

**CHARACTERIZATION INVESTIGATIONS OF POWDER
AND SINTERED Al-SiC AND Al-B₄C COMPOSITES
DEVELOPED VIA MECHANICAL ALLOYING**

**M.Sc Thesis by
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Department : Advanced Technologies

Programme : Materials Science and Engineering

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**MEKANİK ALAŞIMLAMA YÖNTEMİYLE ÜRETİLMİŞ
Al-SiC VE Al-B₄C KOMPOZİTLERİNİN GELİŞTİRİLMESİ
VE KARAKTERİZASYONU**

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ABBREVIATIONS

AMC	: Aluminum Matrix Composites
EDS	: Energy Dispersion Spectrometry
HV	: Vickers Microhardness
MA	: Mechanical Alloying
MMC	: Metal Matrix Composite
PCA	: Process Control Agent
PM	: Powder Metallurgy
PRMMC	: Particulate Reinforced Metal Matrix Composites
PSA	: Laser Particle Size Analyzer
SEM	: Scanning Electron Microscopy
TEM	: Transmission Electron Microscopy
XRD	: X-Ray Diffraction

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SYMBOL LIST

$\mathbf{b}$	: Burgers vector
$\mathbf{f_c}$	: Volume fraction of the reinforcement
$\mathbf{G}$	: Shear modulus of the material
$\mathbf{L}$	: Interparticle spacing
σ_0	: Flow stress of undeformed crystal
σ_c	: Yield strength of the reinforcement
σ_m	: Yield strength of the matrix
σ_{mmc}	: Yield strength of the composite
τ	: Orowan stress

CHARACTERIZATION INVESTIGATIONS OF POWDER AND SINTERED Al-SiC AND Al-B₄C COMPOSITES DEVELOPED VIA MECHANICAL ALLOYING

SUMMARY

Particle-reinforced-metal-matrix composite (PRMMC) materials exhibit a unique combination of microstructure and properties not found in either ceramics or metals alone. Aluminum alloys are widely used as engineering and construction materials. The important characteristics of Al alloys are their lightweight and high specific strength. The mechanical properties of Al alloys can be greatly enhanced by incorporating reinforcing particles to form Al alloy-based metal matrix composites. Al-based or Al alloy-based matrix composites are used in aerospace, automotive and a lot of other applications due to their characteristic isotropic physical and mechanical properties.

In this study, aluminum matrix composites reinforced with SiC and B₄C particles which have attractive properties were developed by mechanical alloying. The effect of different SiC and B₄C amounts on the microstructural and mechanical properties were investigated. Microstructure and phase characterizations of composite powders and sintered samples were carried out via SEM and XRD analyses. Furthermore, the density and hardness of as-consolidated and sintered samples were measured. Also, the effect of addition of Y₂O₃ phase on the mechanical properties and the microstructures of Al-SiC and Al-B₄C composites were investigated. Moreover, in addition to the conventional sintering technique, a two-step sintering regime to inhibit the grain growth was applied to the samples and the effect of these different sintering regimes on microstructural and mechanical properties of the composites was examined.

MEKANİK ALAŞIMLAMA YÖNTEMİYLE ÜRETİLMİŞ Al-SiC VE Al-B₄C KOMPOZİTLERİNİN GELİŞTİRİLMESİ VE KARAKTERİZASYONU

ÖZET

Partikül takviyeli kompozitler, seramik ve metallerde tek başına bulunmayan eşsiz mikroyapıya ve özellik kombinasyonuna sahiptirler. Al alaşımlarının mekanik özellikleri, takviye malzemesi ilavesi ile yüksek oranda geliştirilebilir. Al matrisli kompozitlerin kullanım alanlarına örnek olarak; havacılık, otomotiv ve spor sektörleri verilebilir. Farklı uygulama alanlarında kullanılan bu malzemeler, karakteristik olarak izotropik, kimyasal ve mekanik özellikler içerirler. Bunun yanı sıra, göreceli olarak daha ucuz olmaları, kolay şekil alabilmeleri ve işlenebilmeleri sayılabilecek diğer avantajlarıdır.

Bu çalışmada, değişen sıcaklıklarda iyi özgül mukavemete ve yüksek young modülüne sahip olan, ayrıca iyi bir özgül direngenlik, yüksek erozyon ve korozyon direncine sahip SiC ve B₄C partikülleri ile takviye edilmiş alüminyum matrisli kompozitler, mekanik alaşımlama yöntemi kullanılarak geliştirilmiştir. Değişen SiC ile B₄C oranlarının mikroyapıya ve mekanik özelliklere olan etkisi de araştırılmıştır. Kompozit tozların ve sinterlenmiş numunelerin faz ve mikroyapı karakterizasyonları, SEM ve XRD teknikleri kullanılarak gerçekleştirilmiştir. Ayrıca preslenmiş ve sinterlenmiş numunelerin yoğunluk ve sertlik ölçümleri yapılmıştır. Bunun yanı sıra, Y₂O₃ takviyesinin Al-SiC ve Al-B₄C kompozitlerinin mikroyapı ve mekanik özelliklerine olan etkileri irdelenmiştir. Ayrıca geleneksel sinterleme tekniklerinin dışında, sinterleme sırasındaki tane büyümesini engellemek için iki basamaklı bir sinterleme rejimi kullanılmış ve farklı sinterleme rejimlerinin kompozitin mikroyapı ve mekanik özelliklerine olan etkileri de incelenmiştir.

1. INTRODUCTION

Composite materials have been utilized to solve technological problems for a long time but only in the 1960s did these materials start capturing the attention of industries with the introduction of polymeric-based composites (Schwartz, 1984). Since then, composite materials have become common engineering materials and are designed and manufactured for various applications including automotive components, sporting goods, aerospace parts, consumer goods, and in the marine and oil industries (Ahlatçı, 2003). The growth in composite usage also came about because of an increased awareness regarding product performance and increased competition in the global market for lightweight components. Among all materials, composite materials have the potential to replace widely used steel and aluminum, and often with better performance. Replacing steel components with composite components can save 60 to 80 % in component weight, and 20 to 50% weight by replacing aluminum parts (Akbulut, 2000). Today, it appears that composites are the materials of choice for many engineering applications (Kainer, 2006).

Metal composite materials have found application in many areas of daily life for quite some time. Often it is not realized that the application makes use of composite materials. These materials are produced in situ from the conventional production and processing of metals (Ibrahim et al, 1991). Materials like cast iron with graphite or steel with high carbide content, as well as tungsten carbides, consisting of carbides and metallic binders, also belong to this group of composite materials (Tech Trends, 1990). For many researchers, the term metal matrix composites is often equated with the term light metal matrix composites (MMC's) (Kainer, 2006). Substantial progress in the development of light metal matrix composites has been achieved in recent decades, so that they could be introduced into the most important applications (Eliasson and Sandström, 1995). In traffic engineering, especially in the automotive industry, MMC's have been used commercially in fiber reinforced pistons and aluminum crank cases with strengthened cylinder surfaces as well as particle-strengthened brake disks (Kainer, 2006). These innovative materials open up

unlimited possibilities for modern material science and development; the characteristics of MMC's can be designed into the material, custom-made, dependent on the application. From this potential, metal matrix composites fulfill all the desired conceptions of the designer (Mielke et al., 1987).

New applications are, for example, partially fiber-reinforced pistons and hybrid reinforced crank cases in passenger cars and truck engines, and particle-reinforced brake discs for light trucks, motorcycles, passenger cars and rail-mounted vehicles (Kainer, 2006). A further application area of these materials is in civil and military air and space flight. These innovative materials are of great interest for modern material applications due to the possibility to develop MMC's with specific properties. Ongoing from this potential, the metal matrix composites meet the desired concepts of the design engineer, because they represent custom-made materials. This material group is becoming of interest for construction and functional materials, if the property profile of conventional materials does not meet the requirement of lightweight construction (Kainer, 2006). The advantages of metal matrix composites are of use if a meaningful cost-performance relationship is possible during production of the components. Of special economic and ecological interest is the need for integration of processing residues, cycle scrap and waste products from these materials into the material cycle (Srivatsan et al., 1991).

Aluminum metal matrix composites (Al MMC's) are being considered as a group of new advanced materials for its light weight, high strength, high specific modulus, low coefficient of thermal expansion and good wear resistance properties (Kainer, 2006). Combinations of these properties are not available in a conventional material (Hunt, 2000). The use of Al MMC's has been limited in very specific applications such as aerospace and military weapon due to high processing cost. Recently, Al matrix composites have been used for automobile products such as engine piston, cylinder liner, brake disc/drum etc. (Chung and Zweben, 2000). Processing techniques for Al MMC's can be classified into (1) liquid state processing, (2) semisolid processing and (3) powder metallurgy. From the literature, it can be seen that many researchers were interested in investigating with liquid state processing and semisolid processing (Mortensen, 2000).

The selection of reinforcement depends on the application, the manufacturing methods, and the material cost (Sawtell et al., 1996). Wide range of potential

reinforcements have been considered, including SiC, Al₂O₃, mica, clay, ZrO₂ and graphite (Kainer, 2006). Recently, B₄C has become an attractive reinforcement for Al MMC's due to its lower density and comparable mechanical/ thermal properties to SiC and Al₂O₃ (the two most common reinforcements). In contrast to Al MMC's containing SiC or Al₂O₃ reinforcement, Al MMC's containing B₄C reinforcement paid less attention (Carden, 1996). Furthermore, it is known that reactions between aluminum alloys and B₄C usually produce a variety of phases which affect the mechanical properties of Al/B₄C composites to different extents (Ibrahim et al., 1991). Such reactions are strongly dependent on processing parameters, like consolidation temperature and oxygen content (Ashby, 1993).

The silicon carbide SiC reinforced Al composite (SiC/Al) is perhaps the most successful class of MMC's produced to date. They have found widespread application for aerospace, energy, and military purposes, as well as in other industries for example; they have been used in electronic packaging, aerospace structures, aircraft and internal combustion engine components, and a variety of recreational products (Seleznev et al., 1995). SiC reinforced aluminum alloy composites made by casting techniques are most common because of their low cost and ease of fabrication. However, during the fabrication of the SiC/Al composite, whether reinforced with fibers, whiskers or particulates, a major technical problem occurs with the formation of the Al₄C₃ phase at the SiC/Al interface, because the SiC is thermodynamically unstable in the Al melt. This brittle reactant Al₄C₃, in the shape of thin hexagonal platelets, forms as agglomerates at the SiC/Al interface (Lloyd, 1989). As a result, this reactant degrades the composite strength, modulus, and corrosion resistance (Lin, 1995). So far, the four methodologies have been proposed to prevent the formation of Al₄C₃ reactant at the SiC/Al interface:

- The Si element in the Al melt can effectively inhibit the formation of Al₄C₃ through increased activity a [Si] of Si in the solution. This method is effective but the matrix composition is modified, which may affect the composite global properties (Hunt, 2000),
- Coating the SiC surface to produce diffusional barriers to prevent direct contact of the SiC with the Al matrix, such as Al₂O₃, TiO₂, SiO₂, SnO, Sb₂O₃ and SnO₂ coatings. This method is economically unfavorable and may result in interface instability at elevated temperatures (Lloyd et al., 1990),

- Pre-oxidation of SiC to introduce a thin coating layer of SiO₂ on the SiC surface which is believed to act as an intermediate to form stable interfacial structures, which prevent direct contact of SiC with Al (Han et al., 1993). However, the microstructural details of this type of interface formed from the pre-oxidation SiO₂ layers remain unclear,
- Moreover, the matrix composition being widely imposed by the process needs, there is very limited room for influencing the composite mechanical (and physical) properties by means of matrix alloying (Lee and Kwon, 1997).

Aluminum Powder Metallurgy (PM) offers components with exceptional mechanical and fatigue properties, low density, corrosion resistance, high thermal and electrical conductivity, excellent machinability, good response to a variety of finishing processes, and which are competitive on a cost per unit volume basis. Fatigue is an important decision consideration for PM parts subjected to dynamic stresses (Huda et al., 1995). The most commonly used fatigue property is the fatigue limit, which is the maximum reversed stress the material will withstand if cycled indefinitely. This limit is defined when the fatigue curve becomes horizontal. Fatigue limits for 2xxx and 6xxx aluminum PM alloys are 7.5 and 6.5 ksi, respectively, and are about 50% of the comparable wrought alloys (Nair et al., 1985). This difference is due to the lower density of PM parts. Hot forging the aluminum PM part results in fatigue limits comparable to the wrought alloys (Ashby, 1993).

In addition, the cost of fabrication coupled with a need to improve the part recovery has led to significant growth in the net-shaped component manufacturing processes (Hunt, 2000). In addition, aluminum PM parts can be further processed to eliminate porosity and improve bonding, yielding properties that compare favorably to those of conventional wrought aluminum products. The primary driver for the use of aluminum PM is the unique properties of aluminum coupled with the ability to produce complex net or near net shape parts which can reduce or eliminate the operational and capital costs associated with intricate machining operations. Aluminum PM can replace other PM in certain applications on a direct basis (Eliasson and Sandström, 1995).

Keeping the above concepts in mind, the aim of this study is the development and the characterization of SiC and B₄C particle-reinforced aluminum composite powders

and transformation of these composite powders into end-products via powder consolidation and sintering techniques. A second part of this work is the investigation of the effect of Y_2O_3 addition on the mechanical properties and on the microstructure of Al-SiC and Al-B₄C composites.

2. COMPOSITE MATERIALS

Composite materials (or composites for short) are engineering materials made from two or more constituent materials that remain separate and distinct on a macroscopic level while forming a single component. There are two categories of constituent materials: matrix and reinforcement (Schwartz, 1984). The matrix material surrounds and supports the reinforcement materials by maintaining their relative positions. The reinforcements impart their special mechanical and physical properties to enhance the matrix properties. This synergism produces material properties unavailable by using the individual constituent materials. Due to the wide variety of matrix and reinforcement materials available, the design potentials are incredible (Mazumdar, 2001).

The most primitive composite materials comprised straw and mud in the form of bricks for building construction. The most advanced examples perform routinely on spacecraft in demanding environments. The most visible applications pave our roadways in the form of either steel and aggregate reinforced portland cement or asphalt concrete. Those composites closest to our personal hygiene form our shower stalls and bath tubs made of fiberglass. Solid surface, imitation granite and cultured marble sinks and countertops are widely used to enhance our living experiences.

There are also natural composites like bone and wood. Both of these are constructed by the processes of nature and beyond the scope of this text. Engineered composite materials must be formed to shape. This involves strategically placing the reinforcements while manipulating the matrix properties to achieve a melting event at or near the beginning of the component life cycle. A variety of methods are used according to the end item design requirements. The principle factors impacting the methodology are the natures of the chosen matrix and reinforcement materials. Another important factor is the gross quantity of material to be produced. Large quantities can be used to justify high capital expenditures for rapid and automated manufacturing technology. Small production quantities are accommodated with lower capital expenditures but higher labor and tooling costs at a correspondingly

slower rate (Kainer, 2006). Figure 2.1 shows the development curve of the market for modern materials where composite materials fall in the higher end of the development curve (Tech Trends, 1990).

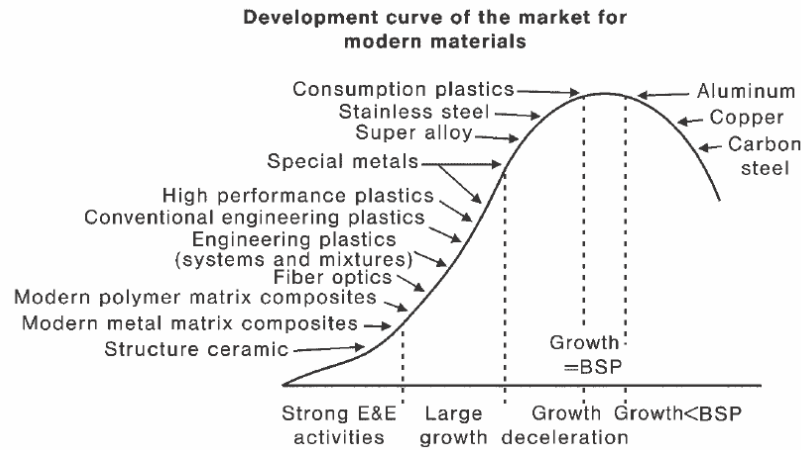


Figure 2.1: Development curve of the market for modern materials (Tech Trends, 1990).

Physical properties of composite materials are generally not isotropic in nature. For instance, the stiffness of a composite panel will often depend upon the directional orientation of the reinforcement. In contrast, an isotropic material has the same stiffness regardless of the directional orientation of the reinforcement. The relationship between forces/moments and strains/curvatures for an isotropic material can be described with the following material properties: Young's Modulus, the Shear Modulus and the Poisson's Ratio, in relatively simple mathematical relationships. For the anisotropic material, it requires the mathematics of a second order tensor and can require up to 21 material property constants. For the special case of orthogonal isotropy, there are three different material property constants for each of Young's Modulus, Shear Modulus and Poisson's Ratio for a total of 9 material property constants to describe the relationship between forces/moments and strains/curvatures (Mazumdar, 2001).

The advantages of the composite materials are only realized when there is a reasonable cost–performance relationship in the component production. The use of a composite material is obligatory if a special property profile can only be achieved by application of these materials. The possibility of combining various material systems (metal–ceramic–nonmetal) gives the opportunity for unlimited variation. The properties of these new materials are basically determined by the properties of their

single components (Schwartz, 1999). Figure 2.2 shows the allocation of the composite materials into groups of various types of materials.

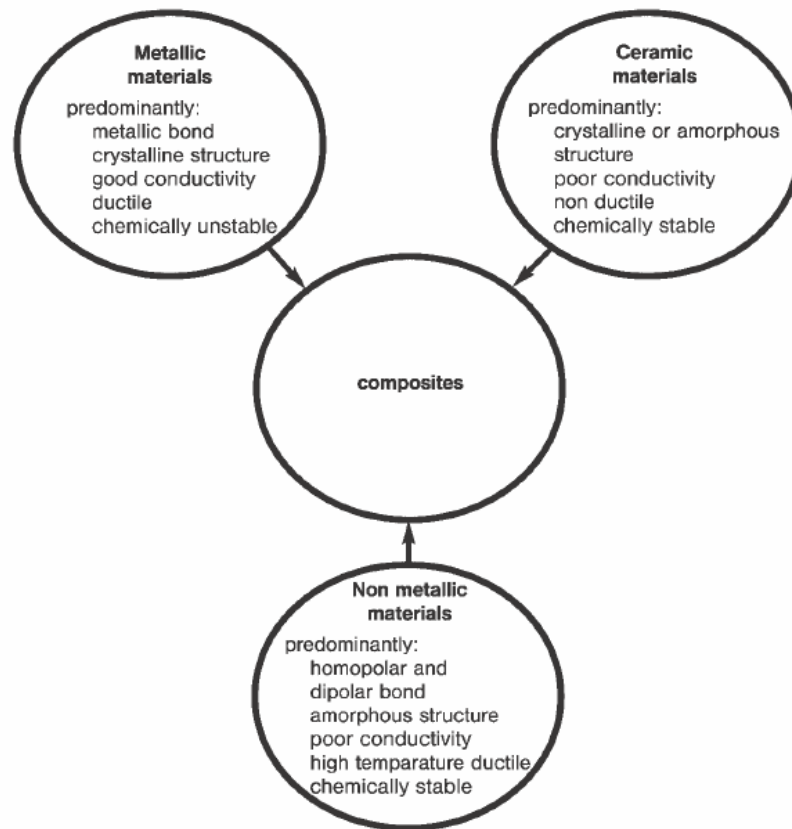


Figure 2.2: Classification of the composite materials with in the group of materials (Kainer, 2006).

In the fabrication of metal matrix composites (MMC), the reinforcement can have many different objectives. The reinforcement of light metals opens up the possibility of application of these materials in areas where weight reduction has first priority. The precondition here is the improvement of the component properties (Kainer, 2006). The development objectives for light metal composite materials are:

- Increase in yield strength and tensile strength at room temperature and above while maintaining the minimum ductility or rather toughness,
- Increase in creep resistance at higher temperatures compared to that of conventional alloys,
- Increase in fatigue strength, especially at higher temperatures,
- Improvement of thermal shock resistance,
- Improvement of corrosion resistance,

- Increase in Young's modulus,
- Reduction of thermal elongation.

To summarize, an improvement in the weight specific properties can result, offering the possibilities of extending the application area, substitution of common materials and optimization of component properties.

3. METAL MATRIX COMPOSITES

Metal matrix composites (MMC) are a group of advanced materials designed for use mainly at elevated temperatures where existing materials are not suitable for use (Huda and Hashmi, 1995). As the name implies, the matrix is a ductile metal. Reinforcements such as intermetallic compounds, oxides, carbides and nitrides improve specific stiffness and specific strength, wear resistance, creep resistance and dimensional stability (Akbulut, 2000). There are many advantages of MMC's when compared with metals. Advantages of MMC's over conventional metals are (Ibrahim et al., 1991):

- High elastic modulus,
- High strength (tensile, compressive, wear, creep and slip),
- Stability at elevated temperatures,
- MMC's possess ductility and toughness of metals and high elastic modulus and strength of ceramics,
- Low density,
- Low sensitivity to temperature differences and thermal shocks,
- High electrical and thermal conductivity.

Disadvantages of MMC's are (Ahlatçı, 2003):

- Low fatigue resistance,
- Complex and expensive production techniques.

Each year, hundreds of new applications of composites are found in different disciplines such as sports, aeronautical and automotive industries. Composite materials offer designers an increasing array of material and system solution. Reducing the weight of a vehicle and therefore reducing the consumption of fuel is very important for high technological applications. Since MMC's are more expensive than matrix alloys, they are used in the fields where material properties are more

important than the cost (Srivatsan et al., 1991). The most important property of MMC's is the wear resistance. They are used in high wear applications (Akbulut, 2000).

Many different metals are used as matrix material in MMC's. The matrix acts as a binder to hold the reinforcement particles together and the main function of the matrix is to transfer and distribute the stress to the reinforcement material. The transfer of stress depends on the bonding interface between matrix and reinforcement, which depends on the type of matrix and the reinforcement as well as on the fabrication technique (Kainer, 2006).

The major problem for attaining a good load transfer is the achievement of proper bonding between the matrix and the reinforcement. Not all combinations of reinforcement and matrix are compatible and many combinations cannot be processed into commercially useful composites. In some composites, the coupling between the reinforcement and the matrix is poor and adhesion promoters are needed (Liu et al., 1994). In others excessive interfacial reactivity can lead to a brittle layer around the reinforcement. The most important parameter for the MMC's is the compatibility between matrix and reinforcement material. In order to enhance wettability and so improve the bonding between matrix and reinforcement, the matrix material can be alloyed (Ibrahim et al., 1991). Researches show that aluminum and aluminum alloys are the best matrix materials when wettability, cost and density are taken into consideration (Akin, 2006).

While chemical composition, morphology, microstructure, physical properties, mechanical properties and cost are important parameters for the reinforcement selection, oxidation resistance, corrosion resistance, density, strength and ductility/toughness ratio are important parameters for the matrix selection (Huda and Hashmi, 1995). Al, Ti, Mg, Ni, Cu, Pb, Fe, Ag, Zn, Sn and super alloys are widely employed as matrix materials. Among these Al, Ti and Mg alloys have the widest application areas when compared to others (Ibrahim et al., 1991).

The main reason for the limited use of MMC's is that they have low fracture toughness and that there is a difference in thermal expansion coefficients of the constituents. The key parameter for MMC's at elevated temperatures is the specific strength (strength/density). Figure 3.1 shows the classification of the composite

materials with metal matrix composite (MMC). MMC's are more reliable than the conventional materials at high temperatures.

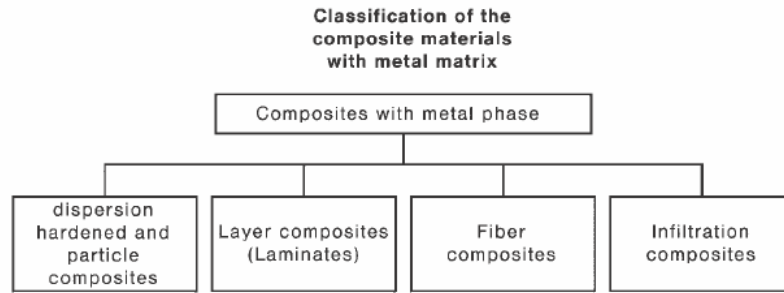


Figure 3.1: Classification of composite materials with metal matrixes.

Although MMC's have been well known over the last forty years, the application of MMC's has been increasing for the last twenty years because of problems related with manufacturing processes and finding fibers that are compatible with a metal matrix (Liu et al., 1994). Since discontinuous reinforcement materials can be produced and obtained easily, in recent years, they are preferred in the manufacturing of MMC's. After production they may be subjected to a secondary process such as forging, rolling and/or extrusion. Easy production techniques lead to the use of MMC's in many fields such as sports equipment and automotive industry (Dinwoodie et al., 1985). Fiber composite materials can be further classified into continuous fiber composite materials (multi and monofilament) and short fibers or, rather, whisker composite materials, as seen in Figure 3.2 (Clyne and Withers, 1993).

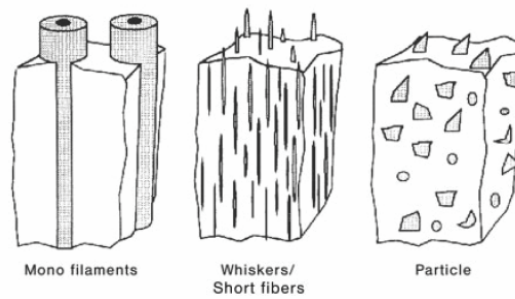


Figure 3.2: Schematic presentation of three shapes of metal matrix composite materials (Clyne and Withers, 1993).

Particle reinforced metal matrix composites are a class of materials that exhibit a blending of properties of the reinforcement and the matrix. According to their chemical compositions, reinforcement materials are classified into three groups; nitrides, oxides and carbides (Lloyd, 1994). Strength of particulate reinforced

composites depends on particle diameter, size of vacancy between particles, volume fraction of reinforcement and matrix/reinforcement interface (Srivatsan et al., 1991). In the selection of reinforcement material, the factors listed below must be taken into consideration (Elliasson and Sandström, 1995):

- Elastic modulus,
- Tensile strength,
- Density,
- Size and shape,
- Thermal stability,
- Thermal expansion coefficient,
- Chemical stability,
- Cost.

If the composite material will be used in structural applications, reinforcement material must have high strength, elastic modulus and low density. Since cornered particles cause stress concentration and decrease the ductility, the shape of the particle has strong influence on mechanical properties (Ahlatçı, 2003).

3.1 Particulate Reinforced Metal Matrix Composites (PRMMC's)

MMC's have become attractive candidate materials for aerospace, automotive and a lot of other applications due to their physical and mechanical properties (Liu et al., 1994). More recently, especially PRMMC's have received increasing attention because of their relatively low costs, good formability and machinability as well as characteristic isotropic properties (Ibrahim et al., 1991; Tjong and Ma, 2000; Sun et al., 2003).

Early studies on MMC's were about the development and investigation of the behavior of continuous fiber reinforced high performance hybrid materials (Kainer, 2006). However, extensive industrial application of these composites has been hindered because of the high production costs of the reinforcement fiber. So, availability of relatively inexpensive reinforcements and the development of various processing methods which result in reproducible microstructures and properties really enhanced the interest on PRMMC's (Ibrahim et al., 1991). These materials

exhibit a unique combination of microstructure and properties which is not found in either ceramics or metals alone (Tjong and Ma, 2000). These properties of PRMMC's mainly depend on the microstructure and properties of the matrix materials, the nature, distribution, size and shape of particles as well as an interfacial behavior between matrix and the reinforcement phase constituents (Liu et al., 1994). An optimum combination of mechanical properties can be achieved when fine and thermally stable ceramic particulates are dispersed uniformly in the metal matrix (Tjong and Ma, 2000). PRMMC's are produced either by melt incorporation and casting technique or powder blending and consolidation (Clyne, 2001).

There are two sub-classifications of PRMMC's: Large particle strengthened composites and dispersion strengthened composites. The distinction between these two groups is based on the reinforcement or strengthening mechanism. The aim of using the term "large" is to point out that particle–matrix interactions cannot be related to the atomic or molecular level; so, preferably, continuum mechanics is used. Generally, the particulate phase is harder and stiffer than the matrix. These reinforcing particles tend to restrain movement of the matrix phase in the neighborhood of each particle.

Basically, the matrix transfers some of the applied stress to the particles, which carry a fraction of the load. The degree of reinforcement or improvement of mechanical behavior depends on strong bonding at the matrix–particle interface. For dispersion-strengthened composites, particles are normally much smaller than particles in large particulate composites, having diameters between 0.01 and 0.1 μm (10 and 100 nm). This time, particle–matrix interactions cause strengthening to occur on the atomic or molecular level (Ibrahim et al., 1991; Tjong and Ma, 2000; Sun et al., 2003). Potential particle or platelet-shaped ceramic compounds for metal reinforcement are shown in Table 3.1.

The mechanism of strengthening is similar to that for precipitation hardening. Since the matrix carries the major portion of an applied load, the small dispersed particles hinder the motion of dislocations. So, plastic deformation is restricted such that yield and tensile strengths, as well as hardness, improve. In addition to that, the volume fraction of the particles in dispersion strengthened composites is very low (%3) comparing to that in large particle strengthened composites (%70-90), (Schwartz, 1984; Demirkesen, 2003).

Table 3.1: Potential particle or platelet-shaped ceramic compounds for metal reinforcement (Kainer, 2006).

<i>Metal-basis</i>	<i>Carbide</i>	<i>Nitride</i>	<i>Boride</i>	<i>Oxide</i>
boron	B ₄ C	BN	–	–
tantalum	TaC	–	–	–
zirconium	ZrC	ZrN	ZrB ₂	ZrO ₂
hafnium	HfC	HfN	–	HfO ₂
aluminum	–	AlN	–	Al ₂ O ₃
silicon	SiC	Si ₃ N ₄	–	–
titanium	TiC	TiN	TiB ₂	–
chromium	CrC	CrN	CrB	Cr ₂ O ₃
molybdenum	Mo ₂ C, MoC	Mo ₂ N, MoN	Mo ₂ B, MB	–
tungsten	W ₂ C, WC	W ₂ N, WN	W ₂ B, WB	–
thorium	–	–	–	ThO ₂

The geometries of the particles are manifold. It is possible to produce spherical, block-shaped, plate-shaped or needle-shaped geometries. However, due to the production process the particles are mostly irregular in shape, having sharp tips and edges. Figure 3.3a shows an example of a SiC particle in block-shaped geometry and Figure 3.3b shows a SiC particle in the spherical form. The geometrical shape can have an unfavorable effect on the composite material. Therefore, attempts have been made to produce, regular shaped particles in platelet (Figure 3.3c and Figure 3.3d) or rod forms, which have a positive influence on the mechanical properties of particle reinforced light metals. Rod-shaped particles act, at an appropriate length–thickness ratio, like short fibers (Kainer, 2006).

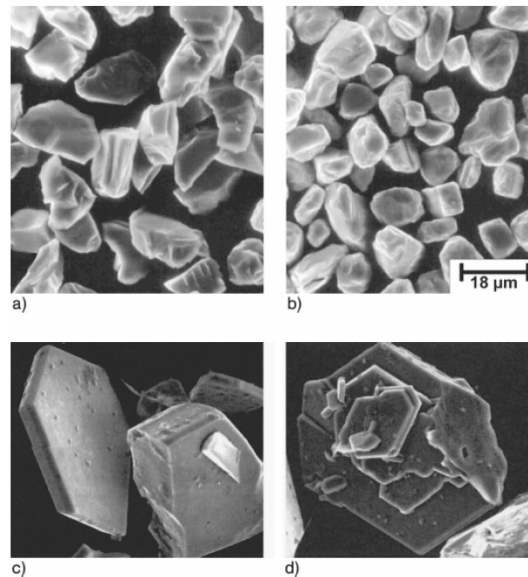


Figure 3.3: (a) SiC, particle in block shaped geometry; (b) SiC, particle in spherical geometry; (c) and (d) (ASM Handbook, Vol. 21, Composites, 2001, p. 54).

3.1.1 Large particle composites

Large-particle composites are utilized with all three material types, namely metals, polymers and ceramics (Tjong and Ma, 2000). However, the most common large-particle composites are cermets which are mixture of ceramics and metals and they offer engineers the opportunity to combine the properties and take advantage of the unique characteristics of both (Schwartz, 1984). The most common cermet is the cemented carbide, which is composed of extremely hard particles of refractory carbide or oxide ceramic such as tungsten carbide (WC), titanium carbide (TiC), alumina (Al_2O_3) or magnesium-oxide (MgO) embedded in a matrix of a metal such as cobalt or nickel.

These composites are used widely as cutting tools for hardened steels. The hard carbide particles provide the cutting surface but, are not themselves capable of withstanding the cutting stresses because they are extremely brittle. Toughness is enhanced by their inclusion in the ductile metal matrix, which isolates the carbide particles from each other and prevents particle-to-particle crack propagation. Both matrix and particulate phases behave like refractory, to withstand the high temperatures generated by the cutting action on materials that are extremely hard (Askeland, 1984; Schwartz, 1984).

3.1.2 Dispersion-strengthened composites

Metals and metal alloys may be strengthened and hardened by the uniform dispersion of several volume percent of fine particles of a very hard and inert material. The particle size in dispersion-strengthened composites is very small, with diameters of 10-250 nm (Askeland, 1984). The dispersed phase may be metallic or nonmetallic; oxide materials are often used (Liu et al., 1994). Again, the strengthening mechanism involves interactions between the particles and dislocations within the matrix, as with precipitation hardening, namely a pronounced strengthening effect is obtained because the particles block the movement of dislocations. However, the strengthening is retained at elevated temperatures and for extended time periods because the dispersed particles are chosen to be unreactive with the matrix phase. For precipitation-hardened alloys, the increase in strength may disappear upon heat treatment as a consequence of precipitate growth or dissolution of the precipitate phase (Askeland, 1984; Demirkesen, 2003).

For instance, the high-temperature strength of nickel alloys may be enhanced significantly by the addition of about 3 vol% of thoria (ThO_2) as finely dispersed particles; this material is known as thoria-dispersed (or TD) nickel. Furthermore, there are tungsten and superalloys which are dispersion-strengthened by adding of about 1-2 vol% of thoria (ThO_2). Yttria (Y_2O_3), alumina (Al_2O_3) and other oxides perform the same function (Askeland, 1984; Schwartz, 1984; Flinn and Trojan, 1995). For instance, as dispersion strengthened phase, La_2O_3 particles exert a significant effect on the microstructure and mechanical properties of materials, such as creep resistance or strength at elevated temperatures (Chen, 2000).

Additionally, a very thin and adherent alumina coating is formed on the surface of extremely small (0.1 to 0.2 μm thick) flakes of aluminum, which are dispersed within an aluminum metal matrix; this material is termed sintered aluminum powder (SAP), (Askeland, 1984; Schwartz, 1984; Flinn and Trojan, 1995).

3.2 Strengthening Mechanisms in PRMMC's

There are a lot of mathematical models which have been formulated for calculating the mechanical properties of PRMMC's. The simplest model is the rule-of-mixture model which is mainly used for fiber reinforced composites. In this model, the composite is assumed to be fully isotropic. Therefore, the mechanical properties, such as strength, shear modulus and normal modulus of PRMMC can be estimated from the weighted average of the individual constituents (Ibrahim et al., 1991; Mital et al, 1996). For instance, for the strength of a PRMMC the equation below can be written;

$$\sigma_{mmc} = f_c \sigma_c + (1 - f_c) \sigma_m \quad (3.1)$$

where σ_{mmc} is the yield strength of the composite, σ_c is the yield strength of the reinforcement, σ_m is the yield strength of the matrix and f_c is the volume fraction of the reinforcement (Zhang, 2003). However, one must first understand the strengthening mechanisms in PRMMC's to be able to formulate a reliable mathematical model.

Particulate reinforced composites fall somewhere between the dispersion strengthened and fiber strengthened composites. A particulate reinforced composite

placed between these extremes is strongly dependent on the size and shape of its reinforcement. In general, as the aspect ratio (l/d) of the reinforcement increases, the composite tends to exhibit increased amounts of fiber strengthening, but as particle size decreases, the composite will tend to be primarily strengthened by dispersion methods (Table 3.2), (Poquette, 2005).

Table 3.2: Metal matrix composite subcategories and the strengthening mechanisms.

Type of MMC	Reinforcement	Primary Strengthening
Fiber Strengthened (Continuously Reinforced)	Long Fibers (aspect ratio >10)	Shear Lag Theory (Load Transfer from Matrix to Fiber)
Discontinuously Reinforced	Short Fibers or Whiskers (aspect ratio <10) and/or Large Particles (diameter >1 μ m)	Combination of Fiber and Dispersion Strengthening Mechanisms
Dispersion Strengthened	Small particles (diameter <1 μ m)	Orowan Inhibition of Dislocation Motion, Boundary Strengthening - Matrix/Reinforcement - Grain Size Refinement in the Matrix Coefficient of Thermal Expansion Mismatch

There are different strengthening mechanisms in PRMMC's. In the following sections, how the reinforcement size and geometry affects the strengthening contributions by these mechanisms will be explained. Most alloys are based on the principle that explaining the strengthening mechanism the strength of the composite is determined by the stress which is required either to generate or move dislocations in the lattice (Ibrahim et al., 1991). Only the Shear lag theory is based on, the more the movement of dislocations is inhibited, the stronger material will be.

3.2.1 Shear lag theory

The shear lag theory assumes that load transfer occurs between a high aspect ratio reinforcement and the matrix by means of shear stresses at the particle-matrix interface (Ibrahim et al., 1991; Mital, 1996). Under an applied load, the load is transferred from the weaker matrix, across the matrix/reinforcement interface, to the

typically higher stiffness reinforcement. In this manner, strengthening takes place by the reinforcement carrying much of the applied load.

Due to the lower aspect ratio of particulate materials, load transfer is not as efficient as in the case of continuous fiber reinforcement, but is still significant in providing strengthening (Poquette, 2005). Through this mechanism, the particle acts to bear some of the applied load. If the original model is modified, considering that the particles are equiaxed, the yield strength of the composite can be found using the equation below;

$$\sigma_{mmc} = \sigma_c + \left(1 + \frac{1}{2}f\right) \quad (3.2)$$

where σ_c is the yield strength of the composite, σ_{mmc} is the yield strength of the unreinforced composite and f is the volume fraction of the reinforcement.

3.2.2 Orowan strengthening

According to Orowan strengthening theory for composites containing small ($<1\mu\text{m}$) particles, the material is strengthened due to the interaction between the particles and dislocations (Mabuchi et al, 1997; Poquette, 2005). A passing dislocation will bow between the small particulates and finally pass by leaving an “Orowan” loop behind, as shown in Figure 3.4.

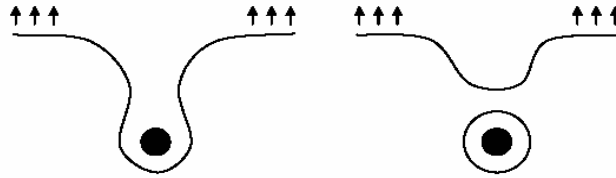


Figure 3.4: The formation of an Orowan Loop.

Thus, the strength of the materials is increased when the applied stress to move the dislocation is increased. This Orowan stress is given below;

$$\tau = \frac{Gb}{L} \quad (3.3)$$

where τ is the Orowan stress, b is the Burgers vector, G is the shear modulus of the material and L is the interparticle spacing.

$$L = 1,23r \left(\frac{2\pi}{3f} \right)^{\frac{1}{2}} \quad (3.4)$$

where r is the average particle radius and f is the fraction of reinforcement. According to this equation the strength of the composite is increased with decreasing particle size and increasing volume fraction of reinforcements. This is especially valid for particles in the submicron range. However, for particle sizes greater than $10\mu\text{m}$ strengthening mechanism is still predicted but not expected to be as effective as in submicron-range (Mabuchi et al, 1997; Poquette, 2005).

3.2.3 Boundary strengthening

For many materials the yield strength σ_y varies with grain size according to Hall-Petch equation;

$$\sigma_y = \sigma_o + k_y d^{-\frac{1}{2}} \quad (3.5)$$

where σ_o is the flow stress of undeformed crystal, k_y is a constant and d is the average diameter of the grains (Callister, 2000; Hansen, 2004; Poquette, 2005).

In this mechanism, again the inhibition of movement or creation of dislocations causes the increase of the strength of the material. However, for boundary strengthened crystallographic discontinuities or boundaries are the reason for improving the strength. When the material is stressed, dislocations tend to pile-up at these incoherent interfaces, so the overall dislocation density thus, the strength of the material is increased (Poquette, 2005). In addition to that, since two grains are different oriented, a dislocation passing to a neighbor grain has to change its direction and this becomes more difficult as the crystallographic misorientation increases (Callister, 2000). According to this, when the amount of the boundaries is increased, the strength of the material will be increased. This increase in the amount of the boundaries is achieved by grain size refinement. Also the boundaries between two different phases hinder the movement of dislocations. So, adding fine particles to a fine grained matrix duplicates the amount of the obstacles (Callister, 2000; Poquette, 2005). Furthermore, grain size refinement improves not only the strength but also the toughness of many alloys (Callister, 2000).

However, not all the explanations of the boundary strengthening mechanism are based on dislocation pileups at grain boundaries. The Hall-Petch behavior can be explained by dislocations which are generated at grain boundary ledges during deformation (Figure 3.5).

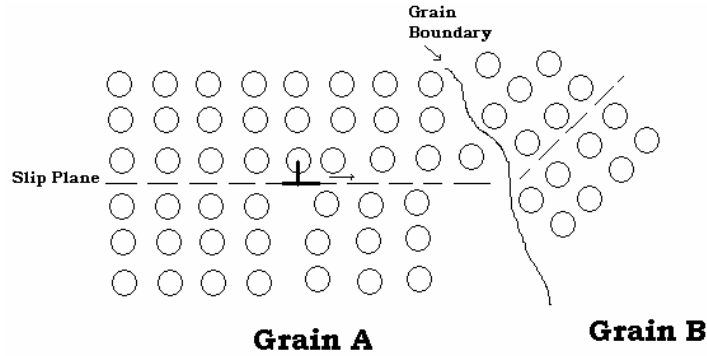


Figure 3.5: The motion of a dislocation through a grain boundary (Callister, 2000).

On the other hand, Meyers and Ashworth (1996) also suggested a model in which the strengthening by grain refinement is based on the generation of dislocation at grain boundaries (Figure 3.6). However, in this model dislocations are generated in the boundary regions where the elastic anisotropy results in stress concentrations, so that a hardened reinforcing second-phase network is formed. So, yielding occurs when the applied stress is high enough to push the dislocations through the hardened layers into the grain interior (Weertman, 2002).

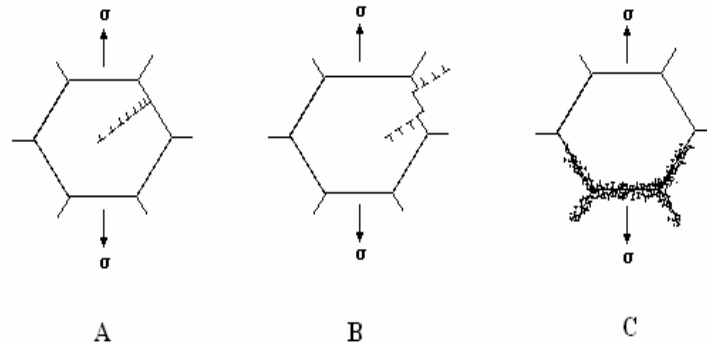


Figure 3.6: Three models explaining the Hall-Petch behavior (Weertman, 2002).

3.2.4 Solid solution hardening

Another mechanism to strengthen metals or composites is alloying with impurity atoms which go either into substitutional or interstitial solid solution. In these mechanism, lattice strain field interactions between dislocations and these impurity

atoms cause to inhibit the movement of dislocations (Callister, 2000). A large difference in atomic size between the solvent atom and the solute atom will increase the strengthening effect because larger size difference produces a greater disruption of the lattice, so that the slip of dislocation is made more difficult (Askeland, 1984). For instance, a solute atom which is smaller than solvent atoms exerts tensile strains on the lattice, whereas a larger atom exerts compressive strains. Thus, these solute atoms tend to diffuse to and segregate around dislocations, so that the overall strain energy is reduced (Figure 3.7). To achieve this, for example a smaller solute atom is located where its tensile strain and some of dislocation's compressive strain cancel each other out (Callister, 2000).

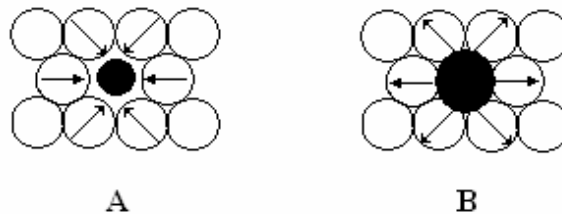


Figure 3.7: Representation of tensile lattice strain (a) Compressive lattice strain (b) Imposed on host atom by impurity atoms (Callister, 2000).

3.2.5 Strain hardening

Strain hardening is a phenomenon whereby a ductile metal becomes stronger as it is plastically deformed. The dislocation density in the material is increased with deformation, due to dislocation multiplication and the formation of new dislocations (Callister, 2000). Primary dislocations produce loops by interaction with secondary dislocations, which give rise to local dislocation tangles gradually developing into three-dimensional networks of sub-boundaries (Smallman and Bishop, 1999). As a result, the average distance between dislocations decreases. On the average, dislocation-dislocation strain interactions are repulsive. The net result is that the motion of a dislocation is hindered by the presence of other dislocations. In this way, the applied stress necessary to deform the material increases with increasing deformation (Callister, 2000).

There are some source mechanisms which explain above mentioned dislocation-dislocation interactions that increase the dislocation density in the material. The most important one is the Frank-Read source mechanism (Smallman and Bishop, 1999). In this mechanism, a dislocation line is fixed at the nodes A and B (fixed, for example,

because the other dislocations that join the nodes do not lie in slip planes) (Figure 3.8). Consequently, a dislocation loop is formed which expands into the slip plane. This sequence is then repeated and as a result the dislocation density is increased.

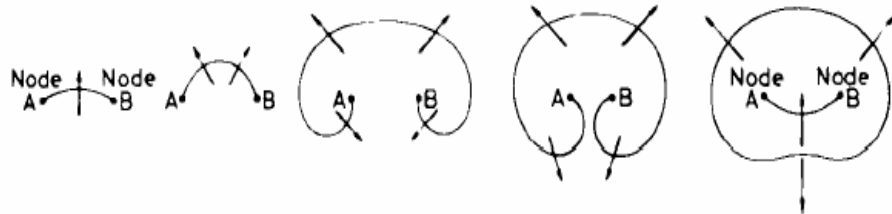


Figure 3.8: Forming of a Frank-Read source.

Another mechanism is the cross-slip mechanism which depends on the Frank-Read principle but does not require dislocation segment to be anchored by nodes (Smallman and Bishop, 1999). Thus, if part of a moving screw dislocation undergoes double cross-slip, the two pieces of edge dislocation on the cross-slip plane effectively act as anchoring points for a new source. The loop expanding on the slip plane parallel to the original plane may operate as a Frank-Read source and any loops produced may in turn cross slip and become a source (Figure 3.9). This process therefore not only increases the number of dislocations on the original slip plane but also causes the slip band to widen (Smallman and Bishop, 1999).

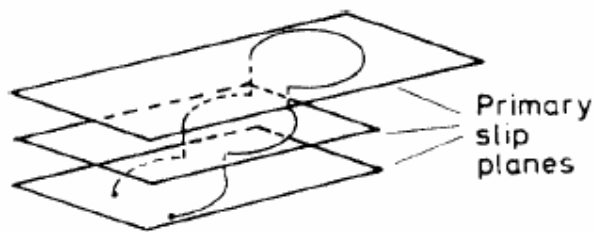


Figure 3.9: Cross-Slip multiplication source.

4. ALUMINUM MATRIX COMPOSITES

Aluminum metal matrix composites (Al MMC's) are being considered as a group of new advanced materials for its lightweight, high strength, high specific modulus, low coefficient of thermal expansion and good wear resistance properties. Since Al has high specific strength, high electric conductivity, low density, high corrosion resistance and is cheaper than other light metals, the use of Al has been increasing rapidly (Elliasson and Sandström, 1995). The chief limitation of aluminum and its alloys is their low melting temperature (~660°C) that limits their maximum service temperature. However, they remain the major materials for airplane construction and are used for many applications due to various advantages such as low specific weight, high specific strength, high elastic modulus and high wear resistance (Burg and Crosky, 2001).

Combinations of these properties are not available in a conventional material (Hunt, 2000). The use of Al MMC has been limited in very specific applications such as aerospace and military weapon due to high processing cost. Recently, Al matrix composites have been used for the automobile products such as engine piston, cylinder liner, brake disc/drum etc. (Chung and Zweben, 2000). Aluminum alloys, 2xxx (AlCuMg), 5xxx (AlMg), 6xxx (AlMgCuSi), 7xxx (AlZnMgCu) and especially due to the wetting characterization of 8xxx (AlLi), are widely used in composite production. For example, 7xxx Al alloys exhibit better strength and toughness combination required for the aviation applications than the 2xxx Al alloys do, but despite this, 2xxx Al alloys are more preferred for aviation applications because of interface reactions that occur between 7xxx Al alloys and reinforcement materials resulting in degradation in the strength of composites (Huda et al., 1995).

Since, the great advantage of AMC materials is a superior combination of different properties of metallic matrix and hard reinforcement. However, these properties can only be obtained with proper selection of matrix material and reinforcement (Lindroos et al., 2004).

The matrix of the composites has to be mainly designed for two major tasks. The first function of the matrix is to bind and support the reinforcing phase. Secondly, it has to satisfy special properties based on the requirements in service. Bond strength between the matrix, whose main function is to transfer and distribute the load to the reinforcement and the reinforcement, depends on the type of matrix and reinforcement (Huda et al., 1995; Lindroos et al., 2004). The interface formed between the matrix and the reinforcement is interesting because the characteristics of this region determine load transfer and crack resistance of the composite during deformation. It is now widely known that in order to maximize interfacial bond strength, it is necessary to promote wetting (when a liquid phase process is present), control chemical interactions and minimize oxide formation (Ibrahim et al., 1991). The hardness of the matrix is the key factor in supporting the reinforcing phase. Furthermore, other considerations such as, cost, weight, fabricability and availability of the matrix materials should be made (Lindroos et al., 2004). Table 4.1 shows the reinforcement materials used in aluminum matrix composites.

Table 4.1: Properties of reinforcement materials used in Al matrix composites (Kainer, 2006).

Reinforcement	Particle size (μm)
Al_2O_3	3-200
SiC, particle	6-120
SiC, whisker	5-10
Graphite, lamellar	20-60
Zirconium	40
Silica sand	75-120
Zirconium oxide	5-80
TiC	46
Mg	40
Boron nitride	46
Mica	40-180
B_4C	50-80

During fabrication of Al MMC's, the selection of reinforcement depends on the application, the manufacturing methods, and the material cost. A wide range of potential reinforcements have been considered, including SiC, Al_2O_3 , mica, clay, ZrO_2 and graphite. Recently, B_4C has become an attractive reinforcement for Al MMC's due to its lower density and comparable mechanical/thermal properties to SiC and Al_2O_3 (the two most common reinforcements) (Huda et al., 1995). In contrast to Al MMC's containing SiC or Al_2O_3 reinforcement, Al MMC's containing B_4C reinforcement have been paid much less attention (Carden, 1996). Furthermore, it is known that reactions between aluminum alloys and B_4C usually produce a

variety of phases which affect the mechanical properties of Al/B₄C composites to different extents. Such reactions are strongly dependent on processing parameters, like consolidation temperature and oxygen content (Ashby, 1993).

The silicon carbide (SiC) reinforced Al composite (SiC/Al) is perhaps the most successful class of MMC's produced to date. They have found widespread application for aerospace, energy, and military purposes, as well as in other industries for example; they have been used in electronic packaging, aerospace structures, aircraft and internal combustion engine components, and a variety of recreational products (Seleznev et al., 1995). SiCp reinforced aluminum alloy composites made by casting techniques are most common because of their low cost and ease of fabrication. However, during the fabrication of the SiC/Al composite, whether reinforced with fiber, whisker or particulate, a major technical problem occurs with the formation of the Al₄C₃ phase at the SiC/Al interface, since SiC is thermodynamically unstable in the Al melt (Lindroos et al., 2004). This brittle reactant Al₄C₃, in the shape of thin hexagonal platelets, forms as agglomerates at the SiC/Al interface (Lloyd, 1989). As a result, this reactant degrades the composite strength, modulus, and corrosion resistance (Lin, 1995).

So far, the following methodologies have been proposed in order to prevent the formation of Al₄C₃ reactant at the SiC/Al interface:

- Si is added to the Al matrix to a thermodynamic equilibrium between the phases involved, thus annihilating the driving force for the reaction. For reactive pressureless infiltration, the critical Si content may be as high as 20 wt% (Seleznev et al., 1995). The Si in the Al melt can effectively inhibit the formation of Al₄C₃ through increased activity $a[\text{Si}]$ of Si in the solution. This method is effective but the matrix composition is modified, which may affect the composite global properties (Hunt, 2000),
- Coating the SiC surface to produce diffusional barriers to prevent direct contact of the SiC with the Al matrix, such as Al₂O₃, TiO₂, SiO₂, SnO, Sb₂O₃ and SnO₂ coatings. This method is economically unfavorable and may result in interface instability at elevated temperatures (Lloyd et al. 1990),
- Pre-oxidation of SiC to introduce a thin coating layer of SiO₂ on the SiC surface which is believed to act as an intermediate to form stable interfacial structures,

which prevent direct contact of SiC with Al (Han et al., 1993). In the presence of SiO₂ layers on the SiC surface, the following reactions may occur in the Al melt containing Mg: thermodynamic calculations were performed for these reactions (Seleznev et al., 1995), and the reactant MgAl₂O₄ was observed as nanoparticles, indicating that these reactions might occur locally at nanoscale. However, the microstructural details of this type of interface formed from the pre-oxidation SiO₂ layers remain unclear. Moreover, when Mg is added, MgAl₂O₄, MgO, Mg₂Si or Al₂O₃ are prone to form, isolatedly or in combination. Such interfacial reactions, however, are known to cause degradation of the SiC particles and to be detrimental to the composites' mechanical properties. The matrix composition being widely imposed by the process needs, there is very limited room for influencing the composite mechanical (and physical) properties by means of matrix alloying (Lee and Know, 1997),

Shorowordi et al., (2003) made a comparative study about microstructure and interface characteristics of B₄C, SiC and Al₂O₃ reinforced Al matrix composites. In this study, the reinforcing particles of SiC and Al₂O₃ were preheated at 900°C for 1 and 2h in air, respectively to increase their surface reactivity, while B₄C was preheated at 175°C for 2h. Then, heat-treated particles were mixed into the melt through the vortex. Finally, the melt had been poured into a 52 mm internal diameter cylindrical graphite mould. Various compositions ranging from 0 to 20 vol.% of Al-SiC, Al-Al₂O₃ and 0–13 vol.% Al-B₄C composites had been processed. Composites had been subjected to hot extrusion at 420°C with an extrusion ratio of 27:1. Hot extruded composites of 10 mm diameter bar had been then heat treated at 400°C for 2h and cooled in furnace to remove the extrusion effect. For Al-B₄C composite, they had detected no clear interaction layer at the interface. The B₄C particles had seemed to adhere well to the Al matrix. They had observed two secondary phases in the matrix away from the interface. From EDX analysis they had thought that these phases were Al₂O₃ and aluminum boron carbide. The alumina particles were small and spread throughout the Al matrix while the second phase consisted of relatively larger particles but were less in number. B₄C decomposes by chemical interaction with solid or liquid aluminum at temperatures ranging from 627 to 1000°C. The reaction products are ternary carbide Al₃BC and diboride, AlB₂ up to 868°C. At temperature higher than 868°C, Al₃BC is still formed while Al₃B₄C₂ replaces AlB₂.

As the processing temperature is below 868°C, the phases present were expected in the Al-B₄C composites to be Al₃BC and AlB₂. But no aluminum boron containing phase had been found. Hence, it was thought that the aluminum boron carbon containing phase was Al₃BC. No Al₄C₃ was present in Al-B₄C composites as it had been processed below 1000°C. This was a specific feature that differentiates the Al-B₄C couple from other reactive couple such as Al-SiC, at the interface of which Al₄C₃ appears as a major reaction product. Moreover, secondary phases that were produced in the Al-B₄C system were not detrimental for the composites like Al₄C₃. These rather improve the properties of the composites.

Hu et al., (2001) studied microstructure of B₄C/Al composites produced by cold isostatic pressing. In their study, B₄C particles with a mean size 10 µm and Al powders had been blended and isostatically cold pressed. Cold isostatically pressed samples had been sintered under vacuum conditions. Sintered samples then had been extruded at a ratio of 35:1. The as-extruded composite had been subsequently solution heat-treated at 493°C for 2h and water quenched and artificially aged at 135°C for 3h. The microstructure of the B₄C: Al-7093 composite that investigation had been characterized by standard metallography and polishing techniques. The primary and secondary phases present in the microstructure had been identified using transmission electron microscopy (TEM), scanning electron microscopy (SEM) and X-ray diffraction. The grain sizes were 3-5 µm, and a large number of precipitates were present in the Al matrix. EDS spectra of these precipitates showed that they were enriched not only with Mg and Zn but also with Cu, suggesting that they were probably Mg (Zn, Cu)₂ precipitates. Higher magnification clearly showed the variation of precipitates in the matrix. Basically, the precipitates exhibited two types of morphologies: plate-shaped precipitates with an average size of 0.10 µm in thickness by 0.55 µm in length, and spherically-shaped precipitates with an average size of 0.15 µm, which was similar to those seen in Al-7075-T651. In some cases, plateshaped precipitates, stacked close to each other, formed precipitate bands in the matrix. The density of these precipitates varied among the specimens. For example, in another specimen, a much lower density of precipitates had been observed. Two types of B₄C: Al-7093 interfaces were observed in the specimens: (a) clean interfaces free of precipitates and (b) interfaces containing dispersed phases. The former type of interface was seldom seen in the composite, although the latter type of interface was

typical. The dispersed phases were equiaxed, a few tens of nanometers across, and often appeared in clusters with no evidence of preferred orientation. In regions with high concentrations of interface phase, the concentration of precipitates in the adjoining matrix was generally reduced. As described above, the amount of precipitates in the aluminum matrix and in grain boundaries was related. EDS spectra consistently showed that the stronger the Mg peak, the stronger the O peak, indicating the presence of MgO or MgAl_2O_4 at the B_4C : Al interfaces. Although it was possible that segregated Mg atoms had been oxidized after results are attributed to the presence of MgO and/or MgAl_2O_4 at the interfaces in B_4C : Al-7093.

Halverson et al., (1989) have studied processing of Al- B_4C composites. They focused on finding the phases in the microstructure. In their study, they mixed B_4C powder (three particle-size distributions with medium sizes of 4, 10 and 56 μm) and aluminum powder (-325 mesh) in isopropyl alcohol, ultrasonically mixed the slurry to achieve homogeneity, and consolidated the solids by filtration in a plaster of Paris mold. They consolidated samples using three different techniques which were pressureless sintering, hot-pressing, and hot isostatic pressing. Hot pressing was achieved under a pressure of 207 MPa at 1000-1200°C. B_4C and aluminum react to form the phase Al_4BC . Under local equilibrium between 800°C and 900°C, AlB_2 and Al_4BC were the major reaction products. Under these conditions, phase Al_4BC is stable, and it will decompose only if all of the free aluminum is depleted from the system. Above 1100°C, there is less of the Al_4BC_3 phase because aluminum is rapidly being depleted through the formation of other more thermodynamically stable phases. Above 900°C, but below 1200°C, the following microstructural differences occur: (1) $\text{AlB}_{12}\text{C}_2$ is thermodynamically favoured over AlB_{12} between 900°C and 1000°C, and (2) AlB_2 , continues to form up to 1000°C; however, above 1000°C, AlB_2 is only present when the microstructure is cooled. Between 1200°C and 1400°C, the following further changes in the microstructure occur: (1) Al_4C_3 is forming very quickly (associated with a decrease of the ternary phase Al_4BC); (2) AlBC_4 is now favored over $\text{AlB}_{12}\text{C}_2$ and becomes the major ternary phase; (3) above 1300°C, XRD patterns indicate the appearance of a phase previously reported as $\text{Al}_4\text{B}_{13}\text{C}_4$ but more recently reported (Lee and Kwon, 1997) as $\text{Al}_8\text{B}_4\text{C}_7$ and (4) at 1400°C, Al_4C_3 begins to crystallize in the shape of short whiskers.

4.1 Application of Aluminum Matrix Composites

Aluminum matrix composites (AMC) are widely used in aeronautical, military, automotive and sport fields due to not only some mechanical properties like high strength, elastic modulus, wear resistance, low density but also low thermal expansion coefficient, high electric conductivity and heat transfer coefficient. Although continuous fiber reinforced aluminum composites are expensive, the best use of continuous fiber reinforced aluminum is in aeronautical area since the volume of production is low and profits with saved weight are high (Hunt, 2000). Compared with aeronautical industry, the production volume of AMC's is large in automotive industry area. In automotive industry, particulate reinforced aluminum composites are of interest (Eliasson and Sandström, 1995).

Aluminum metal matrix composites (AMC's) are candidate materials for automotive industry applications such as brake discs as a means of reducing vehicle weight and brake operating temperatures (Table 4.2). One major limitation for widespread commercial use of AMC's brake discs is their high cost, often more than double the piece cost of gray cast iron discs.

Table 4.2: Development aims of some Al matrix composites (Kainer, 2006).

I.	Drive shaft for people and light load motor vehicles (Fig. 1.61) [65]:
Material:	AlMg1SiCu + 20 vol. % Al ₂ O ₃ P
Processing:	extrusion form cast feed material
Development aims:	– high dynamic stability, high Young's modulus (95 GPa) – low density (2.95 g cm⁻³) – high fatigue strength (120 MPa for $n = 5 \times 10^7$, $R = -1$, RT) – sufficient toughness (21.5 MPa m^{1/2}) – substitution of steels
II.	Vented passenger car brake disk (Fig. 1.62) [65]:
Material:	G-AlSi12Mg + 20 vol. % SiC _p
Processing:	sand- or gravity die casting
Development aims:	– high wear resistance (better than conventional cast iron brake discs) – low heat conductivity (factor 4 higher than cast iron) – substitution of iron materials
III.	Longitudinal bracing beam (Stringer) for planes (Fig. 1.63) [66]:
Material:	AlCu4Mg2Zr + 15 vol. % SiC _p
Processing:	extrusion and forging of casted feed material
Development aims:	– high dynamic stability, high Young's modulus (100 GPa) – low density (2.8 g cm⁻³) – high strength ($R_m = 540$ MPa, $R_{p0.2} = 413$ MPa, RT) – high fatigue strength (240 MPa for $n = 5 \times 10^7$, $R = -1$, RT) – sufficient toughness (19.9 MPa m^{1/2})
IV.	Disk brake calliper for passenger cars (Fig. 1.64) [67]:
Material:	Aluminium alloy with Nextel ceramic fibre 610
Weight reduction:	55 % compared to cast iron.

Light alloy composite materials have, in automotive engineering, a high application potential in the engine area (oscillating construction units: valve train, piston rod, piston and piston pin; covers: cylinder head, crankshaft main bearing; engine block: part-strengthened cylinder blocks). An example of the successful use of aluminum composite materials within this range is the short fiber reinforced aluminum alloy piston in which the recess range is strengthened by Al_2O_3 short fibers (Tech Trends, 1990).

Comparable construction unit characteristics are attainable only with the application of powder metallurgical aluminum alloys or when using heavy iron pistons (Fig.4.1.). The reason for the application of composite materials is, as already described the improved high temperature properties. Potential applications are in the area of undercarriages, e.g. transverse control arms and particle-strengthened brake disks, which can be also applied in the area of rail mounted vehicles, e.g. for undergrounds and railway (ICE).

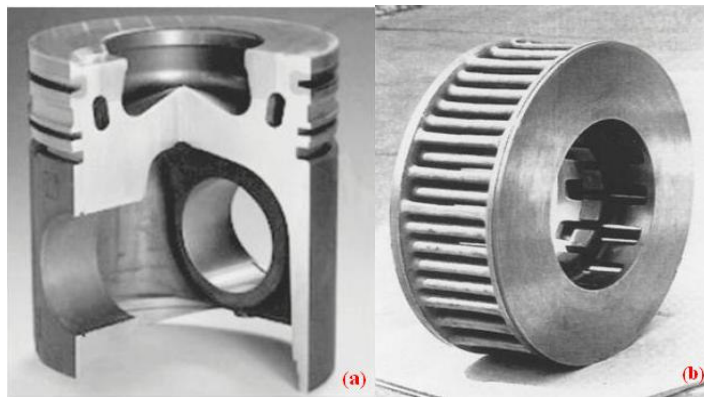


Figure 4.1: (a) Partial short fiber reinforced light metal diesel pistons, (b) Cast brake disk particle of reinforced aluminum.

In the aviation industry, the high specific strength, the high Young's modulus, the small thermal expansion coefficient, the temperature resistance and the high conductivity of the strengthened light alloys are of interest compared with polymer materials, e.g. for reinforcements, axle tubes, rotors, housing covers and structures for electronic devices (Eliasson and Sandström, 1995).

AMC's with high specific stiffness and near-zero coefficient of thermal expansion (CTE) has been developed for space applications. AMC's exhibits high-temperature capability, high thermal conductivity, low CTE, and high specific stiffness and strength. Those potential benefits generated optimism for AMC's for critical space

system applications in the late 1980s. The materials used for aircraft construction can be split into two broad categories; airframe materials and engine materials (Burg and Crosky, 2001).

4.2 Production and Processing of Aluminum Matrix Composites

There are various processing techniques available for fabricating AMC's. These fabrication methods can be grouped according to the temperature of the metal matrix during the process. When the AMC is processed above the liquidus temperature, it is a liquid phase process. If the temperature remains below the solidus temperature, the process is a solid state process. When the temperature range lies in between the solidus and liquidus temperature, it is a two phase process. Main liquid phase processes are molten metal mixing process, melt infiltration process and melt oxidation process. On the other hand, major solid state processes are powder metallurgy and high-energy-high-rate process. Finally, two phase processes are osprey deposition, rheocasting and variable co-deposition of multi-phase materials (VCM) process (Ibrahim et al., 1991).

By altering the manufacturing method, it is possible to obtain different characteristic profiles, although the same composition and amounts of the components are involved. The production of a suitable precursor material, the processing to a construction unit or a semi-finished material (profile) and the finishing treatment must be separated. For cost effective reasons, prototypes, with dimensions close to the final product, and reforming procedures are used, which can minimize the mechanical finishing of the construction units (Mortensen, 2000).

In general the following product engineering types are possible:

- Melting metallurgical processes,
- Infiltration of short fiber, particle or hybrid preforms by squeeze casting, vacuum infiltration or pressure infiltration (Henning and Köhler, 1995).
- Reaction infiltration of fiber or particle preforms (Mielke et al, 1987),
- Processing of precursor material by stirring the particles in metallic melts followed, by sand casting, permanent mold casting or high pressure die casting (Duralcan, 1992b).

Melting metallurgy for the production of AMC's is at present of greater technical importance than powder metallurgy. It is more economical and has the advantage of being able to use well proven casting processes for the production of AMC's. For melting metallurgical processing of composite materials three procedures are mainly used (Henning and Köhler, 1995):

- Compo-casting or melt stirring,
- Gas pressure infiltration,
- Squeeze casting or pressure casting.

Both the terms compo-casting and melt stirring are used for stirring particles into a light alloy melt. Figure 4.2 shows the schematic operational sequence of this procedure. The particles often tend to form agglomerates, which can be only dissolved by intense stirring. Gas access into the melt must be absolutely avoided, since this could lead to unwanted porosities or reactions. Careful attention must be paid to the dispersion of the reinforcement components, so that the reactivity of the components used is coordinated with the temperature of the melt and the duration of stirring, since reactions with the melt can lead to the dissolution of the reinforcement components. Because of the lower surface to volume ratio of spherical particles, reactivity is usually less critical with stirred particle reinforcement than with fibers. The melt can be cast directly or processed with alternative procedures such as squeeze casting or thixocasting (Humphreys, 1988).

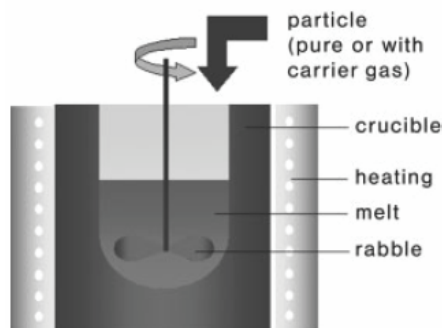


Figure 4.2: Schematic operational sequence during melt stirring.

At the Lanxide Company a similar process is used, with additional reactions between the reinforcement components and the molten matrix being promoted to obtain a qualitatively high-grade composite material (Mielke et al., 1987). In the reaction procedures of the Lanxide Company it may be desirable that the reinforcement

component reacts completely with the melt to form the component in situ, which then transfers the actual reinforcement effect to the second phase in the AMC (Friend, 1987).

In gas pressure infiltration the melt infiltrates the preform with a gas applied from the outside. A gas that is inert with respect to the matrix is used (Figure 4.3). The melting of the matrix and the infiltration take place in a suitable pressure vessel. The advantage of this procedure is that there is no development of pores when completely dense parts are present. Since the reaction time is relatively short with these procedures, more reactive materials can be used than e.g. with the compo-casting. In gas pressure infiltration the response times are clearly longer than in squeeze casting, so that the materials must be carefully selected and coordinated, in order to be able to produce the appropriate composite material for the appropriate requirements (Leatham et al., 1993).

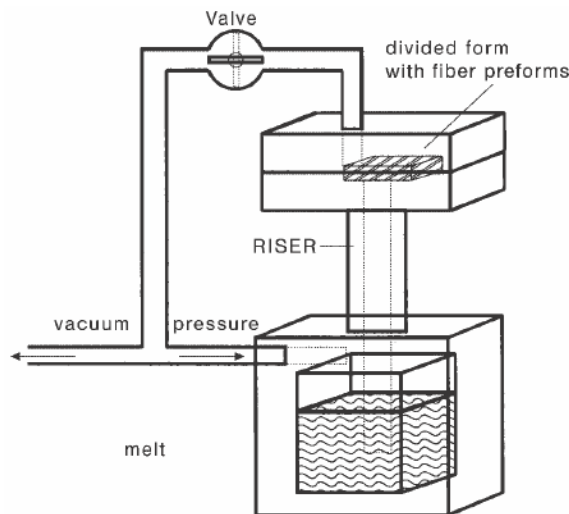


Figure 4.3: Gas pressure infiltration technique.

The interfacial behavior between the particles and matrix is one of the most important variables which affect the properties of the AMC's. Unfortunately, most of the particles used in AMC's possess poor wettability with the matrix, which results in a poor distribution of the reinforcement phase as well as a weak particle-matrix interface (Liu et al., 1994). Various processing techniques have been developed over the last two decades which try to optimize the structure and properties of AMC's (Ibrahim et al., 1991; Schwartz, 1997). Among these techniques, there were some exotic luxurious ones to enhance the wettability by, for instance, introducing some

kind of surface coating to the particles before fabrication. However, this preprocessing of particles increased the cost of AMC's further, so their commercial use was limited. In addition, some recently developed AMC's, using state of the art high performance materials, such as tungsten, molybdenum, niobium and tantalum as the matrix material, are difficult to fabricate by using conventional liquid metallurgy process because these materials have incredible high melting temperatures (Liu et al., 1994). In these cases, powder metallurgy seems more attractive and has become the most important fabrication technique for AMC's.

It has to be pointed out that the powder metallurgy manufacturing route of AMC's is ideally suitable for inserting high percentages by volume of reinforcement components into the material. Values up to approximately 50 vol % are obtainable. This differentiates such systems from particle-strengthened AMC's, which can be manufactured in fusion metallurgical ways; where typically about 20 vol % of reinforcement components can be brought into the matrix (Han et al., 1993). Higher percentages by volume are likewise reported; however, process engineering limits are reached. A further advantage of the powder metallurgy manufacturing of AMC's is the homogeneous structure. Besides mixing source materials with subsequent consolidation, mechanical alloying is used or in situ reaction for aluminum -based PM-MMC (Lloyd, 1989). Examples of mechanically alloyed powders are the systems for dispersion-solidified aluminum ($\text{Al}/\text{Al}_2\text{O}_3$, $\text{Al}/\text{Al}_4\text{C}_3$). Further materials manufactured by mechanical alloying are aluminum alloys, where carbon is ground in an oxygen-containing ball mill atmosphere, which leads to the formation of Al_2O_3 and Al_4C_3 (Seleznev et al., 1995).

4.2.1 Powder metallurgy

As early mentioned, the PM route is the most commonly used method for the preparation of PRMMC's (Liu et al., 1994; Huda et al., 1995). Blending of metallic powders with ceramic particles is a versatile technique for PRMMC production (Clyne, 2001). In the basic process, mixed or prealloyed powders are fed into a die, compacted in a desired shape and then this pressed powder is sintered in a controlled atmosphere furnace to convert the mechanical bonds to the metallurgical bonds that link the powder particles (Newkirk and Kosher, 2004).

The history of powder metallurgy and the art of metals and ceramics sintering are intimately related. Sintering involves the production of a hard solid metal or ceramic piece from a starting powder. There is evidence that iron powders were fused into hard objects as early as 1200 B.C. In these early manufacturing operations, iron was extracted by hand from metal sponge following reduction and was then reintroduced as a powder for final melting or sintering.

A much wider range of products can be obtained using powder processes than from direct alloying of fused materials. In melting operations the "phase rule" applies to all pure and combined elements and strictly dictates the distribution of liquid and solid phases which can exist for specific compositions. In addition, whole body melting of starting materials is required for alloying, thus imposing unwelcome chemical, thermal, and containment constraints on manufacturing as seen in Figure 4.4 (Kainer, 2006).

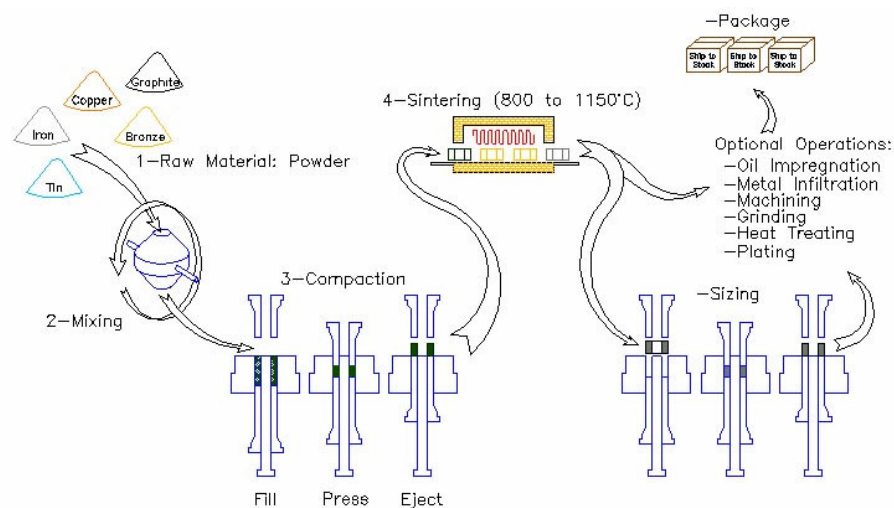


Figure 4.4: Powder metallurgy process.

There are a lot of advantages of PM process. First of all, it is more economical than many other techniques, since no melting and casting is involved. Second, the preparation of PRMMC's is generally easier using PM blending technique than it is using casting technique (Huda et al., 1995). Furthermore, products with complex shapes can be easily produced without any post-machining process. Also, porous products, such as bearings and filters with better properties can be produced by using PM technique. In addition to these, full density products having superior properties are produced by PM technique, which are used in critical applications, such as aerospace applications.

4.2.1.1 Starting materials

The starting material of powder metallurgy has a very important role for the success of the process. Beside the chemistry and the purity of the powders, there are additional issues to concern, such as particle size, size distribution, particle shape as well as the surface texture of the particles (Newkirk and Kosher, 2004).

Regardless of the processing route, all powder metallurgy methods of part fabrication start with the raw material in the form of a powder (Figure 4.5). A powder is a finely divided solid. The particle size is generally smaller than about 1 mm (0.04 in.) in its maximum dimension. There are four major methods used to produce metal powders, involving mechanical comminution, chemical reactions, electrolytic deposition, and liquid-metal atomization. Metal powders exhibit a diversity of shapes ranging from spherical to acicular. Particle shape is an important property, since it influences the surface area of the powder, its permeability and flow, and its density after compaction. Chemical composition and purity also affect the compaction behavior of powders (Liu et al., 1994; Demirkesen, 2003).



Figure 4.5: Sample starting powders.

Virtually any metal can be made into a powder. There are 3 main ways to produce metal powders: atomization, chemical, and electrolytic. The most widely used method is atomization. Atomization involves either spraying or smashing molten metal into smaller particles. There are a few ways of doing this. One method is to spray water at a stream of molten metal, causing it to disintegrate into small particles. Water atomization cools the metal very rapidly, and can cause irregular particles. Water can also corrode some metals. A better way of atomization is to spray the molten metal stream with an inert gas. Because this cools the metal at a slower rate, it creates a more modular circular particle. Another way of atomization is to pour the molten metal onto a rapidly spinning disk, which sprays the metal onto the walls of the container, causing it to create a powder (Clyne, 2001). Chemical reduction is

another process of creating metal powders. It involves a variety of chemical reactions that reduce the metal into elemental powders. A common process involves liberating metals from their oxides by the use of reducing agents, which attach to the oxygen in the oxide, and render metal powders. Electrolysis is a powderization technique that uses electricity to remove the metal, and render a very fine, and highly pure powder. The system is setup so that the anode is made of the metal that the powder is to be made from. The electricity moves the metal from the anode to the cathode, and covers it in a film that is easily washed and dried to make the powder (Newkirk and Kosher, 2004).

❖ Mechanical alloying

After a proper selection of the materials is ensured, the next step is blending or mixing. For getting good parts from the last two operations, the metal powders must be blended and mixed. Blending is a process in which the powders of the same chemical composition make-up but different sizes are combined. Mixing is a process where powders of different chemical compositions make-ups are combined to make an alloy (Newkirk and Kosher, 2004).

Mechanical alloying is an advanced fabrication process that can produce ultra-fine and homogenous powders (Ryu et al., 2000). Even, nanocrystalline materials (with a grain size of few nanometers, usually <100 nm) are also produced by mechanical alloying of powder mixtures (Figure 4.6). Additionally, it has been recognized that this technique can be used to induce chemical (displacement) reactions in powder mixtures at room temperature or at much lower temperatures than normally required to synthesize pure metals (Suryanarayana et al., 2001).

In any mechanical alloying process, starting powder constituents are first mixed or blended according to the required stoichiometry for the given composite formulation. Then, they are put in the milling container with the appropriate ball charge and milled until a steady state of homogeneous dispersion is achieved (Goff, 2003). The central event of MA is the ball-powder collisions (Fecht, 2002). Microstructural refinement during the MA process occurs due to the repeated welding, fracturing, and rewelding of the dry powder constituents during their impact between ball-ball and/or ball-container collisions. Whenever two balls collide, typically, around 1000 particles with an aggregate weight of about 0.2 mg are trapped during each collision.

The force of the impact plastically deforms the powder particles leading to work hardening and fracture (Suryanarayana, 2001; Fecht, 2002).

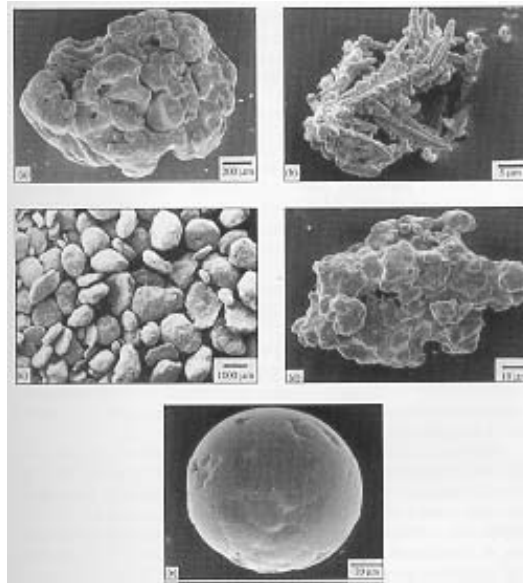


Figure 4.6: Representative metal powders [(a) Chemical; Sponge iron-reduced ore; (b) Electrolytic: Copper; (c) Mechanical: Milled aluminum powder containing disperoids; (d) Water atomization: Iron; (e) Gas atomization: Nickel-base hardfacing alloy. (Atomization - The Production of Metal Powders, A. Lawley, MPIF)].

After a proper selection of the materials is ensured, the next step is blending or mixing. For getting good parts from the last two operations, the metal powders must be blended and mixed. Blending is a process in which the powders of the same chemical make-up but different sizes are combined (Figure 4.7). Mixing is a process where powders of different chemical make-ups are combined to make an alloy (Newkirk and Kosher, 2004).

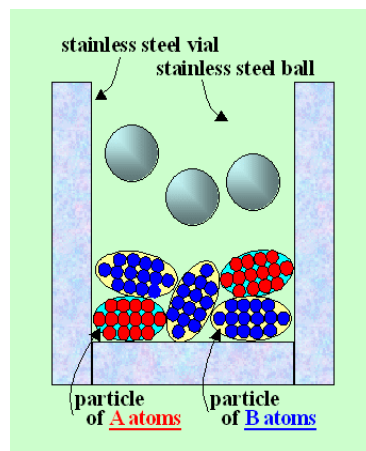


Figure 4.7: Representative mechanical alloying scheme.

In order to understand the physical phenomena that occur during MA processing better it is useful to divide the typical process into three or four stages (Öveçoğlu, 1987; Goff, 2003).

In the early stages of milling, the particles are soft (if we are using either ductile-ductile or ductile-brittle material combination), their tendency to weld together and form large particles is high (Suryanarayana, 2001). A broad range of particle sizes develops, with some as large as three times bigger than the starting particles (Suryanarayana, 2001; Goff, 2003). The composite particles at this stage have a characteristic layered structure consisting of various combinations of the starting constituents (Figure 4.8), (Öveçoğlu, 1987).

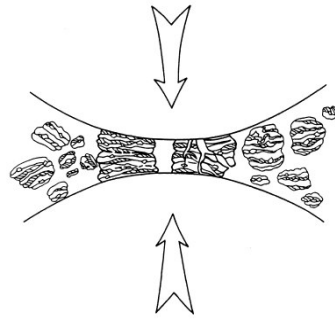


Figure 4.8: Schematic view of a ball powder-ball collision (Suryanarayana, 2001).

As the metallic phases are flattened and overlap during ball collisions, atomically clean surfaces are placed in contact with one another and subsequently coldweld together (Fig.4.9.). At the same time, brittle constituents (intermetallics and dispersoids) are occluded by the ductile constituents, thus becoming trapped along cold-weld interfaces (Goff, 2003).

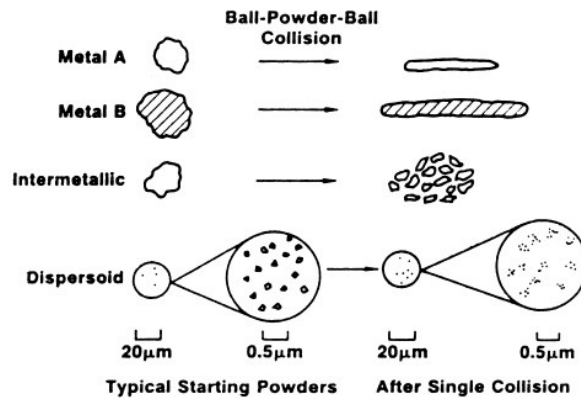


Figure 4.9: Deformation characteristics of starting powders used in a typical MA process (Suryanarayana, 2001).

In the intermediate stage, the composite powder particles are further refined due to continual welding and fracturing of excessively work-hardened metallic phases and continuous brittle intermetallics and/or dispersoids (Goff, 2003). At this stage the tendency to fracture predominates over cold welding (Suryanarayana, 2001). The particles consist of convoluted lamellae. The reduction in particle size, increased microstructural mixing, and elevated temperature of the powder constituents due to the adsorbed kinetic energy of milling balls, all help to form areas of solute dissolution throughout the metallic powder matrix (Öveçoğlu, 1987). So, this potentially may lead to areas where new phases develop which is mainly due to an overall decrease in atomic diffusion distances between individual phases and decreased activation energies for diffusion due to the increase in temperature (Öveçoğlu, 1987; Goff, 2003). Consequently, the inter-layer spacing decreases and the number of layers in a particle increase (Suryanarayana, 2001). Figure 4.10 shows the reduced lamellae thickness, solute dissolution, and formation of new phases in the intermediate stage of processing.

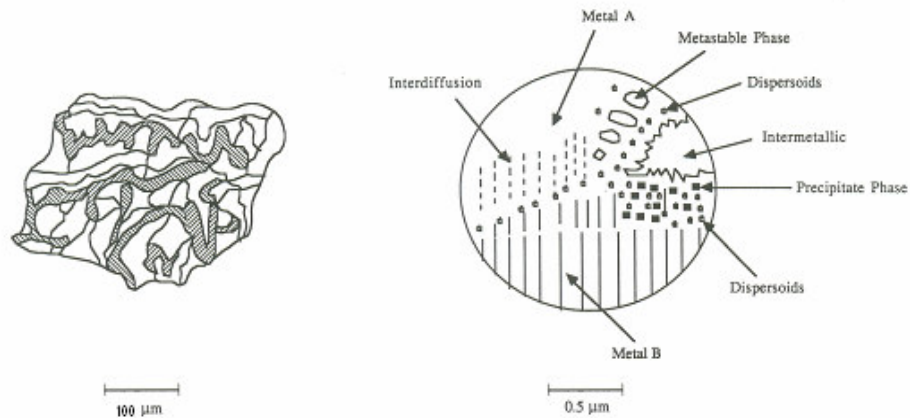


Figure 4.10: Intermediate stage of processing showing reduced lamellae thickness, solute dissolution and formation of new phases (Öveçoğlu, 1987).

In the final stage (Figure 4.11), steady-state equilibrium is attained when the balance is achieved between the rate of welding, which tends to increase the average particle size, and the rate of fracturing, which tends to decrease the average composite particle size. As a result smaller particles are able to withstand deformation without fracturing and tend to be welded into larger pieces, with an overall tendency to drive both very fine and very large particles towards an intermediate size (Suryanarayana, 2001).

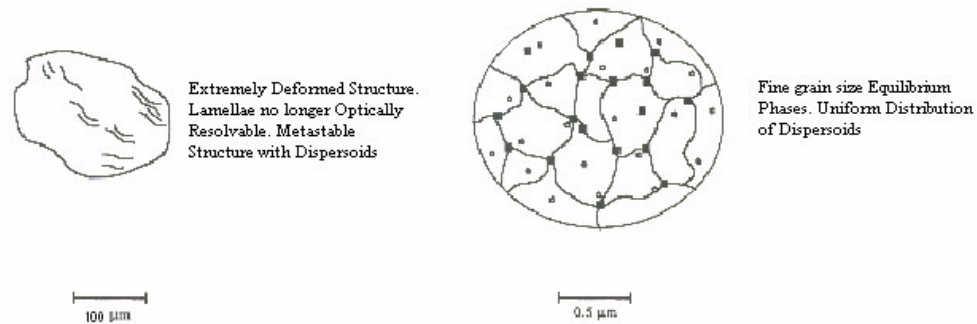


Figure 4.11: The final stage of processing and consolidation (Öveçoğlu, 1987).

Furthermore, individual particle compositions are equal to the starting powder blend composition. The lamellae are no longer optically resolvable and the dispersoid spacing is equal to the distance between weld interfaces (Öveçoğlu, 1987). At this point, further processing would not improve the dispersoid distribution or serve to enhance the homogeneity of the composite microstructure (Öveçoğlu, 1987; Goff, 2003). The particle size distribution at this stage is narrow, because particles larger than average are reduced in size at the same rate that fragments smaller than average grow through agglomeration of smaller particles (Suryanarayana, 2001).

MA is a simple and versatile technique, as well as an economically feasible process with important technical advantages. One of the greatest advantages of MA is in the synthesis of novel alloys, e.g., alloying of normally immiscible elements, which is not possible by any other technique. The reason for that is that MA is a completely solid-state processing technique and therefore limitations imposed by phase diagrams do not apply here (Suryanarayana et al., 2001). Furthermore, mechanical alloying holds an advantage over traditional ball milling processes which is to produce a material whose internal homogeneity is independent of the initial starting particle size. It is not uncommon to obtain mechanically-alloyed dispersions with less than $1\mu\text{m}$ interparticle spacing from initial powder sizes of $50\text{--}100\mu\text{m}$ average diameters (Figure 4.12), (Goff, 2003).

❖ Processing equipment and parameters

Different types of high-energy milling equipment are used to produce mechanically alloyed powders. These equipments include Spex shaker mills, planetary ball mills, attritor mills and commercial mills. They have different capacities, efficiencies of milling and additional arrangements for cooling, heating, etc (Suryanarayana, 2001; Goff, 2003).

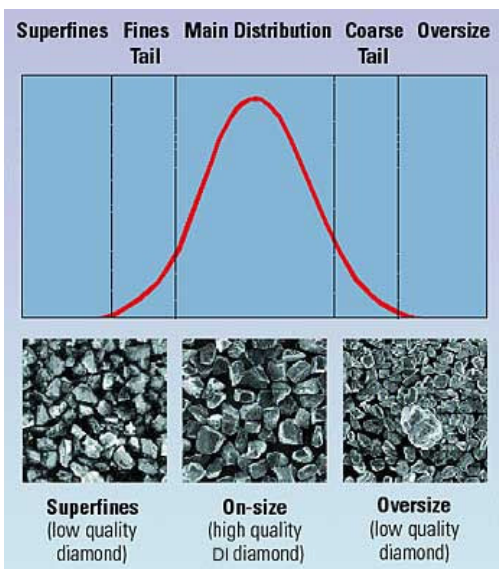


Figure 4.12: Particle size difference after MA.

Spex shaker mills are most commonly used for laboratory investigations and they mill about 10 ± 20 g of the powder (Goff, 2003). All of these mills have one vial, containing the sample and grinding balls, secured in the clamp and shakes the milling container in three-mutually perpendicular directions at about 1200 rpm resulting in powder microstructural refinement with time (Suryanarayana, 2001; Goff, 2003). Ball-ball and ball-container collisions continually trap and refine the powder constituents with time ultimately leading to an overall homogeneously dispersed microstructure (Goff, 2003). There are different vial materials available for the SPEX mills, which are hardened steel, alumina, tungsten carbide, zirconia, stainless steel, silicon nitride, agate, plastic and methacrylate (Suryanarayana, 2001). In Figure 4.13, a typical spex mill and stainless steel vial set can be seen.



Figure 4.13: Particle size reduction by Jar Milling schematic (Powder Metallurgy Science, Second Edition, R.M., German, MPIF).

Another popular mill for conducting MA experiments is the planetary ball mill (Figure 4.14) in which a few hundred grams of the powder can be milled at a time. It is called the planetary ball mill because its vials make a planet-like movement. The centrifugal force produced by the vials rotating around their own axes act on the vial contents, consisting of material to be milled ground and the grinding balls. So, powders are trapped between the rotating balls and the walls of the vial and refined. Even though the linear velocity of the balls in this type of mill is higher than that in the SPEX mills, the frequency of impacts is much more in the SPEX mills. Therefore, comparing to SPEX mills, planetary ball mills can be considered lower energy mills (Suryanarayana, 2001). In Figure 4.15, a schematic view of spex shaker mill can be seen.



Figure 4.14: FritschTM planetary ball mill.



Figure 4.15: (a) A typical spex shaker mill, (b) Stainless steel vial set consisting of the vial, lid and gasket (Suryanarayana, 2001).

Another type of mills is the attritor mills. Attritors are the mills in which large quantities of powder (from about 0.5 to 40 kg) can be milled at a time (Suryanarayana, 2001). It contains a vertical shaft with a series of impellers that rotates in the tank of about 250 rpm (Goff, 2003). As the shaft rotates, the balls drop

on the metal powder that is being ground. The impellers energize the ball charge, causing powder size reduction due to impact between balls, between balls and container wall, and between balls, agitator shaft, and impellers. The rate of grinding increases with the speed of rotation. However, at high speeds the centrifugal force acting on the balls exceeds the force of gravity, and the balls are pinned to the wall of the container. At this point the grinding action stops (Suryanarayana, 2001). In Figure 4.16, a picture of an attritor mill can be seen.

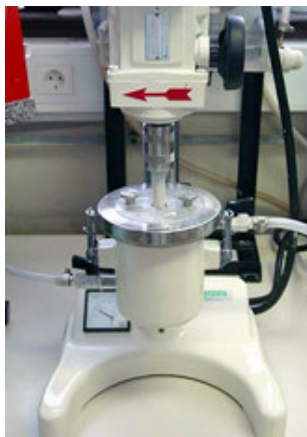


Figure 4.16: Attritor mill.

Finally, commercial mills for MA are much larger in size than the mills described above and can grind several hundred kilograms of powders at a time. Mechanical alloying for commercial production is carried out in ball mills of up to about 1250 kg capacity (Suryanarayana, 2001). The milling time decreases with increasing energy of the mill. Roughly, it can be estimated that a process that takes only a few minutes in the SPEX mill may take hours in an attritor and a few days in a commercial mill. Beside the type of the mill, there are different variables that affect the result of the mechanical alloying process. These include the type (material) of the milling container and the milling medium, ball-to-powder ratio, milling atmosphere, milling time, use of a process control agent (PCA), etc. (Suryanarayana, 2001).

The material used for the milling container (grinding vessel, vial) is important since the impact of the grinding medium on the inner walls of the container will result in tiny fractions of milling container that fracture off and disperse into the composite powder. This can contaminate the powder or alter the chemistry of the powder. If the material of the grinding vessel is different from that of the powder, then the powder may be contaminated with the grinding vessel material. On the other hand, if the two

materials are the same, then the chemistry may be altered (Suryanarayana, 2001; Goff, 2003). Regardless of the type of mechanical alloying process, the most appropriate type of container and milling media for the given system should be chosen. Generally, milling media that are made of a similar material as that of the material to be processed is used to reduce contamination during processing (Goff, 2003). Additionally, the density of the grinding medium should be high enough so that the balls create enough impact force on the powder (Suryanarayana, 2001).

Another important issue is ball-to powder ratio (BPR). This has been varied by different investigators from a value as low as 1:1 to as high as 220:1. Generally, a ratio of 10:1 is most commonly used while milling the powder in a small capacity mill such as a SPEX mill. The BPR has an important effect on the time required to achieve a particular phase in the powder being milled. The higher the BPR, the shorter is the time required (Suryanarayana, 2001).

Milling atmosphere is also an important variable for MA process. The major effect of the milling atmosphere is on the contamination of the powder. Therefore, the powders are milled in containers that are either vacuum or filled with an inert gas such as argon or helium. However, high-purity argon is the most common gas to prevent oxidation and contamination of the powder (Suryanarayana, 2001). The presence of air in the vial causes to produce oxides and nitrides in the powder, especially if the powders are reactive in nature. Thus, the loading and unloading of the powders into the vial has to be carried out inside an atmosphere-controlled glove box (Suryanarayana, 2001; Fecht, 2002).

The time of milling is the most important parameter. In most of the cases, the rate of refinement of the internal structure (particle size, crystallite size, lamellar spacing, etc.) is roughly logarithmic with processing time and therefore the size of the starting particles is relatively unimportant (Figure 4.17). In a few minutes to an hour, the lamellar spacing usually becomes small and the crystallite (or grain) size is refined to nanometer dimensions. Normally, the time is chosen so to achieve a steady state between the fracturing and cold welding of the powder particles. Furthermore, the time required depends on the type of mill used, the intensity of milling, the ball-to-powder ratio, and the temperature of milling. These times have to be decided for each combination of the above parameters and for the particular powder system. However, it should be realized that the level of contamination increases and some

undesirable phases form if the powder is milled for times longer than required. Therefore, the powder has to be milled just for the required duration and not any longer (Suryanarayana, 2001).

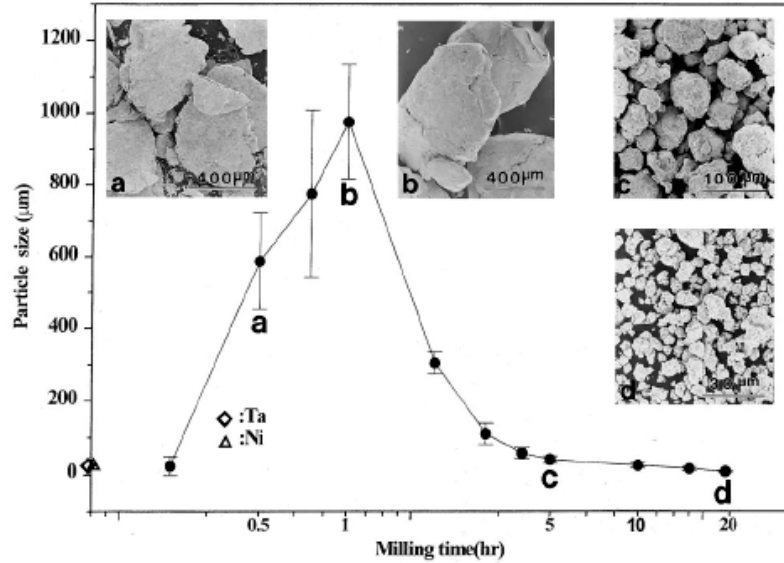


Figure 4.17: Particle size and milling time relationship graph.

The use of process control agents (PCA) is another concern in the MA process. Generally, ductile powder particles get cold-welded to each other, due to the heavy plastic deformation during milling. However, true alloying among powder particles can occur only when a balance is maintained between cold welding and fracturing of particles. So, a process control agent (PCA) is added to the powder mixture during milling to reduce the cold welding (Öveçoğlu, 1987; Suryanarayana, 2001). The PCA's can be solids, liquids, or gases. They are mostly organic compounds, which act as surface-active agents by adsorbing on the surface of the powder particles and minimizing cold welding between powder particles and thereby inhibiting the agglomeration (Suryanarayana, 2001).

4.2.1.2 Compaction

After blending or mixing, the powder mixture is then pressed to form the green compacts (Liu et al., 1994). This step is the one of the most critical steps in the PM process, because it sets the density of the powder and the uniformity of the density throughout the product (Figure 4.18). Because the final properties strongly depend on density, uniform properties require uniform density (Newkirk and Kosher, 2004).

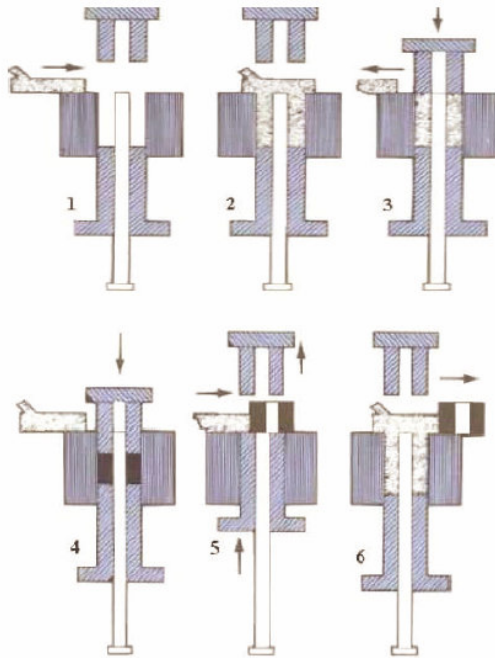


Figure 4.18: Operation sequence in powder metallurgy, single acting press.

The compaction process has the following major functions:

- To consolidate the powders into the desired shape,
- To impart, as much as possible, the desired final dimensions considering any dimensional changes resulting from sintering,
- To give the desired level of porosity,
- To provide sufficient strength for subsequent handling (Upadhyaya, 2000).

In the conventional compaction methods, the pressure is usually applied in one direction resulting in a non-uniform distribution of consolidation and even an insufficient densities (Liu et al., 1994). Mostly, mechanical and hydraulic presses and rigid dies are used (Newkirk and Kosher, 2004). Compacted metal powders are called green packed bodies. Only physical bonds occur between metal powders during pressing. Green packed bodies contain a lot of porosities (Liu et al., 1994).

4.2.1.3 Sintering

Sintering is a process used to produce dense-controlled materials and components from metal and ceramic powders by applying thermal energy (Kang, 2005). Sintering commonly refers to processes involved in the heat treatment of powder compacts at elevated temperatures, usually at $T > 0.5T_m$ (K), in the temperature range where

diffusional mass transport is appreciable. Successful sintering usually results in a dense polycrystalline solid. However, sintering can proceed only locally (i.e. at contact point of grains), without any appreciable change in the average overall density of a powder compact (Chen and Wang, 2000).

The principal goal of sintering is the reduction of compact porosity. Sometimes the initial spaces between compacted grains of ceramics are called “voids”, to differentiate them from the isolated spaces = pores, which occur in the final stages of sintering. The sintering process is usually accompanied by other changes within the material, some desirable and some undesirable (Upadhyaya, 2000). The largest changes occur in:

- Strength, elastic modulus,
- Hardness, fracture toughness,
- Electrical and thermal conductivity,
- Permeability to gases and liquids,
- Average grain number, size and shape,
- Distribution of grain size and shape,
- Average pore size and shape,
- Distribution of pore size and shape,
- Chemical composition and crystal structure.

Sintering is a widely used but very complex phenomenon. The fundamental mechanisms of sintering are still a matter of controversy (Figure 4.19). Experimental quantification of changes in pore fraction and geometry during sintering can be attempted by several techniques, such as:

- Dilatometry,
- Buoyancy,
- Gas absorption,
- Porosimetry,
- Indirect methods (e.g. hardness),
- Quantitative microscopy.

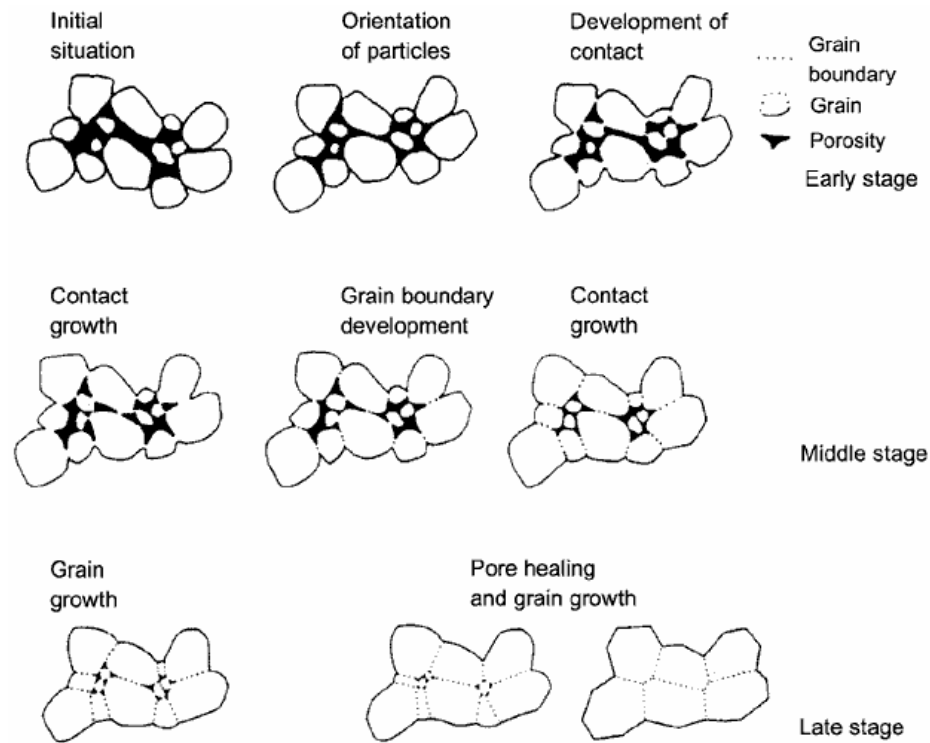


Figure 4.19: Illustration of different stages of sintering (Kang, 2005).

The description of the sintering process has been derived from model experiments (e.g. sintering of a few spheres) and by observing powdered compact behaviour at elevated temperatures. The following phenomena were observed and modelled:

- Increase of interparticle contact area with time,
- Rounding-off of sharp angles and points of contact,
- In most cases, the approach of particle centres and overall densification,
- Decrease in volume of interconnected pores,
- Continuing isolation of pores,
- Grain growth and decrease in volume of isolated pores.

There are different variables which determine sinterability and the sintered microstructure of a powder compact. Basically, the sintering process can be divided into two types:

- Solid-state sintering,
- Liquid phase sintering.

Solid-state sintering occurs when the powder compact is densified fully in a solid state at the sintering temperature, while liquid phase sintering occurs when a liquid phase is present in the powder compact during sintering as seen in Figure 4.20 (Kang, 2005).

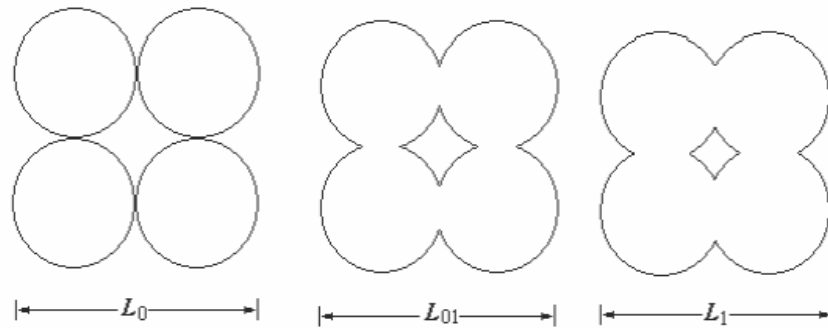


Figure 4.20: Sintering mechanism.

The solid-state sintering is carried out in protective atmosphere within a furnace at a temperature below the melting point of the base metal. The process leads to a decrease in the surface area, an increase in compact strength and mostly in shrinkage of the compact. Sintering longer at above a below T_m temperature decreases the number of pores and makes the pore shape become smooth. Also, grain growth can be expected (Upadhyaya, 2000). The process of sintering is mainly the result of atomic motion aroused by the high temperatures. The initial strains, surface area and curvature of the powder drive the atomic motions which are responsible for sintering (Randall, 1996). In the Figure 4.21, SEM picture of sintering mechanism can be seen.

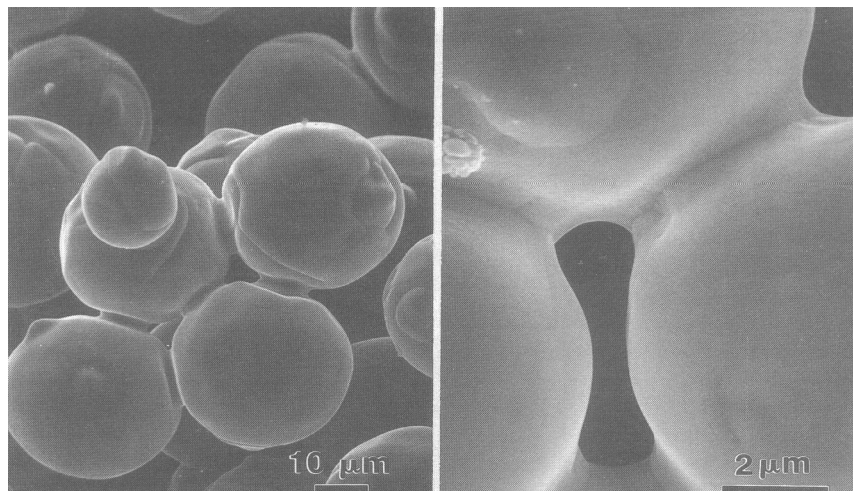


Figure 4.21: SEM micrograph of sintering mechanism.

Liquid state sintering where liquid is present at sintering temperatures aids compaction. Grain rearrangement occurs in the initial stage followed by a solution-reprecipitation stage. Usually, the liquid amount is not sufficient to fill the green-state porosity in normal liquid-assisted sintering of ceramics (Kuczynski, 1984).

Mostly, the sintering kinetics are determined by several parameters including pressed density, material, particle size, sintering atmosphere and temperature. The operation is almost invariably carried out under a protective atmosphere, because of the large surface areas involved, and at temperatures between 60 and 90% of the melting-point of the particular metal or alloys. For powder mixtures, however, the sintering temperature may be above the melting-point of the lower-melting constituent, e.g. copper/tin alloys, iron/copper structural parts, tungsten carbide/cobalt cemented carbides, so that sintering in all these cases takes place in the presence of a liquid phase, hence the term liquid phase sintering. It is, of course, essential to restrict the amount of liquid phase in order to avoid impairing the shape of the part. The selection of a correct isothermal sintering temperature is important in successful densification. Higher temperatures lead to faster densification, however, the rate of coarsening also increases. This increased coarsening rate can lead to abnormal grain growth with pores trapped inside large grains. As a result, the final density may be limited, although densification proceeds faster (Upadhyaya, 2000). So, the sintering process is a complicated process with different variables and one must take all these variables have to be taken into consideration when designing a sintering process.

Control over heating rate, time, temperature and atmosphere is required for reproducible results. An electrically heated furnace is most generally preferred for sintering. The belt and the heating elements are of a modified 80/20 nickel/chromium alloy and give a useful life at temperatures up to 1150°C (Figure 4.22). For higher temperatures walking beam furnaces are preferred, and these are increasingly being used as the demand for higher strength in sintered parts increases. Silicon carbide heating elements are used and can be operated up to 1350°C (German, 1996). For special purposes at still higher temperature molybdenum heating elements can be used, but special problems are involved, notably the readiness with which molybdenum forms a volatile oxide. Molybdenum furnaces must operate in a pure hydrogen atmosphere (Prochazka, 1976).

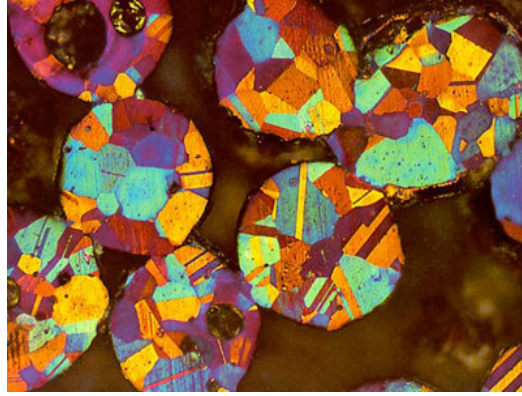


Figure 4.22: Early stage of sintering of powdered bronze made for filter (<http://www.nikonsmallworld.com>).

4.2.2 Aluminum powder metallurgy

The increased demand for light weight components, primarily driven by the need to reduce energy consumption in a variety of societal and structural components, has led to an increased use of aluminum. Additionally, the cost of fabrication coupled with a need to improve the part recovery has led to significant growth in the net-shaped component manufacturing processes (Hunt, 2000).

Aluminum Powder Metallurgy (PM) offers components with exceptional mechanical and fatigue properties, low density, corrosion resistance, high thermal and electrical conductivity, excellent machinability, good response to a variety of finishing processes, and which are competitive on a cost per unit volume basis. In addition, aluminum PM parts can be further processed to eliminate porosity and improve bonding, yielding properties that compare favorably to those of conventional wrought aluminum products. The primary driver for the use of aluminum PM is the unique properties of aluminum coupled with the ability to produce complex net or near net shape parts which can reduce or eliminate the operational and capital costs associated with intricate machining operations. Aluminum PM can replace other PM in certain applications on a direct basis. However, in terms of the potential for ferrous based product substitution, each potential application needs to be considered on a case by case basis (Huda et al., 1995).

The aluminum PM process consists of three basic steps:

- Aluminum powders of controlled purity and particle size are mixed with alloying metal powders in accurately controlled quantities. Generally a powdered lubricant is added to permit the consistent production of high density parts without seizing

of the punches or cold welding to the die walls. This lubricant is carefully chosen to ensure that there is no residual ash to interfere with bonding during sintering,

- The premix is compacted using precision metal dies in specially designed PM presses to yield a green compact. Aluminum premixes exhibit excellent compressibility and obtain a high density parts at low compaction and ejection pressures,
- The green compacts are sintered in a controlled atmosphere furnace at closely regulated temperatures. This process metallurgically bonds the powder particles together and develops the desired physical and mechanical properties. Aluminum powder sintering is difficult to achieve because the aluminum oxide is not reduced by common furnace atmospheres at sintering temperatures (Elliasson and Sandström 1995). However, successful sintering is accomplished in environments containing hydrogen, nitrogen and dissociated ammonia as long as the following conditions are observed:
 - The lubricant is essentially free of moisture and low in ash content,
 - Atmospheres contain low levels of moisture and oxidizing gases,
 - Alloying elements having a high solubility in aluminum are added to generate low melting phases (Nair et al., 1985).

4.2.2.1 Performance properties of aluminum PM components

Aluminum PM mechanical properties are very good and typically dominate in the materials selection process. For certain applications, the dynamic properties as well as other performance properties are more critical and become the determinant criteria. These properties typically include, but are not limited to, fatigue, density, electrical and thermal conductivity, corrosion resistance and machinability (Huda et al., 1995).

Fatigue is an important design consideration for PM parts subjected to dynamic stresses. The most commonly used fatigue property is the fatigue limit, which is the maximum reversed stress the material will withstand if cycled indefinitely. This limit is defined when the fatigue curve becomes horizontal. Fatigue limits for 2xxx and 6xxx aluminum PM alloys are 7.5 and 6.5 ksi, respectively, and are about 50% of the comparable wrought alloys. This difference is due to the lower density of PM parts.

Hot forging the aluminum PM part results in fatigue limits comparable to the wrought alloys (Ashby, 1993).

Aluminum alloys enjoy widespread use in both structural and non structural applications because of their corrosion resistance. Within the aluminum alloy systems, some compositions are more resistant than others. The Al-Mg-Si alloys (6xxx series) exhibit higher resistance to general corrosion than the Al-Cu (2xxx series) but all are significantly better than ferrous based products. The corrosion resistance of aluminum PM alloys can be improved appreciably through application of chemical conversion coating on anodizing treatments (Burg and Crosky, 2001).

Aluminum PM parts offer many of the important advantages of wrought aluminum in machining operations, including high cutting speeds, smooth surface finish and outstanding tool life. In lathe turning tests, 90% density test bars from both 2xxx and 6xxx PM alloys were machined to a fine surface finish with small, broken chips at a cutting speed of 500 sfm. The PM version actually offers an advantage since wrought aluminum can yield long stringy chips that often necessitate a reduction in machining speeds (Elliasson and Sandström, 1995).

4.2.2.2 Aluminum comparison to other PM materials

A direct comparison of mechanical properties of aluminum PM with ferrous based products reveals that, all PM has lower, but competitive, strength levels. However, there are many major property advantages associated with aluminum PM alloys (Huda et al., 1995).

A major advantage is the density of aluminum which is translatable into many property, processing and economic benefits. Parts will weigh less and relatively small changes in part dimensions can yield bulk properties comparable to the ferrous based parts while still maintaining an overall weight advantage. This is a major benefit in today's energy conscious world. In addition, because of the lower density, the relatively high cost per pound of aluminum PM raw materials becomes less significant and more competitive with typical PM materials, when considered on a cost per unit volume or individual part weight basis. This lighter weight can also be translated into a potentially higher volume of parts per inch of belt in the sintering operation (i.e., greater productivity) and also lowers shipping costs (Burg and Crosky, 2001).

Other significant property advantages associated with aluminum PM include corrosion resistance, conductivity and finishing characteristics. The excellent corrosion resistance of aluminum alloys has been well established through years of experience in marine, aerospace and chemical industry applications. In normal outdoor exposure aluminum PM alloys will provide corrosion resistance equivalent to brass, bronze and stainless steel PM parts and significantly better than ferrous based products. This corrosion resistance also means that no special coatings are necessary for normal shipping and storage. Aluminum has excellent conductivity values, both thermal and electrical. Aluminum PM is comparable to its wrought counterparts and significantly better than brass, bronze and ferrous based materials. The natural appearance of aluminum PM parts after chemical or mechanical cleaning is suitable for most applications where good appearance is a requirement. In addition, a wide range of decorative and functional finishes are available with aluminum PM that are not possible with other PM materials (Ashby, 1993).

Aluminum PM parts offer many advantages over other PM products. In addition to properties such as low density, thermal and electrical conductivity, finishing characteristics and corrosion resistance not available with other PM products, aluminum can be economically viable on a direct part replacement basis. An analysis of a hypothetical PM flange part with a flange diameter of 1 inch and the length of 0.06 inches coupled with an overall length and body OD of 0.75 inches suggests a 30% lower cost than 316L SS, a 20% lower cost than Bronze 90-10 and a comparable cost with FC0008 at a density of 6.6 (Humphreys, 1988).

5. MATERIALS SELECTION

The great advantage of MMC materials is a superior combination of different properties of a metallic matrix and a hard reinforcement. However, these properties can only be obtained with proper selection of matrix material and reinforcement (Lindroos et al., 2004).

The matrix of the composites has to be mainly designed for two major tasks, which is firstly to bind and support the reinforcing phase and, secondly, to satisfy special properties based on the requirements in service. Binding strength between the matrix, whose main function is to transfer and distribute the load to the reinforcement, and the reinforcement depends on the type of matrix and reinforcement (Huda et al., 1995; Lindroos et al., 2004). The interface formed between the matrix and the reinforcement is interesting because the characteristics of this region determine load transfer and crack resistance of the composite during deformation. It is now widely known that in order to maximize interfacial bond strength, it is necessary to promote wetting (when a liquid phase process is present), control chemical interactions and minimize oxide formation (Ibrahim et al., 1991). On the other hand, the hardness of the matrix is the key factor in supporting the reinforcing phase. Furthermore, other considerations such as, cost, weight, fabricability and availability of the matrix materials should be made (Lindroos et al., 2004).

The reinforcement phase in the composites is mainly used to increase the strength, stiffness, temperature resistance capacity and to lower the density. Generally, ceramics are used as reinforcement phase, which are typically oxides, carbide and nitrides (Huda et al., 1995). Selection criteria for these ceramic reinforcements include elastic modulus, tensile strength, density, melting temperature, thermal stability, coefficient of thermal expansion, size and shape, compatibility with matrix material and cost (Ibrahim et al., 1991). Common reinforcement elements are SiC, Al₂O₃, SiO₂, TiC, B₄C and Si₃N₄ (Huda et al., 1995). Because of these reasons, in this study aluminum has been chosen as the matrix material.

5.1 Aluminum

5.1.1 History

The ancient Greeks and Romans used aluminium salts as dyeing mordants and as astringents for dressing wounds; alum is still used as a styptic. In 1761 Guyton de Morveau suggested calling the base alum alumine. In 1808, Humphry Davy identified the existence of a metal base of alum, which he at first named aluminum and later aluminum (Venetski, 1969).



Figure 5.1: The statue known as Eros was made in 1893 and is one of the first statues to be cast in aluminium (<http://en.wikipedia.org/wiki/Aluminium>).

Friedrich Wöhler is generally credited with isolating aluminum (Latin alumen, alum) in 1827 by mixing anhydrous aluminum chloride with potassium. The metal, however, had been produced for the first time two years earlier but in an impure form by the Danish physicist and chemist Hans Christian Ørsted. Therefore, Ørsted can also be listed as the discoverer of the metal. Further, Pierre Berthier discovered aluminum in bauxite ore and successfully extracted it. The Frenchman Henri Saint-Claire Deville improved Wöhler's method in 1846 and described his improvements in a book in 1859, chief among these being the substitution of sodium for the considerably more expensive potassium (Duralcan, 1992a).

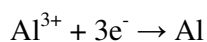
5.1.2 Aluminum metal production and refinement

Although aluminum is the most abundant metallic element in earth's crust (believed to be 7.5% to 8.1%), it is very rare in its free form, occurring in oxygen-deficient environments such as volcanic mud. It was once considered a precious metal more valuable than gold. Napoleon III, Emperor of France, is reputed to have given a

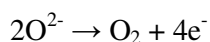
banquet where the most honored guests were given aluminium utensils, while the other guests had to do with gold ones. Aluminium has been produced in commercial quantities for just over 100 years (Davis, 1993).

Aluminium is a reactive metal that is difficult to extract from ore, aluminium oxide (Al_2O_3). Direct reduction with carbon, for example is not economically viable since aluminium oxide has a melting point of about $2,000^\circ\text{C}$. Therefore, it is extracted by electrolysis; that is, the aluminium oxide is dissolved in molten cryolite and then reduced to the pure metal. By this process, the operational temperature of the reduction cells is around 950 to 980°C . Cryolite is found as a mineral in Greenland, but in industrial use it has been replaced by a synthetic substance. Cryolite is a mixture of aluminum, sodium, and calcium fluorides. The aluminium oxide (a white powder) is obtained by refining bauxite in the Bayer process.

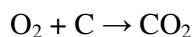
The electrolytic process replaced the Wöhler process, which involved the reduction of anhydrous aluminum chloride with potassium. Both of the electrodes used in the electrolysis of aluminum oxide are carbon. Once the ore is in the molten state, its ions are free to move around. The reaction at the cathode the negative terminal is:



Here the aluminum ion is being reduced. The aluminum metal then sinks to the bottom and is tapped off. At the positive electrode (anode), oxygen is formed:



This carbon anode is then oxidised by the oxygen, releasing carbon dioxide. The anodes in a reduction must therefore be replaced regularly, since they are consumed in the process:



Unlike the anodes, the cathodes are not oxidised because there is no oxygen present at the cathode. The carbon cathode is protected by the liquid aluminium inside the cells (Davis, 1993). Nevertheless, cathodes do erode, mainly due to electrochemical processes. After five to ten years, depending on the current used in the electrolysis, a cell has to be rebuilt because of cathode wear.

Aluminum electrolysis with the Hall-Héroult process consumes a lot of energy, but alternative processes were always found to be less viable economically and/or

ecologically. The world-wide average specific energy consumption is approximately 15 ± 0.5 kilowatt-hours per kilogram of aluminum produced from alumina (52 to 56 MJ/kg). The most modern smelters reach approximately 12.8 kW·h/kg (46.1 MJ/kg). Reduction line current for older technologies are typically 100 to 200 kA. State of the art smelters operate with about 350 kA. Trials have been reported with 500 kA cells (Duralcan, 1992a).

Recovery of the metal via recycling has become an important facet of the aluminium industry. Recycling involves melting the scrap, a process that uses only five percent of the energy needed to produce aluminum from ore. Recycling was a low-profile activity until the late 1960s, when the growing use of aluminum beverage cans brought it to the public consciousness.

Electric power represents about 20% to 40% of the cost of producing aluminium, depending on the location of the smelter. Smelters tend to be situated where electric power is both plentiful and inexpensive, such as South Africa, the South Island of New Zealand, Australia, the People's Republic of China, the Middle East, Russia, Quebec and British Columbia in Canada, and Iceland. In 2004, the People's Republic of China was the top world producer of aluminium (Venetski, 1969).

5.1.3 Properties

Aluminum as seen in Figure 5.2 is a silverish white metal that has a strong resistance to corrosion and like gold, is rather malleable. It is a relatively light metal compared to metals such as steel, nickel, brass, and copper with a specific gravity of 2.7g/cc. Aluminum is easily machinable and can have a wide variety of surface finishes. It also has good electrical and thermal conductivities and is highly reflective to heat and light (Table 5.1.), (Schröder and Kainer, 1991).



Figure 5.2: Bulk aluminum.

Aluminum is nontoxic (as the metal), nonmagnetic, and nonsparking. It has a tensile strength of about 49 MPa in a pure state and 400 MPa as an alloy. Aluminium is about one-third as dense as steel or copper; it is malleable, ductile and easily machined and cast. It has excellent corrosion resistance and durability because of the protective oxide layer.

Aluminium is one of the few metals which retains full silvery reflectance, even in finely powdered form, which makes it a very important component of silver paints. Aluminium's crystal structure is an FCC structure as seen in Figure 5.3 (Davis, 1993).

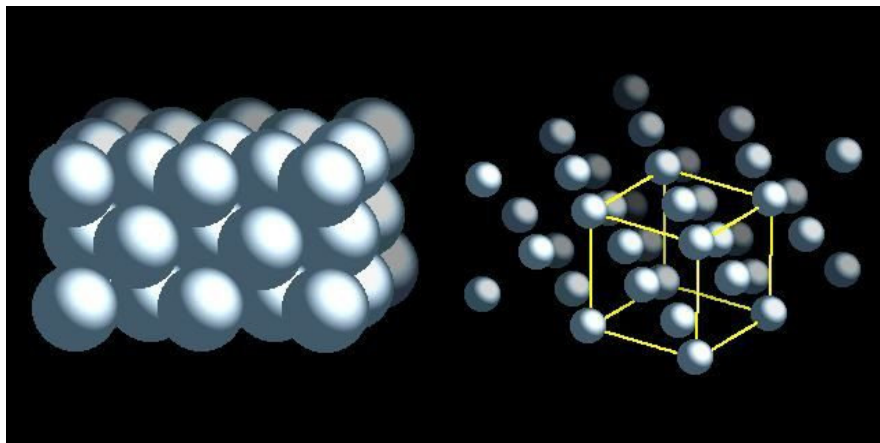


Figure 5.3: The structure of aluminum.

Aluminum mirror finish has the highest reflectance of any metal in the 200–400 nm (UV) and the 3000–10000 nm (far IR) regions, while in the 400–700 nm visible range it is slightly outdone by silver and in the 700–3000 (near IR) by silver, gold, and copper. Aluminum is a good thermal and electrical conductor. It is capable of being a superconductor, with a superconducting critical temperature of 1.2 Kelvin.

Pure aluminum has a low tensile strength, but when combined with thermo-mechanical processing, aluminum alloys display a marked improvement in mechanical properties, especially when tempered. Aluminum alloys form vital components of aircraft and rockets as a result of their high strength-to-weight ratio. Aluminum readily forms alloys with many elements such as copper, zinc, magnesium, manganese and silicon (e.g., duralumin). Today, almost all bulk metal materials that are referred to loosely as "aluminum," are actually alloys. For example, the common aluminum foils are alloys of 92% to 99% aluminum.

Whether measured in terms of quantity or value, the global use of aluminum exceeds that of any other metal except iron, and it is important in virtually all segments of the world economy.

Table 5.1: The properties of pure aluminum.

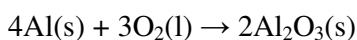
Name	Aluminum
Elastic Modulus	70-79 Gpa
Poisson's Ratio	0.33
Tensile Strength	230-570 MPa
Yield Strength	215-505 MPa
Percent Elongation	10-25%
Density	2700 kg/m ³
Symbol	Al
Atomic Number	13
Atomic Mass	26.981539 amu
Melting Point	660.37 °C (933.52 K, 1220.666 °F)
Boiling Point	2467.0 °C (2740.15 K, 4472.6 °F)
Number of Protons/Electrons	13
Number of Neutrons	14
Classification	Other Metals
Crystal Structure	Cubic
Color	Silver
British Spelling	Aluminium
IUPAC Spelling	Aluminium

Relatively pure aluminum is encountered only when corrosion resistance and/or workability is more important than strength or hardness. A thin layer of aluminum can be deposited onto a flat surface by chemical vapor deposition or chemical means to form optical coatings and mirrors. These coatings form an even thinner layer of protective aluminum oxide that does not deteriorate, as silver coatings do. Nearly all modern mirrors are made using a thin coating of aluminum on the back surface of a sheet of float glass. Telescope mirrors are also made with aluminum, but are front coated to avoid internal reflections, refraction and transparency losses. These first surface mirrors are more susceptible to damage than household back-surface mirrors (Schröder and Kainer, 1991).

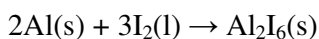
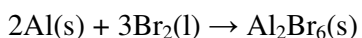
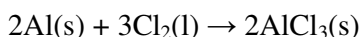
5.1.4 Chemical reactions of aluminum

Fajans rules show that the simple trivalent cation Al^{3+} is not expected to be found in anhydrous salts or binary compounds such as Al_2O_3 . The hydroxide is a weak base and aluminium salts of weak bases, such as carbonate, can not be prepared. The salts of strong acids, such as nitrate, are stable and soluble in water, forming hydrates with at least six molecules of water of crystallization (Friend, 1987).

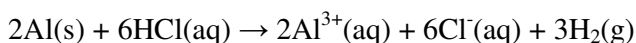
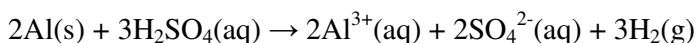
Normally, aluminum metal does not react with air. If the oxide layer is damaged, the aluminium metal is exposed to attack (Davis, 1993). Aluminium will burn in oxygen with a brilliant white flame to form the trioxide aluminum (III) oxide, Al_2O_3 .



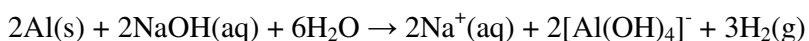
Fajans rules show that the simple trivalent cation Al^{3+} is not expected to be found in anhydrous salts or binary compounds such as Al_2O_3 . The hydroxide is a weak base and aluminium salts of weak bases, such as carbonate, can not be prepared. The salts of strong acids, such as nitrate, are stable and soluble in water, forming hydrates with at least six molecules of water of crystallization. Aluminium metal reacts vigorously with all the halogens to form aluminium halides (Venetski, 1969). So, it reacts with chlorine, Cl_2 , bromine, I_2 and iodine, I_2 to form respectively aluminium (III) chloride, AlCl_3 , aluminium (III) bromide, AlBr_3 and aluminium (III) iodide, AlI_3 .



Aluminium metal dissolves readily in dilute sulphuric acid to form solutions containing the aquated Al(III) ion together with hydrogen gas, H_2 . The corresponding reactions with dilute hydrochloric acid also give the aquated Al(III) ion. Concentrated nitric acid passivates aluminium metal (Davis, 1993).



Aluminium dissolves in sodium hydroxide with the evolution of hydrogen gas, H_2 and the formation of aluminates of the type $[\text{Al(OH)}_4]^-$ (Swain, 1994).



5.1.4.1 Reaction with silicon carbide

The silicon carbide SiC reinforced Al composite (SiC/Al) is perhaps the most successful class of MMC's produced to date. They have found widespread application for aerospace, energy, and military purposes, as well as in other industries for example; they have been used in electronic packaging, aerospace structures, aircraft and internal combustion engine components, and a variety of recreational products (Seleznev et al., 1995). SiC reinforced aluminum alloy composites made by casting techniques are the most common because of their low cost and ease of fabrication. However, during the fabrication of the SiC/Al composite, whether reinforced with fiber, whisker or particulate, a major technical problem occurs with the formation of the Al_4C_3 phase at the SiC/Al interface, because the SiC is thermodynamically unstable in the Al melt. This brittle reactant Al_4C_3 as seen in Figure 5.4, in the shape of thin hexagonal platelets, forms as agglomerates at the SiC/Al interface (Lloyd, 1989).

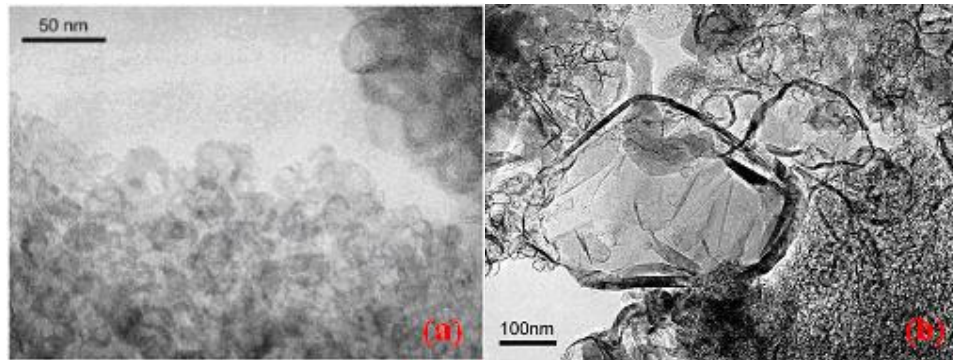


Figure 5.4: (a) TEM picture of nanobarrels from Al_4C_3 , (b) TEM picture of Al_4C_3 (<http://www.skeletonnanolab.com/Al4C3.html>).

Such an interfacial reaction in SiC/Al composites is known to have several undesirable effects on the overall composite properties:

- The composites can be susceptible to corrosive environments owing to the presence of Al_4C_3 , because Al_4C_3 is unstable in some environments such as water, methanol, HCl, etc.,
- Degradation of SiC itself occurs owing to the formation of Al_4C_3 ,
- The elemental Si, formed as a result of the interfacial reaction, produces the Al-Si eutectic during fabrication or the heat treating stage, resulting in undesired mechanical and physical properties of the matrix alloy. Therefore, fabrication of

SiCp/Al alloy composites without the formation of Al_4C_3 has been one of the major concerns (Lin, 1995).

Among various methods which have been proven to be effective in achieving such a goal, two methods have been accepted widely:

- Addition of Si into the Al matrix [7±10],
- Artificial oxidation of SiC to produce a SiO_2 layer on the surface of the SiC [10±12].

In spite of the number of technological approaches reported in the literature, the problem of the potential dissolution of SiC by aluminum remains unresolved, particularly when using the pressureless infiltration method. It has been demonstrated that silicon is a versatile element that can be used to control the reactions at the Al/SiC interface and prevent the potential attack of the SiC reinforcements by liquid aluminum. One of its major benefits is to reduce the activity of aluminum and ameliorate the potential damage caused by the molten metal on the SiC reinforcements. It can be used not only as an alloying element in aluminum, but it may also be present on the surface of the reinforcements as a coating either as an element or as an oxide. As a free-Si coating on the surface of SiC, it improves the wettability by significantly reducing the contact angle between the molten aluminum alloy and the particle (Salvo et al., 1994).

Gacsi et al (2001) investigated the pure Al-SiC system using two different techniques. Solyom and Gacsi (2001) mixed and sintered Al and SiC powders at 640 °C for 6.5 hours. As a result, the ternary $\text{Al}_4\text{Si}_2\text{C}_5$ phase has been detected at the interface between the SiC and Al particles. It should be mentioned that this is the first paper when the formation of a ternary carbide phase is identified, although their existence is clear from diffraction databases (Gacsi et al., 2001). After sintering the same Al/SiC powders during 2 hours, the composite was laser-remelted by Gacsi et al (2001). Although the Si-content of the Al-matrix considerably increased (even up to 7 % from practically 0 %), Al_4C_3 was not possible to identify in the system by XRD, similarly to results of Lee et al (2004).

In addition, the ternary carbide, Al_4SiC_4 , has attracted much attention owing to its lower density (3.03 g/cm^3), higher melting point ($>2000^\circ\text{C}$) and excellent oxidation resistance. In 1961, Barczak (1961) gave the X-ray diffraction of Al_4SiC_4 powders.

The space group of Al_4SiC_4 was identified as P63mc, with unit cell dimensions of $a=3.2771\pm0.0001\text{\AA}$ and $c=21.676\pm0.0002\text{\AA}$ for the corresponding hexagonal lattice. The oxidation behavior of the Al_4SiC_4 powder was studied first in air (Oden and Mccune, 1990). The results showed that the Al_4SiC_4 powder had an excellent oxidation resistance. More recently, Yamamoto et al (2002) synthesized Al_4SiC_4 ceramic with Al, C and Si powders as raw materials. The oxidation resistance and other properties had been studied (Salvo et al., 1994). The results showed that mullite and corundum formed on the surface of the oxidized body after oxidation at 1500°C for 10 h and the protective layer inhibited further oxidation inward to the Al_4SiC_4 body (Oden and Mccune, 1990).

Recently, some studies have been done on the synthesis of Al_4SiC_4 powders and Al_4SiC_4 bulk ceramics (Yamamoto et al., 2002). The oxidation behavior, physical properties and the electrical conductivities of this material were also studied (Barczak, 1961). However, the mechanical properties, especially the high temperature mechanical properties have not been extensively studied so far. Oden and Mccune (1990) investigated the mechanical properties of Al_4SiC_4 ceramics, particularly the enhanced mechanism of fracture toughness at room temperature and the increased bending strength at high temperature in air.

5.1.4.2 Reaction with boron carbide

The selection of reinforcement for AMCs depends on the application, the manufacturing methods, and the material cost (Hunt et al., 2000). A wide range of potential reinforcements have been considered, including SiC, Al_2O_3 , mica, clay, ZrO_2 and graphite. Recently, B_4C has become an attractive reinforcement for Al MMC's due to its lower density and comparable mechanical/ thermal properties to SiC and Al_2O_3 (the two most common reinforcements). In contrast to Al MMC's containing SiC or Al_2O_3 reinforcement, Al MMC's containing B_4C reinforcement have been paid much less attention (Carden, 1996). Furthermore, it is known that reactions between aluminum alloys and B_4C usually produce a variety of phases which affect the mechanical properties of Al/ B_4C composites to different extents. Such reactions are strongly dependent on processing parameters, like consolidation temperature and oxygen content (Ashby, 1993).

Shorowordi et al., (2003) made a comparative study about microstructure and interface characteristics of B_4C , SiC and Al_2O_3 reinforced Al matrix composites. In his study, the reinforcing particles of SiC and Al_2O_3 were preheated at $900^\circ C$ for 1 and 2h in air, respectively to increase their surface reactivity, while B_4C was preheated at $175^\circ C$ for 2h. Then, heat-treated particles were mixed into the melt through the vortex. Finally the melt had been poured into a 52mm internal diameter cylindrical graphite mould. Various compositions ranging from 0 to 20 vol.% of Al-SiC, Al- Al_2O_3 and 0–13 vol.% Al- B_4C composites had been processed. Composites had been subjected to hot extrusion at $420^\circ C$ with an extrusion ratio of 27 at a speed of 1 m/min. Hot extruded composites of 10 mm diameter bar had been then heat treated at $400^\circ C$ for 2h and cooled in furnace to remove the extrusion effect. For Al- B_4C composite, they had detected no clear interaction layer at the interface. The B_4C particles had seemed to adhere well to the Al matrix. They had observed two secondary phases in the matrix away from the interface. From EDX analysis they had thought that these phases were Al_2O_3 and aluminum boron carbide. The alumina particles were small and spread throughout the Al matrix while the second phase consisted of relatively larger particles but were less in number.

Hu et al., (2001) studied microstructure of B_4C /Al composites produced by cold isostatic pressing. In their study, B_4C particles with a mean size $10\mu m$ and Al powders had been blended and isostatically cold pressed. Cold isostatically pressed samples had been sintered under vacuum conditions. Sintered samples then had been extruded at a reduction of 35:1. The as-extruded composite had been subsequently solution heat-treated at $493^\circ C$ for 2h and water quenched and artificially aged at $135^\circ C$ for 3h. The microstructure of the B_4C : Al-7093 composite in the present investigation had been characterized by standard metallography and polishing techniques. The primary and secondary phases present in the microstructure had been identified using transmission electron microscopy (TEM), scanning electron microscopy (SEM) and X-ray diffraction. The grain sizes are 3-5 mm, and a large number of precipitates were present in the Al matrix. EDS spectra of these precipitates showed that they were enriched not only with Mg and Zn but also with Cu, suggesting that they were probably Mg (Zn,Cu)₂ precipitates. Higher magnification clearly showed the variation of precipitates in the matrix.

Halverson et al., (1989) have studied processing of boron carbide-aluminum composites. They focused on finding the phases in the microstructure. In their study, they mixed B_4C powder (three particle-size distributions with medium sizes of 4, 10 and 56 μ m) and aluminum powder (-325 mesh) in isopropyl alcohol, ultrasonically mixed the slurry to achieve homogeneity, and consolidated the solids by filtration in a plaster of Paris mold. They consolidated samples using three different techniques which are pressureless sintering, hot-pressing, and hot isostatic pressing. Hot pressing was achieved under a pressure of 207MPa at 1000-1200°C. B_4C and aluminum react to form phase Al_4BC . Under local equilibrium between 800°C and 900°C, AlB_2 and Al_4BC are the major reaction products. Under these conditions, phase Al_4BC is stable, and it will decompose only if all of the free aluminum is depleted from the system. Above 1100°C, there is less of the Al_4BC_3 phase because aluminum is rapidly being depleted through the formation of other more thermodynamically stable phases. Above 900°C, but below 1200°C, the following microstructural differences occur: (1) $AlB_{12}C_2$ is thermodynamically favoured over AlB_{12} between 900°C and 1000°C, and (2) AlB_2 , continues to form up to 1000°C; however, above 1000°C, AlB_2 is only present when the microstructure is cooled. Between 1200°C and 1400°C, the following further changes in the microstructure occur: (1) Al_4C_3 is forming very quickly (associated with a decrease of the ternary phase Al_4BC); (2) $AlBC_4$ is now favored over $AlB_{12}C_2$ and becomes the major ternary phase; (3) above 1300°C, XRD patterns indicate the appearance of a phase previously reported as $Al_4B_{13}C_4$ but more recently reported (Lee, 1997) as $Al_8B_4C_7$ and (4) at 1400°C, Al_4C_3 begins to crystallize in the shape of short whiskers.

5.2 Silicon Carbide (SiC)

Among the various non-oxide ceramics that have found commercial applications, SiC is the leader. The attractive properties, such as good specific strength and Young modulus as a function of temperature, the specific stiffness, corrosion and erosion resistance have made SiC an attractive alternative to the hard metal compositions (Rafaniello and Srinivasan, 1997). Furthermore, it is an important ceramic used in structural applications, such as automotive engines, cutting tools, heat exchange and mechanical seals (Marchi et al., 2001). The characteristics and the properties of SiC are summarized in Table 5.2.

Table 5.2: Summary of characteristics and properties of SiC.

Composition	SiC (very narrow range)
Molecular Weight	40.097 g/mol
Density	α SiC 3.211 g/cm ³ β SiC 3.214 g/cm ³
Melting Point	2545 °C @ 1atm(β SiC) 2830 °C @ 35 atm(β SiC)
Specific Heat	α SiC 27.69 J/molK β SiC 28.63 J/molK
Heat of Formation(ΔH)	α SiC -25.73 $\pm$ 0.63 kJ/molK @ 298.15K β SiC -28.03 $\pm$ 2 kJ/molK @ 298.15K
Thermal Conductivity	α SiC 41 W/m °C β SiC 25.5 W/m °C
Thermal Expansion	α SiC 5.12 x10 ⁻⁶ /°C β SiC 3.8 x10 ⁻⁶ /°C
Vickers Hardness	30-35 GPa
Modulus of Elasticity	300-475 GPa
Shear Modulus	192 GPa (β SiC)
Bulk Modulus	96.6 GPa (β SiC)
Flexural Strength	350-600 MPa
Poisson's Ratio	0.183-0.192
Oxidation Resistance	Excellent due to the formation of a layer of SiO ₂
Chemical Resistance	Essentially inert at room temperature

SiC has a close-packed crystal structure depending on the stacking order which can exist in either cubic or hexagonal orientations (Rafaniello and Srinivasan, 1997). Silicon carbide exists in a large number of different polytypes. Basically, all polytypes have a hexagonal frame with C atoms in center of mass of a triangle of Si atoms (Figure 5.5)The structural unit of the tetrahedron consists of primarily covalent Si-C bonds (88% covalent and 12% ionic), (Marchi, 2001).

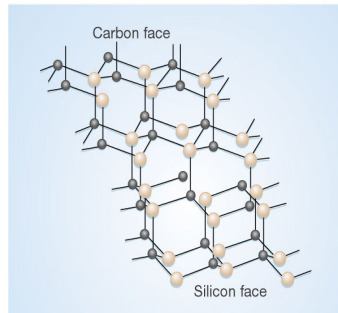


Figure 5.5: C atoms in center of mass of a triangle of Si atoms
(<http://www.nature.com/nature/journal/v430/n7003/images/430974a-f1.2.jpg>).

The crystal structures of SiC are cubic, hexagonal and rhombohedral and often the Ramsdell notation is used for describing the polytypes (Figure 5.6). This notation system indicates the number of layers in the unit cell and a letter representing the crystal symmetry of the polytype (C for cubic, H for hexagonal and R for rhombohedral), (Rafaniello and Srinivasan, 1997). Generally, the 3C-SiC polytype is referred to as β -SiC and the hexagonal polytypes as α -SiC. The 3C-SiC polytype has a zinc-blende structure, and is the only polytype which is cubic. Furthermore, the 2H polytype represents the wurtzite structure of the SiC polytype.



Figure 5.6: (a) A silicon carbide nanobouquet, (b) A silicon carbide nanotree (<http://nanotechweb.org/objects/news/3/6/11/NanobouquetWelland.jpg>).

There are various applications where SiC is used. Because of its thermal mechanical and chemical properties it can be used in extremely harsh environments. Firstly, it is used in powder form as deoxidizer in steel production and other metallurgical processes, as powder, bonded and coated abrasives and as filler materials in refractory cements. Additionally, it is used in bulk form as refractory products, as electric heating elements and resistors, as igniters for gas appliances, as ceramic burners, as mechanical seal faces, as radiation sensors, as low-weight high-strength mirrors, as high power and high temperature semiconductor devices, as radiation resistant semiconductors and as light-weight armors (Pierson, 1996; Rafaniello and Srinivasan, 1997). Furthermore, it is used as coatings for fusion reactor applications, for nuclear waste containers, for oxidation resistance of carbon-carbon composites and for blue light emitting diodes (LED), (Pierson, 1996).

5.3 Boron Carbide (B_4C)

Boron Carbide (Figure 5.7) is one of the hardest materials known, originally discovered in mid 19th century as a by-product in the production of metal borides, boron carbide was only studied in detail since 1930.

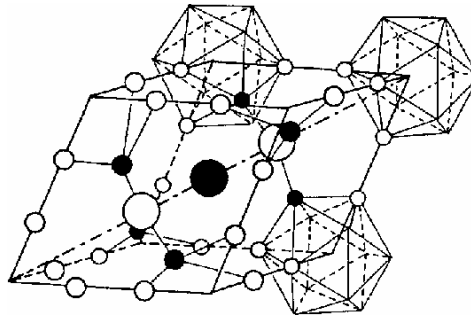


Figure 5.7: B₄C structure.

Boron carbide powder is mainly produced by reacting carbon with B₂O₃ in an electric arc furnace, through carbothermal reduction or by gas phase reactions. For commercial use B₄C powders usually need to be milled and purified to remove metallic impurities.

In common with other non-oxide materials boron carbide is difficult to sinter to full density, with hot pressing or sinter HIP being required to achieve greater than 95% of theoretical density. Even using these techniques, in order to achieve sintering at realistic temperatures (e.g. 1900-2200°C), small quantities of dopants such as fine carbon, or silicon carbide are usually required.

Due to its high hardness, boron carbide powder is used as an abrasive in polishing and lapping applications (Table 5.3), and also as a loose abrasive in cutting applications such as water jet cutting. It can also be used for dressing diamond tools. The extreme hardness of boron carbide gives it excellent wear and abrasion resistance and as a consequence it finds application as nozzles for slurry pumping, grit blasting and in water jet cutters (Figure 5.8).

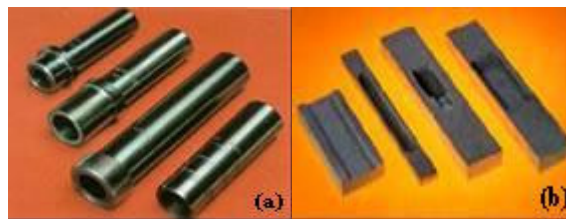


Figure 5.8: (a) B₄C nozzles (Photo Courtesy of CERAM Research Ltd), (b) B₄C evaporating boats (Photo Courtesy of CERAM Research Ltd).

Boron carbide, in conjunction with other materials also finds use as ballistic armour (including body or personal armour) where the combination of high hardness, high elastic modulus, and low density give the material an exceptionally high specific stopping power to defeat high velocity projectiles.

Table 5.3: Summary of characteristics and properties of B₄C.

Property	Unit	B₄C	SiC
Density	g/cm ³	>2.48	>3.07
Hardness (Vickers)	GPa	32	24
Compressive Strength	MPa	2760	2100
Flexural Strength	MPa	360	290
Young's Modulus	GPa	455	320
Poisson-Ratio	-	0.16	0.17
Weibull Modulus	-	10	12
Thermal Expansion (20-1000°C)	10 ⁻⁶ K ⁻¹	5.6	4,6
Thermal Conductivity (20°C)	W/mK	30	80
Specific Electrical Resistivity (20°C)	Ohm cm	0.1	0.1

6. EXPERIMENTAL PROCEDURE

The experimental part of this study was designed in order to provide useful information about sintering, microstructural and mechanical properties of Al-SiC, Al-B₄C, Al-SiC-Y₂O₃ and Al-B₄C-Y₂O₃ composites prepared by the mechanical alloying technique.

The first group of experiments deals with the effect of SiC addition on the microstructural and mechanical properties of Al, the second group of experiments investigates the effect of Y₂O₃ addition on the microstructural and mechanical properties of Al-SiC composites, third group of experiments deals with effect of B₄C addition on the microstructural and mechanical properties of Al, fourth and also the last group of experiments investigates the effect of Y₂O₃ addition on the microstructural and mechanical properties of Al-B₄C composites. In each group, the influence of the amount of alloying addition is investigated together with the influence of the duration of mechanical alloying. In the first group of experiments, powder mixtures of;

- Al-%5 SiC (weight), Al-%10 SiC (weight) and Al-%15 SiC (weight),

in the second group of experiments powder mixtures of;

- Al-%5 B₄C (weight), Al-%10 B₄C (weight) and Al-%15 B₄C (weight).

in the third group of experiments powder mixtures of;

- Al-%5 SiC-%5 Y₂O₃ (weight), Al-%10 SiC-%5 Y₂O₃ (weight) and Al-%15 SiC-%5 Y₂O₃ (weight).

in the last group of experiments powders mixtures of;

- Al-%5 B₄C-%5 Y₂O₃ (weight), Al-%10 B₄C-%5 Y₂O₃ (weight) and Al-%15 B₄C-%5 Y₂O₃ (weight) were prepared as experimental batches of this investigation.

In Figure 6.1, flowchart of the experiments is given. All aspects in this schema will be explained in further paragraphs.

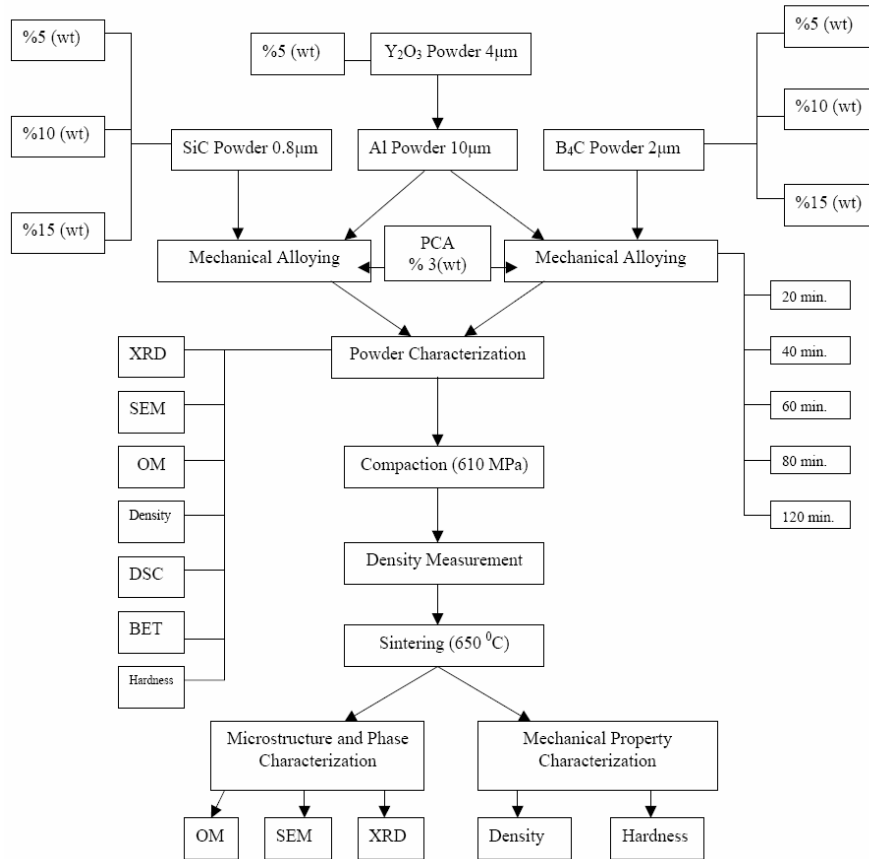


Figure 6.1: Flowchart showing experimental procedures of this investigation.

6.1 Preparation of Green Compacts

6.1.1 Mechanical alloying (MA)

In this study, Al, SiC, B₄C and Y₂O₃ powders were used with an average particle size of 10 µm, 0.8 µm, 2.464 µm and 1 µm, respectively. Furthermore, 3 wt % fine zinc stearate powder was used as a process control agent (PCA) to minimize cold welding between powder particles and thereby inhibit agglomeration.

The powders were mechanically alloyed (MA'd) in a stainless steel vial using a 8000D™ Spex mill (Fig.6.2a) with a speed of 1200 rpm. Stainless steel balls with a diameter of ¼ inches were used as milling media. A ball-to-powder weight ratio of 7:1 was used in all MA experiments. The degree of contamination of the milled powder with stainless steel was determined by weighing the media before and after milling. The mechanical alloying procedure of all powder mixtures were carried out in Argon atmosphere in a glove-box. All the powder mixtures were MA'd for 20, 40, 60, 80 and 120 minutes.

During dry MA, the ball and vial surface were covered with powder and wear of the balls was not detected. After milling, the balls and vial surface were cleaned with isopropyl alcohol (IPA).

High-purity argon was chosen as the milling atmosphere to prevent oxidation and contamination of the powder. The presence of air in the vial causes the formation of oxides and nitrides in the powder, especially if the powders are reactive in nature. Thus, loading and unloading of the powder batches into the vial was carried out inside a “Plaslabs™” atmosphere-controlled glove box (Figure 6.2b).



Figure 6.2: (a) 8000D™ spex mill, (b) Plaslabs™ glove box.

6.1.2 Compaction

Mechanically alloyed powders were compacted by cold pressing in a tool-steel die with a pressure of 610-620 MPa (100 bar) into cylinder shaped green compacts with a diameter of $\approx 12\text{mm}$ for 1 minute by using “APEX™ 3010/4” one-action hydraulic press (Figure 6.3). Zinc stearate was applied to the walls of the die to remove the samples easily from the die.



Figure 6.3: APEX™ 3010/4 one-action hydraulic press.

6.1.3 Sintering

Sintering was performed in a high temperature 1700 Anter™ dilatometer (Fig.6.4a). In addition to its function for measuring the thermal expansion behaviour of materials, 1700 Anter™ dilatometer was also used as a high temperature furnace with reducing atmosphere to understand the sintering behavior of the samples in this study. The samples were first sintered in the 1700 Anter™ dilatometer (Figure 6.4). According to their sintering behaviour, other samples were sintered in the same sintering regime. All samples were sintered under Argon atmosphere accordance with the sintering regime determined by using 1700 Anter™ dilatometer, as seen in Fig. 6.5. A reductive high temperature 1800 HT Vac Molybdene Linn™ furnace was also used for sintering the Al-B₄C-Y₂O₃ samples at the Katholieke Universiteit Leuven.



Figure 6.4: (a) 1700 Anter™ vertical dilatometer, (b) Linn™ HT 1800 furnace.

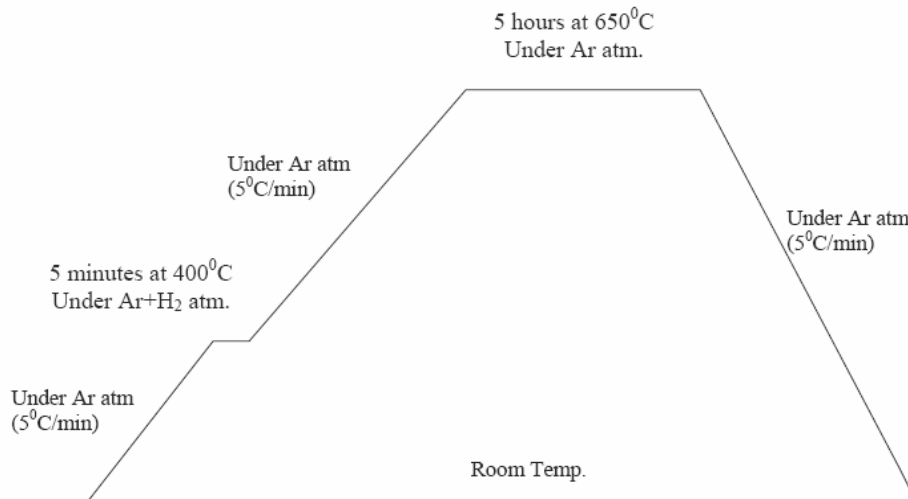


Figure 6.5: Sintering regime in the 1700 Anter™ dilatometer.

6.2 Characterization of Powder Mixtures and Sintered Samples

6.2.1 Powder characterization

Zetasizer can measure a combination of three of the most important parameters for the colloid and polymer chemist: particle size, zeta potential and molecular weight. A new technology incorporated in these systems provides unequalled sensitivity and versatility. Zetasizer enables measurements of particles and molecules from 0.6 nm to 6 microns. For Zeta potential measurements, MalvernTM Zetasizer M3-PALS technology enables accurate measurements of zeta potential in aqueous and non-aqueous dispersions (Figure 6.6).



Figure 6.6: MalvernTM zetasizer equipment.

This is achieved by a combination of laser Doppler velocimetry and phase analysis light scattering MalvernTM Zetasizer M3-PALS. Even samples of very low mobility can be analyzed and their mobility distributions can be calculated. This device was used for analyzing the behavior of Al-SiC and Al-B₄C composites in liquid media (aqueous dispersions).

Stability, chemical reactivity, opacity, flow ability and material strength of many materials are affected by the size and characteristics of the particles within them. MalvernTM particle size analyzer has a range of particle size measurement solutions from sub-nanometer to millimeters in size (Figure 6.7). In some cases, sample materials are not plentiful and a smaller volume sample dispersion unit is a practical choice to minimize sample consumption. This instrument was used for obtaining particle size of the samples.

QuantachromeTM Autosorb-1 (Figure 6.8.) operates by measuring the quantity of gas adsorbed onto or desorbed from a solid surface at some equilibrium vapor pressure by the static volumetric method (QuantachromeTM Autosorb User Manual, 2006). The data are obtained by admitting or removing a known quantity of adsorbate gas

into or out of a sample cell containing the solid adsorbent maintained at a constant temperature below the critical temperature of the adsorbate. All experiments are performed under controlled atmosphere with liquid nitrogen (N_2). Quantachrome™ Autosorb-1 has the capability of measuring adsorbed or desorbed volumes of N_2 at relative pressures in the range 0.001 to slightly under 1.0 bar.



Figure 6.7: Malvern™ particle size equipment.

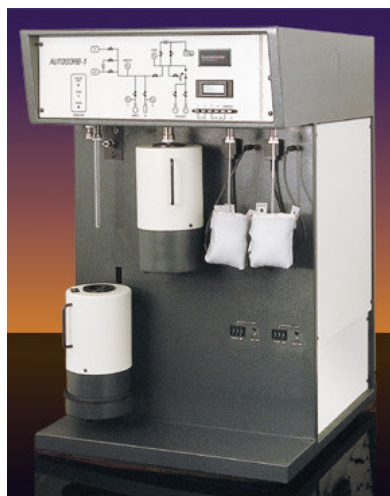


Figure 6.8: Quantachrome™ Autosorb-1 AS-1 BET analysis instrument.

As adsorption or desorption occurs, the pressure in the sample cell changes until equilibrium is established. The quantity of gas adsorbed or desorbed at the equilibrium pressure is the difference between the amount of gas admitted or removed and the amount required to fill the space around the adsorbent (void space). This volume-pressure data can be reduced by the Autosorb-1 software into BET surface area (single and/or multipoint), Langmuir surface area, adsorption and/or desorption isotherms, pore size and surface area distributions, micropore volume and surface area using an extensive set of built-in data reduction procedures.

6.2.2 Microstructural and phase characterization

Microstructural and phase characterizations were carried out by an optical microscope, a scanning electron microscope (SEM) and an X-Ray diffraction (XRD) analyse. Before the sintered samples were characterized, they were mounted in using standard metallographical procedures. After that, the samples were polished on a Struers™ TegraPol-15 automatic polishing machine shown in Figure 6.9.



Figure 6.9: Struers™ TegraPol-15 automatic polishing machine.

XRD analyses were carried out on a Rigaku™ X-Ray Diffractometer in Istanbul Technical University and Seifert XRD 3003 PTS-HR Diffractometer at a generator voltage of 40kV and current of 30mA in the Katholieke Universiteit Leuven. CoK_α radiation was used to irradiate the samples (Figure 6.10).



Figure 6.10: (a) Rigaku™ X-Ray diffractometer, (b) Seifert XRD 3003 PTS-HR diffractometer.

The Nikon™ Eclipse L150 specification for infinity corrected optics is presented to allow introduction of auxiliary components, such as differential interference contrast (DIC) prisms, polarizers, and epi-fluorescence illuminators, into the parallel optical path between the objective and the tube lens with only a minimal effect on focus and aberration corrections.

In order to reveal the grain boundaries, polished surfaces were etched by using Keller-Murakami for 10 seconds before the microscopic analyses. Optical microscope analyses were carried out on a Nikon™ Eclipse L150 optical microscope shown in Figure 6.11. On the other hand SEM analyses were carried out on two different SEM equipment, one in Istanbul Technical University and the other in Katholieke Universiteit Leuven (Figure 6.12). These are Jeol™-JSM-T330 scanning electron microscope and Philips™ XL 30 FEG field emission scanning electron microscope, respectively. Second one was used for higher magnifications (3000x-6000x).

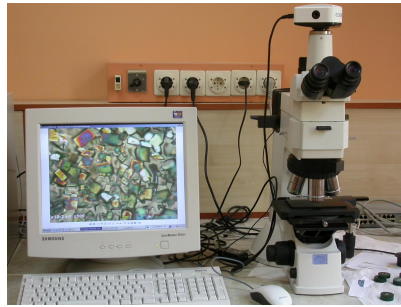


Figure 6.11: Nikon™ Eclipse L150 optical microscope.



Figure 6.12: (a) Jeol™-JSM-T330 scanning electron microscope, (b) Philips™ XL 30 FEG field emission scanning electron microscope.

6.2.3 Density measurements

Densities of green compacts were calculated dimensionally. On the other hand density measurements of the compacted and sintered samples were carried out by simply using the relationship between volume and mass. In this method, the density is determined by using liquid displacement (Archimedes' method). First, the sample is weighted in air and then in a liquid. After that, the mass in air is divided with the difference of these results and then multiplied with the density of the liquid (Figure

6.13a). In this study, ethyl alcohol (EA) is used as the liquid because of the oxidation risk of the samples.

The density of the powder can also be determined with a pycnometer. The Quantachrome™ Pycnometer instrument shown in Figure 6.13 measures compacted and sintered powder density. The pycnometer is a flask with a close-fitting ground glass stopper with a fine hole through it, so that a given volume can be obtained accurately. This enables the density of a fluid to be measured accurately, by reference to an appropriate working fluid such as water or mercury, using Archimedes' principle.



Figure 6.13: (a) Precisa™ XB220A balance, (b) Quantachrome™ pycnometer

During pycnometer measurements, if the flask is weighed empty, full of water or with full of a fluid whose specific gravity is desired, the specific gravity of the fluid can then easily be calculated. In these experiments, helium is used. The particle density of a powder, to which the usual method of weighing cannot be applied, can also be determined with a pycnometer. The powder is added to the pycnometer, which is then weighed, giving the weight of the powder sample. The pycnometer is then filled with a fluid of known density, in which the powder is completely insoluble. The weight of the displaced fluid can then be determined, and hence the specific gravity of the powder.

6.2.4 Hardness measurements

Hardness measurements were carried out on a Shimadzu™ microhardness tester shown in Figure 6.14 with a Vickers indenter under a load of 50 g for 15 seconds for powder samples and 1 kg for 15 seconds for bulk samples. Results of hardness tests were averaged out of 25 successive indentations.



Figure 6.14: Shimadzu™ microhardness tester.

6.2.5 Thermal analysis

A Thermal Analysis™ (TA™) DTA-DSC-TGA instrument shown in Figure 6.15 measures the amount and the rate of change in the weight of a material as a function of temperature or time in a controlled atmosphere. Measurements are used primarily to determine the composition of aluminum based materials and to predict their thermal stability at temperatures up to 650°C under Argon atmosphere. The typical heating rate is 10°C/min. By using this DTA/DSC/TGA, it is possible to characterize the materials that exhibit weight loss or gain due to decomposition, oxidation, or dehydration.

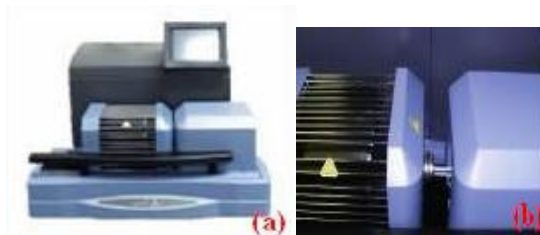


Figure 6.15: SDT Q Series™ DTA-DSC instrument (a) General view, (b) Furnace.

The thermal analytical equipment is used as an analytical tool to measure the following physical and reactive properties of substances based on temperature: thermal decomposition of solids and liquids kinetic study of consecutive decompositions, solid-solid and solid-gas chemical reactions, material specification, purity and identification of inorganic solid material adsorption phase transformations (Thermal Analysis™ (TA™) DTA-DSC-TGA User Manual, 2006).

Differential Scanning Calorimetry (DSC) is a thermal analysis technique which is used to measure the temperatures and heat flows associated with transitions in

materials as a function of time and temperature (Thermal AnalysisTM (TATM) DTA-DSC-TGA User Manual, 2006). Such measurements provide qualitative and quantitative information about physical and chemical changes that involve endothermic and exothermic processes, or changes in heat capacity. All powder samples of different compositions have been tested at temperatures up to 650°C under argon atmosphere. Typical heating rate is 10°C/min.

7. RESULTS AND DISCUSSIONS

7.1 Characterization of Powders

7.1.1 Starting powders

As major constituent, Al powders with a purity of 99.99 wt % were used for all experiments. Black and green silicon carbide powders of different grades (SiC content is greater than 98 wt %) commercially produced by Herman Starck Inc. and boron carbide (97.5 wt %) raw materials commercially produced by Kayseri Boron Technologies Inc. (BMBT), Turkey were used for reinforcing phases. Y_2O_3 commercially produced by Alfa Aesar Inc. was also used for different experiment sets as a reinforcing agent. The chemical analysis results of the chemical analysis of starting powders performed with acid titrimetric analyses are shown in Table 7.1.

Table 7.1: Chemical analysis of starting powders.

SiC	Al	B ₄ C	Y ₂ O ₃
%0.050 Fe	%99.630 Al	%64.56 B	%99.9 Y ₂ O ₃
%0.001 Mn	%0.102 Fe	%18.31 C (depends on boron carbide)	50 ppm Fe
%0.011 Ca	%0.003 Mn	%14.64 C (free)	30 ppm Ca
%35.470 Si	%0.040 Ca	%0.54 Fe	13 pm Al
%3.390 C	%0.400 Si	%1.21 Si + %0.75 Al	20 ppm La

BET surface areas of the powders which were measured a BET are shown in Table 7.2. All BET surface area measurements were performed under controlled atmosphere with liquid nitrogen according to multi-point BET principle. All data were collected from 5 points. BET surface analyses were carried out in two stages: degass stage was the first stage. In this stage, all the humid in the powders was removed away. For this process, helium was used as a backfill gas. The temperature for degassing was selected as 150⁰C. After the degassing section, the absorbate gas nitrogen was used for obtaining surface area. The specific area of Al powders is 22.5 m²/g. Specially selected ratios of these powders were used in specific ceramic compositions.

Table 7.2: Surface area results of the powders.

Powder Type	Surface Area (m²/g)	Corelation Coefficient
Al	4.57	0.9534
SiC	22.25	0.9989
B ₄ C	8.37	0.9932
Y ₂ O ₃	5.27	0.9878

The densities of the powders which were measured with pycnometer before mechanical alloying are shown in Table 7.3. The density of the studied SiC powders is relatively low. The achievement of these low values is connected with some porosity of ceramics. The studied B₄C powders have a density around 2.51 g/cc, Al has density of 2.68 g/cc and Y₂O₃ has density of 5.01 g/cc.

Table 7.3: Density data of the starting powders.

Powder Type	Density (g/cc)
Al	2.68
SiC	3.05
B ₄ C	2.51
Y ₂ O ₃	5.01

The starting powders which were used for this project did not dissolve in water. For this reason, particle size measurements were applied in wet conditions using distilled water (Figure 7.1). To prevent agglomeration, powders were dispersed and deagglomerated in an ultrasonic bath for 15 min. before analyzing the particle sizes.



Figure 7.1: Aluminum powders in distilled water.

Al, SiC, B₄C and Y₂O₃ powders have different average particle sizes and particle size distributions. As can be seen from Figure 7.2., the distributions of average particle size SiC and B₄C powders are bimodal. Their particle sizes are distributed around

two mean values. For SiC, these mean values are 0.8 μm and 20 μm . For B_4C , two mean values are 0.1 μm and 5 μm . For Al and Y_2O_3 powders, the distribution is Gaussian like around a mean value. For Al, this mean value is about 10 μm particle size and the average median particle size of Y_2O_3 is about 4 μm . The particle size distribution curves of the starting powders are given in Figure 7.2.

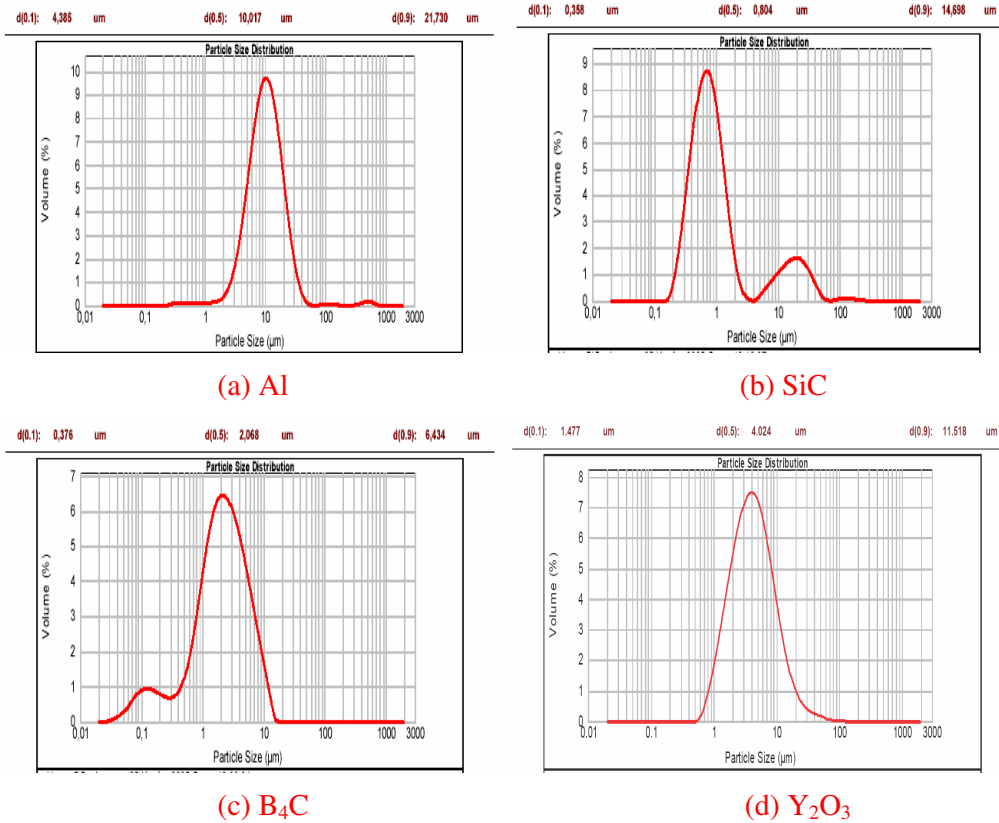


Figure 7.2: Particle size and particle size distribution of the starting powders.

Microstructures of powders were characterized before mixing procedure by X-Ray diffraction (XRD) at a low incident angle ($\theta=3^\circ$), (Figure 7.3a-b-c-d). X-ray diffraction analysis has been carried out to check the absence of foreign phases. As a result of these experiments, no foreign phases were detected as seen in Fig.7.3.

The powder morphology was examined using Scanning Electron Microscopy (SEM) techniques, SEM pictures of starting materials taken with 20 kV and different enlarge sizes (x500–x1500) are shown in Figure 7.4. The SEM photographs show that Al and Y_2O_3 particles have a more spherical or oblong shape and are smoother than B_4C and SiC powders. Moreover, the particle sizes of powders can be investigated from SEM pictures.

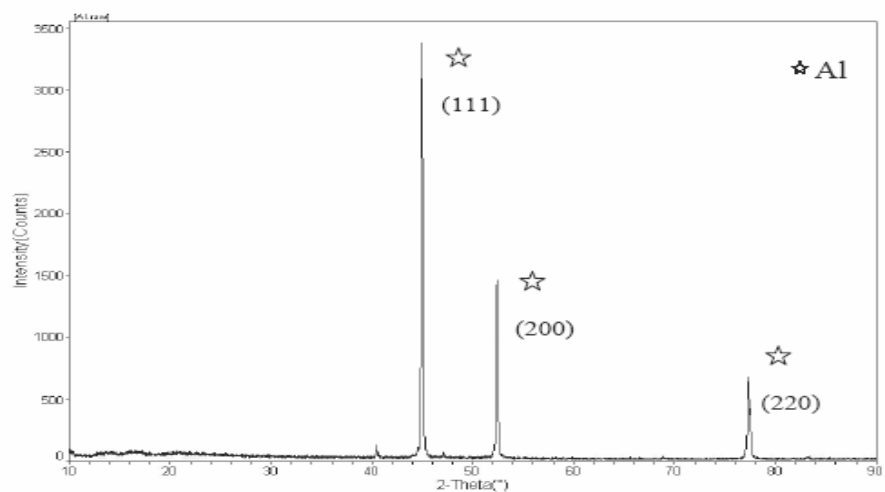


Figure 7.3a: XRD pattern of the Al powder used in this investigation.

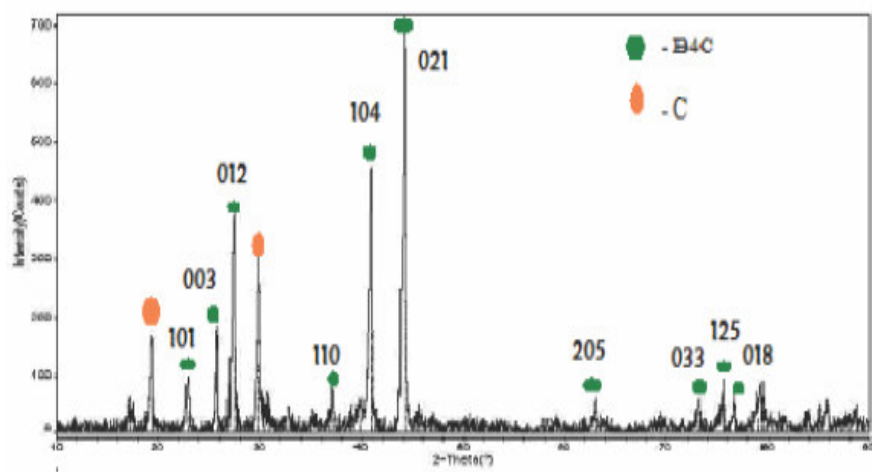


Figure 7.3b: XRD pattern of the B₄C powder used in this investigation.

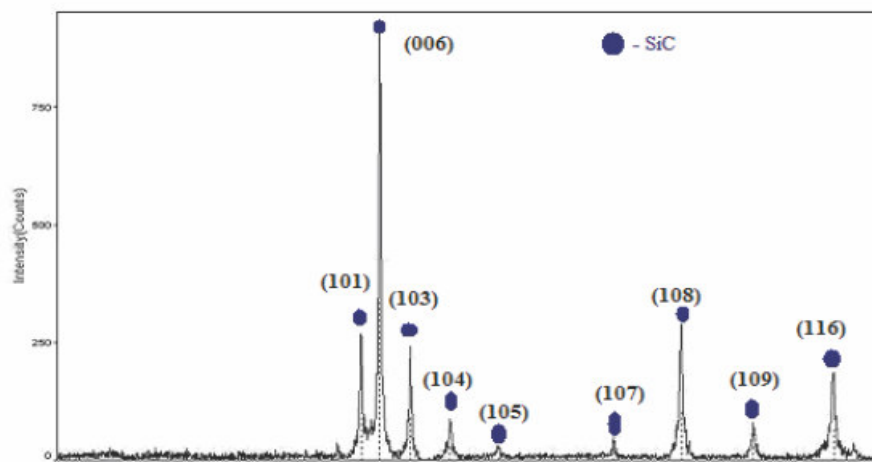


Figure 7.3c: XRD pattern of the SiC powder used in this investigation.

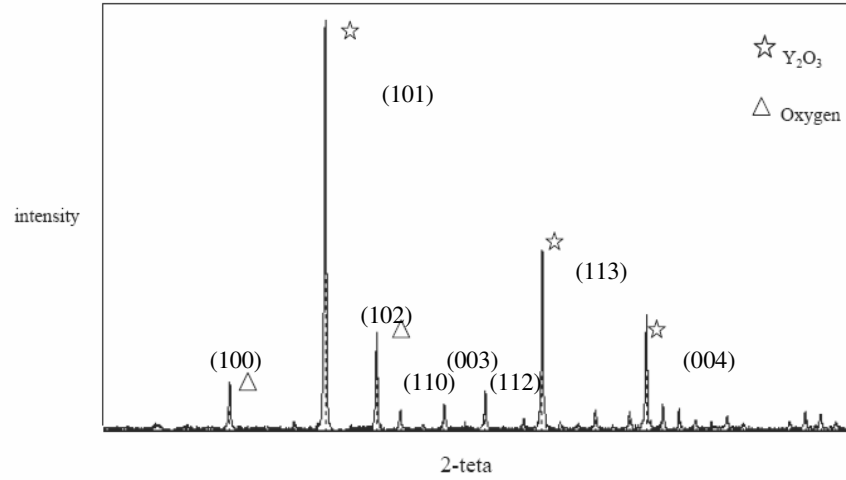


Figure 7.3d: XRD pattern of the Y_2O_3 powder used in this investigation.

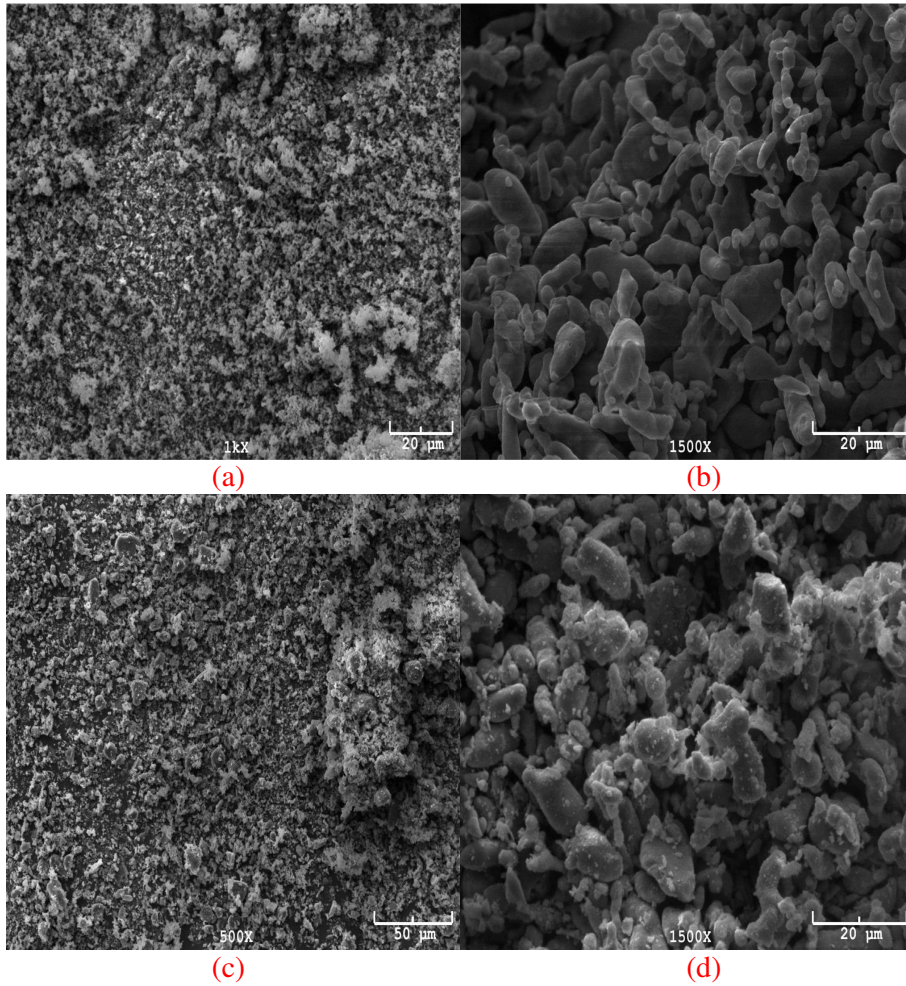


Figure 7.4: SEM micrographs of (a) SiC (x1000), (b) Al (x1500), (c) B_4C (x500), (d) Y_2O_3 (x1500) powders used in this investigation.

7.1.2 Phase analyses and microstructural characterizations

The compositions and grades of raw materials used have been developed and selected to achieve an optimal particle size distribution and compaction. Since there are a lot of samples to discuss, sample codes are given to all samples, such as AS5MA2006 or AB15Y5MA12006 as seen in Tables 7.4a-b-c-d.

Table 7.4a: Sample codes for Al-SiC compositions of this investigation.

Sample Name	Powder Composition Information	Mechanical Alloying Time (min.)
AS5MA2006	Al-%5 SiC(wt)	20
AS5MA4006	Al-%5 SiC(wt)	40
AS5MA6006	Al-%5 SiC(wt)	60
AS5MA8006	Al-%5 SiC(wt)	80
AS5MA12006	Al-%5 SiC(wt)	120
AS10MA2006	Al-%10 SiC(wt)	20
AS10MA4006	Al-%10 SiC(wt)	40
AS10MA6006	Al-%10 SiC(wt)	60
AS10MA8006	Al-%10 SiC(wt)	80
AS10MA12006	Al-%10 SiC(wt)	120
AS15MA2006	Al-%15 SiC(wt)	20
AS15MA4006	Al-%15 SiC(wt)	40
AS15MA6006	Al-%15 SiC(wt)	60
AS15MA8006	Al-%15 SiC(wt)	80
AS15MA12006	Al-%15 SiC(wt)	120

Table 7.4b: Sample codes for Al-B₄C compositions of this investigation.

Sample Name	Powder Composition Information	Mechanical Alloying Time (min.)
AB5MA2006	Al-%5 B ₄ C (wt)	20
AB5MA4006	Al-%5 B ₄ C (wt)	40
AB5MA6006	Al-%5 B ₄ C (wt)	60
AB5MA8006	Al-%5 B ₄ C (wt)	80
AB5MA12006	Al-%5 B ₄ C (wt)	120
AB10MA2006	Al-%10 B ₄ C (wt)	20
AB10MA4006	Al-%10 B ₄ C (wt)	40
AB10MA6006	Al-%10 B ₄ C (wt)	60
AB10MA8006	Al-%10 B ₄ C (wt)	80
AB10MA12006	Al-%10 B ₄ C (wt)	120
AB15MA2006	Al-%15 B ₄ C (wt)	20
AB15MA4006	Al-%15 B ₄ C (wt)	40
AB15MA6006	Al-%15 B ₄ C (wt)	60
AB15MA8006	Al-%15 B ₄ C (wt)	80
AB15MA12006	Al-%15 B ₄ C (wt)	120

Table 7.4c: Sample codes for Al-SiC-Y₂O₃ compositions of this investigation.

Sample Name	Powder Composition Information	Mechanical Alloying Time (min.)
AS5Y5MA2006	Al-%5 SiC (wt)-%5 Y ₂ O ₃ (wt)	20
AS5Y5MA4006	Al-%5 SiC (wt)-%5 Y ₂ O ₃ (wt)	40
AS5Y5MA6006	Al-%5 SiC (wt)-%5 Y ₂ O ₃ (wt)	60
AS5Y5MA8006	Al-%5 SiC (wt)-%5 Y ₂ O ₃ (wt)	80
AS5Y5MA12006	Al-%5 SiC (wt)-%5 Y ₂ O ₃ (wt)	120
AS10Y5MA2006	Al-%10 SiC (wt)-%5 Y ₂ O ₃ (wt)	20
AS10Y5MA4006	Al-%10 SiC (wt)-%5 Y ₂ O ₃ (wt)	40
AS10Y5MA6006	Al-%10 SiC (wt)-%5 Y ₂ O ₃ (wt)	60
AS10Y5MA8006	Al-%10 SiC (wt)-%5 Y ₂ O ₃ (wt)	80
AS10Y5MA12006	Al-%10 SiC (wt)-%5 Y ₂ O ₃ (wt)	120
AS15Y5MA2006	Al-%15 SiC (wt)-%5 Y ₂ O ₃ (wt)	20
AS15Y5MA4006	Al-%15 SiC (wt)-%5 Y ₂ O ₃ (wt)	40
AS15Y5MA6006	Al-%15 SiC (wt)-%5 Y ₂ O ₃ (wt)	60
AS15Y5MA8006	Al-%15 SiC (wt)-%5 Y ₂ O ₃ (wt)	80
AS15Y5MA12006	Al-%15 SiC (wt)-%5 Y ₂ O ₃ (wt)	120

Table 7.4d: Sample codes for Al-B₄C-Y₂O₃ compositions of this investigation.

Sample Name	Powder Composition Information	Mechanical Alloying Time (min.)
AB5Y5MA2006	Al-%5 B ₄ C (wt)-%5 Y ₂ O ₃ (wt)	20
AB5Y5MA4006	Al-%5 B ₄ C (wt)-%5 Y ₂ O ₃ (wt)	40
AB5Y5MA6006	Al-%5 B ₄ C (wt)-%5 Y ₂ O ₃ (wt)	60
AB5Y5MA8006	Al-%5 B ₄ C (wt)-%5 Y ₂ O ₃ (wt)	80
AB5Y5MA12006	Al-%5 B ₄ C (wt)-%5 Y ₂ O ₃ (wt)	120
AB10Y5MA2006	Al-%10 B ₄ C (wt)-%5 Y ₂ O ₃ (wt)	20
AB10Y5MA4006	Al-%10 B ₄ C (wt)-%5 Y ₂ O ₃ (wt)	40
AB10Y5MA6006	Al-%10 B ₄ C (wt)-%5 Y ₂ O ₃ (wt)	60
AB10Y5MA8006	Al-%10 B ₄ C (wt)-%5 Y ₂ O ₃ (wt)	80
AB10Y5MA12006	Al-%10 B ₄ C (wt)-%5 Y ₂ O ₃ (wt)	120
AB15Y5MA2006	Al-%15 B ₄ C (wt)-%5 Y ₂ O ₃ (wt)	20
AB15Y5MA4006	Al-%15 B ₄ C (wt)-%5 Y ₂ O ₃ (wt)	40
AB15Y5MA6006	Al-%15 B ₄ C (wt)-%5 Y ₂ O ₃ (wt)	60
AB15Y5MA8006	Al-%15 B ₄ C (wt)-%5 Y ₂ O ₃ (wt)	80
AB15Y5MA12006	Al-%15 B ₄ C (wt)-%5 Y ₂ O ₃ (wt)	120

The first three terms of each code indicates (A for Al; S for SiC; Y for Y₂O₃ or B for B₄C) the composition of the powder and amount of weight. MA stands for mechanical alloying and 40 or 20 indicates the duration of mechanical alloying. For example, AS10MA4006 is that this sample contains SiC wt % 10 in an Al matrix, it is MA'd for 40 minutes or AB15Y5MA12006 is that this sample contains B₄C wt % 15 and Y₂O₃ wt % 5 in Al matrix and is MA'd for 120 minutes.

XRD analysis has been carried out to verify the absence of foreign phases. Microstructures of powders were characterized after mechanical alloying procedure by XRD at a low incident angle ($\theta=3^0$) as seen in Figure 7.5a-b-c, Figure 7.6a-b-c, Figure 7.7a-b-c and Figure 7.8a-b-c.

XRD patterns of MA'd Al-SiC powders in Figure 7.5a-b-c show that with increasing mechanical alloying, peaks are broadened and heights of peaks are decreased because of the decrease in the crystalline size and increase in the lattice strain. This is believed to be because of the recrystallization triggered by severe plastic deformation due to mechanical alloying. New grains might have pumped the excess Si and C in and carbides out. As a result, new strain free grains of Al and SiC might have been formed. XRD results of mechanical alloyed Al-SiC powder system shown in Fig. 7.5a, 7.5b, 7.5c, Al_4SiC_4 and Al_4C_3 were formed. These phases were formed by the decomposition of SiC.

XRD patterns of MA'd Al- B_4C powders in Figure 7.6a-b-c again show that with increasing mechanical alloying, peaks are broadened and heights of peaks are decreased because of the decrease in the crystalline size and increase in the lattice strain. As a result, new strain free grains of Al and B_4C have been formed. XRD results of MA'd Al- B_4C powder system, AlB_2 was formed.

XRD patterns of MA'd Al- B_4C - Y_2O_3 powders in Figure 7.7a-b-c show that with increasing mechanical alloying, peaks are broadened and heights of peaks are decreased because of the decrease in the crystalline size and increase in the lattice strain. According to the XRD results of mechanical alloyed Al- B_4C - Y_2O_3 powder system, AlB_2 , Al and Y_2O_3 phases were detected. AlB_2 was formed as a result of the decomposition of B_4C .

XRD results of mechanical alloyed Al-SiC- Y_2O_3 powder system, $\beta\text{-AlFeSi}$, Al, Al_4C_3 and Al_4SiC_4 phases were detected. It is believed that both Al_4SiC_4 and Al_4C_3 were formed by the decomposition of B_4C . The formation of Al_3FeSi ($\beta\text{-AlFeSi}$) is an unexpected result. Because in all systems, Fe was not used, but in XRD analyses iron-silicon-aluminum intermetallic was detected. This presence might have occurred due to the Y_2O_3 addition. In studied Al-SiC- Y_2O_3 composite, there is Fe in the system about 50 ppm because of Y_2O_3 . In the chemical analyses of starting powders, Y_2O_3 contains 50 ppm Fe. From the literature concerning the intermetallic phases

there is a consensus among the researchers that iron is the main impurity of the Al-Si alloys. Due to its reduced solubility in α -Al, iron promotes the formation of intermetallics with Al and Si. Earlier investigations have demonstrated the detrimental effect of iron-containing intermetallics causing a significant reduction in the mechanical properties, including impact energy and fracture toughness (Ferrarini et al., 2003). Especially in casting systems, the hypoeutectic Al-Si alloys represent the most widely used alloy system for the production of aluminium cast parts. The use of very high cooling rates to produce finely distributed iron phases, or additions of trace elements to alter the morphology of the β -needles can counteract the negative effect of iron (Dahle et al., 2000). Considering the volumetric fraction, morphology and size of enriched iron phases in aluminium, these phases may appear as Chinese script or needles (platelets). Therefore, rapid or near rapid solidification processes are possible routes to influence the formation of intermetallics phases increasing the solubility of the iron in the aluminium matrix and providing metastable conditions to the formation of less deleterious phases. Among the Fe-containing intermetallics in Al-Si alloys, the β -AlFeSi (Al_5FeSi) phase is the most undesirable due to its needle form that acts as a stress concentrator which reduces strongly the ductility of the alloys (Fatahalla et al., 1999).

In addition to high Fe amount in Y_2O_3 , milling medium might have effected the system. Stainless steel high-energy balls were used for this investigation and the balls might have been grinded by SiC- Y_2O_3 powders during the mechanical alloying time. This is a result of iron contamination and phase transformation during high-energy ball milling from high-purity elemental powder. With respect to the high-energy ball milling process, the repetitive cold-welding and fracture mechanisms between the powder particles of different compositions lead to the chemical and microstructural homogenization. In addition, metastable structures such as extended solid solutions and amorphous phases can be formed. In some cases, the iron contamination can occur from the milling medium, depending on the composition and milling parameters (Fernandes et al., 2005).

Thus, the presence of a small amount of Fe to form β -AlFeSi (Al_5FeSi) needles in the MA'd Al-SiC- Y_2O_3 powders is most likely due to iron contamination from the milling media.

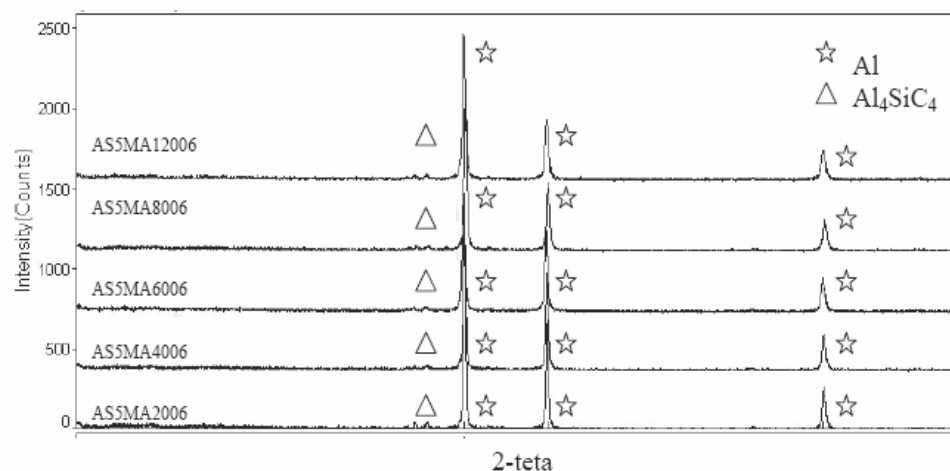


Figure 7.5a: XRD patterns of MA'd Al-5 wt % SiC powders starting from a MA time of 20 min. (bottom) to 120 min. (top).

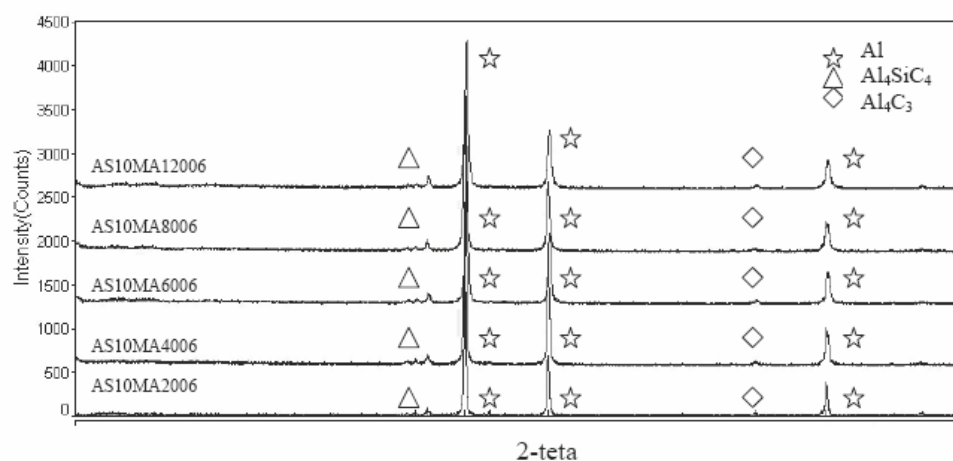


Figure 7.5b: XRD patterns of MA'd Al-10 wt % SiC powders starting from a MA time of 20 min. (bottom) to 120 min. (top).

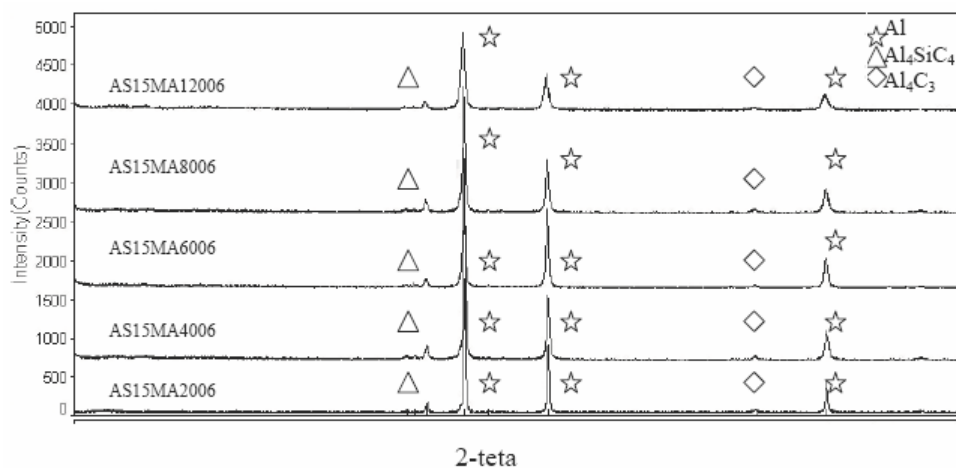


Figure 7.5c: XRD patterns of MA'd Al-15 wt % SiC powders starting from a MA time of 20 min. (bottom) to 120 min. (top).

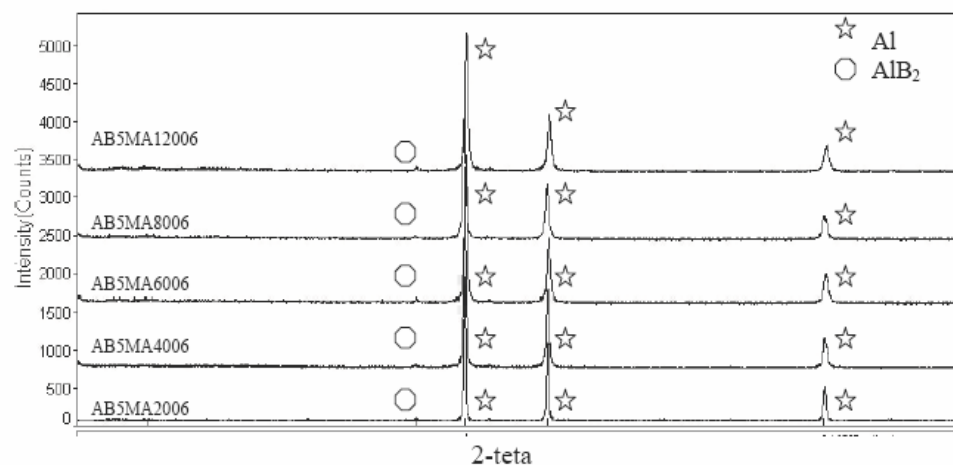


Figure 7.6a: XRD patterns of MA'd Al-5 wt % B₄C powders starting from a MA time of 20 min. (bottom) to 120 min. (top).

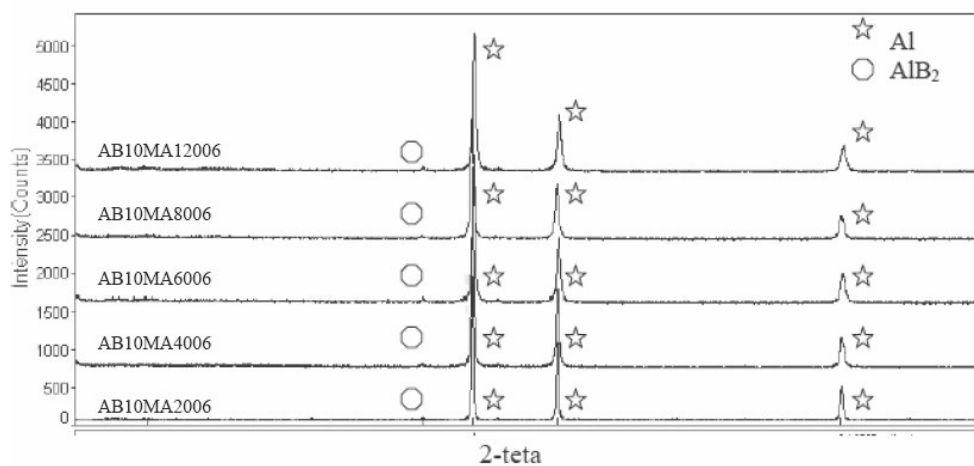


Figure 7.6b: XRD patterns of MA'd Al-10 wt % B₄C powders starting from a MA time of 20 min. (bottom) to 120 min. (top).

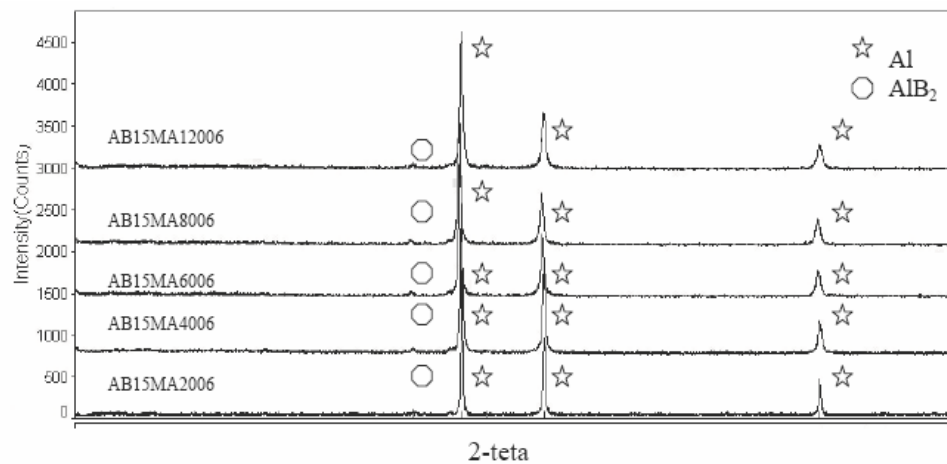


Figure 7.6c: XRD patterns of MA'd Al-15 wt % B₄C powders starting from a MA time of 20 min. (bottom) to 120 min. (top).

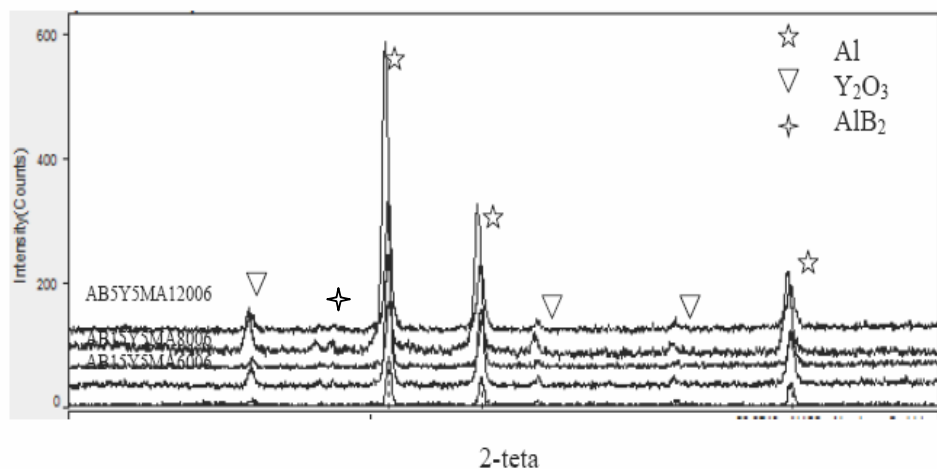


Figure 7.7a: XRD patterns of MA'd Al-5 wt % B₄C-5 wt % Y₂O₃ powders starting from a MA time of 20 min. (bottom) to 120 min. (top).

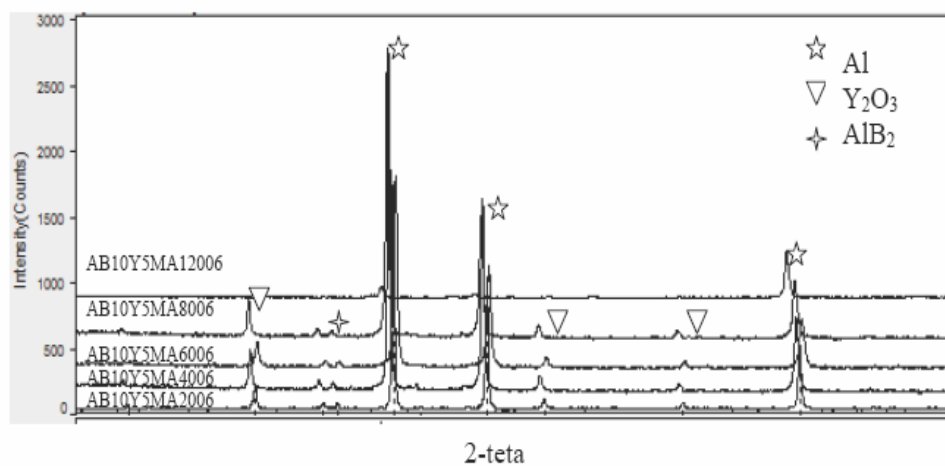


Figure 7.7b: XRD patterns of MA'd Al-10 wt % B₄C-5 wt % Y₂O₃ powders starting from a MA time of 20 min. (bottom) to 120 min. (top).

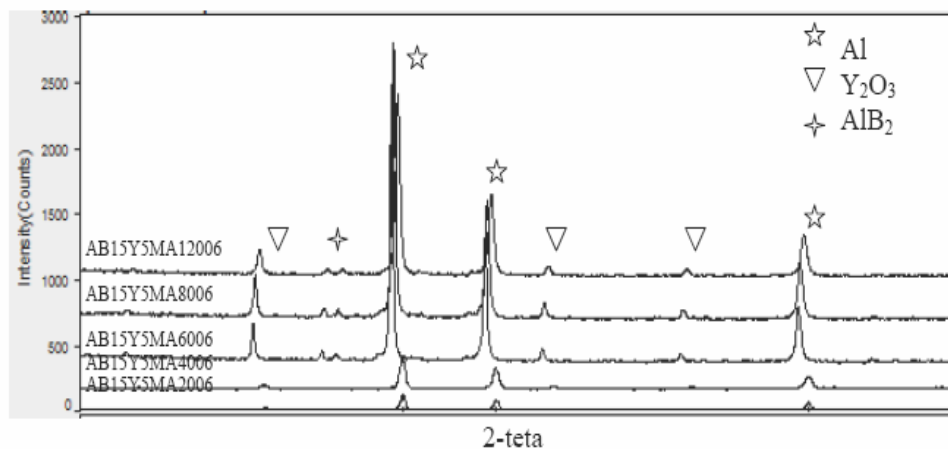


Figure 7.7c: XRD patterns of MA'd Al-15 wt % B₄C-5 wt % Y₂O₃ powders starting from a MA time of 20 min. (bottom) to 120 min. (top).

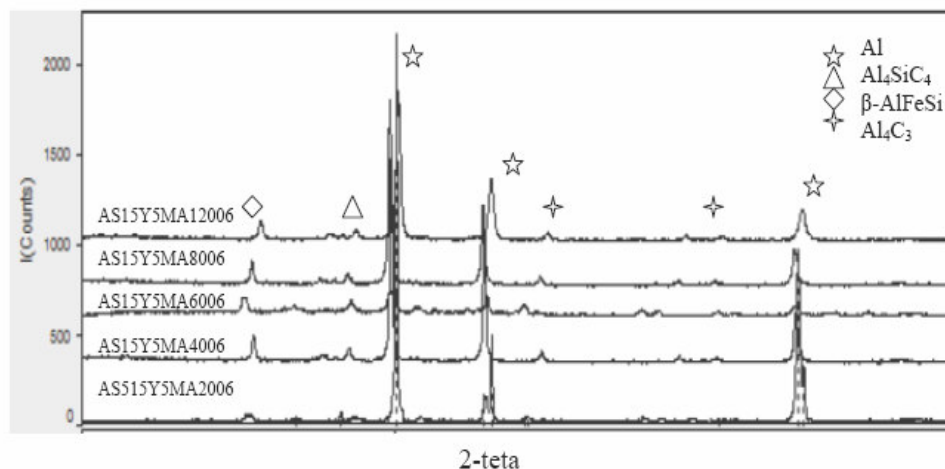


Figure 7.8a: XRD patterns of MA'd Al-5 wt % SiC-5 wt % Y_2O_3 powders starting from a MA time of 20 min. (bottom) to 120 min. (top).

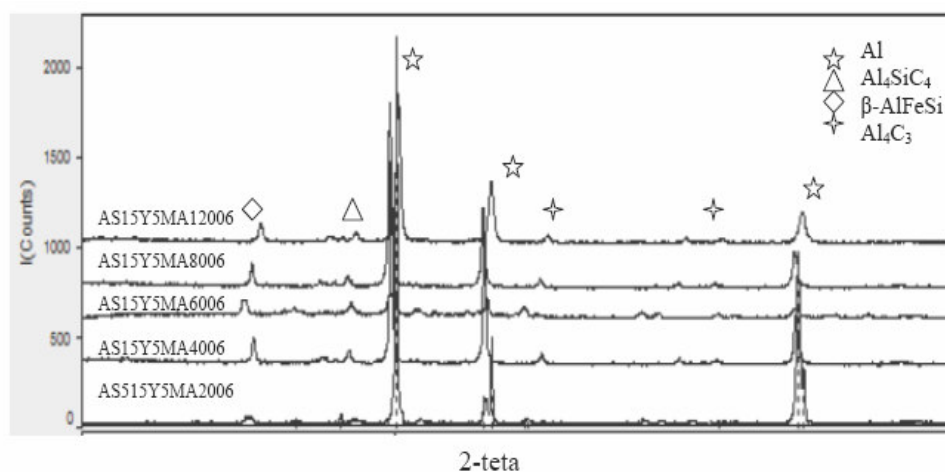


Figure 7.8b: XRD patterns of MA'd Al-10 wt % SiC-5 wt % Y_2O_3 powders starting from a MA time of 20 min. (bottom) to 120 min. (top).

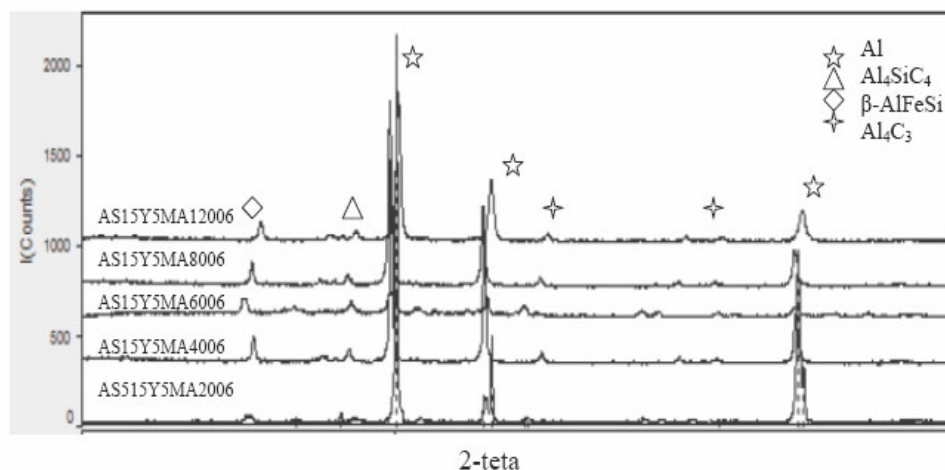


Figure 7.8c: XRD patterns of MA'd Al-15 wt % SiC-5 wt % Y_2O_3 powders starting from a MA time of 20 min. (bottom) to 120 min. (top).

Mechanically alloyed powders used in this investigation did not dissolve in water. For this reason, particle size and zetasize measurements were carried out in wet conditions using distilled water (Figure 7.9). To determine optimum liquid media and optimum particle distribution, optimum pH value should have been found from zeta potential experiments.



Figure 7.9: (a) Powders in particle size analysis instrument, (b) Al-based composite powders in distilled water.

From the experiments which can be seen in Figure 7.10 and Figure 7.11, which were made for observing mobility of the samples in different liquids, the mobility distributions in water, water-alcohol solution and different pH values such as 1.03 and 3.09 were investigated. Using water media which had a pH of 7.4, the particles were not dispersed in liquid and the experiment took long time. The mobility of the particles were low and according to these measurements which were performed with 10 runs, the average value of the zeta potential was found as 1.8 mV. This means that, it is impossible to measure exact particle size of powders using a media having a pH value of 7.4 and a zeta potential of 1.8 mV.

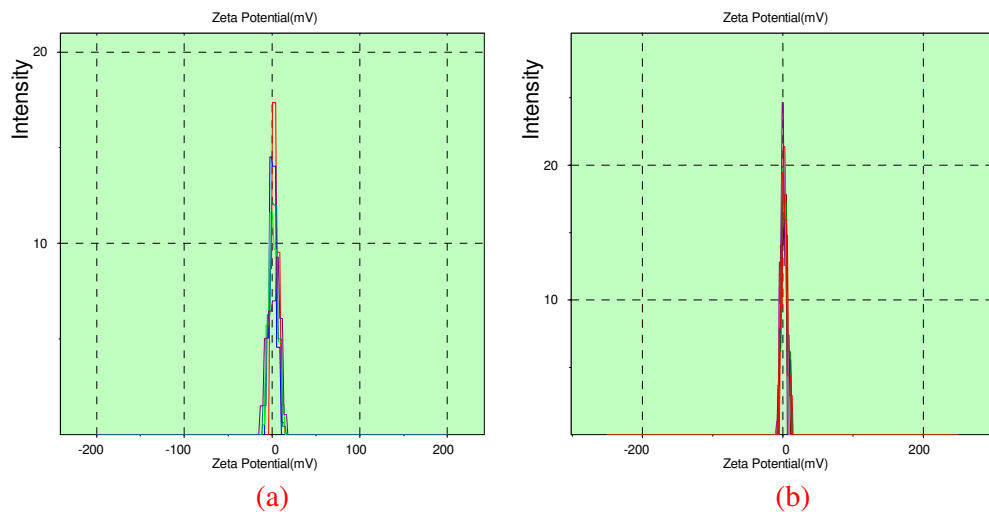


Figure 7.10: (a) The dispersion and mobility behaviour of Al composite in water (pH:7.4), (b) The dispersion and mobility behaviour of Al composite in water and alcohol solution (pH:7.3).

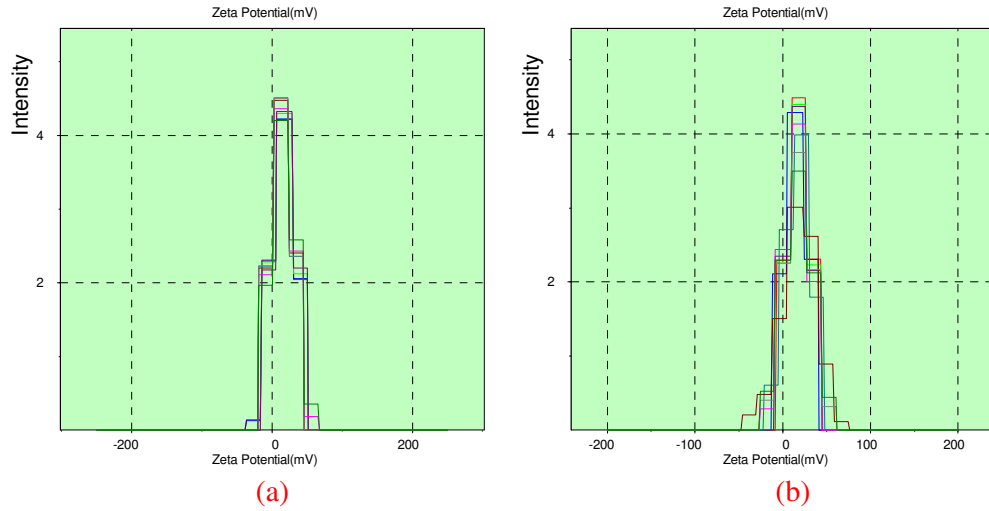


Figure 7.11: (a) The dispersion and mobility behaviour of Al composite in pH:1.03, (b) The dispersion and mobility behaviour of Al composite in pH:3.09.

In water-alcohol media which has a pH of 7.3, the particles were not dispersed in the media completely but the experiment time was not long as before. The average value of the zeta potential was found as 1.6. For low pH values such as 1.03, the experiments were better than higher pH values. The mobility of the particles were relatively high but, this pH value may have a negative effect on powders. Because of the possibility that powders could resolve in very high and very low pH medias, pH value was selected in the range between 3 and 8. The average value of the zeta potential was found as 1.22. So the pH of 3.09 was used for experiments. The particles were dispersed in the media and the experiment took little time compared to other experiments. The mobility of the particles were high enough for analyzing and according to these measurements, the average value of the zeta potential was found as 16.5 as seen in Figure 7.12. This means that, this pH value is optimum for particle size analyzing.

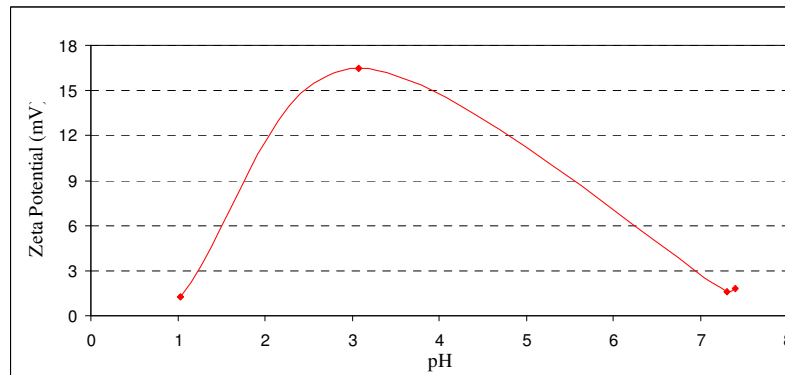


Figure 7.12: Zeta potential (mV)-pH diagram.

Particle size analysis experiments were performed in liquid media. For preventing agglomeration, powders were dispersed and deagglomerated in an ultrasonic bath for 15 min. before analyzing the particle sizes. All the experiments were done in liquid media which has 3.08 pH.

In Figures 7.13a and 7.13b, results of particle size analyses are shown. One of the most important problems associated with the composite materials production is the presence of reinforcement agglomerates. The possibility of obtaining a composite material setting from a composite powder, where reinforcement particles are fine and homogeneously distributed by means of mechanical alloying process, eliminates the possibility of the formation of these segregations (Friend, 1987).

Initial Al powders have an average diameter of 10 μm according to SEM and particle size analysis; however the result in Figure 7.14 is around 22 μm despite mechanical alloying because of the agglomeration of powders. High amount of refining of particles occurred up to 60 minutes and after that the grains were refined, as also verified by the XRD scans shown in Figures 7.5, 7.6, 7.7 and 7.8.

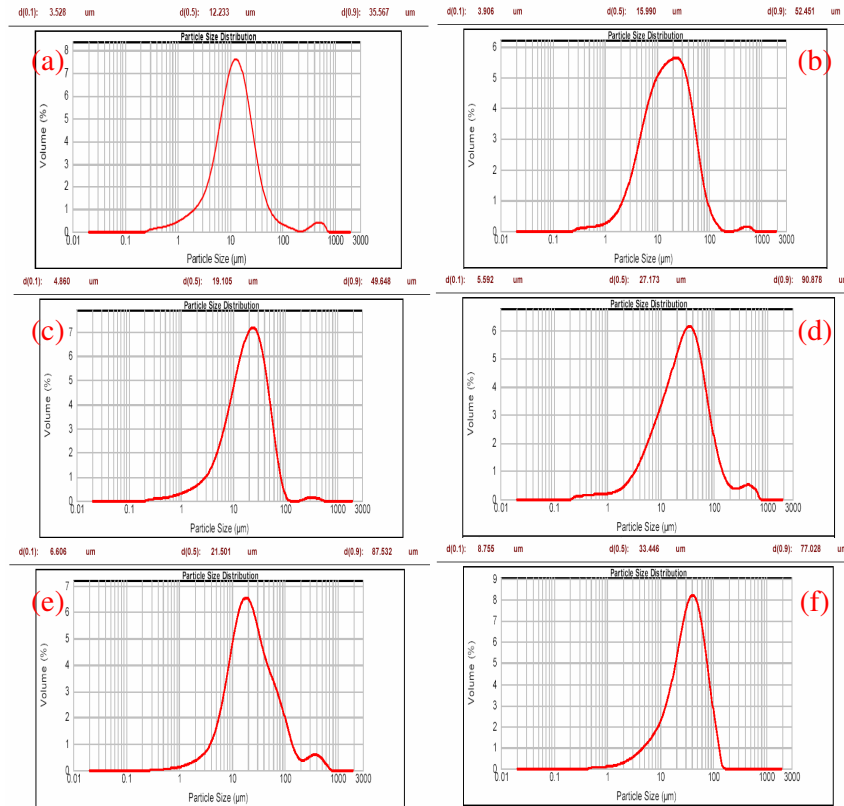


Figure 7.13a: Particle size distributions of (a)AS5MA2006 (b)AS5MA12006 (c)AS10MA2006 (d)AS10MA12006 (e)AS15MA2006 (f)AS15MA12006.

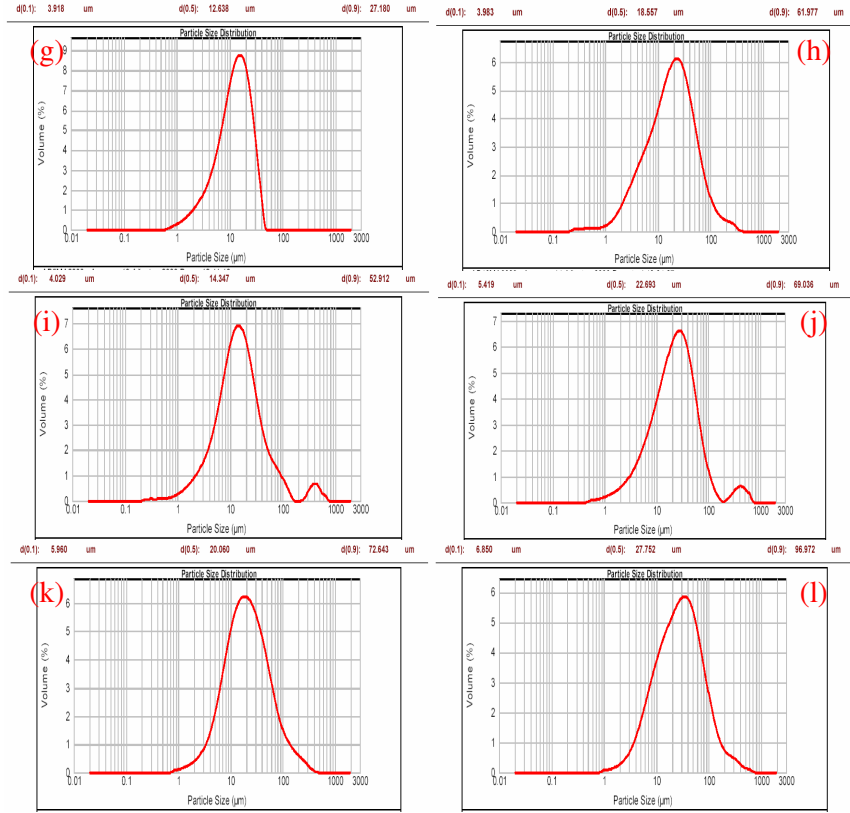


Figure 7.13b: Particle size distributions of (g)AB5MA2006 (h)AB5MA12006 (i)AB10MA2006 (j)AB10MA12006 (k)AB15MA2006 (l)AB15MA12006.

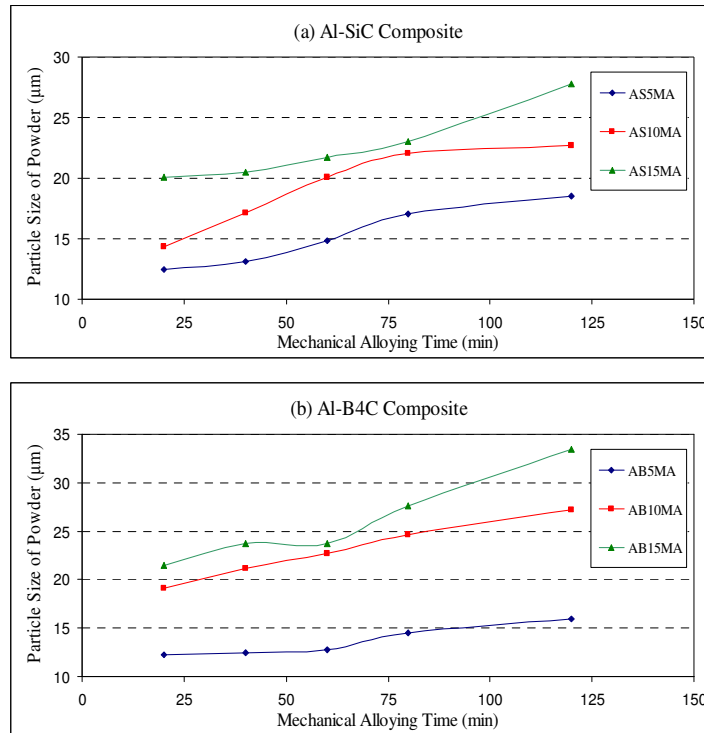


Figure 7.14: Average powder particle sizes of the (a) Al-SiC composite, (b) Al-B₄C composite as a function of MA time.

In Figure 7.15, results of particle size analyses are shown. Initial Al powders have an average diameter of 10 μm according to SEM and particle size analysis results, but that shown in Figures 7.15 and 7.16; the result in Figures 7.16 is around 25 μm despite mechanical alloying because of the agglomeration of powders. High amount of refining of particles occurred up to 60 minutes and after that the grains were refined, as also verified by the XRD scans shown in Figure 7.5, 7.6, 7.7 and 7.8.

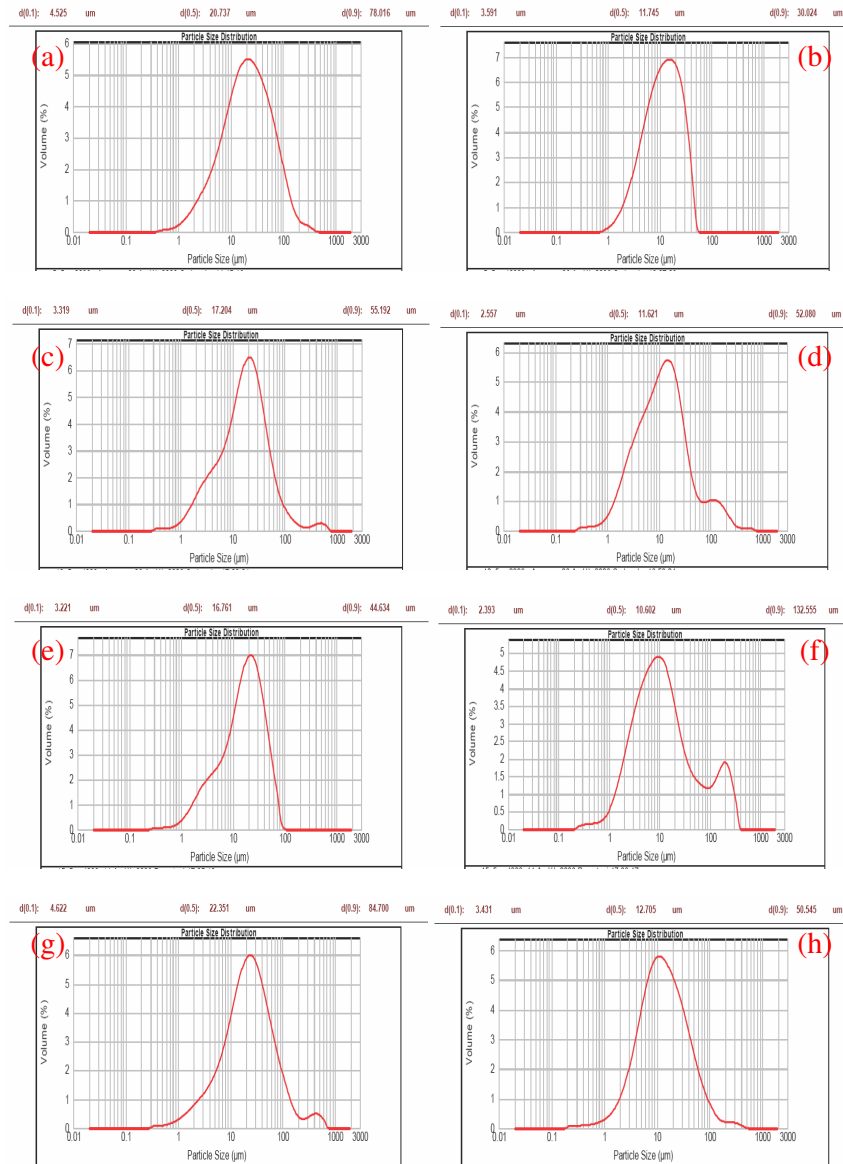


Figure 7.15: Particle size distributions of (a)AS5Y5MA2006 (b)AS5Y5MA12006 (c)AS10Y5MA2006 (d)AS10Y5MA12006 (e)AS15Y5MA2006 (f)AS15Y5MA12006, (g)AB5Y5MA2006, (h)AB5Y5MA12006.

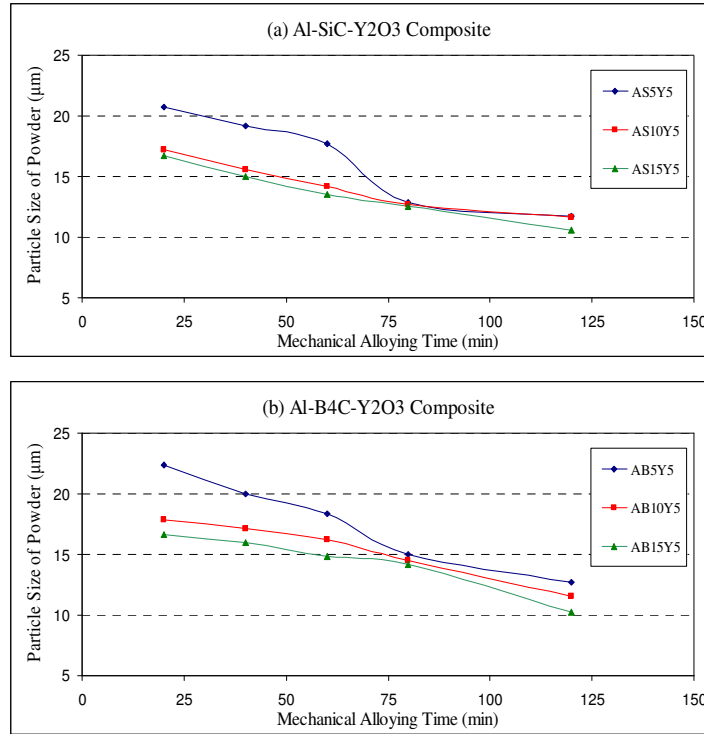


Figure 7.16: Average powder particle sizes of the (a) Al-SiC-Y₂O₃ composite, (b) Al-B₄C-Y₂O₃ composite as a function of MA time.

One of the most important problems associated with the composite materials production is the presence of reinforcement agglomerates. The possibility of obtaining a composite material setting from a composite powder, where reinforcement particles are fine and homogeneously distributed by means of mechanical alloying process, eliminates the possibility of these segregations formation.

When short milling times are employed the cross-section of the powders reveals that only a small fraction of carbide particles has been introduced into the alloy and their size and distribution is not homogeneous.

SEM images of (Figure 7.17a and Figure 7.17b) 20 min., 40 min., 60 min., 80 min. and 120 min. mechanically alloyed powders show that the particle sizes of powders are decreasing with increasing mechanical alloying. When short milling times are employed the cross-section of the powders reveals that only a small fraction of carbide particles has been introduced into the alloy and their size and distribution is not homogeneous.

When longer milling times are used, the morphology of particles changes, there is a higher reinforcement incorporation and the thickness of layers is reduced milling: a fully well distribution of both the alloying elements and the carbides is now evident. Also a good bonding between matrix and reinforcement without voids or discontinuities was observed and no defects in the reinforcement were found, possibly eliminated by the continuous colliding.

During milling, Al-SiC and Al-B₄C powders were mixed and fractured. As seen from the images in Figure 7.17, the round and nearly equiaxed particles are Al particles, sharp-edged particles at the left-top of the image are SiC and Al₄C₃ particles. It can be clearly seen that in the initial stages of milling, the ductile metal (here Al) powder particles get flattened by the ball-powder-ball collisions, while the brittle SiC particles get fragmented as expected. With continuous milling, these flattened structures get fragmented and finally composite powder particles are formed with compositions similar to starting powder blend composition. As a result, powders were successfully and completely mechanical alloyed after 120 min.

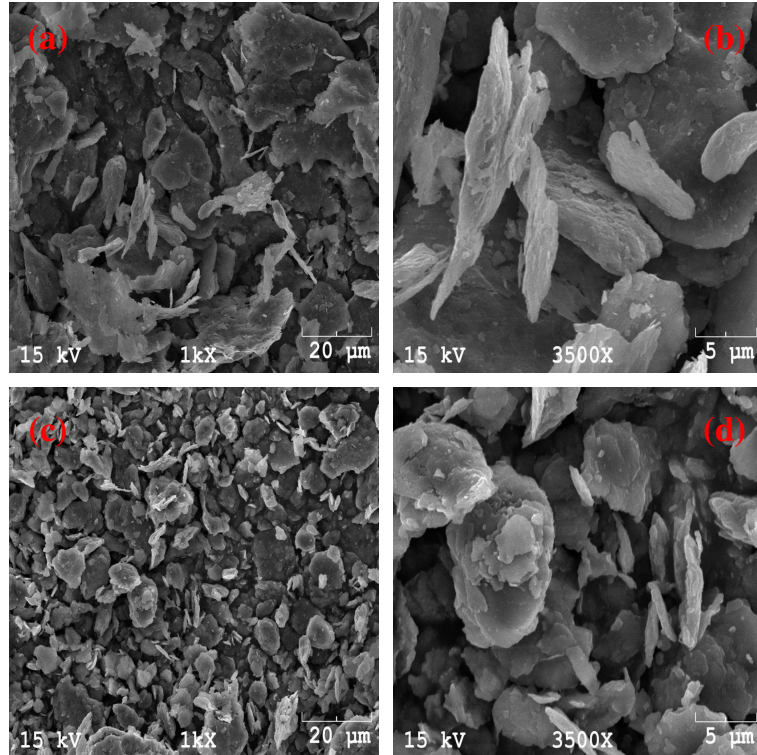


Figure 7.17a: SEM micrographs of (a)AS5MA2006 (x1000), (b)AS5MA2006 (x3500), (c)AS5MA12006 (x1000), (d)AS5MA12006 (x3500)

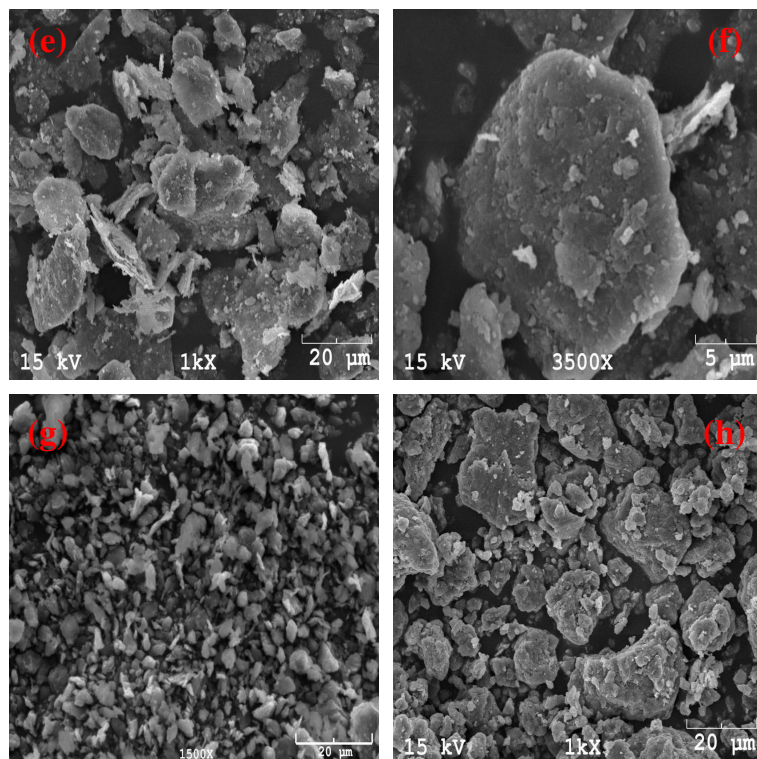


Figure 7.17b: SEM micrographs of (e)AS15MA2006 (x1000), (f)AS15MA2006 (x3500), (g)AS15MA8006, (h)AS15MA12006.

According to EDS results in Figure 7.18, the round and nearly equiaxed grey particles are Al particles, sharp-edged dull white particles at the left-top of the image are SiC and grey particles are Al_4C_3 .

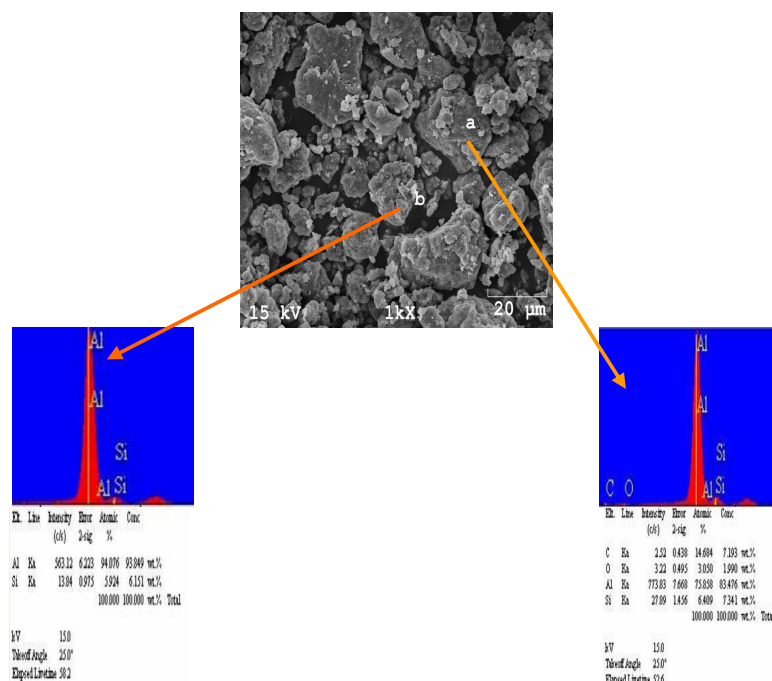


Figure 7.18: EDS analysis of AS15MA12006.

As seen from the images in Figure 7.19, flattening of powder particles took place during the initial stages of mechanical alloying. This was followed by particle welding resulting in an increase of number of lamellar particles. Afterwards, the particles became more equiaxed. Finally, the steady stage was reached.

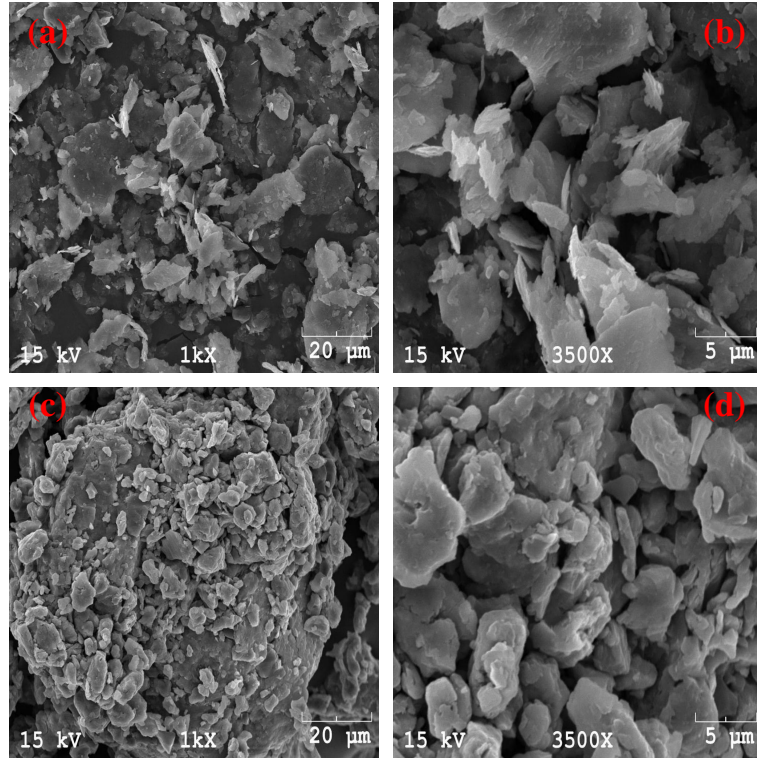


Figure 7.19: SEM micrographs of (a)AB5MA2006 (x1000), (b)AB5MA2006 (x3500), (c)AB5MA12006 (x1000), (d)AB5MA12006 (x3500).

According to EDS results in Figure 7.20, the round and nearly equiaxed grey particles are Al particles, sharp-edged black particles at the left top of the image are B_4C and AlB_2 particles.

SEM images of (Figure 7.21) 20 min., 40 min., 60 min., 80 min. and 120 min. the mechanically alloyed Al-SiC- Y_2O_3 and Al- B_4C - Y_2O_3 powders show that the particle sizes of the powders decrease with increasing mechanical alloying. As seen from the images, the round and nearly equiaxed particles are Al and Y_2O_3 particles, sharp-edged particles at the left-top of the images are SiC and β -AlFeSi intermetallic particles. It can be clearly seen that in the initial stages of milling the ductile metal (here Al) powder particles get flattened by the ball-powder-ball collisions, while the brittle SiC particles get fragmented as expected. With continuous milling, these

flattened structures get fragmented and finally composite powder particles are formed with compositions similar to starting powder blend composition.

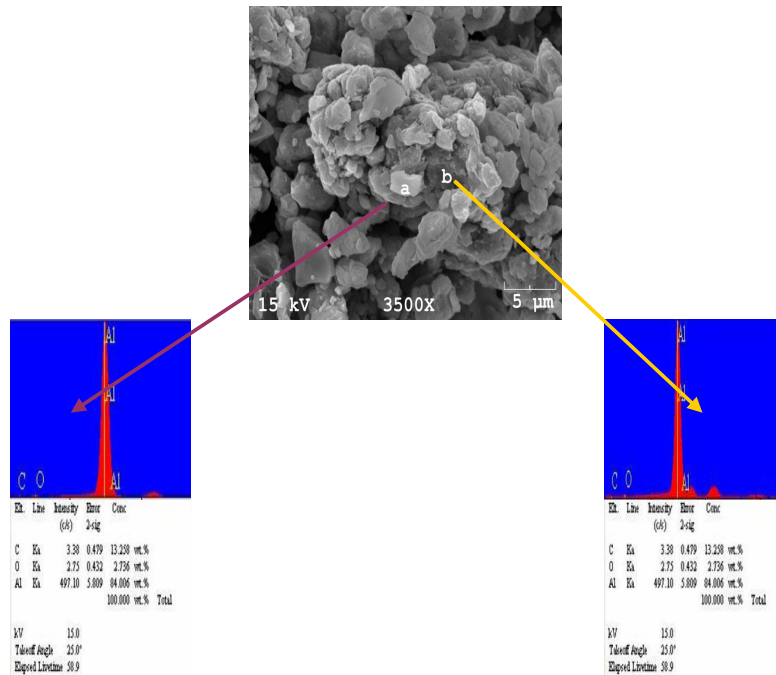


Figure 7.20: EDS analysis of AB15MA12006.

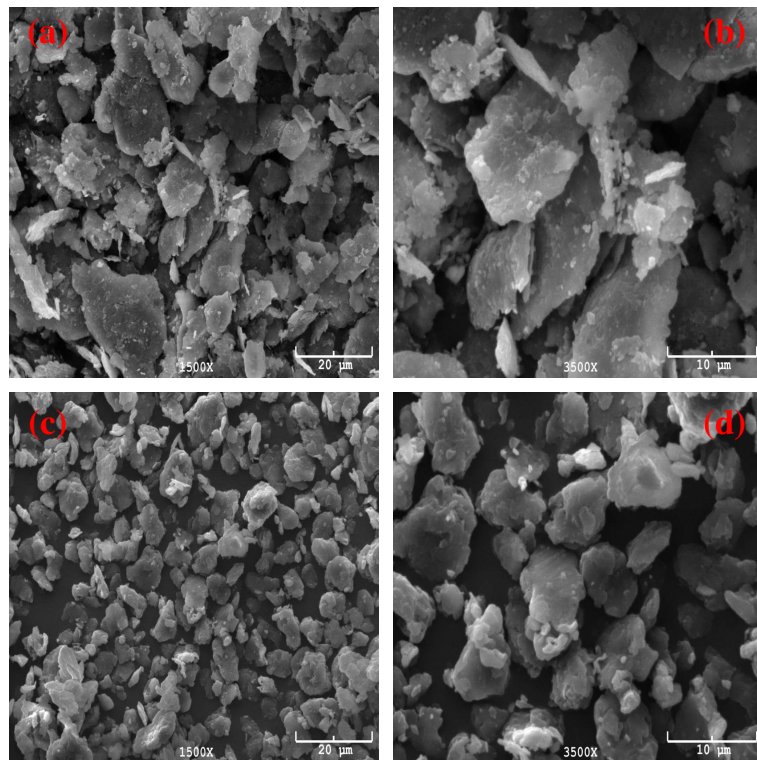


Figure 7.21: SEM micrographs of (a)AS5Y5MA2006 (x1500), (b)AS5Y5MA2006 (x3500), (c)AS5Y5MA12006 (x1500), (d)AS5Y5MA12006 (x3500).

As seen in Figure 7.22, the round and nearly equiaxed particles are Al and Y_2O_3 particles, sharp-edged particles at the left-top of the image are B_4C particles. Flattening of powder particles took place during the initial stages of mechanical alloying.

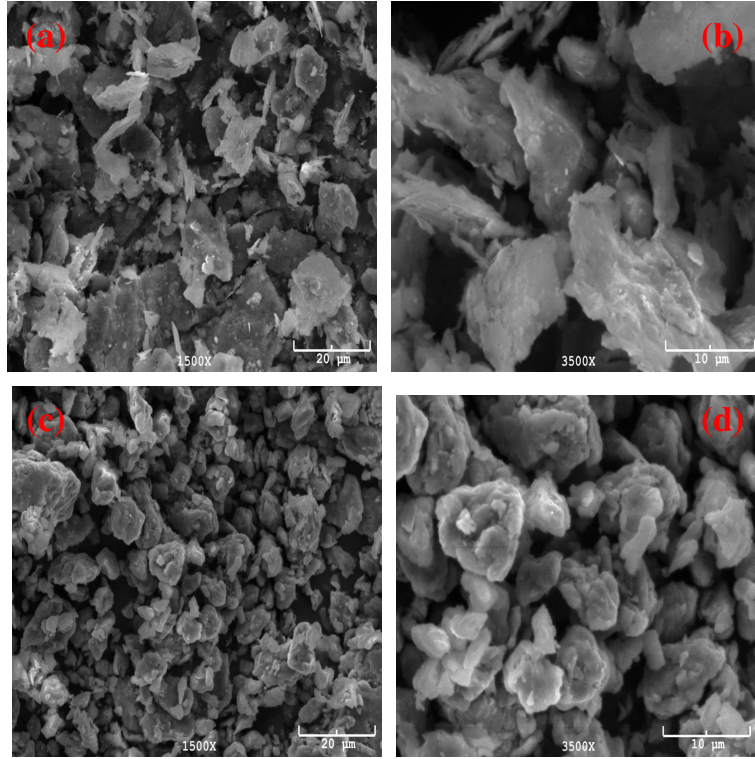


Figure 7.22: SEM micrographs of (a)AB5Y5MA2006 (x1000), (b)AB5Y5MA2006 (x3500), (c)AB5Y5MA12006 (x1000), (d)AB5Y5MA12006 (x3500).

This was followed by particle welding resulting in an increase of number of lamellar particles. With continuing milling, these flattened structures get fragmented and finally composite powder particles are formed with compositions similar to starting powder blend composition. Afterwards the particles became more equiaxed. Finally steady stage was reached.

According to EDS results in Figure 7.23a-b, the round and nearly equiaxed black particles are Al particles, sharp-edged grey particles at the left-top of the image are β -AlFeSi intermetallic particles.

According to EDS results in Figure 7.24, the round and nearly equiaxed black particles are Al, sharp-edged grey particles at the left-top of the image are B_4C and AlB_2 particles.

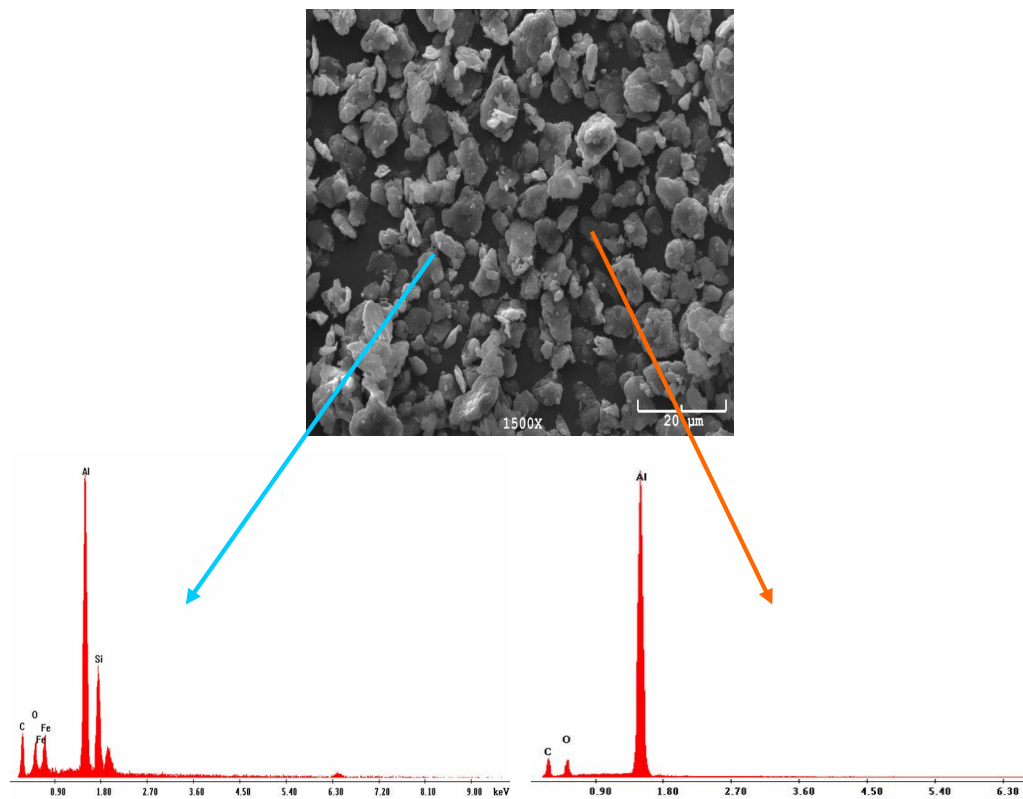


Figure 7.23a: EDS analysis of AS5Y5MA12006.

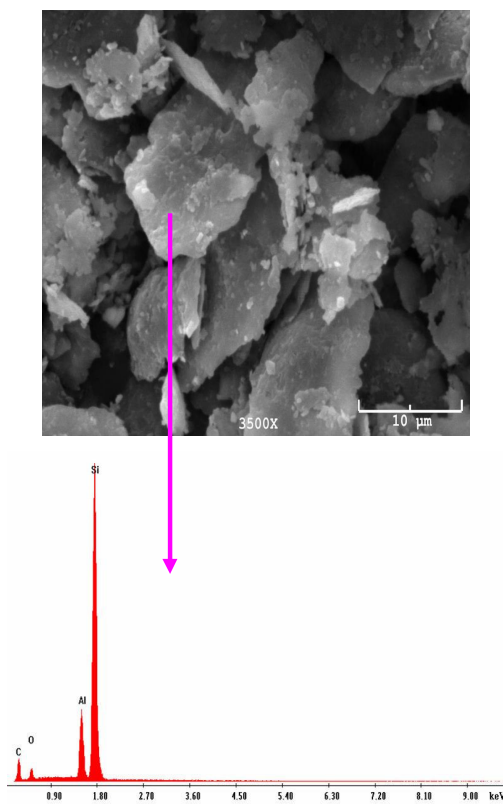


Figure 7.23b: EDS analysis of AS5Y5MA2006.

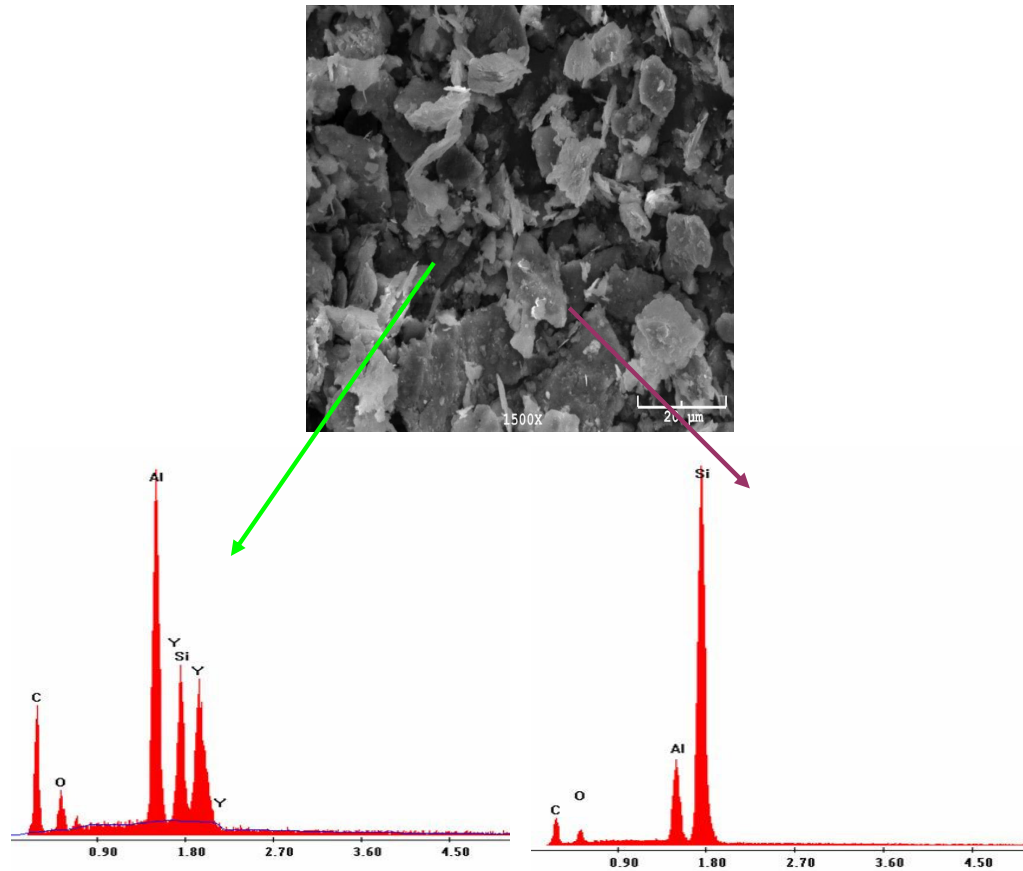


Figure 7.24: EDS analysis of AB5Y5MA2006.

Figures 7.25, 7.26, 7.27 and 7.28 are representative optical micrographs taken from MA'd Al-SiC, Al-B₄C, Al-SiC-Y₂O₃ and Al-B₄C-Y₂O₃ powders, respectively.

From the optical microscope images in Figures 7.25, 7.26 and 7.28, it can be said that Al-SiC and Al-B₄C composites are good examples for ductile-brittle systems. Dull white areas in Figure 7.25 and bright yellow areas in Figure 7.26 consist of SiC and black areas in Figure 7.25 and brown areas in Figure 7.26 consist of Al and Al carbide phases. In the initial stages of milling the ductile metal (here Al) powder particles get flattened by the ball-powder-ball collisions, while the brittle SiC/B₄C particles get fragmented as expected. With continued milling, these flattened structures get fragmented and finally composite powder particles are formed with compositions similar to starting powder blend composition.

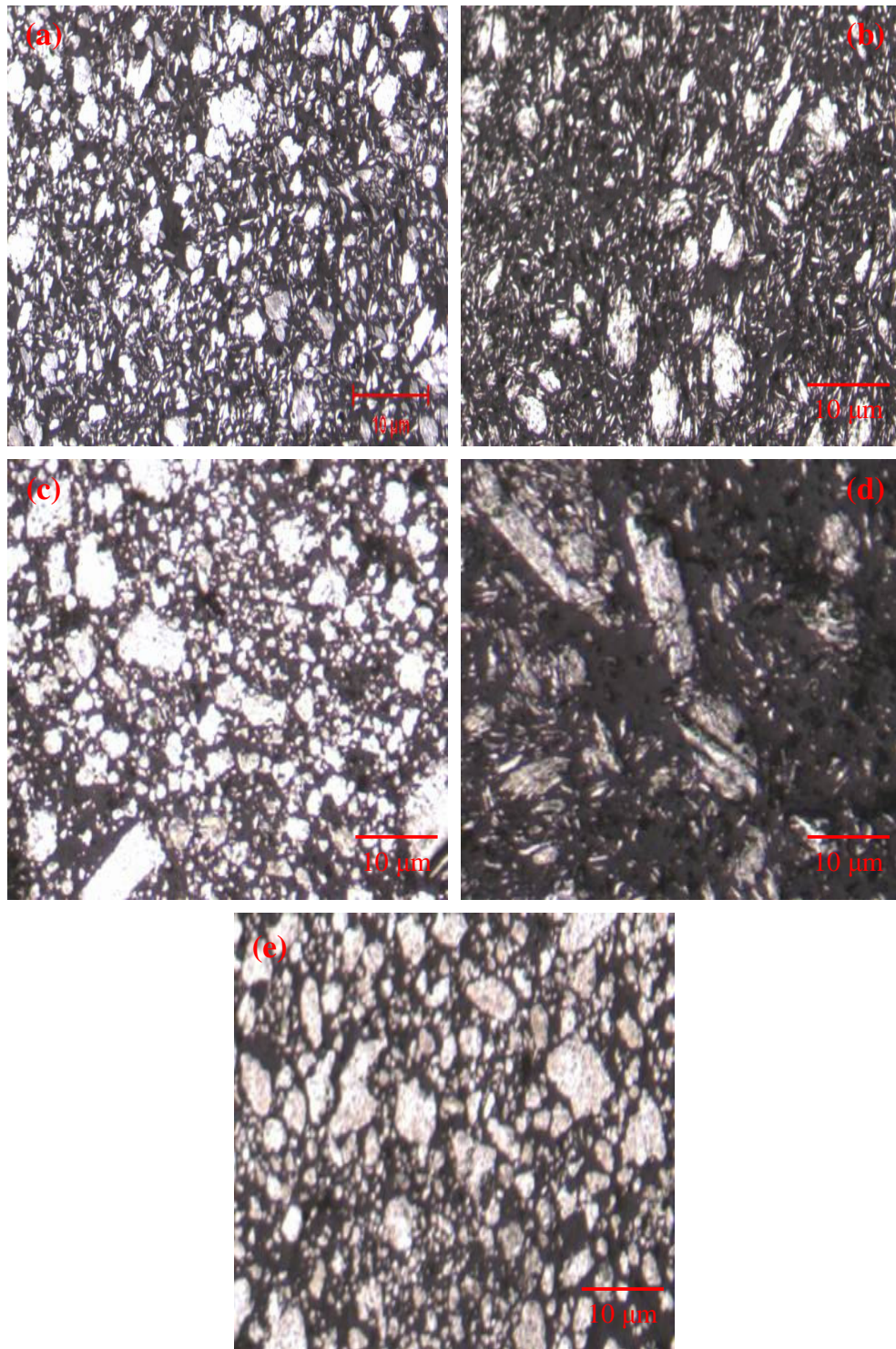


Figure 7.25: Optical microscope images of (a)AS5MA8006, (b)AS5MA2006, (c)AS10MA12006, (d)AS10MA2006, (e)AS15MA12006.

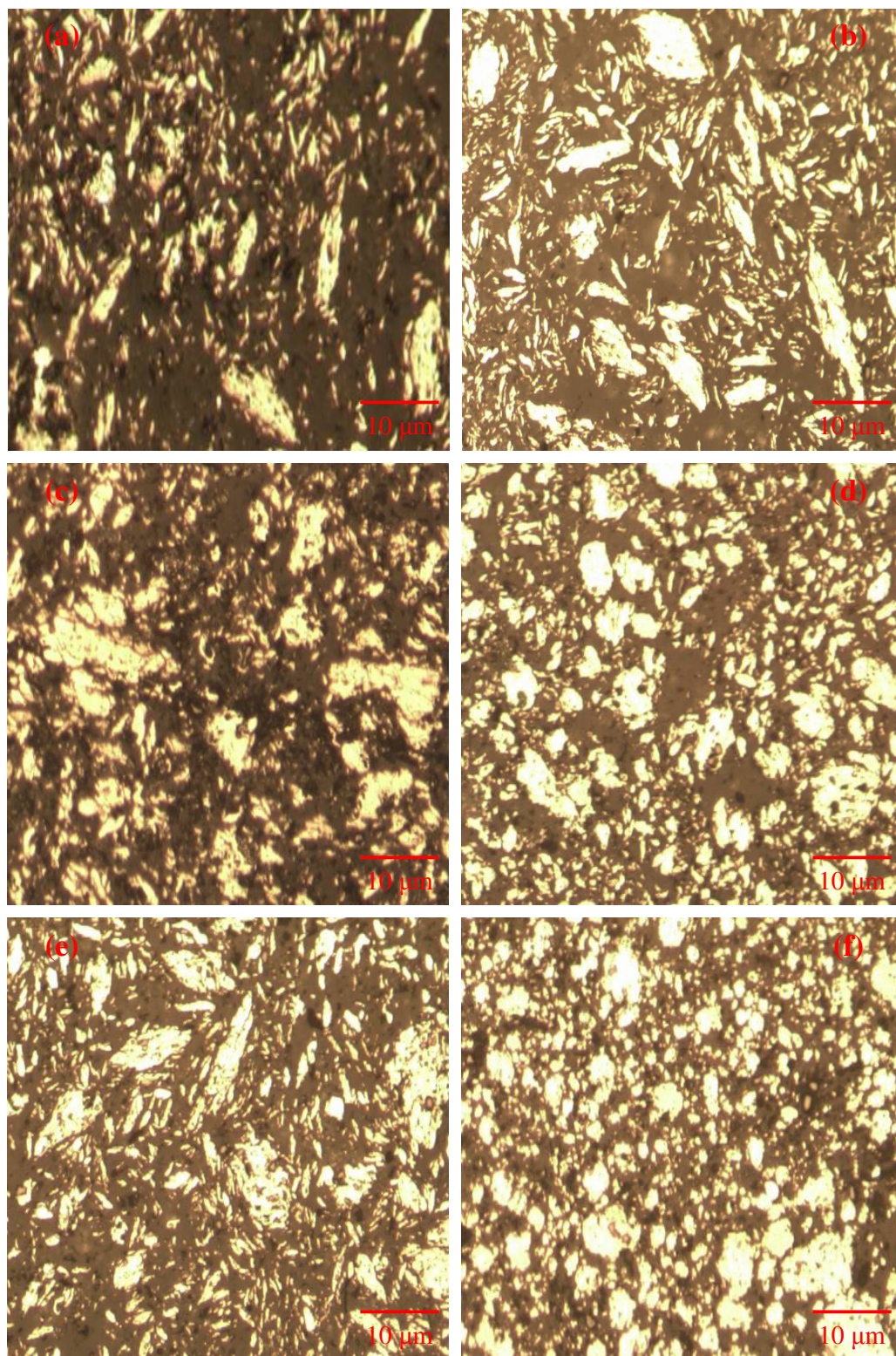


Figure 7.26: Optical microscope images of (a)AB5MA2006, (b)AB5MA4006, (c)AB10MA2006, (d)AB10MA6006, (e)AB15MA2006, (f)AB15MA12006.

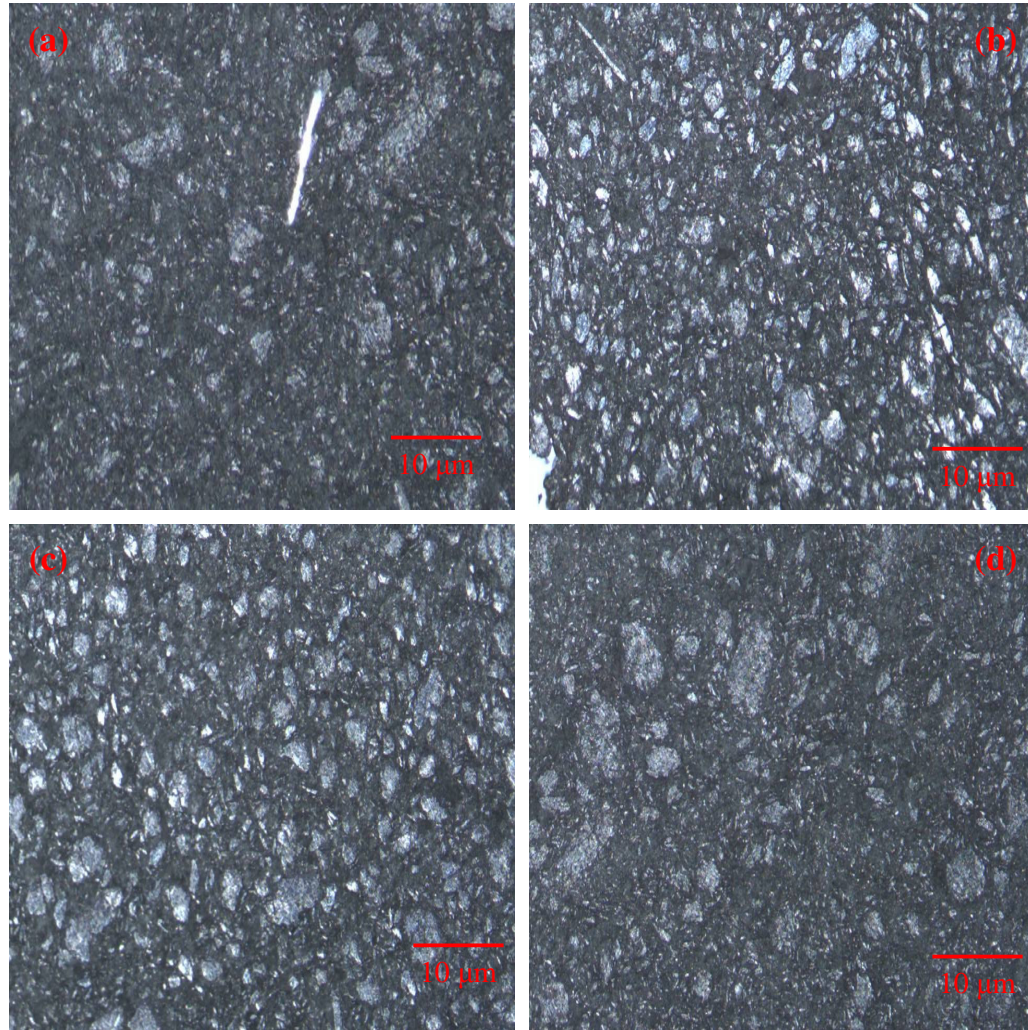


Figure 7.27: Optical microscope images of (a)AS5Y5MA6006, (b)AS10Y5MA2006, (c)AS15Y5MA12006, (d)AS15Y5MA6006.

From the optical microscope images in Figure 7.27; in the initial stages of milling, there are needle-like structures in the microstructure. Dull grey areas in Figure 7.27 consist of SiC, dark grey areas in Figure 7.27 consist of Al and white needle like areas consist of β -AlFeSi phases. As known from the XRD results, the β -AlFeSi intermetallic phase was expected to be seen in optical microscope images. With respect to the high-energy ball milling process, the repetitive cold-welding and fracture mechanisms between the powder particles of different compositions lead to the chemical and microstructural homogenization. The volumetric fraction, morphology and size of enriched iron phases in aluminium, these phases may appear as Chinese script or needles (platelets). The size of these phases became smaller as milling time increased in Figures 7.27c and 7.27d. A microstructure of Al-SiC-Y₂O₃ system composed of plate-like silicon particles and coarse intermetallics embedded

in an Al matrix. With continuing milling, flattened structures of Al-SiC get fragmented and finally composite powder particles are formed with compositions similar to starting powder blend composition.

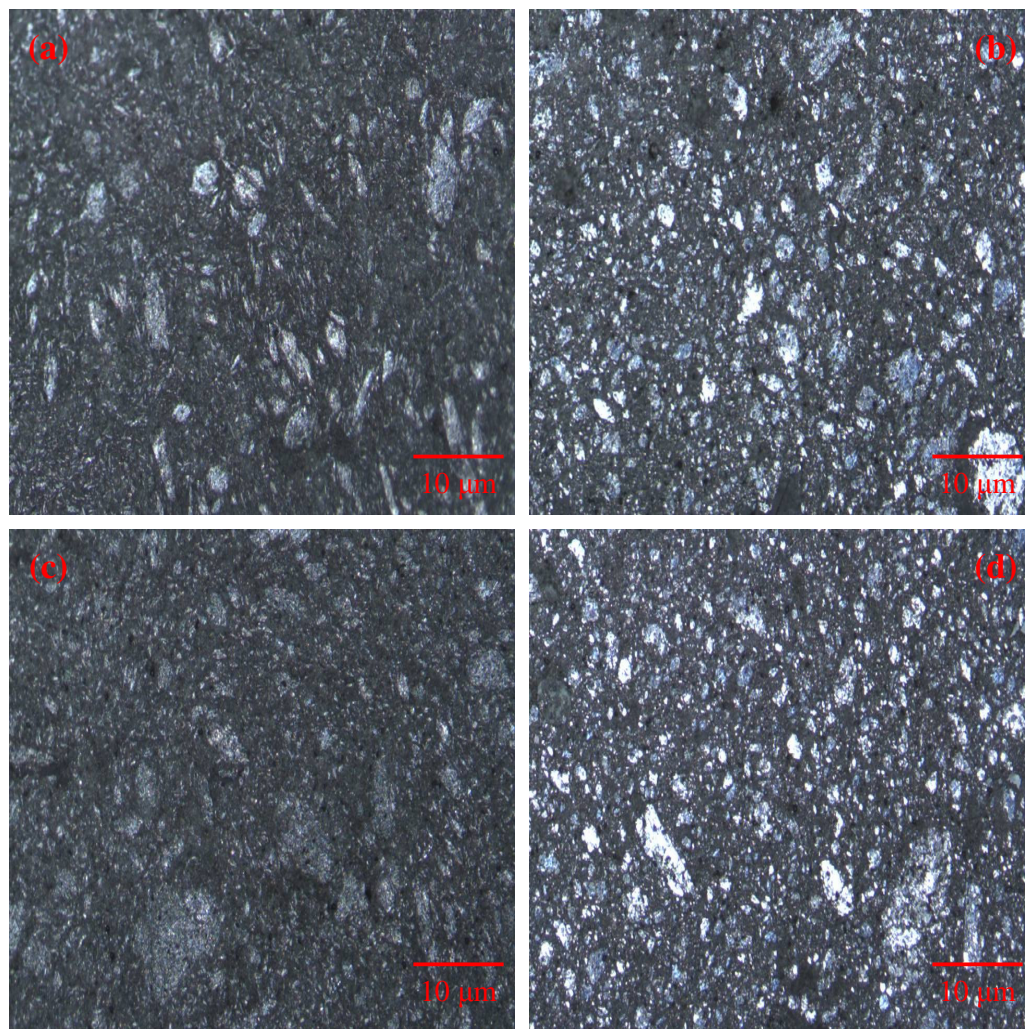


Figure 7.28: Optical microscope images of (a)AB5Y5MA2006, (b)AB10Y5MA6006, (c)AB15Y5MA2006, (d)AB15Y5MA6006.

The surface areas of the powders which were obtained from a BET surface area analysis are shown in Figure 7.29a-b and Figure 7.30a-b. Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or, more rarely, a liquid (adsorbent), forming a molecular or atomic film (Quantachrome™ Autosorb User Manual, 2006). It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. The term sorption encompasses both processes, while desorption is the reverse process. Adsorption, ion exchange and chromatography are sorption processes in which certain adsorptives are selectively transferred from the fluid phase to the surface of insoluble, rigid particles suspended

in a vessel or packed in a column. Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements (be they ionic, covalent or metallic) of the constituent atoms of the material are filled. But atoms on the (clean) surface experience a bond deficiency, because they are not wholly surrounded by other atoms. Thus it is energetically favourable for them to bond with whatever happens to be available. The exact nature of the bonding depends on the details of the species involved, but the adsorbed material is generally classified as exhibiting physisorption or chemisorption. In all analyses in Figure 7.29 and 7.30, the physisorption analyses were done. The studied composite powders formed multilayers, that is, some are adsorbed on already adsorbed molecules. The biggest step in BET isotherm is to consider that the successive equilibria for all the layers except for the first are equal to the liquefaction of the adsorbate. This consideration is done in next graphics.

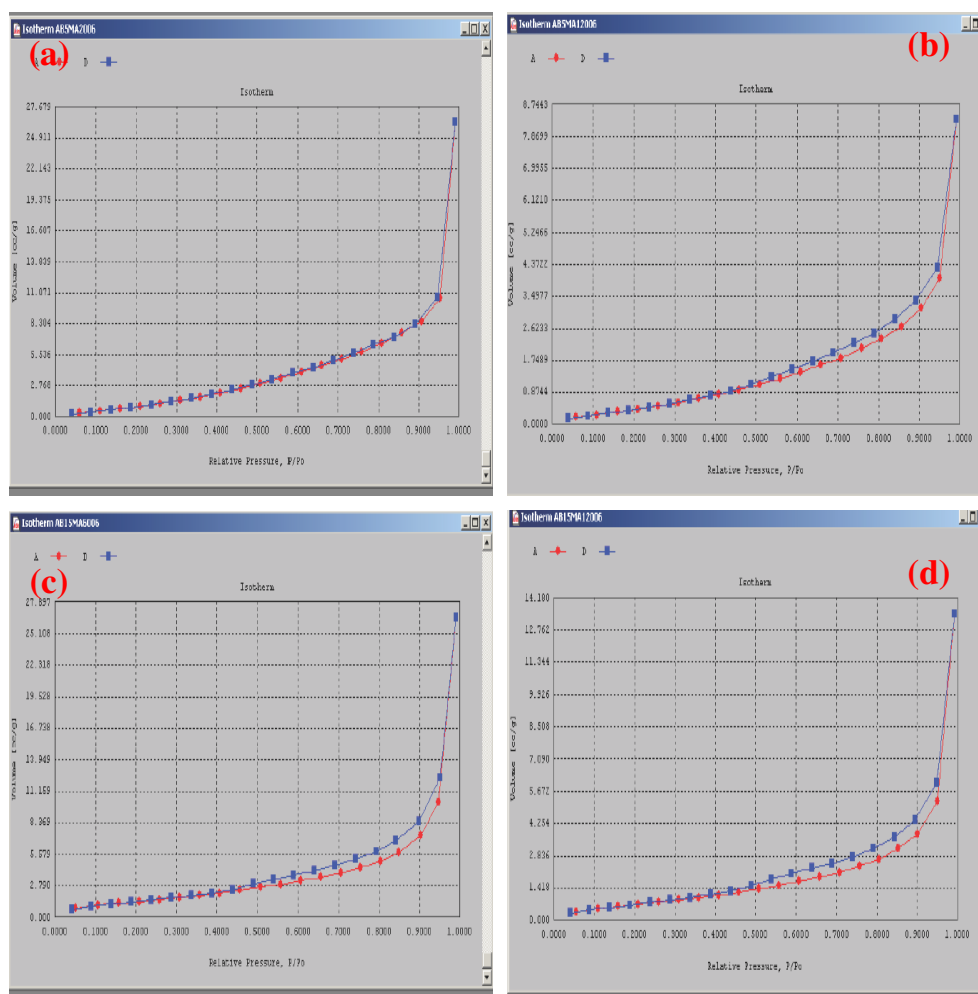


Figure 7.29a: BET surface area isotherms; (a)AB5MA2006, (b)AB5MA12006, (c)AB10MA2006, (d)AB10MA12006.

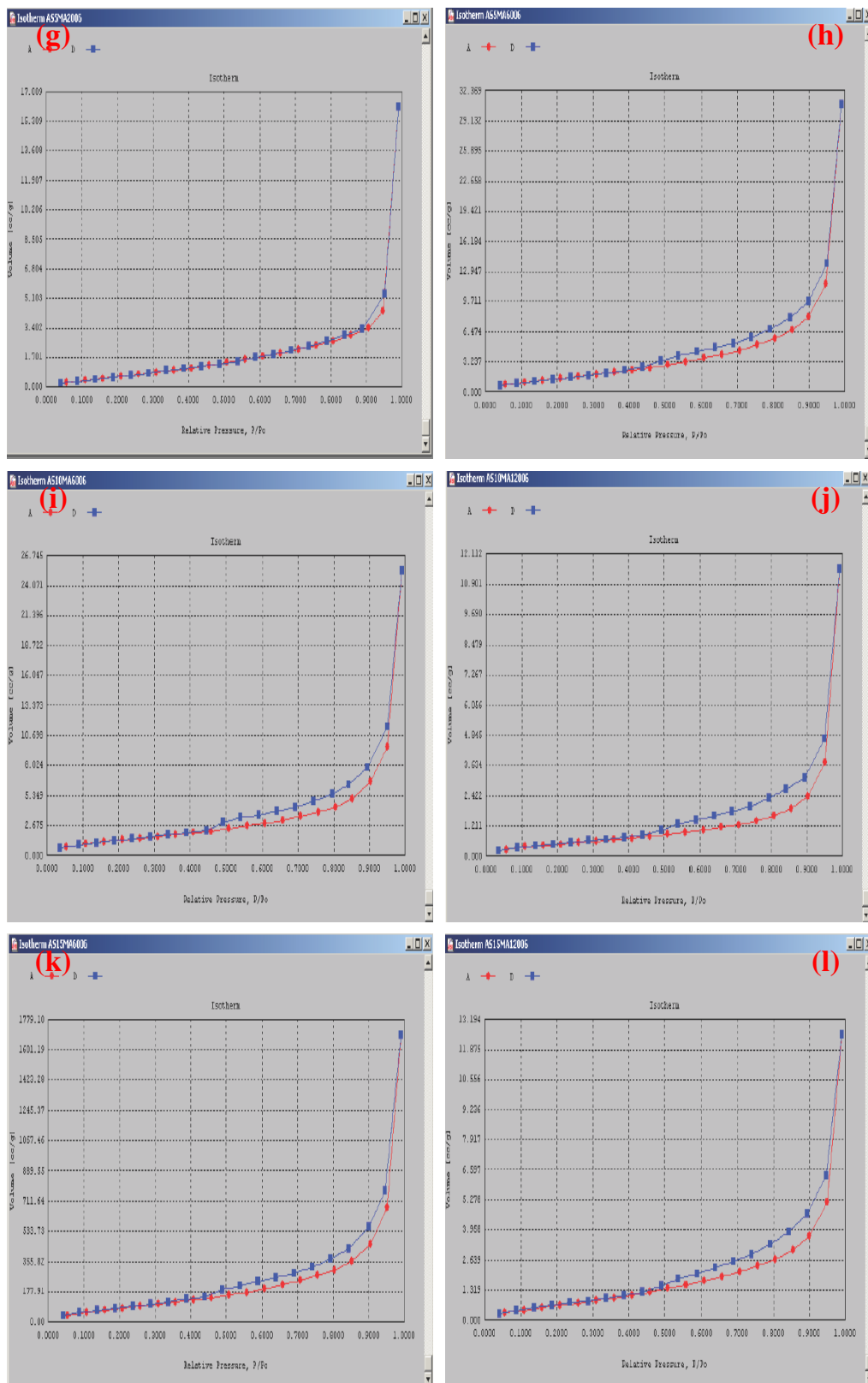


Figure 7.29b: BET surface area isotherms; (g)AS5MA2006, (h)AS5MA12006, (i)AS10MA2006, (j)AS10MA12006, (k)AS15MA2006, (l)AS15MA12006.

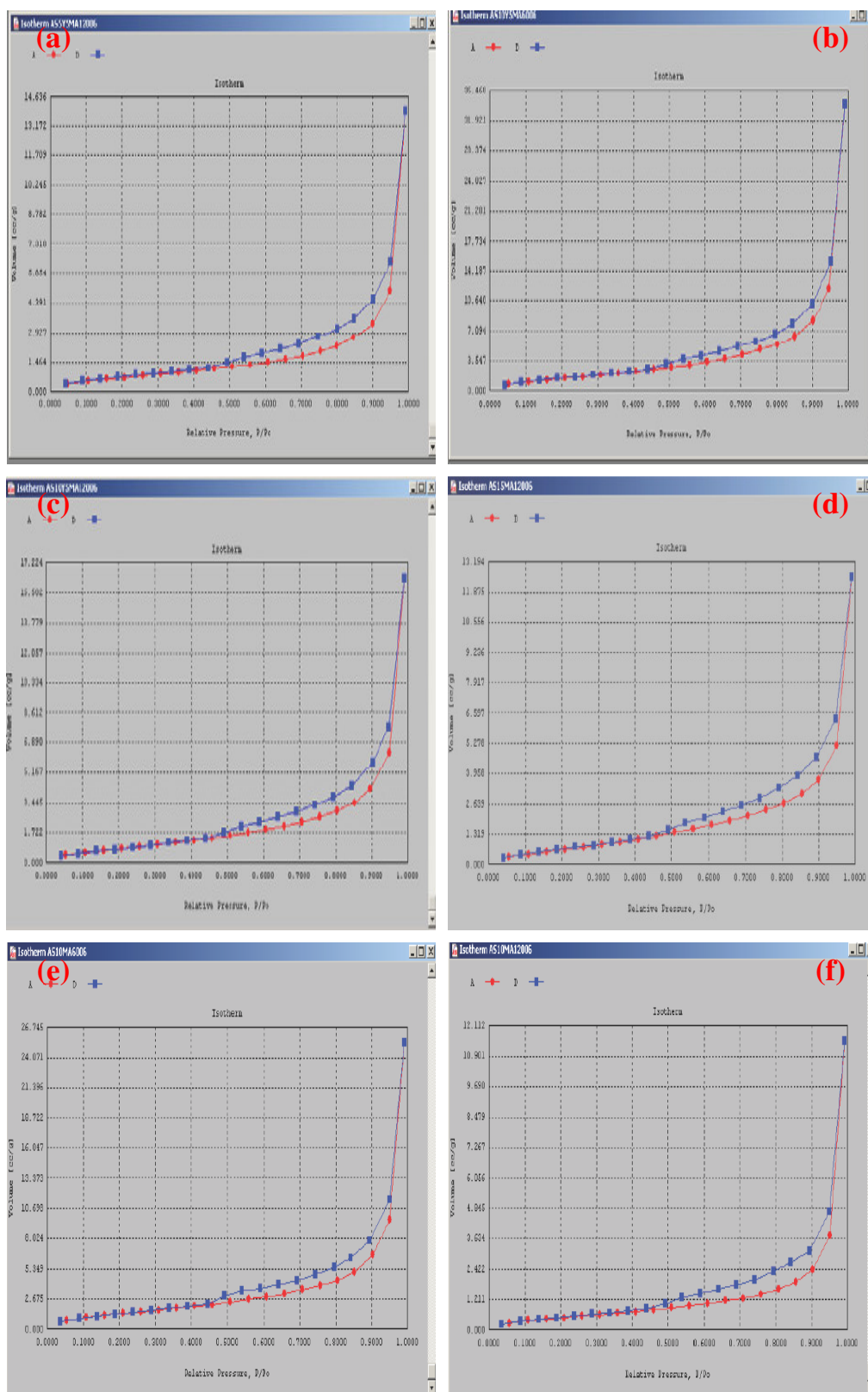


Figure 7.30a: BET surface area isotherms; (a)AS5Y5MA2006, (b)AS5Y5MA12006, (c)AS10Y5MA2006, (d)AS10Y5MA12006, (e)AS15Y5MA2006, (f)AS15Y5MA12006.

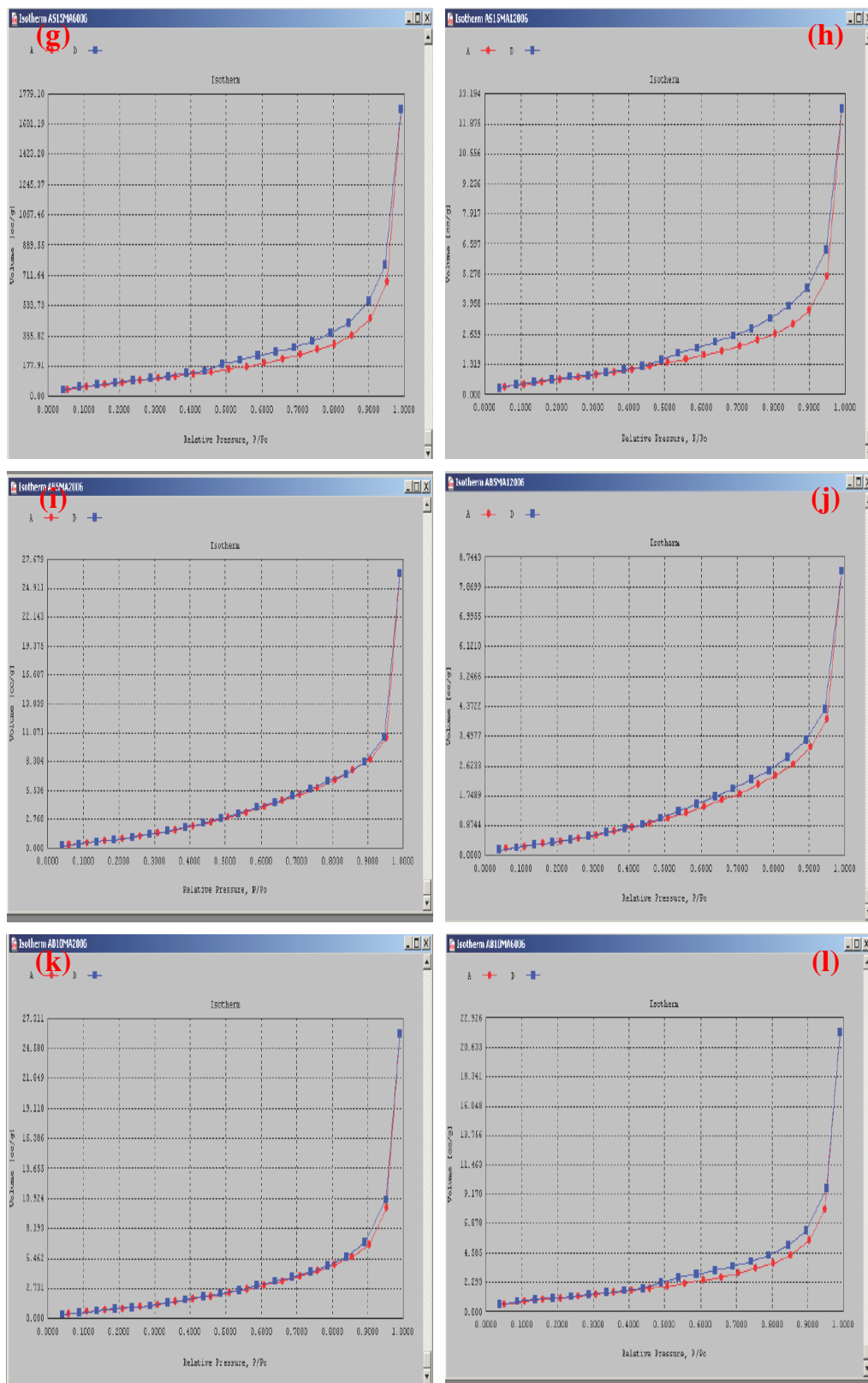


Figure 7.30b: BET surface area isotherms; (g)AB5Y5MA2006, (h)AB5Y5MA12006, (i)AB10Y5MA2006, (j)AB10Y5MA12006, (k)AB15Y5MA2006, (l)AB15Y5MA12006.

All BET surface area measurements were performed under controlled atmosphere with liquid nitrogen according to multi-point BET principle. All data were collected from 5 points. BET surface analyses were carried out in two stages: degass stage was the first stage. In this stage, all the humid in the powders was removed away. For this process, helium was used as a backfill gas. The temperature for degassing was selected as 150⁰C. After the degassing section, the absorbate gas nitrogen was used for obtaining surface area.

From Figure 7.31 and Figure 7.32, it can be seen that, as known from the previous analyses, in the initial stages of milling the ductile metal (here Al) powder particles get flattened by the ball-powder-ball collisions, while the brittle SiC/B₄C particles get fragmented as expected. With increasing mechanical alloying time, the particle size of the powders increased, also fresh surfaces also occurred. The powders get flattened until alloying time of 60 minutes. A high amount of refinement of particles occurred up to 60 minutes and after that the grains began to refine according to the BET surface analysis. These flattened structures get fragmented and finally composite powder particles are formed with compositions similar to starting powder blend composition.

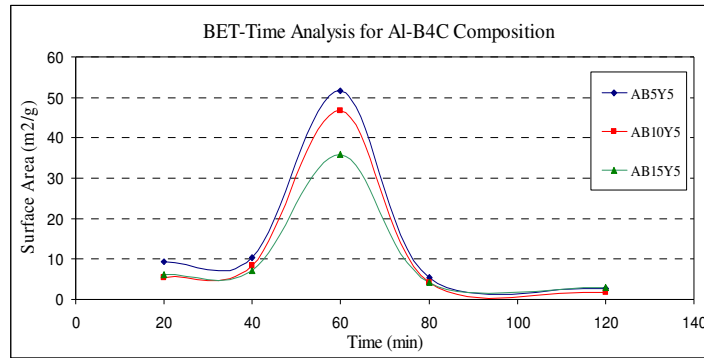


Figure 7.31: BET-Time analysis for Al-B₄C composition.

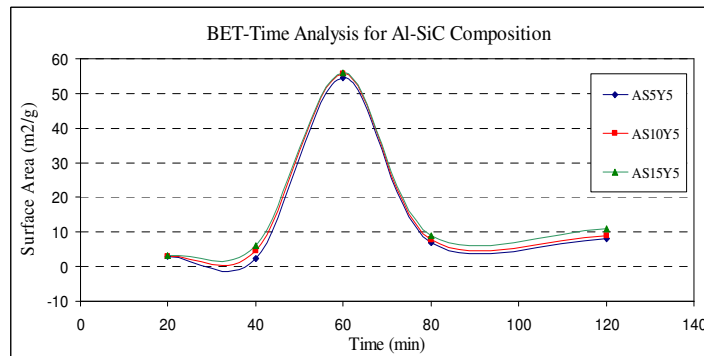


Figure 7.32: BET-Time analysis for Al-SiC composition.

From Figure 7.33 and Figure 7.34, it can be seen that again the powders get flattened until alloying time of 60 minutes. Surface area of the particles are increasing with mechanical alloying time until 60 minutes. After 60 minutes, particles get larger again. High amount of refining of particles occurred up to 60 minutes and after that the grains began to refine according to the BET surface analyses. These flattened structures get fragmented and finally composite powder particles are formed with compositions similar to starting powder blend composition.

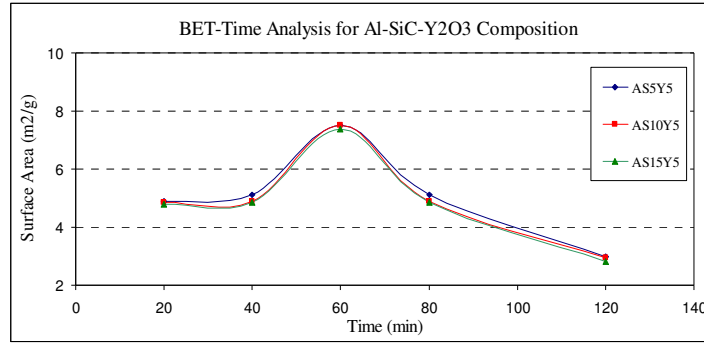


Figure 7.33: BET-Time analysis for Al-SiC-Y₂O₃ composition.

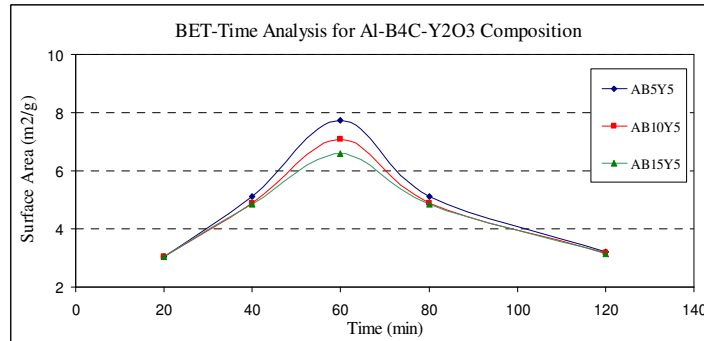


Figure 7.34: BET-Time analysis for Al-B₄C-Y₂O₃ composition.

7.1.3 Mechanical properties

A Vickers indenter under a load of 50 g for 15 seconds was intended on embedded powder samples (Figure 7.35). For every sample, 15 indentations were done to obtain average values and standard deviations (Table 7.5; Table 7.6). Hardness values are mainly consistent with SEM and XRD results.

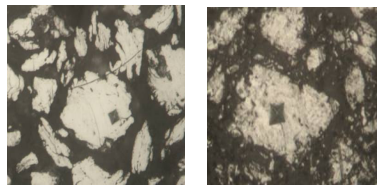


Figure 7.35: Pictures of Vickers indentations on powders.

Table 7.5: Hardness results of the Al-SiC and Al-B₄C samples with standard deviations.

Sample	Hardness (HV)	Standard Deviation
AS5MA2006	24.82	±13,22
AS5MA4006	25.26	±12,71
AS5MA6006	27.41	±13,13
AS5MA8006	44.96	±3,84
AS5MA12006	48.13	±4,93
AS10MA2006	25.25	±11,69
AS10MA4006	29.31	±12,59
AS10MA6006	47.41	±2,90
AS10MA8006	66.04	±5,44
AS10MA12006	68.38	±5,79
AS15MA2006	31.79	±13,95
AS15MA4006	44.91	±4,88
AS15MA6006	69.13	±8,56
AS15MA8006	105.19	±9,78
AS15MA12006	127.47	±10,53
AB5MA2006	29.82	±11,53
AB5MA4006	44.61	±13,13
AB5MA6006	70.62	±5,21
AB5MA8006	73.75	±5,78
AB5MA12006	102.37	±9,52
AB10MA2006	40.53	±5,29
AB10MA4006	57.76	±11,78
AB10MA6006	71.27	±3,36
AB10MA8006	108.92	±8,65
AB10MA12006	130,00	±5,45
AB15MA2006	35.59	±11,75
AB15MA4006	45.47	±2,90
AB15MA6006	77.34	±8,95
AB15MA8006	112.14	±6,34
AB15MA12006	154.36	±7,95

Table 7.6: Hardness results of the Al-SiC-Y₂O₃ and Al-B₄C-Y₂O₃ samples with standard deviations.

Sample	Hardness (HV)	Standard Deviation
AS5Y5MA2006	30.22	±11,31
AS5Y5MA4006	31.14	±11,95
AS5Y5MA6006	50.54	±5,32
AS5Y5MA8006	71.23	±6,67
AS5Y5MA12006	97.32	±5,41
AS10Y5MA2006	25.47	±12,81
AS10Y5MA4006	31.53	±13,91
AS10Y5MA6006	59.73	±8,51
AS10Y5MA8006	101.76	±3,42
AS10Y5MA12006	127.06	±1,15
AS15Y5MA2006	52.13	±4,27
AS15Y5MA4006	45.15	±5,35
AS15Y5MA6006	75.16	±3,12
AS15Y5MA8006	112.95	±2,11
AS15Y5MA12006	135,00	±2,05
AB5Y5MA2006	32,67	±10,99
AB5Y5MA4006	50.54	±6,76
AB5Y5MA6006	85,95	±5,74
AB5Y5MA8006	100,00	±2,52
AB5Y5MA12006	120,24	±3,78
AB10Y5MA2006	43,65	±14,77
AB10Y5MA4006	59,37	±13,57
AB10Y5MA6006	85,25	±5,64
AB10Y5MA8006	126.06	±5,41
AB10Y5MA12006	135,65	±5,98
AB15Y5MA2006	77,12	±7,54
AB15Y5MA4006	80,35	±8,98
AB15Y5MA6006	135,23	±5,86
AB15Y5MA8006	146,42	±5,61
AB15Y5MA12006	168,55	±7,75

Generally, the hardness is increasing with increasing mechanical alloying, also with decreasing grain size. On the other hand, all the hardness values of samples containing more reinforcement materials are higher than other samples. This is the direct effect of increasing amount of SiC or B₄C. In addition, B₄C reinforced composites have higher hardness values compared to SiC reinforced composites because of higher hardness value of B₄C compared to SiC (Figures 7.36, 7.37 and 7.38). In some samples, there are very high standard deviation values because the pores are non-uniform, so different hardness values obtained from a region with pores and from a region without any pores increase standard deviation.

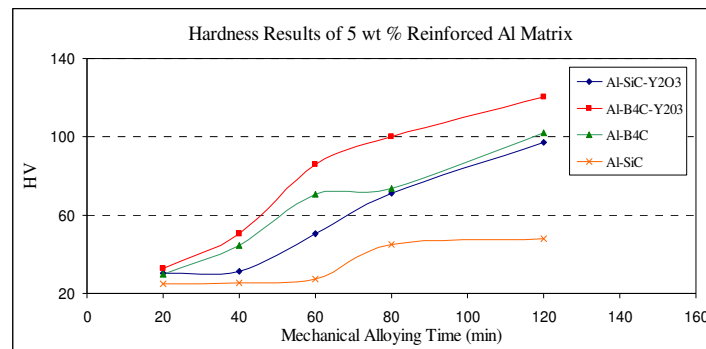


Figure 7.36: Hardness results of 5 wt % reinforced Al matrix.

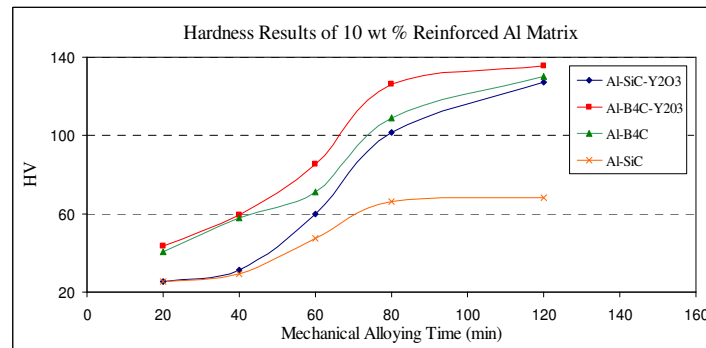


Figure 7.37: Hardness results of 10 wt % reinforced Al matrix.

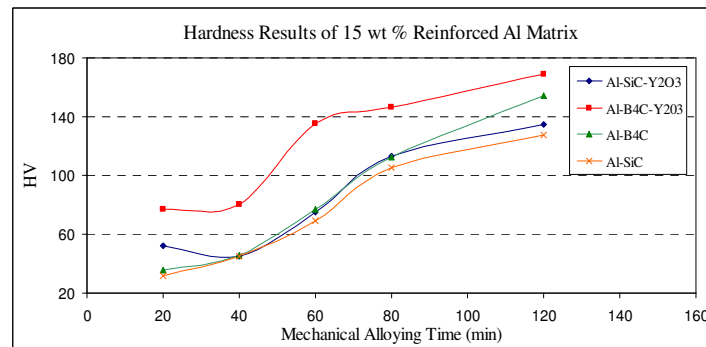


Figure 7.38: Hardness results of 15 wt % reinforced Al matrix.

7.1.4 Thermal analysis

The measurements are used primarily to determine the composition of aluminum based materials and to predict their thermal stability at temperatures up to 650°C under argon-hydrogen atmosphere. The typical heating rate is 10°C per minute. From the Figure 7.39; the heat behavior of all samples looks the same. At 400°C, there is a heat flow change because of vaporization of zinc stearat.

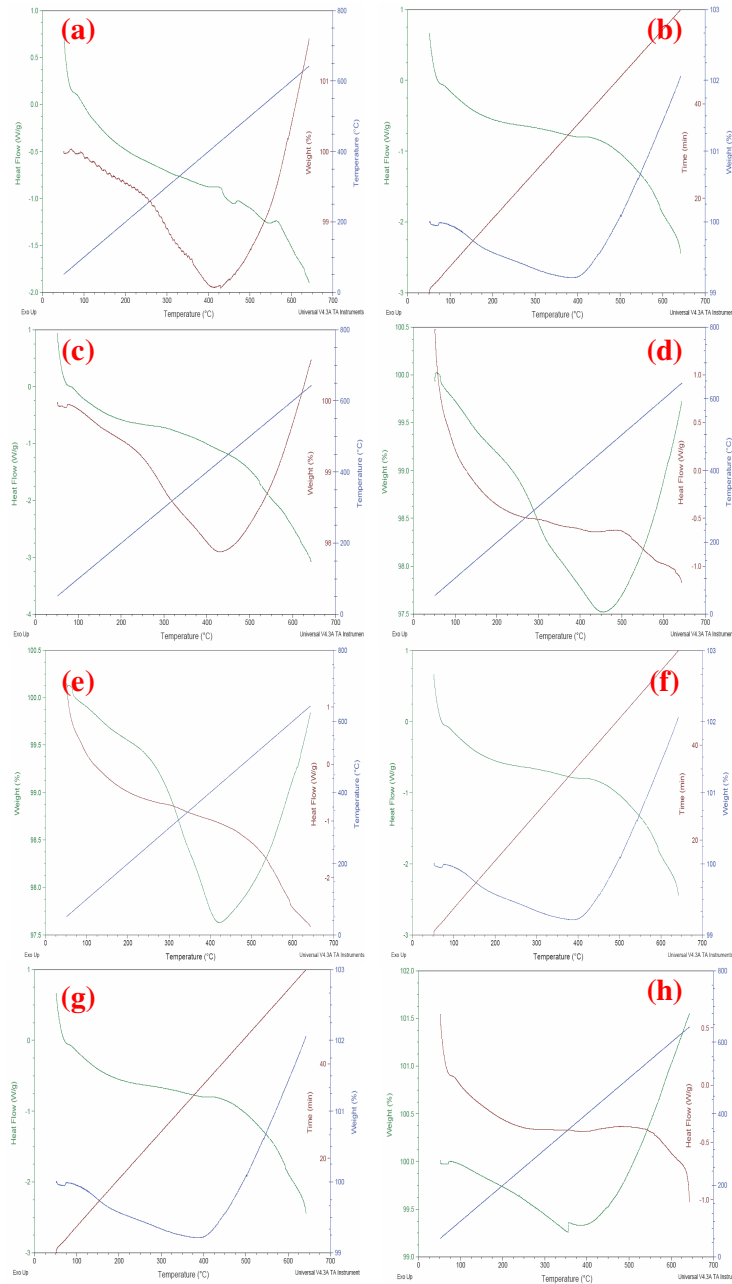


Figure 7.39: DSC analyse of (a)AS5MA2006, (b)AS5MA12006, (c)AB10MA2006, (d)AB15MA12006, (e)AS5Y5MA2006, (f)AS5Y5MA12006, (g)AB5Y5MA2006, (h)AB15Y5MA12006.

This information is very useful for determining sintering regime in next step. All the same, there is a weight gain due to oxidation in the powders around 380-400⁰C. The reason should be the oxidation; this means that unfortunately the hydrogen amount in the system was not enough for protecting the powders from oxidation. Oxygen in the argon atmosphere has oxidized the powders. The DSC reactions are exothermic because of oxidation.

7.2 Characterization of Compacted Powders

The mechanically alloyed powders were compacted by cold pressing in a tool-steel die with a pressure of 610-620 MPa (100 bar) into cylinder shaped green compacts with a diameter of ≈ 12 mm and height of ≈ 6 mm (Figure 7.40).



Figure 7.40: Compacted powder.

The results of the density measurements of both green compacts are given in Table 7.7 and Table 7.8. The densities of the samples are increasing with increasing mechanical alloying. This is because of the mechanically activated process which is enhanced by the stored energy with severe cold working and homogeneous distribution of matrix phase by MA.

However, the densities of samples with 15 wt. % SiC are slightly decreasing again compared to those of with wt. %10 SiC or wt. %5 SiC. The same conclusion can be made also for B₄C containing composites. The reason is that the increased amount of SiC or B₄C phases, which are very brittle, make the compressibility of the powder difficult.

Moreover, the surface tensions of the powders are increased with decreasing particle size, due to the increasing surface area. This also makes the compressibility of the powder difficult. So, these samples all have similar low green densities. Some samples have low densities and the reason for that is that the pore formation in the structure.

Table 7.7: Density measurements of green compacts of Al-SiC and Al-B₄C compositions.

Sample	Density (g/cc)	Relative Density
AS5MA2006	1.562	55.00%
AS5MA4006	1.717	58.35%
AS5MA6006	1.795	61.00%
AS5MA8006	1.883	64.00%
AS5MA12006	1.942	66.00%
AS10MA2006	1.450	53.00%
AS10MA4006	1.504	55.00%
AS10MA6006	1.545	56.53%
AS10MA8006	1.668	61.00%
AS10MA12006	1.742	63.70%
AS15MA2006	1.404	51.00%
AS15MA4006	1.487	54.00%
AS15MA6006	1.542	56.00%
AS15MA8006	1.597	58.25%
AS15MA12006	1.707	62.65%
AB5MA2006	1.536	57.10%
AB5MA4006	1.604	59.60%
AB5MA6006	1.618	60.10%
AB5MA8006	1.736	64.50%
AB5MA12006	1.797	66.80%
AB10MA2006	1.493	55.70%
AB10MA4006	1.531	57.10%
AB10MA6006	1.582	59.98%
AB10MA8006	1.646	61.40%
AB10MA12006	1.689	63.54%
AB15MA2006	1.443	54.45%
AB15MA4006	1.510	56.50%
AB15MA6006	1.564	58.54%
AB15MA8006	1.628	60.95%
AB15MA12006	1.657	62.31%

Table 7.8: Density measurements of green compacts of Al-SiC-Y₂O₃ and Al-B₄C-Y₂O₃ compositions.

Sample	Density (g/cc)	Relative Density
AS5Y5MA2006	1.559	58.45%
AS5Y5MA4006	1.661	62.31%
AS5Y5MA6006	1.745	65.43%
AS5Y5MA8006	1.784	66.90%
AS5Y5MA12006	1.811	67.89%
AS10Y5MA2006	1.524	56.90%
AS10Y5MA4006	1.538	57.40%
AS10Y5MA6006	1.607	60.00%
AS10Y5MA8006	1.688	63.76%
AS10Y5MA12006	1.741	64.98%
AS15Y5MA2006	1.509	55.95%
AS15Y5MA4006	1.535	56.95%
AS15Y5MA6006	1.546	57.34%
AS15Y5MA8006	1.612	59.80%
AS15Y5MA12006	1.687	62.56%
AB5Y5MA2006	1.562	59.10%
AB5Y5MA4006	1.597	60.40%
AB5Y5MA6006	1.660	62.80%
AB5Y5MA8006	1.726	65.30%
AB5Y5MA12006	1.769	66.90%
AB10Y5MA2006	1.519	57.80%
AB10Y5MA4006	1.563	59.50%
AB10Y5MA6006	1.637	62.30%
AB10Y5MA8006	1.700	64.70%
AB10Y5MA12006	1.708	65.66%
AB15Y5MA2006	1.487	56.80%
AB15Y5MA4006	1.495	57.10%
AB15Y5MA6006	1.584	60.50%
AB15Y5MA8006	1.647	62.90%
AB15Y5MA12006	1.649	63.54%

7.3 Characterization of Sintered Samples

7.3.1 Determination of the sintering regime

As mentioned in section.6, the sintering regime is mainly determined by several additional experiments using a dilatometer. Examples of the curves obtained from the dilatometer experiments are shown below.

According to these curves, Ar flow was regulated. In every experiment, different flow rates and flow durations were applied. As a result, a similar sintering behavior was observed. Furthermore, it was observed that the initial reductive effect of Ar began at approximately same temperatures. Moreover, it is known that the zinc stearat evaporates around 400 °C. For this reason, a holding time is foreseen at this temperature. During this period, the sintering atmosphere is changed to a gas mixture of Ar and H₂ to avoid oxidation.

To determine the whole sintering regime, literature research was done and a sintering regime was chosen to inhibit the grain growth (see the Figure 7.41a and 7.41b). Sintering at 650 °C is a conventional sintering temperature which is to heat the powder compact at a certain rate, holding it at the highest temperature until the maximum density is reached. The feasibility of densification without grain growth relies on the suppression of grain-boundary migration while keeping grain-boundary diffusion active. However, the important thing here is to obtain a sufficiently high starting density during the first step of sintering.

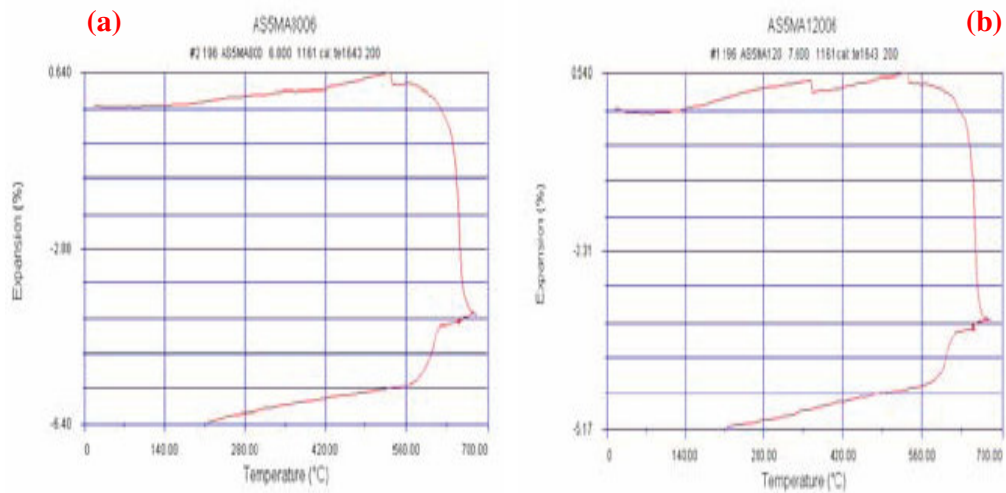


Figure 7.41a: Sintering curves of; (a)AS5MA2006, (b)AS5MA12006.

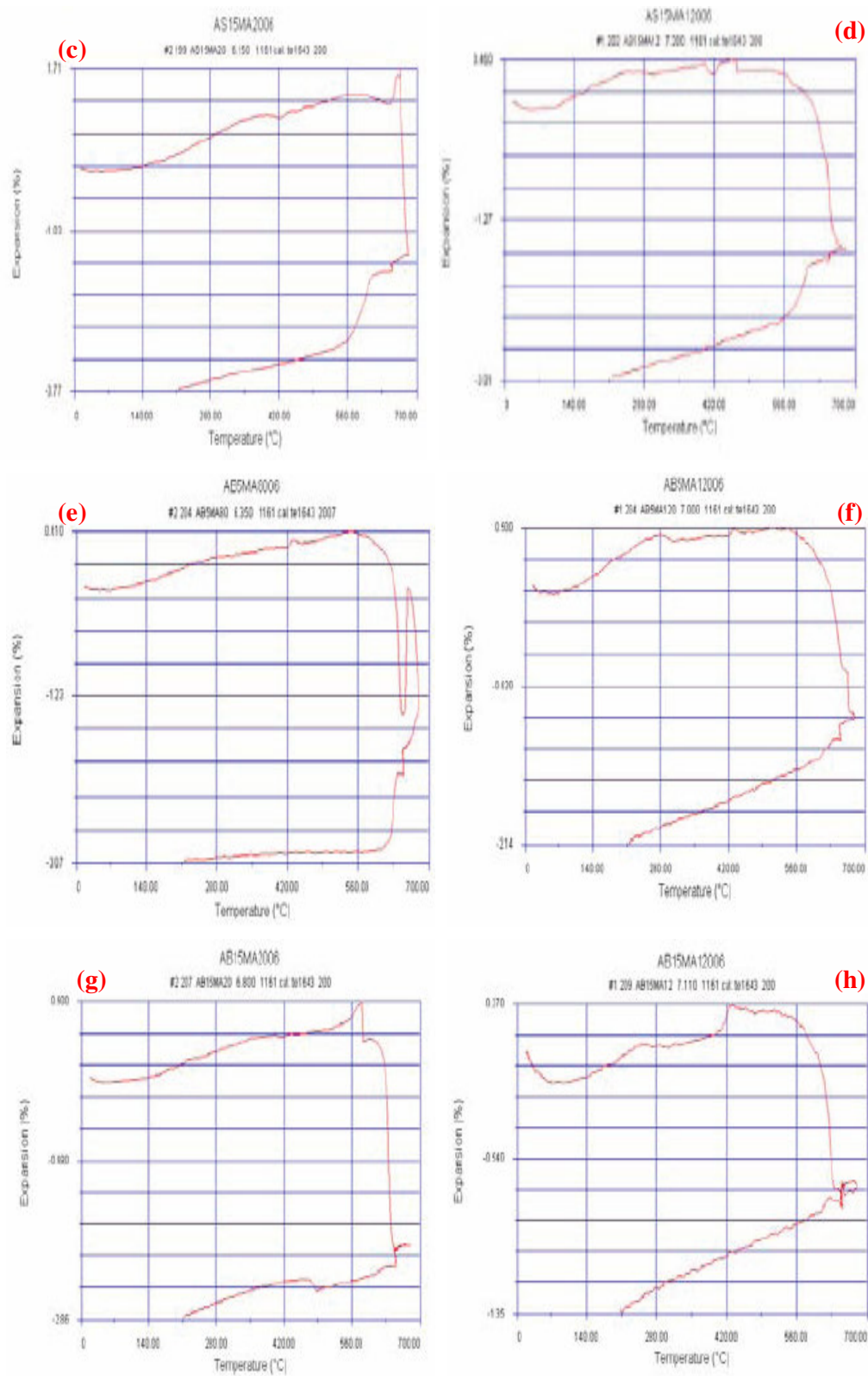


Figure 7.41b: Sintering curves of; (c)AS15Y5MA2006, (d)AS15Y5MA12006, (e)AB5MA2006, (f)AB5MA12006, (g)AB15MA2006, (h)AB15MA12006.

7.3.2 Density measurements

The results of the density measurements of sintered samples are given in Table 7.9 and Table 7.10.

Table 7.9: Density measurements of sintered compacts of Al-SiC and Al-B₄C compositions.

Sample	Sintered Density (g/cc)	Relative Density
AS5MA2006	2,80	92,10%
AS5MA4006	2,83	93,35%
AS5MA6006	2,86	94,44%
AS5MA8006	2,87	94,82%
AS5MA12006	2,88	95,29%
AS10MA2006	2,76	91,19%
AS10MA4006	2,77	91,37%
AS10MA6006	2,79	92,29%
AS10MA8006	2,83	93,46%
AS10MA12006	2,86	94,56%
AS15MA2006	2,74	90,32%
AS15MA4006	2,77	91,51%
AS15MA6006	2,78	91,92%
AS15MA8006	2,80	92,38%
AS15MA12006	2,81	92,60%
AB5MA2006	2,74	91,31%
AB5MA4006	2,75	91,70%
AB5MA6006	2,77	92,45%
AB5MA8006	2,80	93,47%
AB5MA12006	2,83	94,22%
AB10MA2006	2,72	90,61%
AB10MA4006	2,73	90,90%
AB10MA6006	2,75	91,80%
AB10MA8006	2,76	92,17%
AB10MA12006	2,80	93,32%
AB15MA2006	2,70	89,93%
AB15MA4006	2,72	90,72%
AB15MA6006	2,74	91,53%
AB15MA8006	2,76	91,95%
AB15MA12006	2,78	92,66%

Table 7.10: Density measurements of sintered compacts of Al-SiC-Y₂O₃ and Al-B₄C-Y₂O₃ compositions.

Sample	Sintered Density (g/cc)	Relative Density
AS5Y5MA2006	2,90	93,56%
AS5Y5MA4006	2,91	93,78%
AS5Y5MA6006	2,93	94,54%
AS5Y5MA8006	2,96	95,66%
AS5Y5MA12006	2,99	96,89%
AS10Y5MA2006	2,88	92,98%
AS10Y5MA4006	2,89	93,23%
AS10Y5MA6006	2,90	93,67%
AS10Y5MA8006	2,92	94,38%
AS10Y5MA12006	2,95	95,12%
AS15Y5MA2006	2,85	91,98%
AS15Y5MA4006	2,86	92,36%
AS15Y5MA6006	2,88	92,87%
AS15Y5MA8006	2,90	93,50%
AS15Y5MA12006	2,91	93,80%
AB5Y5MA2006	2,85	92,54%
AB5Y5MA4006	2,85	92,65%
AB5Y5MA6006	2,87	93,12%
AB5Y5MA8006	2,87	93,31%
AB5Y5MA12006	2,89	93,69%
AB10Y5MA2006	2,82	91,47%
AB10Y5MA4006	2,82	91,71%
AB10Y5MA6006	2,84	92,21%
AB10Y5MA8006	2,88	93,58%
AB10Y5MA12006	2,88	93,63%
AB15Y5MA2006	2,73	88,70%
AB15Y5MA4006	2,75	89,35%
AB15Y5MA6006	2,76	89,78%
AB15Y5MA8006	2,79	90,67%
AB15Y5MA12006	2,83	91,96%

According to these results, it is clear that the density is increased with increasing sintering temperatures because the diffusivity of the atoms, which is the key factor for sintering, is enhanced with increasing temperature. Furthermore, the densities of the sintered samples containing 5 wt %, 10 wt % and 15 wt % SiC are increasing with increasing mechanical alloying just like the sintered samples containing 5 wt %, 10 wt % and 15 wt % B₄C. This is because of the mechanically activated sintering which is caused by the stored energy of the severe cold working and homogeneous distribution of matrix phase by mechanical alloying. In addition, the reason of increasing sintered densities is the small amount of Y₂O₃ phase. However, the densities of samples with wt. %15 SiC slightly change and the sintered densities are lower than those of with wt. %10 SiC or wt. %5 SiC. The same conclusion can be made also for B₄C containing composites. The reason for that is that the increased amount of SiC or B₄C phases which are very brittle make the compressibility of the powder difficult. Moreover, the surface tensions of the powders are increased with decreasing particle size, due to the increasing surface area and this also makes the compressibility of the powder difficult. So, all these samples have similar low sintered densities.

7.3.3 Phase analyses and microstructure characterizations

The phases in microstructures of the sintered samples were characterized by X-Ray diffraction (XRD) at a low incident angle ($\theta=3^{\circ}$) as seen in Figures 7.42a, 7.42b and 7.42c, Figures 7.43a, 7.43b and 7.43c, Figures 7.44a, 7.44b and 7.44c and Figures 7.45a, 7.45b and 7.45c.

XRD patterns of sintered Al-SiC samples in Figures 7.42a, 7.42b and 7.42c show that with increasing mechanical alloying, the intensity of Al₄SiC₄ diffraction patterns increases. Al₄SiC₄ phase is more stable after sintering. This may be a result of the SiC contamination during the MA process. The excess amount of SiC could have reacted with Al. There is Al₄Si₂C₅ formation in the system. The Al₄C₃ phase is unstable at 650⁰C, so that this phase no longer exists after the sintering process. Also, there is a decrease in the height of Al peaks and new Al and SiC peaks were formed. This is believed to be caused by the recrystallization triggered by severe plastic deformation of MA. As a result, new strain free grains of Al and SiC have been formed.

XRD patterns of sintered Al-B₄C samples in Figure 7.43a show that increasing MA, did not drastically effect on AlB₂ peak. There is a decrease in the height of Al peaks also. In Figure 7.43b, new AlB₂ peaks appeared. There is a formation of Al₃BC. In addition, there is a decrease in the height of Al peaks also. In Figure 7.43c, new AlB₂ peaks appeared and with increasing MA time, the intensity of AlB₂ diffraction patterns increases. The excess amount of B₄C could have been reacted with Al. Again, there is a formation of Al₃BC. Also, there is a decrease in the height of Al peaks and new Al and B₄C peaks were formed. This is believed to be because of the recrystallization triggered by the severe plastic deformation due to the MA. New grains might have pumped the excess B and C in carbides out. As a result, new strain free grains of Al and B₄C have been formed.

XRD patterns of sintered Al-SiC-Y₂O₃ powders in Figures 7.44a, 7.44b and 7.44c show that with increasing mechanical alloying, the intensities of Al₄SiC₄ and β -AlFeSi intermetallic diffraction patterns get stronger. Al₄SiC₄ phase is more stable after sintering. Al₄SiC₄ was formed by the decomposition of B₄C. The β -AlFeSi intermetallic is a result of iron contamination. No Y₂O₃ peaks were detected. β -AlFeSi and Al₄SiC₄ phases are more stable after sintering and their heights of peaks increased. Also, there is a decrease in the height of Al peaks. In Figure 7.44b and Figure 7.44c, new Al and SiC peaks were formed. The excess amount of SiC could have reacted with Al. There is Al₄Si₂C₅ formation in the system. This is believed to be because of the recrystallization triggered by severe plastic deformation due to the mechanical alloying. New grains might have pumped the excess Si and C in silicides and carbides out. As a result, new strain free grains of Al and SiC have been formed.

XRD patterns of sintered Al-B₄C-Y₂O₃ powders in Figures 7.45a, 7.45b and 7.45c AlB₂ phase is more stable and its height of peak has increased. Again, there is a formation of Al₃BC. Also, there is a decrease in the height of Al peaks and new Al and B₄C peaks were formed.

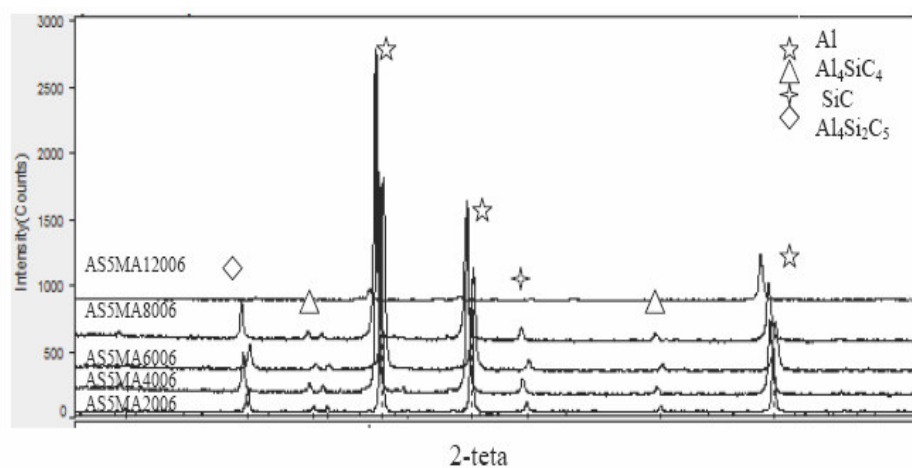


Figure 7.42a: XRD patterns of sintered Al-5 wt % SiC powders starting from a MA time of 20 min. (bottom) to 120 min. (top).

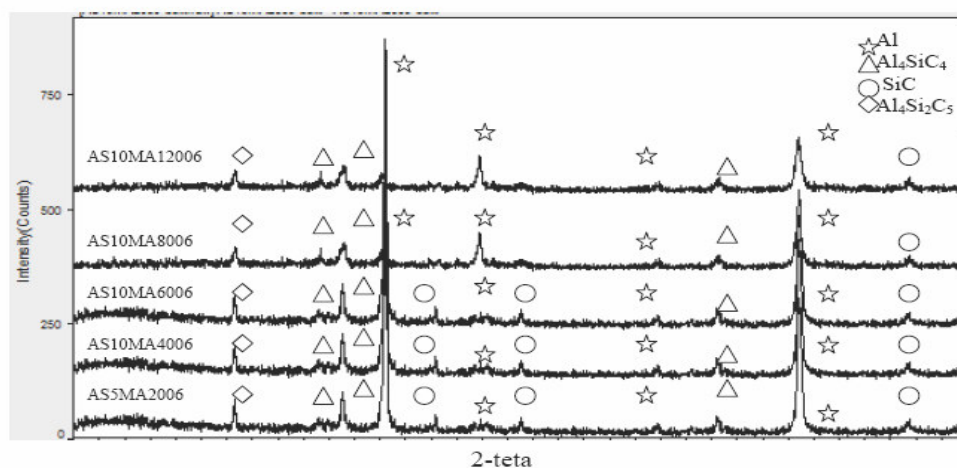


Figure 7.42b: XRD patterns of sintered Al-10 wt % SiC powders starting from a MA time of 20 min. (bottom) to 120 min. (top).

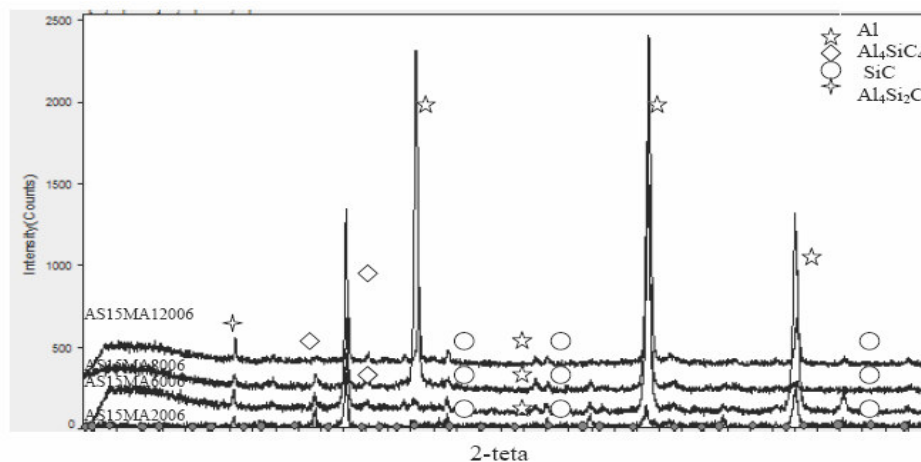


Figure 7.42c: XRD patterns of sintered Al-15 wt % SiC powders starting from a MA time of 20 min. (bottom) to 120 min. (top).

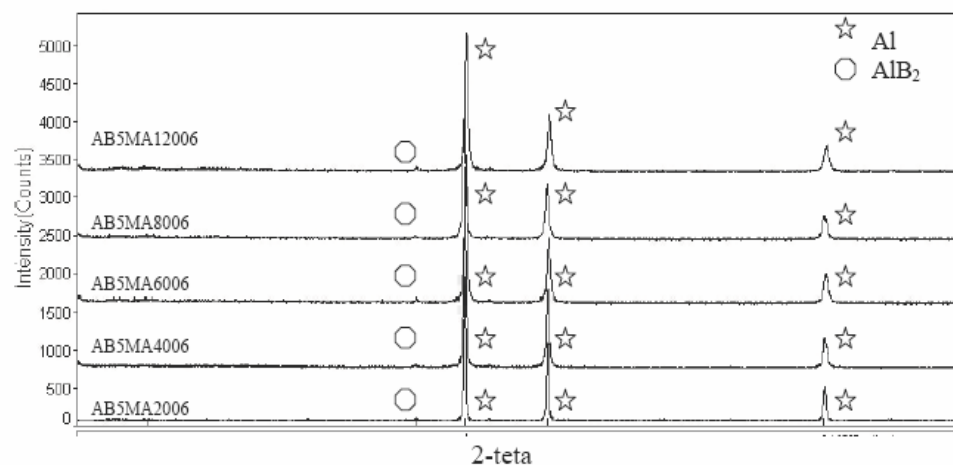


Figure 7.43a: XRD patterns of sintered Al-5 wt % B₄C powders starting from a MA time of 20 min. (bottom) to 120 min. (top).

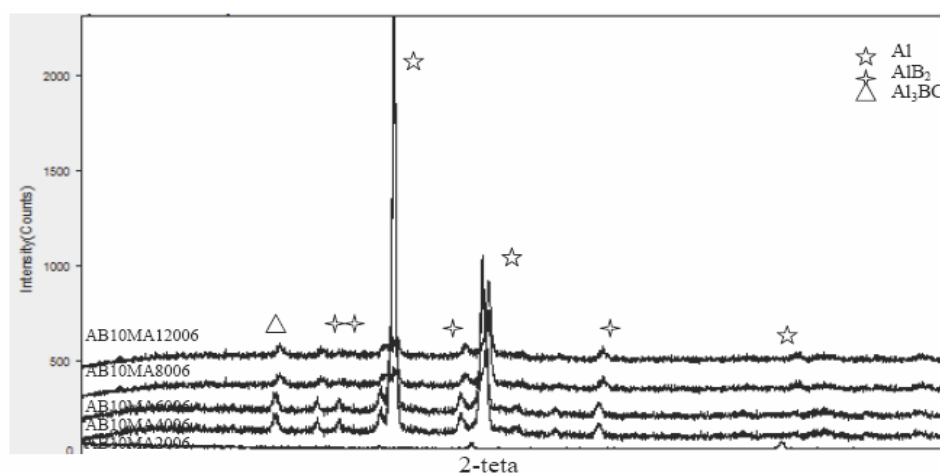


Figure 7.43b: XRD patterns of sintered Al-10 wt % B₄C powders starting from a MA time of 20 min. (bottom) to 120 min. (top).

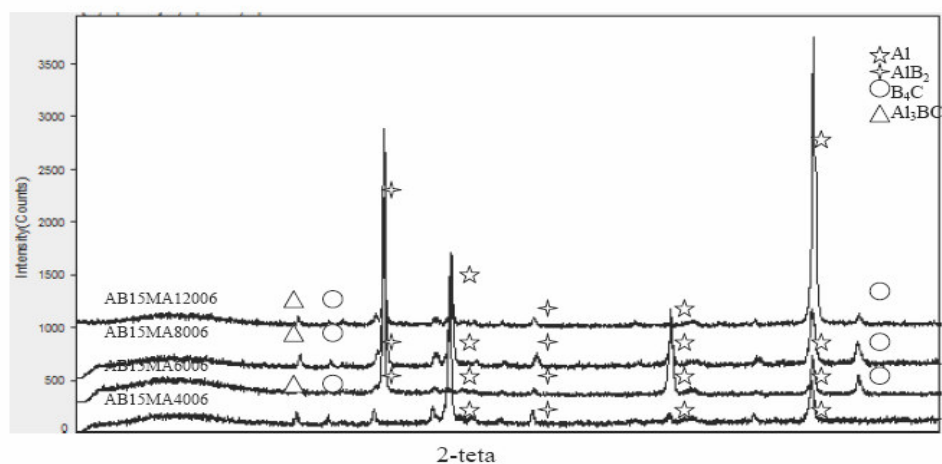


Figure 7.43c: XRD patterns of sintered Al-15 wt % B₄C powders starting from a MA time of 20 min. (bottom) to 120 min. (top).

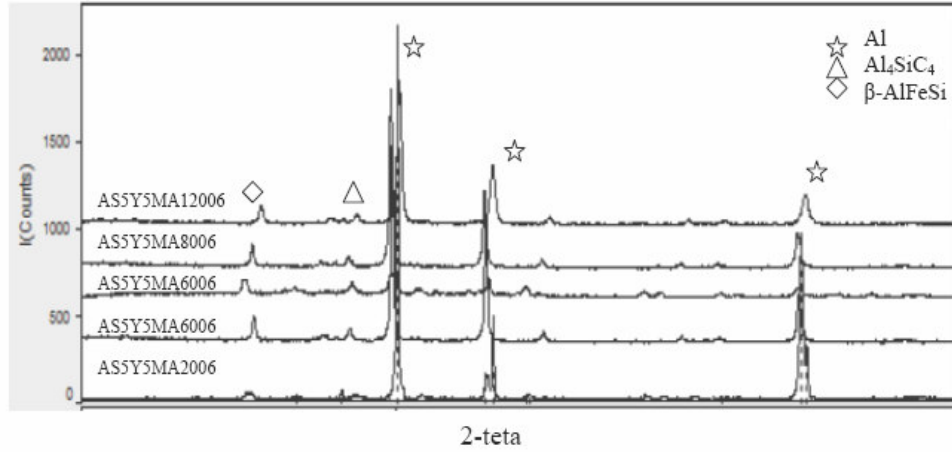


Figure 7.44a: XRD patterns of sintered Al-5 wt % SiC-5 wt % Y₂O₃ powders starting from a MA time of 20 min. (bottom) to 120 min. (top).

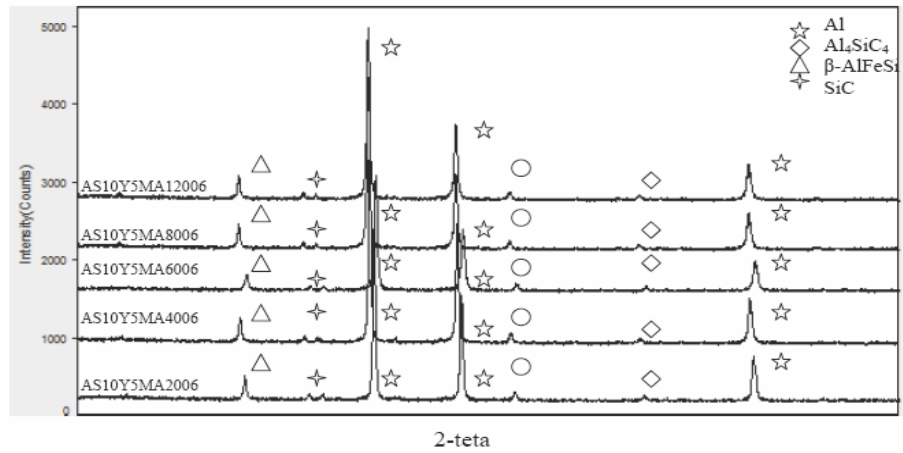


Figure 7.44b: XRD patterns of sintered Al-10 wt % SiC-5 wt % Y₂O₃ powders starting from a MA time of 20 min. (bottom) to 120 min. (top).

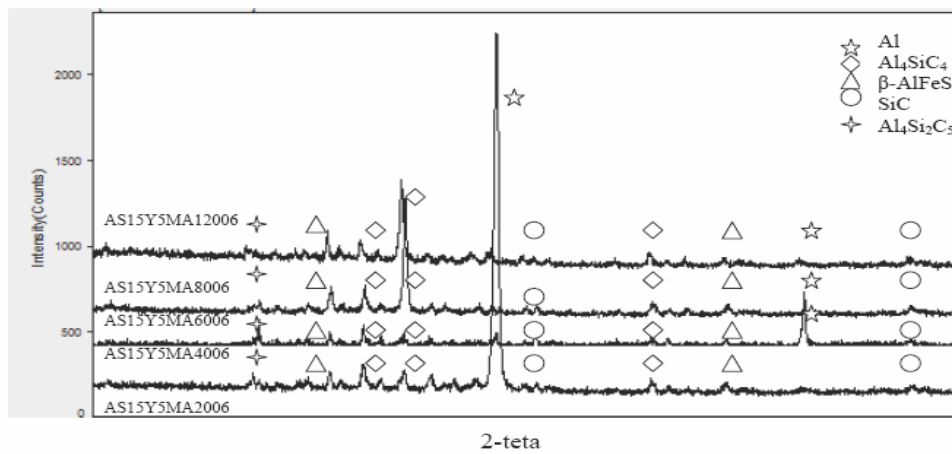


Figure 7.44c: XRD patterns of sintered Al-15 wt % SiC-5 wt % Y₂O₃ powders starting from a MA time of 20 min. (bottom) to 120 min. (top).

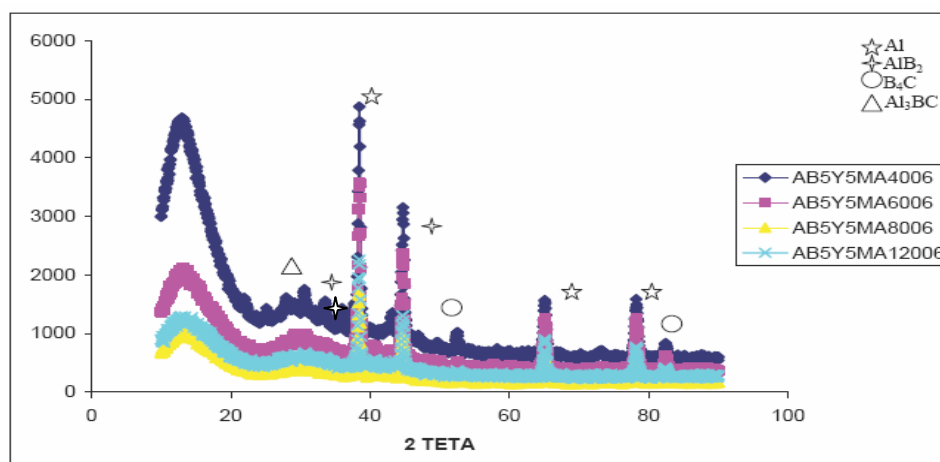


Figure 7.45a: XRD patterns of sintered Al-5 wt % B_4C -5 wt % Y_2O_3 powders starting from a MA time of 20 min. (bottom) to 120 min. (top).

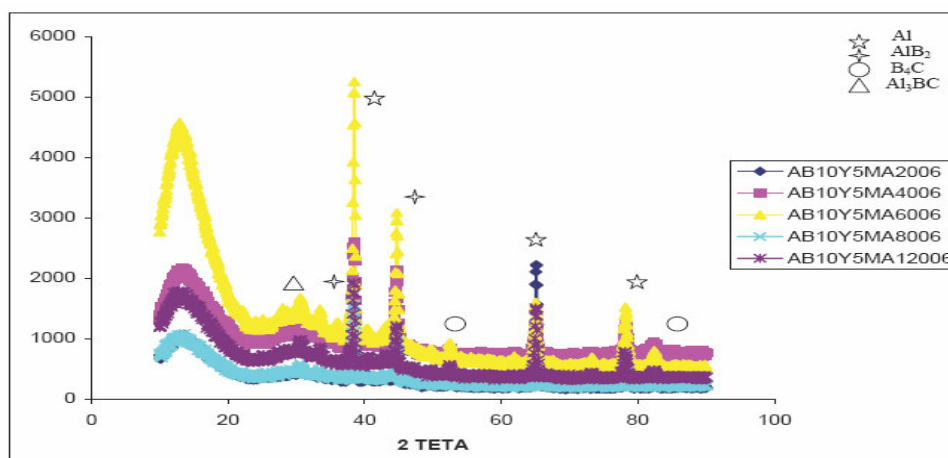


Figure 7.45b: XRD patterns of sintered Al-10 wt % B_4C -5 wt % Y_2O_3 powders starting from a MA time of 20 min. (bottom) to 120 min. (top).

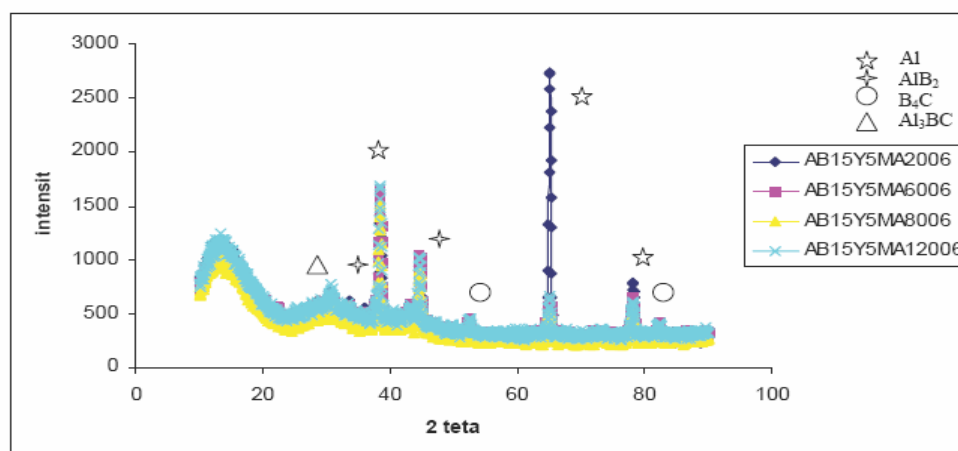


Figure 7.45c: XRD patterns of sintered Al-15 wt % B_4C -5 wt % Y_2O_3 powders starting from a MA time of 20 min. (bottom) to 120 min. (top).

SEM images are consistent with XRD patterns. The SEM pictures of sintered materials with 10 kV and different enlarge sizes (x500–x1500) are shown in Figure 7.46. It can be clearly seen that Al-SiC sintered samples and Al-B₄C sintered samples have similar microstructures. Both of them have a lot of pores, mostly smaller than 0.5 μm . The only difference is that the AB5MA6006 sample contains some cracks and some bigger pores. SiC and B₄C particles were found to be distributed homogeneously in the Al matrix by sintering process in Figure 7.46. It was observed that the Al matrix of the sintered powders consists mainly of fine subgrains with a wide range of misorientations. In Figure 7.46, a-b, dull white areas consist of SiC and black areas consist of Al+Al₄SiC₄+Al₄Si₂C₅. In addition, grey areas consist of the silicate phases and spherical shaped dark grey areas consist of SiC. Spherical shaped black areas are mainly pores. H₂ might have reacted with the free carbon in the structure and escaped as C_xH_y gas which is believed to be the reason of pore formation. On the other hand, vaporization of zinc stearate from the system may cause also these pores. For more reliable results transition electron microscope (TEM) analyses should be done. In Figure 7.46, c-d-e-f-g, dull white areas consist of B₄C and black areas consist of Al+AlB₂. Spherical shaped black areas are mainly pores. The reason of the pores may be C_xH_y gas and vaporization of zinc stearate. In addition to all these information, in Figure 7.46, e black areas have Al₃BC phase also. For Al-SiC system, the bonding seems to be weaker than that of Al-B₄C due to the relatively low adherence of matrix alloy to the particulate. SEM images in Figure 7.47 show that Al-SiC-Y₂O₃ sintered samples and Al-B₄C-Y₂O₃ sintered samples do not have similar microstructures. Al-SiC-Y₂O₃ sintered samples have a needle-like β -AlFeSi structures. Al-B₄C-Y₂O₃ contains some cracks. The results are consistent with XRD results where the silicide peaks are barely visible. In Figure 7.47, a-b-c-d-e, grey phase is aluminum, white phases are β -AlFeSi, Al₄SiC₄ and Al₂Si₄C. White needle-like phases are β -AlFeSi. In addition, grey areas consist of the silicate phases and spherical shaped dark grey areas consist of SiC. Spherical shaped black areas are mainly pores. This composite have a lot of pores, mostly smaller than 0.5 μm . H₂ might have reacted with the free carbon in the structure and escaped as C_xH_y gas which is believed to be the reason of pore formation. On the other hand, vaporization of zinc stearate from the system may cause also these pores. For more reliable results transition electron microscope (TEM) analyses should be done. In Figure 7.47, f-g-h;

dull white areas consist of B_4C and black areas consist of $Al+AlB_2+Al_3BC$. This composite does not contain a lot of pores compared to other compositions.

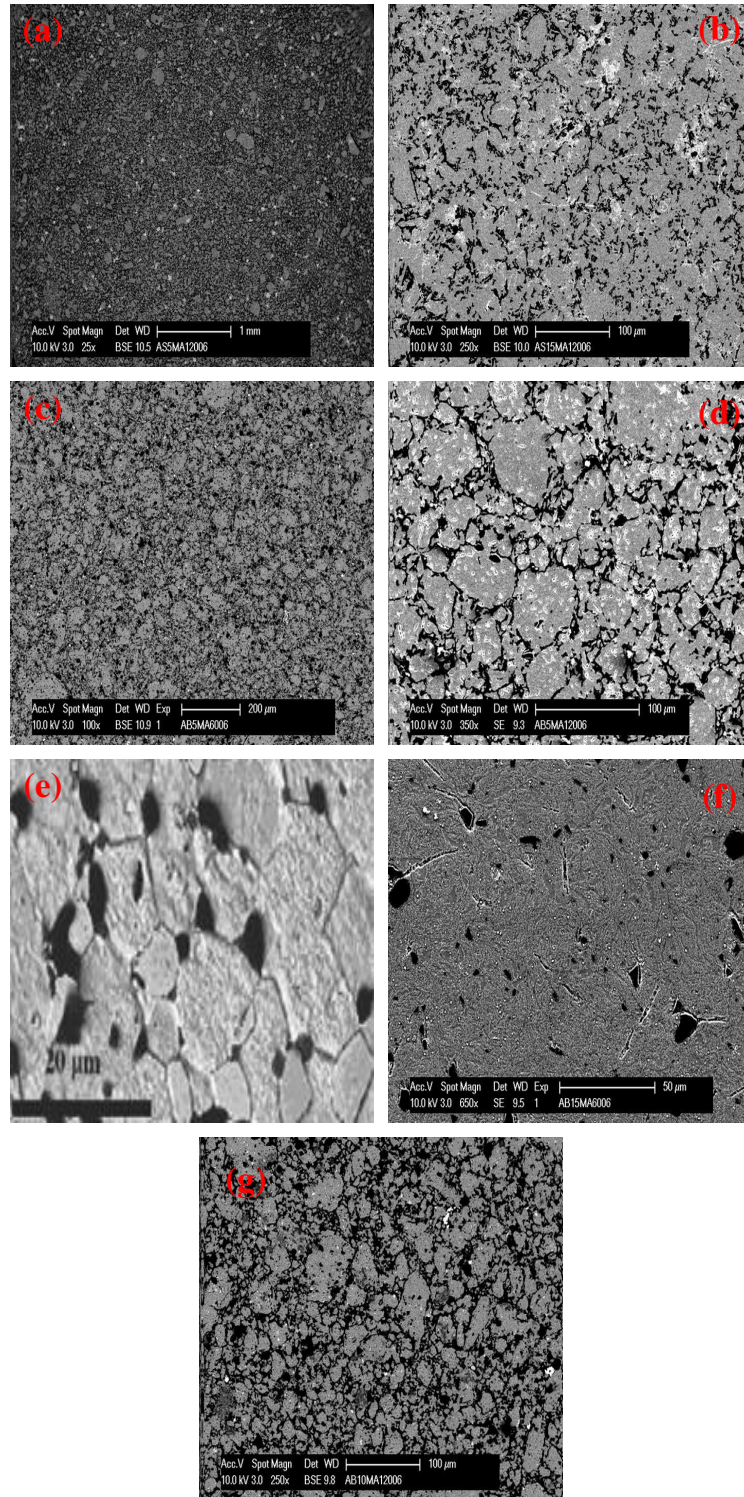


Figure 7.46: SEM micrographs of (a)AS5MA12006, (b)AS15MA12006, (c)AB5MA6006, (d)AB5MA12006, (e)AB5MA12006 (x6000), (f)AB15MA6006, (g)AB10MA12006.

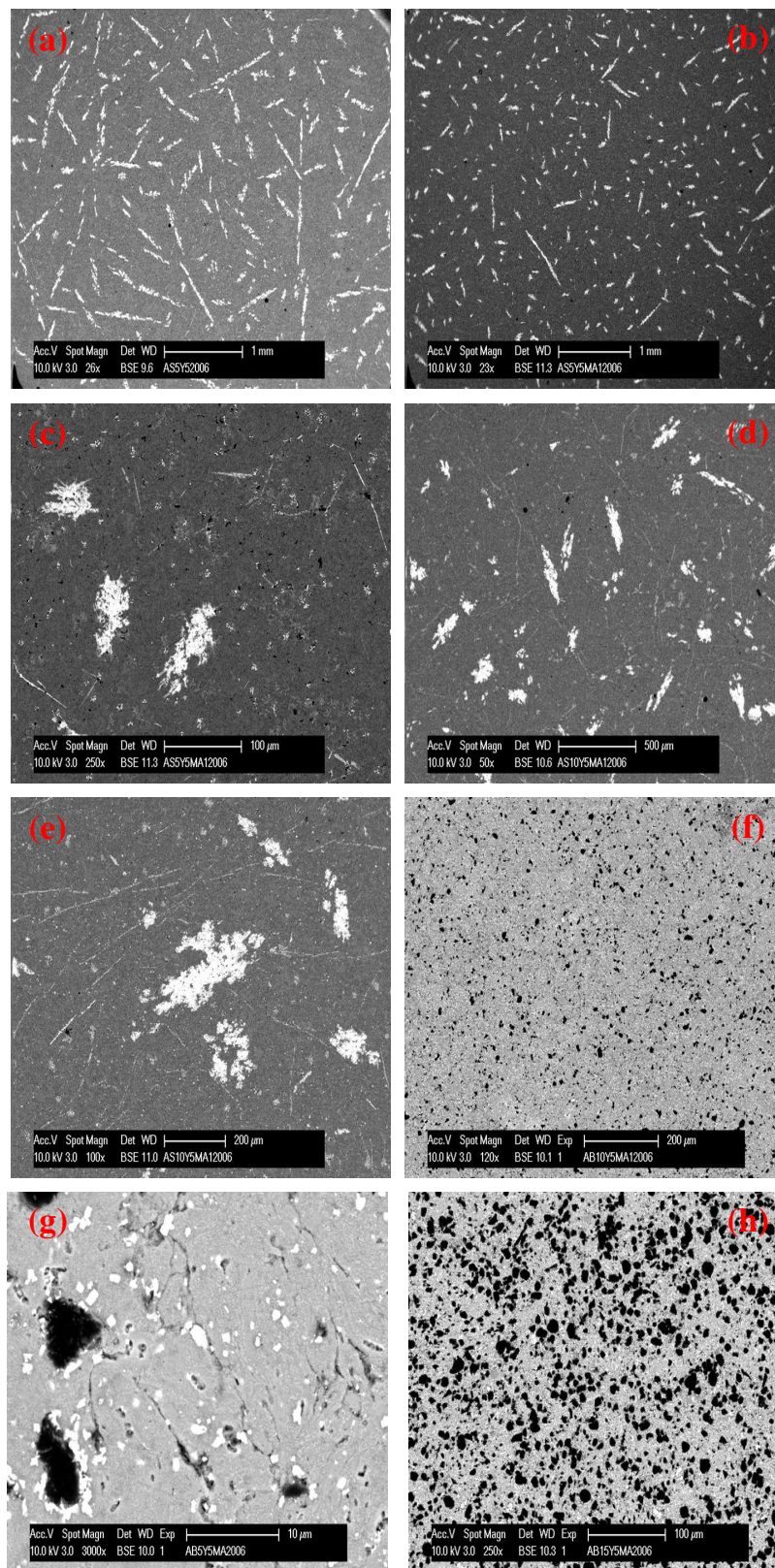


Figure 7.47: SEM micrographs of (a)AS5Y5MA2006, (b)AS5Y5MA12006, (c)AS5Y5MA12006 (x250), (d)AS10Y5MA2006, (e)AS10Y5MA2006 (x100), (f)AB10Y5MA12006, (g)AB5Y5MA2006, (h)AB15Y5MA2006.

The objective of the sintering regime at 650°C was grain growth inhibition. However, as seen in Figure 7.48a-b, in Al-SiC and Al-B₄C composites, there is a growth of the crystallites during sintering. The reason for that is believed to be that these samples did not have a sufficient starting density during the sintering regime.

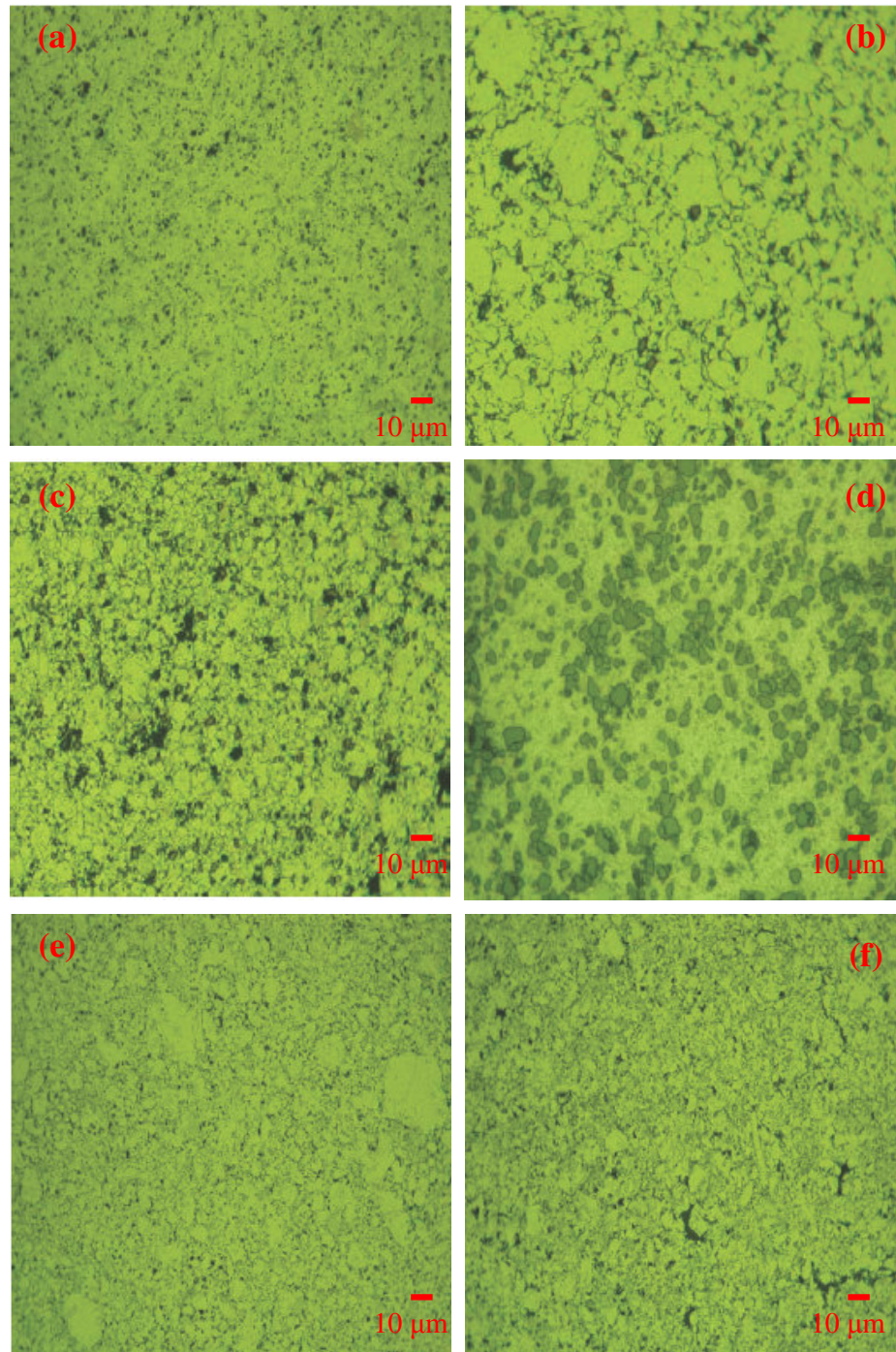


Figure 7.48a: Optical microscope images of (a)AB5MA2006, (b)AB5MA12006, (c)AB10MA8006, (d)AB15MA6006, (e)AS5MA12006, (f)AS15MA4006.

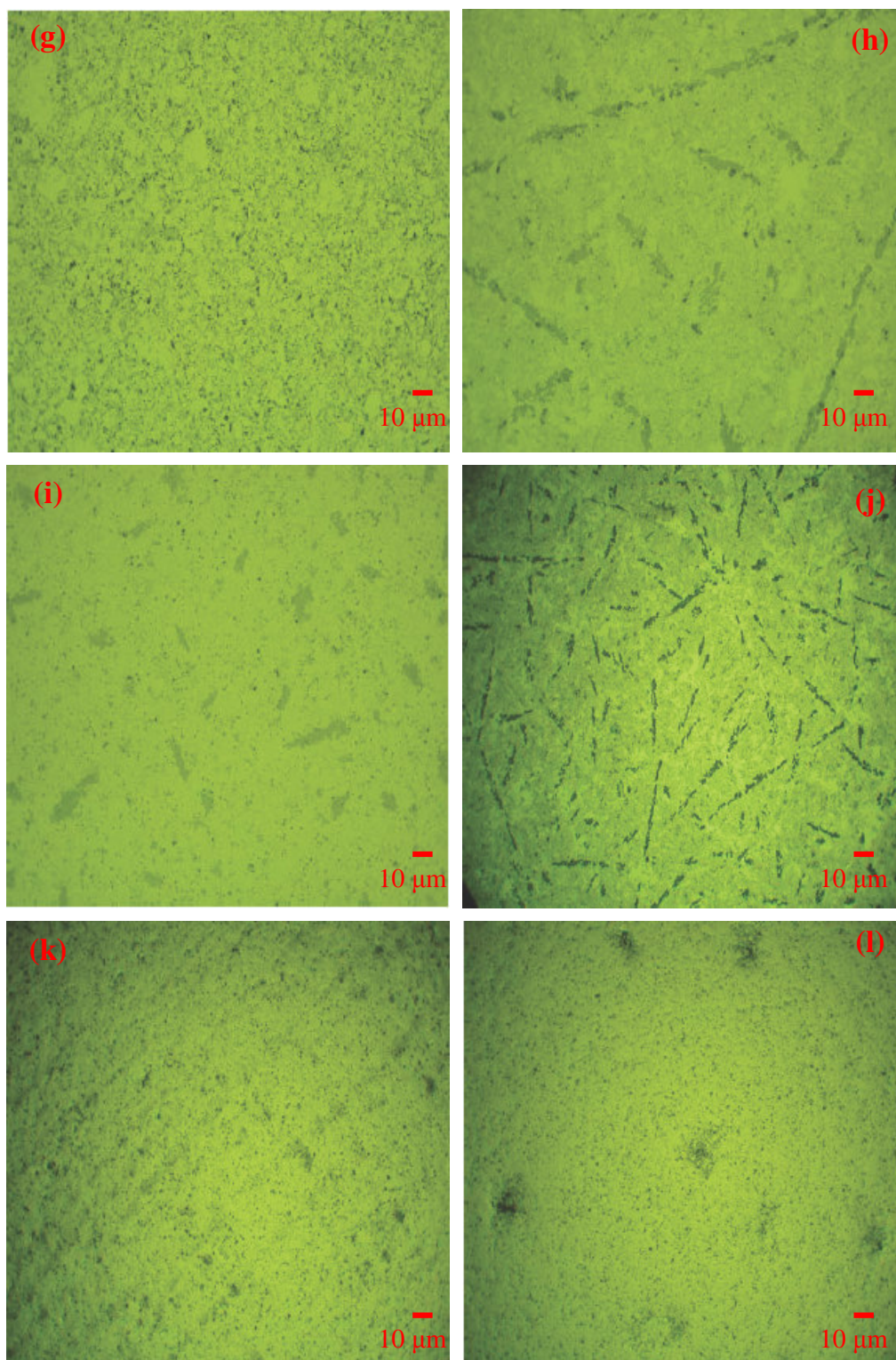


Figure 7.48b: Optical microscope images of (g)AS10MA12006, (h)AS5Y5MA2006, (i)AS5Y5MA12006, (j)AS15Y5MA12006, (k)AB15Y5MA12006, (l)AB10Y5MA12006.

Moreover, it can be stated that microstructure of Al-SiC samples was refined with increasing amount of SiC. The homogeneity of the distribution of the second phase was also improved with increasing amount of SiC. The same explanation is valid for Al-B₄C. With increasing amount of B₄C, the homogeneity of the distribution of the second phase was also improved. Furthermore, the amount and sizes of the pores were increased in all samples with wt %15 reinforcement phase. After the longest milling times, the quality of the second phases distribution is more convenient than after the first steps of milling. On the other hand, the microstructure of Al-SiC-Y₂O₃ is slightly different than others. It includes needle-like structures. Particle distribution in Al-B₄C-Y₂O₃ composites is found to be better. This is due to the fact that the addition of yttria of ceramics particles in aluminum controls the quality of sintering process. Among the four composites, Al-B₄C-Y₂O₃ system showed the strongest bonding as revealed by the good matrix/particulate adherence. No gap or micro-void is observed at the particle/matrix interface in the analysis. All the same the grain growth did not occur in this system. For Al-SiC system, the bonding seems to be weaker than that of Al-B₄C due to the relatively low adherence of matrix alloy to the particulate.

7.3.4 Mechanical properties

Because the samples were too small only the hardness tests were carried out. The Table 7.11 and 7.12 show the hardness results of the samples. Vickers hardness was obtained under a 1 kg load. For every sample, 15 indentations were done to obtain the average values and standard deviations. Hardness values are mainly consistent with SEM and XRD results. Generally, the hardness is increasing with increasing mechanical alloying, also with decreasing grain size (Figures 7.49, 7.50 and 7.51).

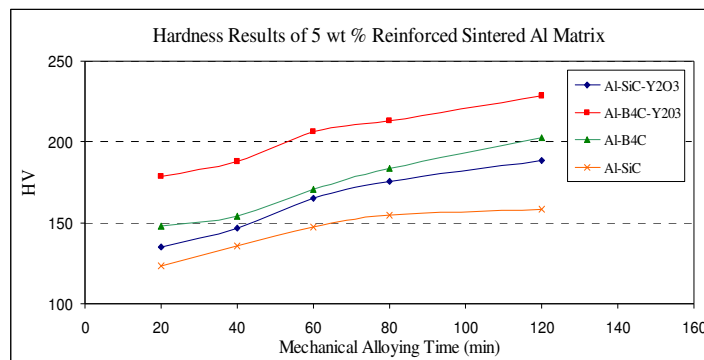


Figure 7.49: Hardness results of 5 wt % reinforced sintered Al matrix.

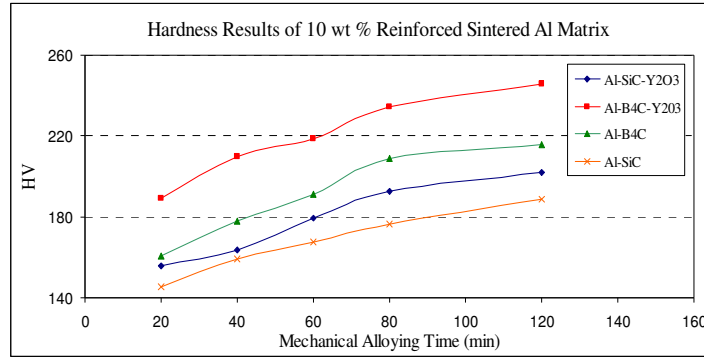


Figure 7.50: Hardness results of 10 wt % reinforced sintered Al matrix.

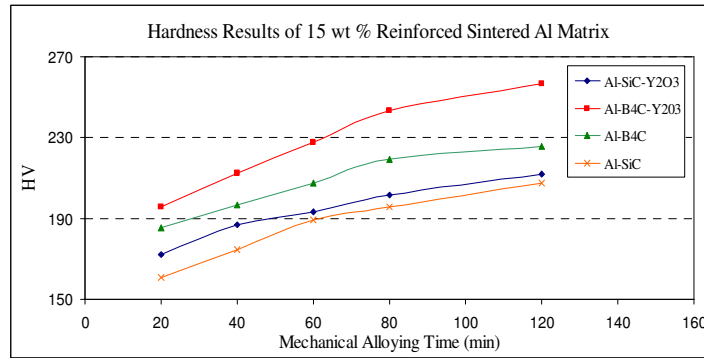


Figure 7.51: Hardness results of 15 wt % reinforced sintered Al matrix.

All the hardness values of samples containing more reinforcement materials are higher than other samples. This is the direct effect of increasing amount of SiC or B₄C. In addition, B₄C reinforced composites have higher hardness values compared to SiC reinforced composites because of higher hardness value of B₄C compared to SiC.

In some samples, there are very high standard deviations and the reason for that is that the pore and crack distributions are non-uniform, so different hardness values obtained from a region with pores and cracks and from a region without any pores and cracks increase the value of standard deviation.

Aluminum silicon carbide composites have low hardness values compared to all other samples. The reason for that is that grain sizes are larger than others. Because of uniformly distributed pores and cracks the standard deviations for these samples are low. Sintering regime is believed to be effective on grain sizes and distribution of pores and cracks.

Table 7.11: Hardness results of the sintered Al-SiC and Al-B₄C samples with standard deviations.

Sample	Hardness (HV)	Standard Deviation
AS5MA2006	123.5	±13,22
AS5MA4006	135.8	±12,72
AS5MA6006	147.4	±13,13
AS5MA8006	154.6	±23,84
AS5MA12006	158.1	±24,93
AS10MA2006	145.2	±21,69
AS10MA4006	159.4	±22,30
AS10MA6006	167.6	±32,58
AS10MA8006	176.2	±35,44
AS10MA12006	188,8	±25,79
AS15MA2006	161,0	±33,66
AS15MA4006	174.8	±34,28
AS15MA6006	189.2	±38,16
AS15MA8006	195,8	±29,73
AS15MA12006	207,4	±40,79
AB5MA2006	147.8	±31,14
AB5MA4006	154.3	±23,39
AB5MA6006	170.5	±25,77
AB5MA8006	183.7	±15,88
AB5MA12006	202.4	±19,52
AB10MA2006	160.5	±25,28
AB10MA4006	177.9	±31,72
AB10MA6006	191,2	±33,42
AB10MA8006	208,9	±28,56
AB10MA12006	215,6	±15,44
AB15MA2006	185,6	±21,96
AB15MA4006	196,5	±32,56
AB15MA6006	207,3	±28,42
AB15MA8006	219,2	±36,43
AB15MA12006	225,6	±32,55

Table 7.12: Hardness results of the sintered Al-SiC-Y₂O₃ and Al-B₄C-Y₂O₃ samples with standard deviations.

Sample	Hardness (HV)	Standard Deviation
AS5Y5MA2006	135,2	±16,28
AS5Y5MA4006	146,6	±19,95
AS5Y5MA6006	164,9	±23,52
AS5Y5MA8006	175,8	±26,92
AS5Y5MA12006	188,6	±25,6
AS10Y5MA2006	155,9	±28,13
AS10Y5MA4006	163,7	±33,9
AS10Y5MA6006	179,3	±29,25
AS10Y5MA8006	192,5	±33,14
AS10Y5MA12006	202,2	±35,15
AS15Y5MA2006	177,2	±24,9
AS15Y5MA4006	186,7	±25,3
AS15Y5MA6006	193,4	±33,4
AS15Y5MA8006	201,8	±32,9
AS15Y5MA12006	211,8	±29,32
AB5Y5MA2006	178,9	±30,99
AB5Y5MA4006	188,2	±26,7
AB5Y5MA6006	206,3	±33,4
AB5Y5MA8006	212,9	±26,76
AB5Y5MA12006	228,7	±32,98
AB10Y5MA2006	189,3	±34,5
AB10Y5MA4006	209,8	±28,9
AB10Y5MA6006	218,9	±25,7
AB10Y5MA8006	234,6	±29,66
AB10Y5MA12006	245,9	±32,1
AB15Y5MA2006	195,6	±23,46
AB15Y5MA4006	212,3	±23,92
AB15Y5MA6006	227,9	±34,12
AB15Y5MA8006	243,6	±26,99
AB15Y5MA12006	256,7	±27,22

Hardness values in Al-B₄C-Y₂O₃ composites are found to be better. This is due to the fact that the addition of yttria of ceramics particles in aluminum controls the quality of sintering process. The grain growth did not occur in this system and this effected hardness positively. The highest hardness values are obtained in Al-B₄C-Y₂O₃ system.

8. CONCLUSION

The results of this study can be discussed in two parts which are the results of powder characterization experiments and the results of characterization experiments of as-consolidated and sintered samples.

In case of powder characterization results, it can be clearly stated that the grain sizes were extremely decreased and the internal strains were increased with increasing amount of mechanical alloying according to SEM and XRD investigations. Generally, the hardness is increasing with increasing mechanical alloying, also with decreasing grain size. On the other hand, all the hardness values of samples containing more reinforcement materials are higher than other samples. This is the direct effect of increasing amount of SiC or B₄C. In addition, B₄C reinforced composites have higher hardness values compared to SiC reinforced composites because of higher hardness value of B₄C compared to SiC. However, the green densities of samples with 15 wt % SiC are slightly decreasing compared to those of with wt. %10 SiC or wt. %5 SiC. The same conclusion can be made also for B₄C containing composites. The reason is that the increased amount of SiC or B₄C phases, which are very brittle, make the compressibility of the powder difficult. Moreover, the surface tensions of the powders are increased with decreasing particle size, due to the increasing surface area. According to the XRD results of mechanical alloyed Al-B₄C powder system, AlB₂ was formed. In Al-B₄C-Y₂O₃ powder system, AlB₂, Al and Y₂O₃ phases were detected. In XRD result of Al-SiC powder system, Al₄SiC₄ and Al₄C₃ were identified. In Al-SiC-Y₂O₃ powder system, β -AlFeSi, Al, Al₄C₃ and Al₄SiC₄ phases were formed. The β -AlFeSi intermetallic is an unexpected result. Because in all systems, Fe was not used, but in XRD analyses iron-silicon-aluminum intermetallic was detected. This presence might have occurred due to the Y₂O₃ addition.

In case of as-consolidated and sintered samples, it is clear that the density is increased with increasing sintering temperatures because the diffusivity of the atoms, which is the key factor for sintering, is enhanced with increasing temperature.

Furthermore, the densities of the sintered samples containing 5 wt %, 10 wt % and 15 wt % SiC are increasing with increasing mechanical alloying just like the sintered samples containing 5 wt %, 10 wt % and 15 wt % B₄C. This is because of the mechanically activated sintering which is caused by the stored energy of the severe cold working and homogeneous distribution of matrix phase by mechanical alloying. In addition, the reason of increasing sintered densities is the small amount of Y₂O₃ phase. However, the densities of samples with wt. %15 SiC slightly change and the sintered densities are lower than those of with wt. %10 SiC or wt. %5 SiC. The same conclusion can be made also for B₄C containing composites. The reason for that is that the increased amount of SiC or B₄C phases which are very brittle make the compressibility of the powder difficult.

According to the XRD diffraction patterns of sintered aluminum-silicon carbide samples show that with increasing mechanical alloying, the intensity of Al₄SiC₄ diffraction patterns increases. Al₄SiC₄ phase is more stable after sintering. There is Al₄Si₂C₅ formation in the system. The Al₄C₃ phase is unstable at 650⁰C, so that this phase no longer exists after the sintering process. XRD diffraction patterns of sintered aluminum-boron carbide and aluminum-boron carbide-yttria samples show that increasing mechanical alloying, did not drastically effect on AlB₂ peak. There is a decrease in the height of Al peaks also. New AlB₂ peaks appeared and there is a formation of Al₃BC. XRD diffraction patterns of sintered aluminum-silicon carbide-yttria powders show that with increasing mechanical alloying, the intensities of Al₄SiC₄ and β-AlFeSi intermetallic diffraction patterns get stronger. The β-AlFeSi intermetallic is a result of iron contamination. Also, there is a decrease in the height of Al peaks and new Al and SiC peaks were formed. This is believed to be caused by the recrystallization triggered by severe plastic deformation of mechanical alloying. As a result, new strain free grains of Al and SiC have been formed.

Considering the microstructure characterizations, among the four composites, Al-B₄C-Y₂O₃ system showed the strongest bonding as revealed by the good matrix/particulate adherence after sintering. No gap or micro-void is observed at the particle/matrix interface in the analysis. All the same the grain growth did not occur in this system. For Al-SiC system, the bonding seems to be weaker than that of Al-B₄C due to the relatively low adherence of matrix alloy to the particulate.

Finally, hardness values are mainly consistent with SEM and XRD results. Generally, the hardness is increasing with increasing mechanical alloying, also with decreasing grain size. B_4C reinforced composites have higher hardness values compared to SiC reinforced composites because of higher hardness value of B_4C compared to SiC. Hardness values in Al- B_4C - Y_2O_3 composites are found to be better. This is due to the fact that the addition of yttria of ceramics particles in aluminium controls the quality of sintering process. The grain growth did not occur in this system and this effected hardness positively. The highest hardness values are obtained in Al- B_4C - Y_2O_3 system.

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BIOGRAPHY

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