculated by using peak areas of XRD analysis results for the samples containing *% 30 B_4C (Cerac) and % 70 Al_2O_3 (Ceralox)* which were exposed to sintering from 0,5 hour to 5 hour at *1950 °C*

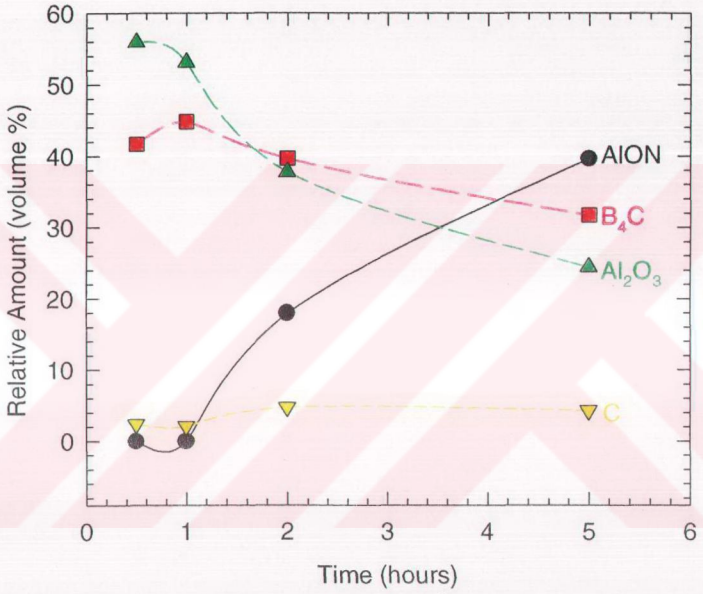


Figure 4.13 Volume percentage of phases calculated by using peak areas of XRD analysis results for the samples containing *% 50 B_4C (Cerac) and % 50 Al_2O_3 (Ceralox)* which were exposed to sintering from 0,5 hour to 5 hour at *1750 °C*

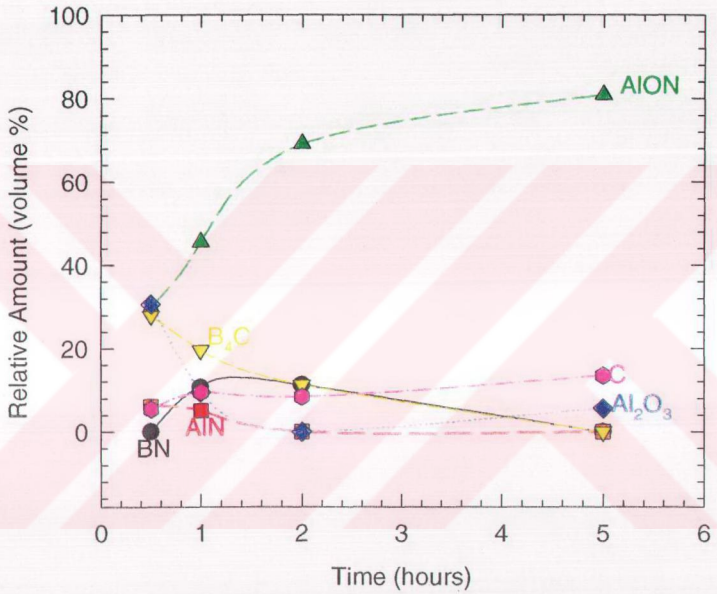


Figure 4.14 Volume percentage of phases calculated by using peak areas of XRD analysis results for the samples containing *% 50 B_4C (Cerac) and % 50 Al_2O_3 (Ceralox)* which were exposed to sintering from 0,5 hour to 5 hour at *1850 °C*

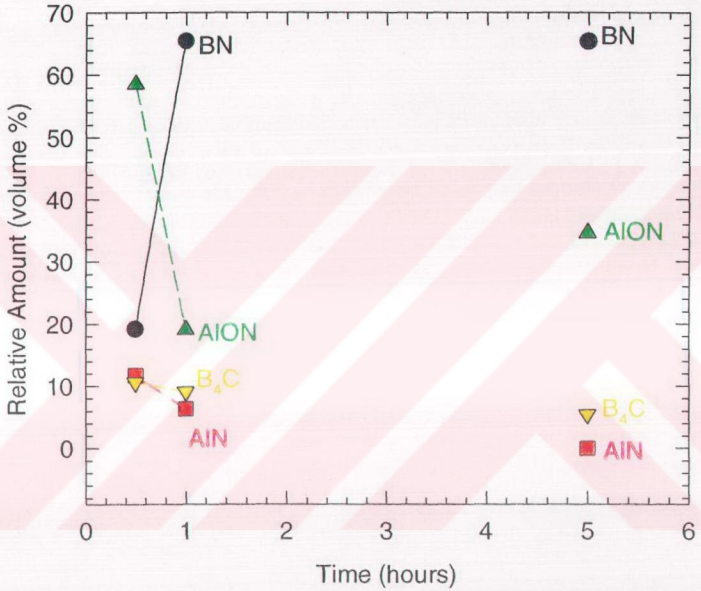


Figure 4.15 Volume percentage of phases calculated by using peak areas of XRD analysis results for the samples containing *% 50 B_4C (Cerac) and % 50 Al_2O_3 (Ceralox)* which were exposed to sintering from 0,5 hour to 5 hour at *1950 °C*

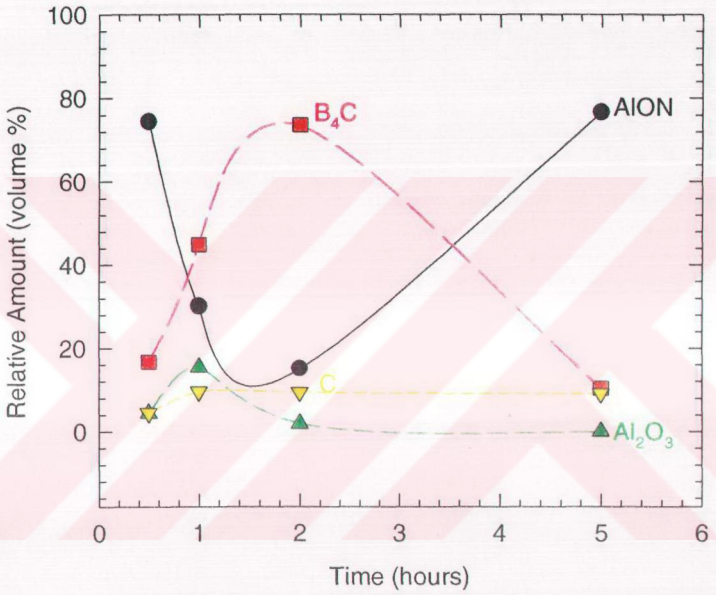


Figure 4.16 Volume percentage of phases calculated by using peak areas of XRD analysis results for the samples containing *% 30 B_4C (ITU) and % 70 Al_2O_3 (Ceralox)* which were exposed to sintering from 0,5 hour to 5 hour at *1750 °C*

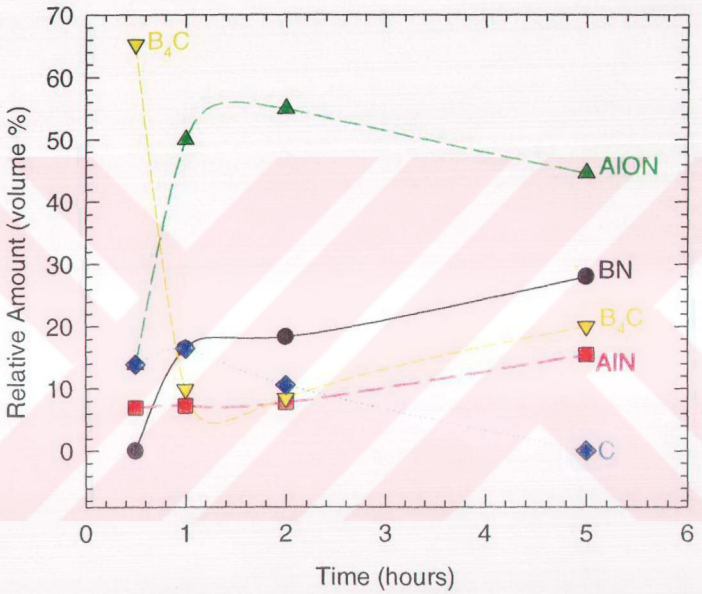


Figure 4.17 Volume percentage of phases calculated by using peak areas of XRD analysis results for the samples containing *% 30 B_4C (ITU) and % 70 Al_2O_3 (Ceralox)* which were exposed to sintering from 0,5 hour to 5 hour at *1850 °C*

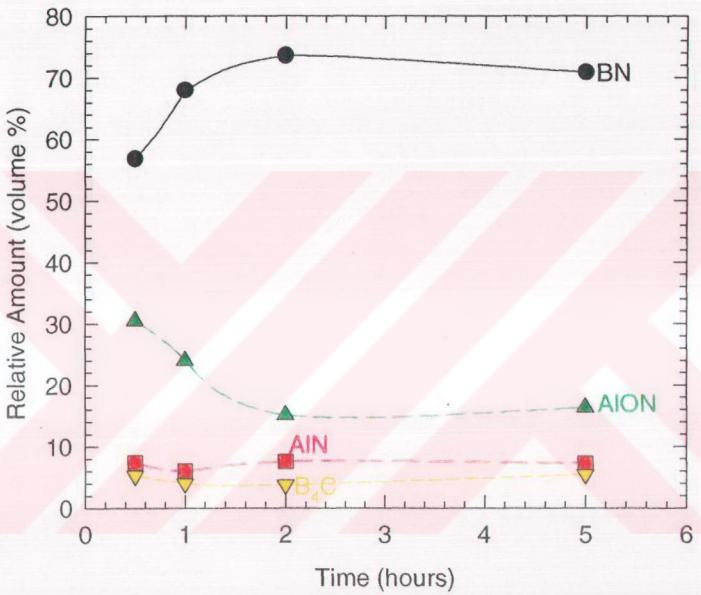


Figure 4.18 Volume percentage of phases calculated by using peak areas of XRD analysis results for the samples containing *% 30 B_4C (ITU) and % 70 Al_2O_3 (Ceralox)* which were exposed to sintering from 0,5 hour to 5 hour at *1950 °C*

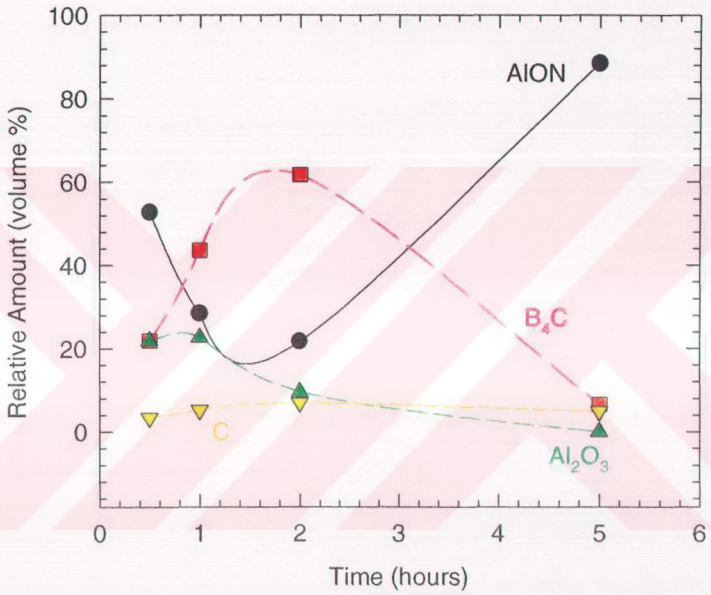


Figure 4.19 Volume percentage of phases calculated by using peak areas of XRD analysis results for the samples containing *% 50 B_4C (Cerac) and % 50 Al_2O_3 (Ceralox)* which were exposed to sintering from 0,5 hour to 5 hour at *1750 °C*

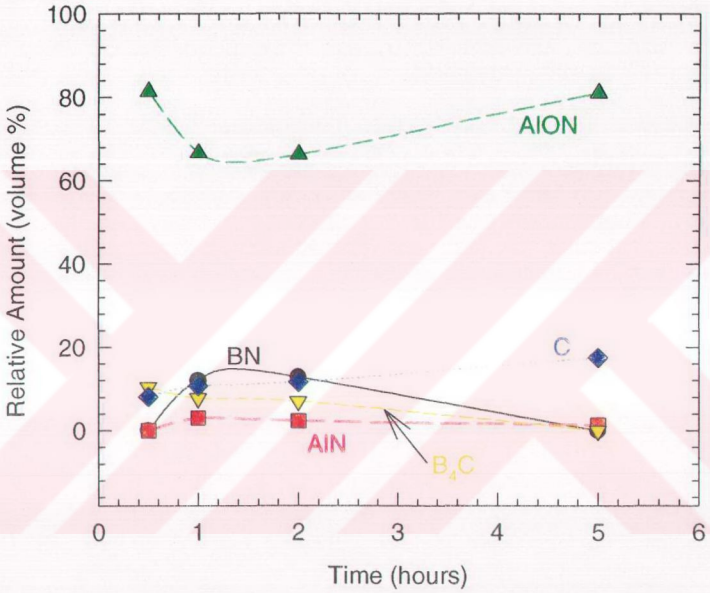


Figure 4.20 Volume percentage of phases calculated by using peak areas of XRD analysis results for the samples containing *% 50 B_4C (Cerac) and % 50 Al_2O_3 (Ceralox)* which were exposed to sintering from 0,5 hour to 5 hour at *1850 °C*

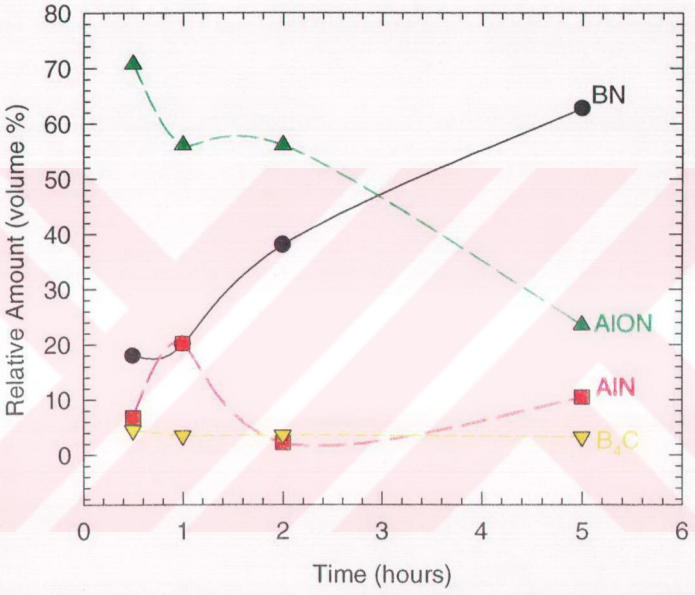


Figure 4.21 Volume percentage of phases calculated by using peak areas of XRD analysis results for the samples containing *% 50 B_4C (Cerac) and % 50 Al_2O_3 (Ceralox)* which were exposed to sintering from 0,5 hour to 5 hour at *1950 °C*

As a result, processing conditions of AlN-BN reaction have been investigated. It is understood that sintering 5 hours at 1850 °C can be optimum condition for producing such system. ITU originated B_4C powders containing free carbon have a very good effect on reaction sintering.

4.1. CONCLUSIONS

The reaction sintering of BN-AlN ceramic composite were studied. The following conclusions were obtained.

The study of nitridation of Al_2O_3 and B_4C in N_2 atmosphere and densification of this composite system in N_2 atmosphere at 1850-1950 °C were carried out by using Al_2O_3-B_4C (ITU) powders as a starting materials.

Excess carbon in the system appears to have positive effect for processing of BN-AlN ceramic composites. B_4C powders by ITU were indicated good results in composite synthesis due to reasonably high carbon content.

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CURRICULUM VITAE

Cem Çeliker was born Ankara-Turkey in 1970. He graduated from Suadiye High School in 1987 and attended to İstanbul Technical University, Sakarya Engineering Faculty in 1988. He received his B.Sc degree in Metallurgical Engineering in 1992. He started graduate study in 1993 at the Institute of Science and Technology in Materials Science program at Istanbul Technical University.

He had a fellowship from United Nations Development Organization (UNIDO) for a short term training in Quest Integrated Inc., Kent, WA., USA in 1996.