PREPARATION OF IN-SITU CARBIDES REINFORCED HYBRID COPPER-BASED COMPOSITE BY MECHANICAL ALLOYING AND ITS CHARACTERIZATION

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PREPARATION OF IN-SITU CARBIDES REINFORCED HYBRID COPPER-BASED COMPOSITE BY MECHANICAL ALLOYING AND ITS CHARACTERIZATION

by

Le Minh Hai

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I declare that the content which is presented in the dissertation is my own work which was done at University Science Malaysia unless informed otherwise. The dissertation has not been previously summated for any other degree.

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Penyediaan komposit hibrid berasas kuprum diperkuat karbida in situ secara pengaloian mekanikaldan pencirian

ABSTRAK

Matlamat utama kajian ini adalah untuk menyiasat kemungkinan penghasilan dua jenis karbida (NbC dan TiC) serentak di dalam matrik kuprum melalui pengaloian mekanikal dan metalurgi serbuk daripada serbuk unsur seperti Cu, Nb, Ti dan grafit. Tiga campuran bahan mula berdasarkan kepada komposisi Cu-10vol.%NbC-10vol.%TiC, Cu-15vol.%NbC-15vol.%TiC dan Cu-20vol.%NbC-20vol.%TiC telah dialoikan secara mekanikal dengan menggunakan planetary kempaan bebola selama 5, 10, 20 dan 30 jam. Serbuk yang diperolehi dimanpatkan pada tekanan di antara 500-1000MPa dan disinter di dalam relau vakum selama satu jam pada suhu di antara 700-1000^{o}C. Keputusan pembelauan sinar-X dan mikroskop imbasan elektron menunjukkan bahawa fasa-fasa NbC dan TiC termendak di dalam serbuk yg dikisar selama 10 jam dan mencapai pecahan isipadu maksimum pada 20 jam tempoh pengisaran. Pelanjutan tempoh pengisaran telah meningkatkan ketumpatan dan mikrokekerasan bagi komposit hibrid kuprum yang telah disinter disertai dengan pengurangan dalam kekonduksian elektriknya disebabkan oleh saiz butir yang halus dan peningkatan terhadap terikan dalaman semasa proses pengaloian mekanikal. Ketumpatan, mikrokekerasan dan kekonduksian elektrik komposit Cu-TiC-NbC meningkat dengan peningkatan tekanan penekanan serbuk hasil daripada penurunan nilai keliangan. Peningkatan suhu pensinteran juga membawa kepada peningkatan dalam ketumpatan dan kekonduksian elektrik bagi komposit ini. Bagaimanapun, penurunan dalam mikro kekerasan diperhatikan hasil daripada kadar penghabluran yang tinggi dan penyingkiran kehelan pada suhu pensinteran yang lebih tinggi. Peningkatan terhadap kandungan karbida pula memberikan peningkatan dalam mikro kekuatan dan penurunan dalam kekonduksian elektrik. Pembolehubah proses yang paling optimum adalah pada tempoh pengisaran 20 jam dengan kelajuan 400 rpm, tekanan pemejalan 800 MPa dan suhu pensinteran 900^{o}C selama satu jam kerana telah menghasilkan komposit Cu-TiC-NbC dengan mikrokekerasan dan kekonduksian elektrik yang tinggi.

Preparation of in-situ carbides reinforced hybrid copper-based composite by mechanical alloying and its characterization

ABSTRACT

The goal of this research work is to investigate the feasibility of the synthesis of two distinct in-situ carbides (NbC and TiC) simultaneously in a copper matrix via mechanical alloying and powder metallurgy from elemental powders of Cu, Nb, Ti and graphite. Three mixtures of starting powders with compositions corresponding to Cu-10vol.%NbC-10vol.%TiC, Cu-15vol.%NbC-15vol.%TiC and Cu-20vol.%NbC-20vol.%TiC were mechanical alloyed using a planetary ball mill for 5, 10, 20 and 30 hours. The as-milled powders then were cold pressed at compaction pressure in range of 500-1000 MPa and sintered in a vacuum sintering furnace for 1 hour at different temperatures from 700 to 1000^{o}C. The results of X-ray diffraction, energy dispersive X-ray analysis and scanning electron microscopy showed that the NbC and TiC phases were co-precipitated after 10 hours of milling and reached maximum volume fraction after 20 hours. Extension of milling time increased the density and microhardness of the sintered composite with a decreasing in electrical conductivity because of the refinement of the grain size and the increase of internal strain during the MA process. Density, microhardness and electrical conductivity of the sintered composite increased with increasing compaction pressure due to better powder packing which led to decreasing porosity. Higher sintering temperature led to an increase in density and electrical conductivity of the bulk composite with a decrease in microhardness as a result of higher rate of recrystallization and the elimination of dislocation at higher sintering temperature. Increasing carbide content resulted in an increase in microhardness and a decrease in electrical conductivity of in-situ Cu-NbC-TiC composite. The optimum processing parameters to produce Cu-15vol.%NbC-15vol.%TiC composite with high microhardness and electrical conductivity are 20 hours of milling time at a speed of 400 rpm, 800 MPa of compaction pressure and 900^{o}C of sintering temperature for 1 hour.

1 CHAPTER 1

INTRODUCTION

1.1 Introduction

The aim of fabricating copper-based composites reinforced with dispersed ceramic particles is to enhance the mechanical properties of copper, such as their specific strength and good mechanical properties at elevated temperatures, whist still maintaining their high electrical and thermal conductivities (Takahashi and Hashimoto, 1992; Botcharova *et al.*, 2003; Marques *et al.*, 2005; Liu *et al.*, 2008; Marques *et al.*, 2008; Sheibani *et al.*, 2009).

Presently, copper based composites can be fabricated using two main routes which are ex-situ and in-situ processes. In the ex-situ process, the dispersed reinforcing phase is prepared separately and then embedded in the copper matrix using powder metallurgy, casting or pressure infiltration techniques. However, the coarse size of the reinforced particles and the difficulties of achieving strong interfacial reinforcement-matrix bonding limit the improvement in the mechanical and physical properties of the copper-based composite. On the other hand, in the in-situ synthesis technique, the reinforcing ceramic phases are synthesized in the metallic matrix by a chemical reaction during composite fabrication. Consequently, the in-situ routes introduce significant advantages over ex-situ techniques, notably the fine, well-distributed and thermodynamically stable reinforcing phases (Froyen and Wildle, 2003), which considerably enhance the properties of the composites. Zuhailawati *et al.* (2009) produced Cu-NbC composites by both ex-situ and in-situ processes and the characterizations revealed that the microhardness and the electrical conductivity of in-situ Cu-NbC composite surpass those of the ex-situ composite.

Mechanical alloying (MA) is a potential powder metallurgical route for preparing in- situ ceramic particle-reinforced metal matrix composites (MMCs) from a mixture of starting elemental powders by high energy ball-milling. The greatest advantage of this route is it is able to develop nanostructured materials such as nanocomposites (Froyen and Wildle, 2003). For example, Krasnowski *et al.* (2002) have produced FeAl–30%TiC nanocomposite by mechanical alloying and hot-pressing consolidation from pure elemental Fe, Al, Ti, and C powders. Nanocomposite materials provide the possibility for enhanced functionality and multifunctional properties in contrast with their more limited single component counterparts (Hanif *et al.*, 2002).

1.2 Problem statements

Although many papers have reported the synthesis of in-situ copper-based composites reinforced by carbide particles, most of them have focused on the synthesis of one certain kind of carbides (Takahashi and Hashimoto, 1992; Botcharova *et al.*, 2003; Marques *et al.*, 2005; Marques *et al.*, 2008; Zuhailawati *et al.*, 2008). Zuhailawati *et al.* (2008) have successfully synthesized in-situ NbC-reinforced copper-based composite by mechanical alloying with subsequent heat treatment at $900^{o}C$ for 1 hour. It is interesting to investigate whether two distinct in-situ carbides could be synthesized simultaneously in a copper matrix and how microstructure and properties of such hybrid composite are correlated. To date, only Takahashi and Hashimoto (1992) have synthesized hybrid in-situ copper composite reinforced by two different kinds of carbides which are NbC and TaC. On the other hand, there are limited papers reported on the effect of consolidation process including compaction and sintering on the properties of bulk in-situ copper-based composites prepared by mechanical alloying and powder metallurgy route.

1.3 Objectives

The primary objectives of this work are:

1. To investigate the feasibility of the formation of two distinct in-situ carbides (NbC and TiC) simultaneously in a copper matrix via mechanical alloying and powder metallurgy.
2. To study the effect of milling time and sintering temperature on the formation of NbC and TiC in Cu-Nb-Ti-C systems and the properties of bulk Cu-NbC-TiC composite.
3. To study the effects of compaction pressure and carbides content on the properties of the bulk Cu-NbC-TiC composite.

1.4 Research Scope

In the present investigation, a hybrid in-situ copper nanocomposite reinforced with 15vol.%NbC-15vol.%TiC was synthesized by mechanical alloying. The milling time was varied to investigate both the formation of niobium and titanium carbides during mechanical alloying and the changes in properties, such as density, microhardness and electrical conductivity, of the sintered in-situ Cu-TiC-NbC composites.

Secondly, the present work studied the effects of consolidation parameters on the properties of the in-situ Cu-NbC-TiC composite. The compaction pressure, sintering temperature and carbides content were varied to investigate the changes in properties, such as density, microhardness and electrical conductivity, of the sintered in-situ Cu-TiC-NbC composites.

2 CHAPTER 2

LITERATURE REVIEW

2.1 Composite Materials

Our modern technologies require materials with unusual combinations of properties that cannot be met by the conventional metal alloys, ceramics and polymeric materials. This is especially true for materials that are needed for aerospace, underwater and transportation applications. Materials property combinations and ranges have been, and are yet being, extended by the development of composite materials. In designing composite materials, scientists and engineers have combined various metals, ceramics, and polymers to produce a new generation of extraordinary materials. In the broad sense the word “composite” means “made of two or more different parts” (Berthelot, 1999). One is termed as matrix, which is continuous and surrounds the other phase, often called the dispersed phase. In addition, the constituent phases must be chemically dissimilar and separated by a distinct interface. The properties of the composites are a function of the properties of the constituent phases, their relative amount, and the geometry of the dispersed phase (Callister, 2000).

2.1.1 Introduction to Metal Matrix Composites

Metal Matrix Composites (MMC) is a kind of composite materials in which a continuous metallic phase (the matrix) is combined with another phase (the reinforcement). These innovative materials open up unlimited possibilities for modern material science and development; the characteristics of MMCs can be designed into the material, custom-made, depending on the application. Thus, metal matrix composites potentially fulfill all the desired conceptions of the designer. This material group becomes interesting for use as constructional and functional materials.

Reinforcement for MMCs has a manifold demand profile, which is determined by production and processing, and by the matrix system of the composite material. The possibility of combining various material systems (metal – ceramic – non-metal) gives opportunity for unlimited variation. MMCs combine metallic properties (ductility and toughness) with ceramic characteristics (high strength and modulus), leading to greater strength to shear and compression and to higher service temperature capability. The properties of these new materials are basically determined by the properties of their single components. The reinforcement of metals can have different objectives. For example, for light materials the objectives are to increase in yield and tensile strength, creep resistance at higher temperature and so on (Kainer *et al*., 2006).

With functional materials there is another aim, the precondition of maintaining the appropriate function of the materials. The objectives are, for example, to increase in strength of conducting materials while maintaining the high conductivity, improvement in low temperature creep resistance and improvement of wear behaviour. For other applications, different development objectives are given. For example, in medical technology, mechanical properties, like extreme corrosion resistance and low degradation as well as bio-compability are expected.

Metal matrix composites (MMCs) are recently under attention for many applications in many areas of daily life. The examples are carbides-reinforced metals for machining of materials in product engineering, noble metal composite systems for contacts in electronics and electro-technology, copper-graphite sliding contacts for generators and electric motors and multi-compound systems for brake linings in high speed brakes.

2.1.2 Classification of Metal Matrix Composites

Metal matrix composites can be classified by the form of the components or by their nature. As a function of the form of the reinforcement, metal matrix composites are generally divided into three types: particle-reinforced, fibre-reinforced and structural composites. This classification is shown in Figure 2.1.

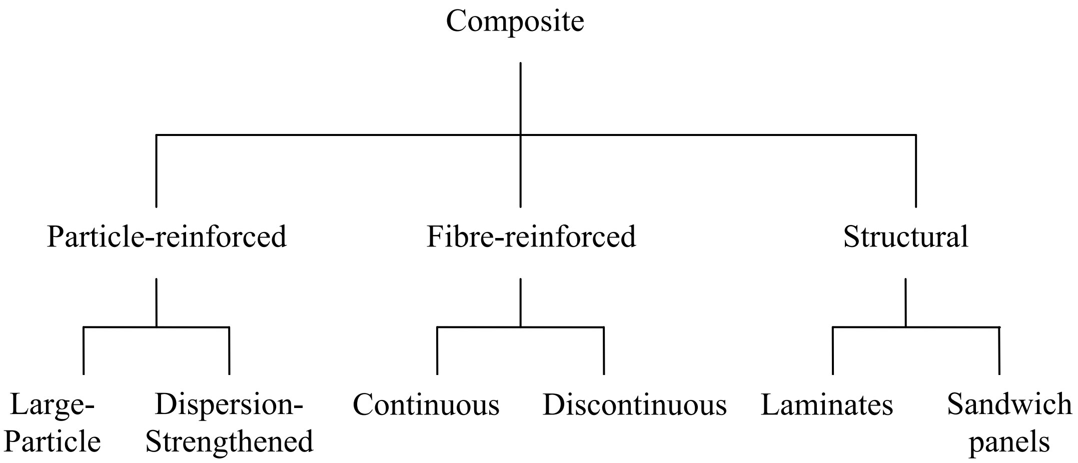

Figure 2.1 Scheme of classification of composites (Callister, 2003)

2.1.2.1 Particle-reinforced composites

Particle-reinforced composite is a kind of composite where the reinforcement is made of particles. Particles are generally used to improve certain properties of materials or matrices, such as stiffness, temperature behavior, resistance to abrasion and decrease of shrinkage. In some cases, particles are simply used as filler to reduce the cost of material without degrading the characteristics.

The choice of the particle-matrix combination depends upon the desired properties. In most cases, the particulate phase is harder and stiffer than the matrix. For example, particles of brittle ceramic materials incorporated in ductile metals improve their mechanical properties at higher temperatures whilst preserving their properties at room temperatures. A large number of different oxides, carbides, nitrides and borides are suitable for reinforcement.

On the other hand, the properties of particle-reinforced composite are mainly dependent on the composition and the microstructure of the matrix, shape and volume content of reinforcement and matrix-reinforcement interface. Usually, small particles with size in the range of 10-1000 nm are used.

Wanga *et al.* (2004) studied the influence of volume fraction of particulate reinforcement TiB_2 on the properties of magnesium based composite. In this research, the magnesium based composites reinforced with 10, 20 and 30 %vol. TiB_2 particulates fabricated by powder metallurgy introduced an increase in hardness (HB) values by 41%, 106% and 181%, respectively as compared with pure Mg. The abrasive wear tests also showed that the wear resistance of this composite was increased with an increase of the reinforcement volume fraction. In addition, Liu *et al.* (1998) observed that with the same volume fraction of reinforcement, stainless steel-based composites reinforced with TiN show higher ductility and toughness with narrower particle-size distribution and larger mean particle size of reinforcement.

2.1.2.2 Fibre-reinforced composites

A composite is a fibre-reinforced composite if the reinforcement is in the form of fibres. The fibres used are either continuous or discontinuous in form of flakes, whiskers, chopped fibres or short fibres (Fridlyander, 1995).

The arrangement of the fibres and their orientation (Figure 2.2) allow us to tailor the mechanical properties of composites to obtain materials ranging from strongly anisotropic to isotropic in one plane. The physical properties and behavior of the composite is tailored by adjusting the nature of the constituent, the proportions of the constituents and the orientation of the fibres according to the performances required.

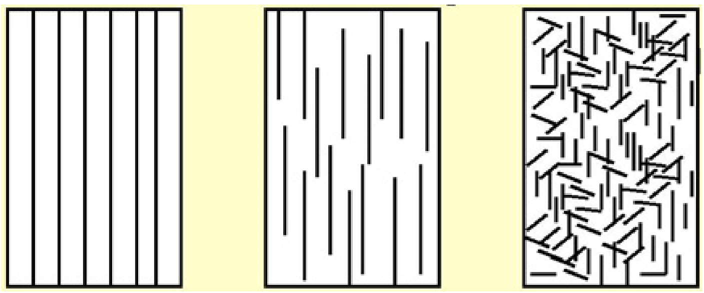

Figure 2.2 Fibre orientations in fibre-reinforced composites, (a) continuous and aligned fibres, (b) discontinuous and aligned fibres, (c) discontinuous and randomly oriented fibres (Callister, 2003)

The basic requirements of fibre reinforcements are high strength and high modulus of elasticity in combination with low density, which determines their high specific values of strength and rigidity. In addition, the melting temperature of the fibres should be higher than that of the matrix alloy and the fibre have to maintain their properties at elevated temperature. The most widely used are fibres of boron, silicon carbide, carbon, oxide, metal wire and whisker (Chawla, 1998).

2.1.2.3 Structural Composites

A structural composite is normally composed of both homogenous layers and cores, the properties of which depend not only on the properties of the constituent materials but also on the geometrical design of the various structural elements. Laminar and sandwich panels are two of the most common structural composites (Callister, 2003).

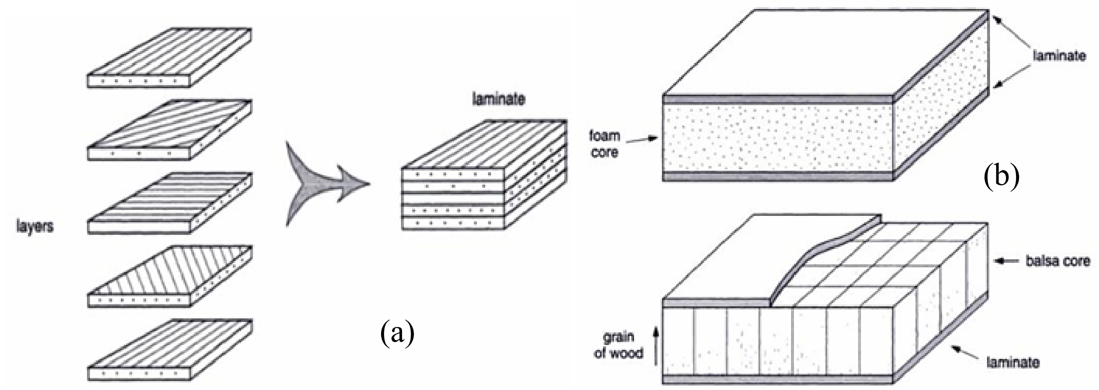

Figure 2.3 (a) Constitution of a laminate, (b) Sandwich composite with solid core (Berthelot, 1999)

Laminar composites (Figure 2.3 a) are composed of two-dimensional sheets that have preferred high strength direction. The layers are stacked and subsequently cemented together such that the orientation of the high-strength direction varies with successive layer. Thus a laminar has relatively high strength in a number of directions in the two-dimensional plane. On the other hand, sandwich panels (Figure 2.3 b) consist of two strong outer sheets separated by a layer of less-dense materials or core. Various materials and structures are utilized such as foam materials. Figure 2.4 shows a multi-layered Al/Cu composites produced by accumulative roll bonding (ARB) process using Al 1100and Cu strips (Eizadjou *et al.*, 2008).

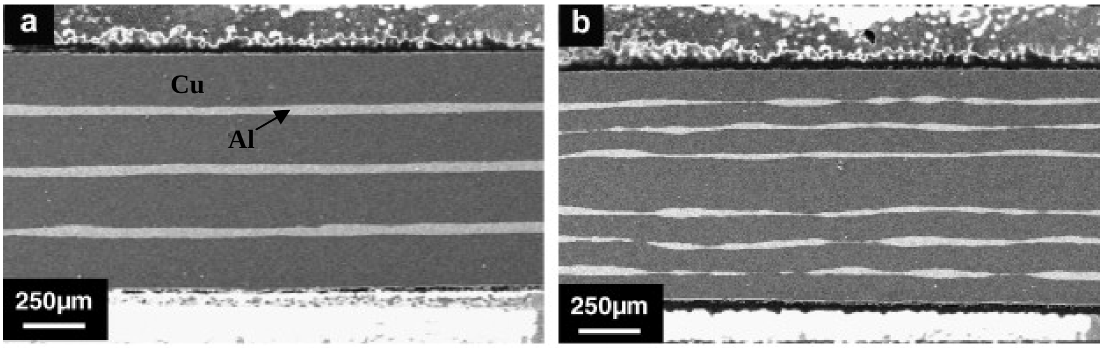

Figure 2.4 SEM micrograph of laminar Al/Cu composite cross sections (a) primary sandwich, (b) 1st cycle (Eizadjou et al., 2008)

2.1.3 Fabrication Methods of Metal Matrix Composites

Many processes exist for fabricating metal matrix composites. For the most part, these processes involve processing in the liquid and solid state. Some processes may involve a variety of deposition techniques or an in-situ process of incorporating reinforcement phases.

2.1.3.1 Solid State Processing

Solid state processing involves bringing the particles or foils into close contact with the reinforcement, with the application of a suitable combination of temperature and pressure (Matthews, 1994).

The method of using foils as a form of starting materials is usually called diffusion bonding as shown in Figure 2.5. The first stage in diffusion bonding is to sandwich a fibre mat, which has the fibres held in place by a polymer binder, between two sheets of foil to form a ply. In some cases, this is followed by consolidation of the ply. The plies are cut and stacked in the required sequence. After that, the stack is hot pressed in a die to form the component.

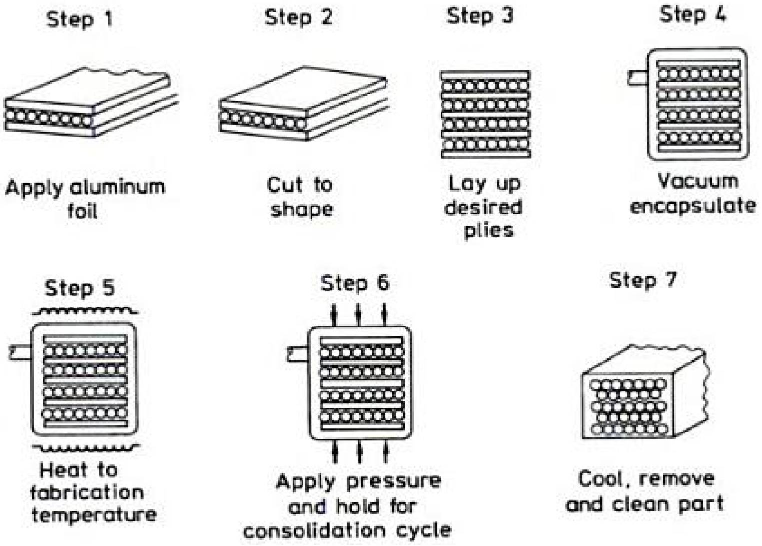

Figure 2.5 Schematic diagram of diffusion bonding technique (Chawla, 1998)

When the starting materials used are in form of powders, the technique is referred to as powder metallurgy. Powder metallurgy is especially suited for production of discontinuous fibre, whisker and particulate reinforced metal. The mixture of powders are compacted into a desired shape and then sintered to form the solid pieces. The mixing stage is critical to produce a homogeneous mixture with good properties. Clean conditions are required because large surface area of the particles leads to contamination. Several mechanical methods can be used for pressing such as forging, extrusion and rolling (Matthews, 1994).

2.1.3.2 Liquid State Processing

Metals with melting temperatures that are not too high can be incorporated easily as a matrix by liquid routes (Chawla, 1998).

Casting adapted from the conventional technique was used to fabricate metal composite. The main problems of this technique are non-wetting of the reinforcement and adverse matrix-reinforcement reactions due to the high temperature involved (Matthews, 1994). Various approaches are being pursued to overcome these problems such as adding an additive substance to improve wettability between the matrix and the reinforcement and applying melt stirring method. In recent years, many researchers used external pressure during processing: spontaneous infiltration, squeeze casting (Figure 2.6), and gas pressure infiltration.

In Daoud's work (2004), a 2014 Al alloy was used as a matrix to fill in fibres preform Ni-coated continuous carbon fibre. The processing of the composite was carried out by gas pressure infiltration method. It was observed that the fibres were uniformly distributed in the aluminum alloy matrix and there is no sign of fibre cluster or residual porosity. In Onat study (2009), Al–4.5Cu–3Mg/15 vol.% SiCp matrix composites were manufactured by direct squeeze casting technique. The results showed that the composites have homogeneously distributed porosity free SiC particles and good bonding between matrix and particles

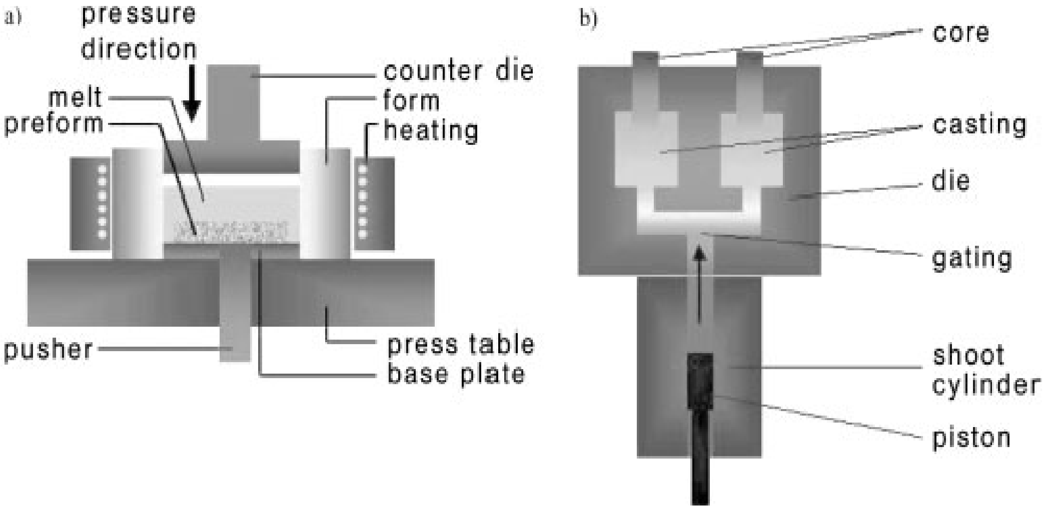

Figure 2.6 Direct and indirect squeeze casting (Kainer *et al.*, 2006)

The metal matrix composites reinforced by fibres also can be fabricated by either high-pressure or low-pressure infiltration process. According to Peng *et al.*, (2004), high-volume-fraction of Si_3N_4–Al-based composite has been fabricated by high-pressure casting method. Ceramic–metal composites were fabricated by infiltrating the molten Al alloys into the porous preform using a vertical type, high-pressure casting machine. The ceramic preforms were preheated to 800°C and positioned within the mold cavity, which was preheated to 300°C. The matrix alloy, heated to 800°C, was poured into the mold cavity, and pressure of 85 MPa was applied to the casting during solidification. The cast composite samples were then subjected to a heat treatment at 500^oC.

2.1.3.3 Deposition Processing

A deposition process which has considerable potential is spray co-deposition (Figure 2.7) which involves atomizing a melt and introducing the reinforcement particle into the spray of fine metal droplets. The metal and the reinforcement particles are then co-deposited on the substrate. The atomized exists as discrete droplets for a short time, of the order of a few milliseconds, and the rapid solidification leads to a matrix with a fine microstructure and reduces of possibility of extensive chemical reaction (Matthews, 1994).

Many other deposition techniques have been tried in fabrication of MMCs, such as chemical and physical deposition, sputtering and plasma spraying. An attractive feature of some of these techniques is that they operate at low temperature, therefore reactions at the reinforcement-fibre interface is minimized.

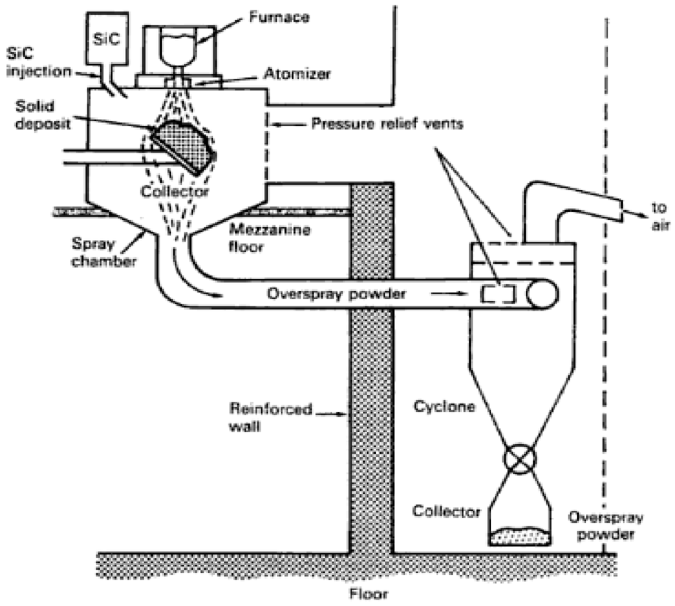

Figure 2.7 Diagram of spray co-deposition production of SiC particulate reinforced metal (Matthews, 1994)

In Srivastava *et al.* study (2005), aluminium alloy (2014-Al alloy)-based metal matrix composites containing SiC$_P$ particulates were produced by spray co-deposition. Optical microscopy showed a uniform distribution of SiC particulates in the aluminium alloy matrix. Smaller size particles were pushed towards the grain boundaries during solidification of the deposit, in contrast to their large size counterparts. The matrix grain size varies from 15 to 50 µm with a variation in the size and content of the reinforcement particles.

2.1.3.4 In-situ Processing

Traditionally, discontinuously reinforced MMCs have been produced by several processing routes such as powder metallurgy, spray deposition, mechanical alloying and various casting techniques. All these techniques are based on the addition of ceramic reinforcements to the matrix materials, which may be in molten or powder form. The reinforcing phases are prepared separately prior to the composite fabrication. Thus, conventional methods can be viewed as ex-situ MMCs. In this case, the scale of the reinforcing phase is limited by the starting powder size (rarely below 1 µm). Other drawbacks are reinforcement-matrix interfacial reactions and poor wettability between the reinforcement and the matrix due to surface structure as well as contamination (Ajayan *et al*., 2003).

In-situ synthesis or reactive processing offers interesting ways to produce intermetallics or metal matrix composite by powder metallurgy or casting (Froyen and Wilde, 2003). In-situ composite material is a material class which uses the reactions of different components during the production to produce new components. The reaction between components can happen during mixing or in the subsequent process. A minimum energy must first be introduced to get the reaction going. This can take place, for example, with the thermal energy of hot pressing, with subsequent thermal heat-treatment, or by high kinetic energy of mechanical alloying (Kainer, 2006).

In-situ composites possess a number of advantages as compared to ex-situ composites, i.e. thermodynamical stability of the reinforcing phases, clean particle-matrix interfaces with improved wettability, finer reinforcing particle size, more uniform particle distribution, no difficulties or safety risks in handling fine reinforcing particles, and good mechanical characterization (Froyen and Wilde, 2003; Krasnowski and Kulik, 2008; Xiuquing *et al*., 2007).

In Zuhailawati *et al*. study (2008), the Cu-NbC composites were produced by both ex-situ and in-situ processes and their characterization revealed that the microhardness and the electrical conductivity of in situ Cu-NbC composite surpassed those of ex situ composite.

Mechanical alloying and reactive milling are powder metallurgical routes for preparing composite powders from a mixture of starting powders by high energy ball milling. In-situ MMCs can be successfully produced by MA plus subsequent eventually heat-treatment (Froyen and Wilde, 2003). Using these routes, in-situ composites with a wide range of matrix materials (including Al, Cu, Mg, Ti, Ni and Fe) and second-phase particles (including borides, carbides, nitrides and oxides) have been produced. An example is the synthesis of in-situ TiC/Fe composites (Figure 2.8) through ball-milling a mixture of pure Fe, Ti and graphite powders followed by subsequent sintering process (Jing and Jisan, 2007).

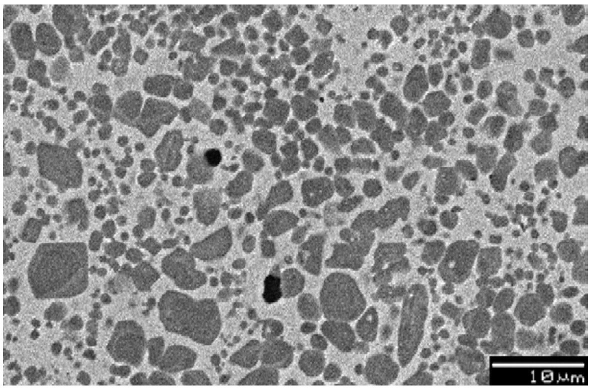

Figure 2.8 Microstructure of Fe-TiC composite sintered at 1420°C (Jing and Jisan, 2007)

2.1.4 Metal Matrix Nanocomposites

Nano-sized materials now emerged as one of the focal points of modern research. Nanomaterials have received much attention because they are expected to be used in various applications based on their excellent and optical, electrical magnetic, catalytic, biological, or mechanical properties (Botcharova *et al.*, 2006).

The field of nanocomposites involves in the study of multiphase material where at least one of the constituent phases has one dimension less than 100nm. The common processes used to synthesize metal matrix nanocomposites are mechanical alloying, sol-gel synthesis and thermal spray synthesis (Ajayan *et al.*, 2003).

In the last few years, the synthesis of nanocrystalline alloys, intermetallic compounds and nanocomposite by mechanical alloying has been successfully achieved (Hamzaoui *et al.*, 2004; Krasnowski and Kulik, 2008; Zheng *et al.*, 2008). In Krasnowski and Kulik's work (2008), the nanocomposites powders with Fe(Al) solid solution matrix reinforced by TiC carbide were produced through mechanical alloying. The final products were nanocrystallite, with the estimated mean crystallite size in range of 8-15 nm. Another example is the synthesis of NiAl-30vol.% Al_2O_3 nanocomposite (Figure 2.9) from the NiO–Al–Ni powder mixture by carrying out reactive milling subsequent heat-treatment. After heating to 1120 °C, the 20 h milled powder consists of nanocrystalline NiAl phase and α-Al_2O_3 with a crystallite size of 115 ± 40 nm size and 11 ± 3 nm, respectively (Udhayabanu *et al.*, 2009).

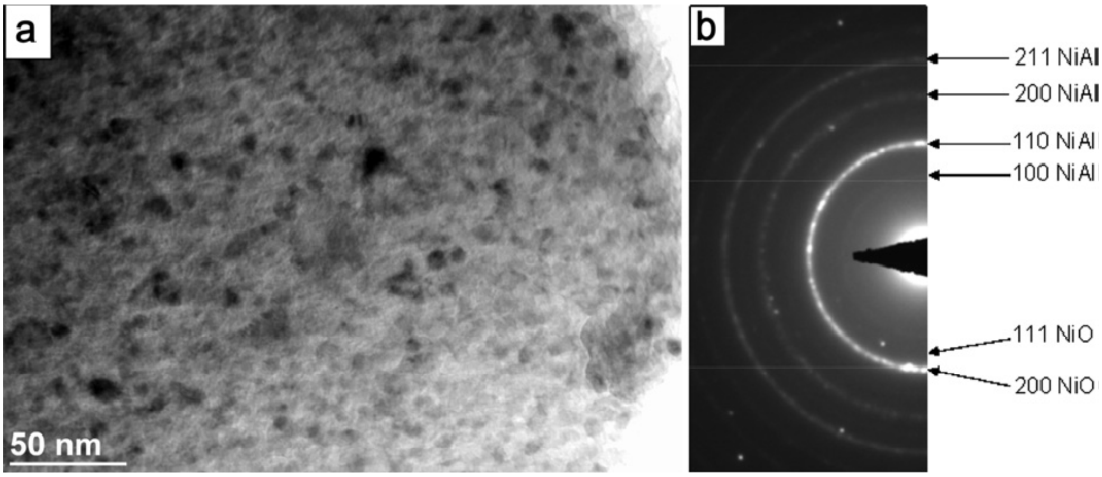

Figure 2.9 TEM micrographs of as milled NiO–Al–Ni powder mixture corresponding to NiAl-30 vol.%Al_2O_3 composition (a) bright field image, (b) selected area diffraction pattern (Udhayabanu *et al.*, 2009)

2.2 An overview of in-situ copper composites reinforced by ceramic particles

Whenever electrical and thermal conductivities are important for the application in mind, copper is the most common metal used, as it shows high conductivity and is, at the same time, cost-effective. However, since copper presents very low strength, it must be strengthened. Dispersion strengthening of copper with fine ceramic particles has long been considered as an ideal method for preparing materials with good high-temperature strength and high conductivity (Marques *et al.*, 2005).

MA route has successfully produced in-situ nanostructured copper based composites reinforced by ceramic particles such as oxide (Sheibani *et al.*, 2009; Ying and Zhang, 2000), nitride (Chi *et al.*, 1995), boride (Biselli *et al.,* 1994) and carbides (Takahashi and Hashimoto, 1991; Marques *et al.*, 2005, 2007; Hussain *et al.*, 2007; Zuhailawati and Mahani, 2008; Zuhailawati *et al.*, 2010). Additional heat treatment is usually required to promote the formation of fine particles of reinforcement phases.

Biselli *et al.* (1994) have prepared the in-situ TiB_2 particle reinforced copper composites by means of mechanical alloying techniques, followed by suitable heat treatments. They reported that the reaction between Ti and B does not occur during milling, but instead takes place during annealing for short time periods at temperatures of 600-800^{o}C.

Sheibani *et al.* (2009) have fabricated Cu-50wt.%MnO nanocomposite powder by combustion reaction between CuO and Mn induced by high energy ball milling. It was observed that the combustion reaction ignited after about 45 min and with continuing mechanical milling, the MnO was formed in the nanocrystalline Cu matrix. Also, Cu–MnO nanocomposite powder after 60 min milling had relatively equiaxed shape with uniformly distributed MnO phase in Cu matrix. The mean crystallite size of the Cu matrix was about 43 nm.

So far, there have been few articles about fabrication of in-situ copper based composites reinforced by NbC and even fewer in case of in-situ Cu-TiC. The first fabrication of in-situ copper composite reinforced by NbC has been reported by Takahashi and Hashimoto (1992). In their study the copper alloys reinforced with in-situ NbC particles have been synthesized by mechanical alloying. The in situ formation of the carbide phases was not observed in the as-milled powder but only after appropriate heat-treatment in the temperature range 600-1100^{o}C.

However, Marques *et al.* (2005) have produced in-situ copper-niobium carbide (Cu-NbC) nanocomposites via mechanical alloying without additional heat-treatment. The authors observed that relatively short milling time (less than 20 hours) is sufficient to form NbC nanoparticles in a copper matrix. Their result showed that the NbC phase starts to form in the early stages of milling, after 1 hour. The maximum volume fraction of niobium carbide in copper matrix is achieved after 8 hours of milling

Recently, Mahani (2008) has observed NbC phase in as-milled Cu-Nb-C in situ powders after 32 hours of milling from XRD pattern. The peaks of NbC appear, however, in low intensities meaning that only a small volume of NbC phase formed in the copper matrix at this time. The peak intensities of NbC become much more intense and well defined after subsequent heat-treatment at 900^{o}C for 1 hour in argon atmosphere.

Palma (2007) has been the only person who has synthesized in-situ Cu-TiC composite by reaction milling in a high-energy mill. In their research, an in-situ composite Cu-5vol.%TiC was synthesized after 10 hours of milling with subsequent heat-treatment at 700^{o}C for 1 hour.

2.3 Mechanical Alloying

In present work, mechanical alloying method was used to synthesize the copper composite reinforced by NbC and TiC from elemental Cu, Nb, Ti and graphite powders. As a result, a review on mechanical alloying is needed to provide the necessary knowledge to understand more clearly about this process and what factor affects the properties of the products.

2.3.1 Introduction

Mechanical alloying (MA) is a powder processing technique that was developed in the mid-1960s by John Benjamin to produce oxide dispersion strengthened (ODS) nickel-based superalloys for gas turbine applications. The processing involves repeated cold welding, fracturing, and rewelding of powder particles in a high-energy ball mill resulting in the formation of alloy phases.

The technique of MA has now branched out to the synthesis of a variety of equilibrium and non-equilibrium alloy phases including solid solutions, intermetallics, quasicrystals, amorphous alloys and bulk metallic glasses. Nanostructured materials and even exotic materials are also being synthesized by this simple and inexpensive technique (Suryanarayana, 2004). Accordingly, the term mechanical alloying (MA) is becoming increasingly common in the materials science and metallurgy literatures. MA presents status as an important method for the preparation of either materials with enhanced physical and mechanical properties or, indeed, new phases, or new engineering materials (El-Eskandarany, 2001). Various application areas where the MA technology has been utilized are illustrated in Figure 2.10.

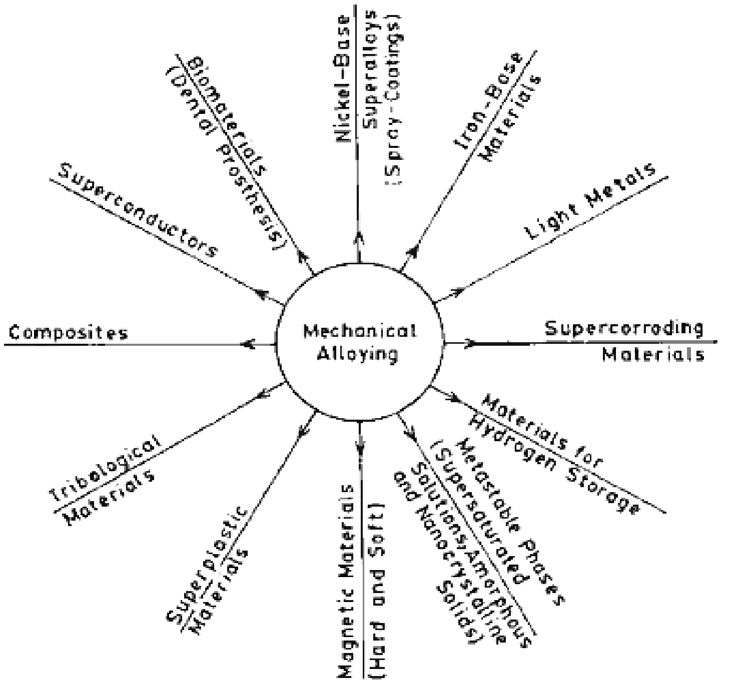

Figure 2.10 Application areas of mechanical alloying (Soni, 2001)

2.3.2 Planetary ball mill

Among many types of high-energy milling equipment have been used, planetary ball mill is one of the most popular mills used in MA research for synthesizing almost all materials. The planetary balls mill owes its name to the planet-like movement of its vials (milling bowl). In this type of mill, the milling media have considerably high energy, because milling stock and balls come off the inner wall of the vial and the effective centrifugal force reaches up to twenty times gravitational acceleration. The centrifugal forces caused by the rotation of the supporting disc and autonomous turning of the vial act on the milling charge (balls and powders). Since the turning directions of the supporting disc and the vial are opposite, the centrifugal forces alternately are synchronized and opposite. Therefore, the milling media and the charged powders alternatively roll on the inner wall of the vial, and are lifted and thrown off across the bowl at high speed, as schematically presented in Figure 2.11 (El-Eskandarany, 2001).

The impact energy acquired depends on the speed of the planetary mills. As the speed is reduced, the grinding balls lose the impact energy, and when the energy is sufficiently low there is no grinding involved; only mixing occurs in the sample (Suryanarayana, 2004). One advantage of this type of mill is the ease of handling the vials (45 ml to 500 ml in volume) inside the glove box (El-Eskandarany, 2001).

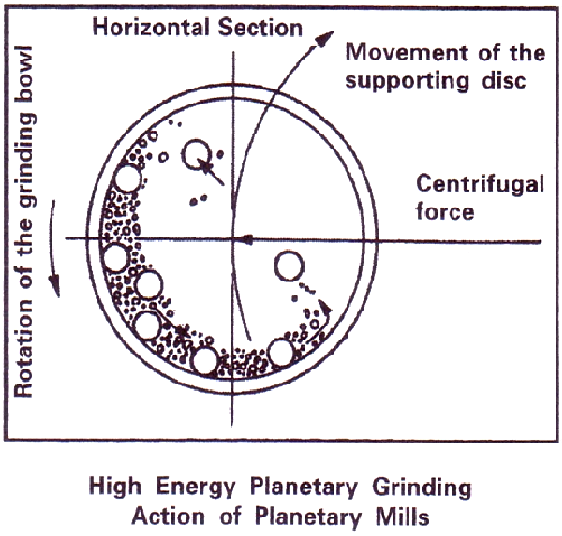

Figure 2.11 Schematic diagram depicting the ball motion inside a planetary ball mill (Suryanarayana, 2004)

Three different sizes of vials, with capacities of 80, 250, and 500 ml, are available. Various materials for grinding vials and balls are available such as agate, silicon nitride, sintered corundum, chrome steel, tungsten carbide and plastic. Advantage of plastic inner wall is noiseless but there was a limit in operation temperature. Larger or heavier-density ball is used to shorten the milling time, e.g. tungsten carbide balls in a steel bowl or zirconia oxide balls in a silicon nitride bowl. In normal cases, grinding bowls and balls of the same material are used, and grinding bowl material must also be harder than the material to be ground.

2.3.3 Mechanism of Mechanical Alloying

The main processes which take place in a mill during the MA method to produce quality powders with controlled microstructure are the repeated welding, fracturing, and rewelding of a mixture of powders of the diffusion couples. It is