FABRICATION AND CHARACTERISATION OF COPPER COMPOSITES REINFORCED WITH TRANSITION METAL CARBIDES VIA MECHANICAL ALLOYING

NUR HAWADAH MOHD SUBHI

UNIVERSITI SAINS MALAYSIA

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By

NUR HAWADAH MOHD SUBHI

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LIST OF SYMBOLS

Symbol	Description
D	Crystallite size
D_o	Pre-exponential constant
σ	Electrical conductivity
ρ	Resistivity
ρ_t	Individual thermal resistivity distribution
ρ_i	Impurity resistivity distribution
ρ_d	Deformation resistivity distribution
ρ_0	Constant for particular metal
C_i	Concentration in terms of atom
n	Order of diffraction
λ	Wavelength of X-ray beam
2θ	Angle of diffraction
d	Distance between each of set of atomic plane of the crystal
m	Weight
β	Line broadening
l	Scherrer constant
β_t	Full width at half maximum
ε	Internal Strain
β_o	Instrumental broadening
d	Average grain diameter

d_0	Initial grain diameter
k	Arrhenius constant
t	Time
h	Hour
v	Velocity

LIST OF ABBREVIATIONS

BPR	Ball to powder ratio
BM	Ball milling
BSE	Backscattered electron
CTE	Coefficient of thermal expansion
EDX	Energy Dispersive X-ray
FESEM	Field emission scanning electron microscopy
GD	Green density
MA	Mechanical alloying
MMC	Metal matrix composite
ODS	Oxide dispersion super-alloy
PM	Powder metallurgy
SD	Sintered density
SE	Secondary electron
SEM	Scanning electron microscopy
TD	Theoretical density
XRD	X-ray diffraction

LIST OF PUBLICATIONS

Fabrikasi Dan Pencirian Komposit Kuprum Diperkuat Logam Peralihan Karbida Melalui Pengaloian Mekanikal

ABSTRAK

Dalam kajian ini, kempaan bebola bertenaga tinggi juga dikenali sebagai pengaloian mekanikal (PM) digunakan untuk mensintesis komposit *in situ* matrik kuprum. Campuran serbuk Cu, (M=W atau Ti) dan grafit dilakukan pengaloian mekanikal selama beberapa masa kempaan di dalam kempa planetari. Komposisi nominal adalah Cu-28.72wt%W-1.87wt%C dan Cu-9.67wt%Ti-2.42wt%C berdasarkan kepada komposisi Cu-20vol%WC dan Cu-20vol%TiC. Berdasarkan komposisi dan masa kempaan yang hampir sama, campuran komposit *ex situ* bagi kuprum diperkuat WC dan TiC dikempa menggunakan kempaan bebola bertenaga rendah. Serbuk bagi komposit *in situ* dan *ex situ* ditekan pada 200 hingga 400 MPa dan disinter di dalam relau vakum pada suhu 900˚C. Keputusan pembelauan sinar-X, mikroskop imbasan elektron dan penyerakan tenaga sinar-X menunjukkan bahawa pembentukan tungsten karbida (fasa W_2C dan WC) berlaku selepas pensinteran Cu-W-C komposit manakala TiC termendak di dalam serbuk Cu-Ti-C komposit selepas 5 jam dan semakin amorfus dengan peningkatan masa kempaan. Mekanisma PM menjelaskan tentang kejadian kimpalan sejuk dan pemecahan yang berlaku semasa kempaan. Sistem Cu-W-C menunjukkan bahawa prosess pemecahan adalah lebih dominan pada peringkat awal kempaan dan partikel W masih wujud walaupun selepas kempaan selama 60 jam. Manakala dalam system Cu-Ti-C, kimpalan sejuk adalah lebih dominan dan semua partikel Ti terlarut ke dalam matrik Cu. Fenomena ini telah meningkatkan sifat kekerasan bagi kedua-dua Cu-W-C dan Cu-Ti-C komposit dan penurunan dalam sifat kekonduksian elektrik. Kekerasan yang lebih tinggi dan kekonduksian elektrik yang lebih rendah didapati dalam komposit *in situ* berbanding komposit *ex situ* disebabkan oleh kesan PM dan pemendakan serbuk penguatan karbida yang halus.

Fabrication and Characterisation of Copper Composites Reinforced with Transition Metal Carbides via Mechanical Alloying

ABSTRACT

In this study, high-energy ball milling also called mechanical alloying (MA) was applied to synthesis *in situ* copper based composite. Cu, M (M=W or Ti) and graphite powder mixture were mechanically alloyed for various milling time in a planetary ball mill. The nominal composition was Cu-28.72wt%W-1.87wt%C and Cu-9.67wt%Ti-2.42wt%C which corresponds to Cu-20vol%WC and Cu-20vol%TiC, respectively. With similar composition and milling time, the *ex situ* WC and TiC reinforced copper composite was also mixed by ball milling. Then the as-milled powder for both *in situ* and *ex situ* composites were compacted at 200 to 400 MPa and sintered in vacuum furnace at 900ºC. The results of X-ray diffraction, scanning electron microscopy and energy dispersive spectroscopy analysis showed that formation of tungsten carbide (W_2C and WC phases) observed after sintering of Cu-W-C composite while TiC precipitated in as-milled powder of Cu-Ti-C composite after 5 h and become amorphous with longer milling. Mechanism of MA explained the cold welding and fracturing event during milling. Cu-W-C system shows fracturing event is more dominant at early stage of milling and W particle still existed after milling up to 60 h. While in Cu-Ti-C system, cold welding is more dominant and all Ti particles dissolved into Cu matrix. These phenomena results in increased the microhardness properties of both *in situ* Cu-W-C and Cu-Ti-C composite and decreased in electrical conductivity by increasing the milling time. Higher microhardness and lower electrical conductivity are obtained in both *in situ* composite compared to *ex situ* composite due to the effect of MA and the fine carbides particles precipitation.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Copper provides the best electrical and thermal conductivity among the common base metals (Marques *et al.,* 2005). It is used extensively as an electrical conductor and suitable for thermal management application (Chawla and Chawla, 2006). However, copper presents as a very low strength metal. It must be strengthened to perform adequately and precipitation or solid solution hardening usually compromises the electrical conductivity. Dispersion strengthening of copper (Groza and Gibeling, 1993) has been considered as a promising method to produce good high temperature strength of copper to help in maintaining good electrical conductivity. Carbide reinforcement of copper has been considered as an ideal method for preparing materials with good high-temperature strength and high conductivity (Marques *et al.,* 2005). Several transition element carbides have been synthesised *in situ* in copper matrix using mechanical alloying such as Cu-NbC (Marques *et al.*, 2008) and Cu-TiC (Shen *et al.,* 2000).

In this study, copper reinforced by WC and TiC was chosen because both carbides have high melting point and microhardness values. Previous study conducted by Takahashi and Hashimoto (1992) was limited to the fabrication of copper composites reinforced by several types of transition metal carbides but did not include tungsten carbide (WC) as reinforcement. They also studied Cu-Ti-C system with various volume fraction of TiC reinforcement; that were 2.5vol%, 4.15vol%, 10 vol%, and 30 vol% of TiC. It was confirmed that the very fine transition metal carbide particles began to precipitate in Cu-30vol%TiC by mechanical alloying for about 20 h. Their research was focused on microstructure of composite powder not include consolidation and sintering process to relate with properties of copper composite. For these reasons, further investigation on the synthesis and characterisation of 20vol% WC and 20vol% TiC reinforced copper matrix composite by *in situ* method especially their bulk properties become the focus of the present work.

The strengthening effect of copper matrix by reinforcement particles depends on inter-particle distance, distribution and particle size of the reinforcement material (Rajkovic *et al.,* 2008). The most widely used method in producing metal matrix composite reinforced with dispersion particles is based on casting and powder metallurgy (PM) techniques (Hussain and Kit, 2008). In PM, two mixing methods can be used to incorporate the dispersed particle in the matrix, namely ball milling and mechanical alloying. Ball milling (BM), a low energy process, is relatively simple but does not ensure a uniform distribution of the dispersed particles since the produced fine powder often agglomerates. This process, which is also referred as *ex situ* processing, normally generates problem of contaminated interface in the composite and it is also difficult to produce strong interfacial bonding.

The second process for incorporating the fine dispersoid particles is high energy milling or mechanical alloying (MA) (Benjamin and Volin, 1974; Benjamin and John, 1992), which has been employed widely in developing composite material because it has the capability to incorporate reinforcement particle into the metal matrix at a close distance. This technique generally involves the *in situ* generation of the reinforcing phase which has emerged as a preferred synthesis route for these materials. *In situ* techniques of MMC relate to a method that involves a chemical reaction resulting in the formation of a very fine and thermodynamically stable ceramic phase within a metal matrix. As a result, the reinforcement surfaces are likely to be free from gas absorption, oxidation or other detrimental surface reaction contamination, and the interface between the matrices, and therefore, the reinforcement bond tends to be stronger (Wang and Wang, 2007).

The deformation structures of materials under MA were rarely reported, and such are very important for one to get a better understanding of the mechanisms governing the MA process, since it is still not well understood. It has been shown that enhanced reaction rates can be achieved and dynamically maintained during milling as a result of microstructural refinement (Khitouni *et al.,* 2009) and mixing processes accompanying repeated fracture, deformation and welding of particles during collision events (Suryanarayana, 2003).

In order to get direct formation of reinforcement in metal matrix additional heat treatment at appropriate temperature after MA sometimes is needed. In previous studies for Cu-W-C system, WC and W_2C phases are observed after MA with heat treatment at 940 ˚C for 5 hours. This is because long milling time (exceeding 50 min) led to Fe contamination due to collision of ball and jar (Baikalova and Lomovsky, 2000).

Wang and Wang (2007) have succeeded in producing *in situ* Fe-TiC by powder metallurgy and MA. They give a particular attention on reaction path of Fe-Ti-C system and microstructure of the final product. The microstructure observation of Fe-TiC composite shows the TiC particles are uniformly dispersed in iron matrix. The reaction path results showed that allotropic change $Fe\alpha \rightarrow Fe\gamma$ at 765.6 °C , formation of the compound Fe_2Ti at 1078.4 °C is because of the eutectic reaction between Ti and Fe, reaction between carbon and melted Fe_2Ti causing the formation of TiC at 1138.2 °C and formation of Fe_3C due to the eutectic reaction between remnants C and Fe at 1146.4 °C.

Another research on *in situ* composite processing was reported by Zuhailawati and Mahani (2009) who studied the effect of milling time on hardness and electrical conductivity of *in situ* Cu-NbC composite by MA was found that NbC particles was precipitated in the Cu-Nb-C after sintering process. The precipitated NbC particles improved the hardness properties of the *in situ* composite but low of electrical conductivity was obtained in *in situ* composite as a result of electron scattering by fine NbC particle and copper grain.

1.2 Problem Statement

Literature shows that *in situ* copper composites provide better properties such as high strength (Yih and Chung, 1997), and high electrical conductivity (Tu *et al.*, 2002). Potential alloying element that has been widely used as particle strengthening is transition metal carbides such as CrC, WC, TaC, NbC, MoC, VC (Botcharova *et al.*, 2003). Among other ceramic particles, this compound is a superior choice as a reinforcement particle for metal matrix composite.

Mechanical alloying is the promising route for the development of *in situ* composite. Most of the literatures reported synthesis of *in situ* composites with one single mixture such as synthesis of Cu-TiB (Tu *et al.*, 2002), Cu-WC (Naiqin Zhao and Yang, 2004) and Cu-NbC (Hussain *et al.*, 2010). The mechanism of carbide formation depends on the powder mixture because properties of element influence the fracturing and cold welding of powder during mechanical alloying. Properties of the composite also depend on fabrication process such as pressing and sintering. Morphology of the milled powder affects the consolidation during sintering and pressing. Hence, the aim of this project is to study the mechanism of MA for two mixtures which are copper-tungsten-graphite (Cu-W-C) and copper- titanium-graphite (Cu-Ti-C) and to investigate the properties of these two composites that had been fabricated almost under similar condition.

1.3 Objectives

The objectives of this research work are:

i. To explain the mechanism of carbide formation in copper matrix during mechanical alloying and sintering process for Cu-W-C and Cu-Ti-C mixtures.

ii. To compare the structure, hardness and electrical conductivity properties of *in situ* copper composite reinforced by tungsten carbide and titanium carbide particles prepared by powder metallurgy.

iii. To compare the structure, hardness and electrical conductivity properties of the *in situ* tungsten and titanium carbides reinforced copper composite with the *ex situ* prepared composites.

1.4 Scopes of Study

In this work, an *in situ* technique is developed for the fabrication of WC and TiC particle-reinforced Cu matrix composite. The technique called mechanical alloying (MA) was used to disperse both carbides in copper matrix using the elemental powders of copper, tungsten, titanium and graphite. The effect of milling time on the microstructure and properties of the milled composite powders and as-consolidated composite was revealed in this study. The properties of copper composite are depend on the mechanism of carbide formation, morphology of as-milled powder and consolidation and sintering process. Hence, this study was aim to explain the formation of carbide dispersion in Cu matrix with 20vol%WC and 20vol%TiC.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The most interesting properties of copper composites are the high mechanical properties and moderate electrical conductivity. This chapter discusses topics that are related to the development of copper composites.

2.2 Metal Matrix Composites (MMC)

Metal matrix composite (MMC) is a type of composite that is reinforced with another material to improve its strength, wear or some other characteristics. It consists of a metallic matrix combined with a ceramic (such as oxides and carbides) or metallic dispersed phase (such as tungsten and molybdenum). Over the last 45 years or so, metal matrix composites have merged as an important class of materials. During this period, very substantial research efforts have been directed towards an improved understanding of their potential and limitations, invoking principles of physical metallurgy, stress analysis and processing science (Clyne and Withers, 1995). The properties of composites are a function of the properties of the constituent phases, their relative amounts and the geometry of the dispersed phase. “Dispersed phase geometry” in this context means the shape of the particles and the particle sizes, distribution and orientation. These characteristics are represented in Fig. 2.1.

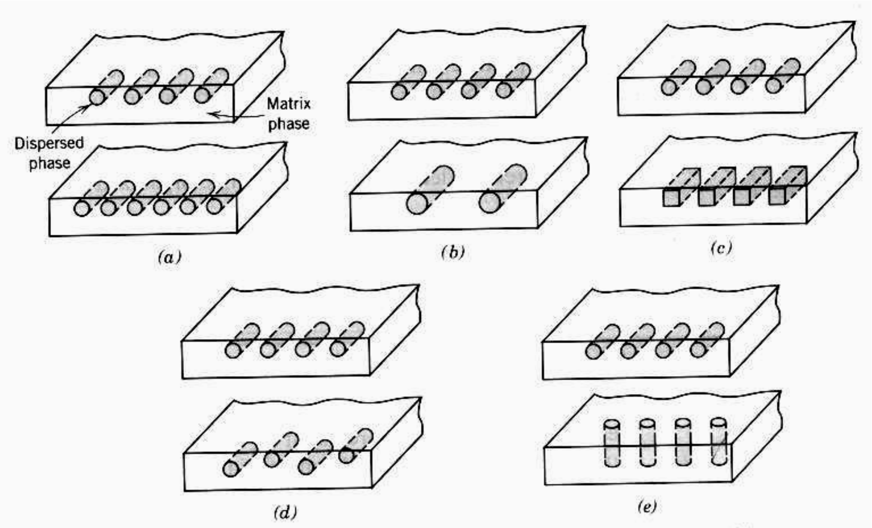

Figure 2.1: Various geometrical and spatial characteristics of particles of the dispersed phase that may influence the properties of composites: (a) concentration, (b) size, (c) shape, (d) distribution and (e) orientation (Callister, 2003).

The physical and mechanical properties that can be obtained with MMCs have made them attractive candidate materials for aerospace, automotive and numerous others applications. More recently, particulate reinforced MMCs have attracted considerable attention as a result of their relatively low costs and characteristic isotropic properties. Reinforcement materials include carbides, nitrides and oxides. In an effort to optimise the structure and properties of particulate reinforced MMCs various processing techniques have evolved over the last 40 years. The processing method utilised to manufacture particulate reinforced MMCs can be grouped depending on the temperature of the metallic matrix during processing (Ibrahim *et al.,* 1991).

The classification of composite materials can be categorised into three main groups, namely particle-reinforced, fibre-reinforced, and structural composites with at least two subdivisions for each. Fig. 2.2 shows the classification scheme for the various composites types (Callister, 2003).

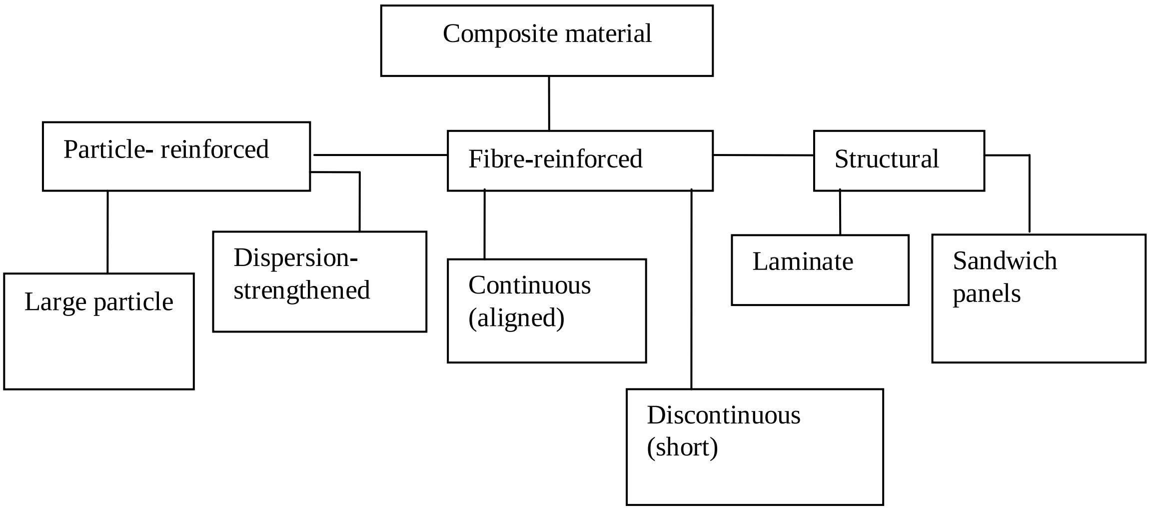

Figure 2.2: A classification scheme for the various composites types.

There are two types of particle-reinforced in metal matrix composite. The first one is large-particle reinforcement. One of the familiar large-particle composite is concrete, being composed of cement (matrix) and sand and gravel (particulates). The particles in these composite are larger than in dispersion-strengthened composites. The particle diameter is typically on the order of a few microns. In this case, the particles carry a major portion of the load. The particles are used to increase the modulus and decrease the ductility of the matrix. Fig. 2.3 shows a photomicrograph of WC-Co cemented carbide.

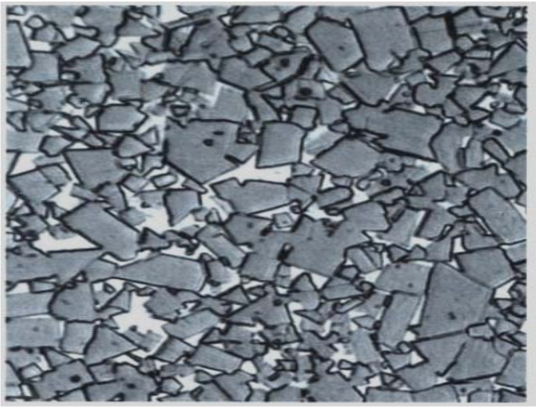

Figure 2.3: Photomicrograph of a WC-Co cemented carbide. Light areas are the cobalt matrix while dark regions are the particles of tungsten carbides (Callister, 2003).

According to Zhang *et al.* (1995), transition load increase with increasing the particle volume fraction but for the given average particle size, the higher the particle volume fraction, the higher the hardness of the composite. Therefore, particle size influences the transition load more pronouncedly then particle volume fraction. They studied the wear mechanisms in SiC or Al_2O_3 particles reinforced aluminium matrix composites with volume fractions of 10% and 20%, respectively. It is observed that a transition of mild wear to severe wear occurs when the applied normal load reaches a certain critical value. The transition behaviour is both load and microstructure-dependent.

Particulate reinforced composites, which contain hard particles dispersed homogeneously in a ductile matrix, have the potential as engineering materials because of their good formability and machinability as well as improved mechanical properties. The technique has been applied to metal matrix and polymer matrix composites. These composites have enhanced performance on the basis of the Young's modulus, yield strength, fatigue strength, and resistance to wear, while they generally exhibit poor ductility, low fracture toughness and strong dependency on processing (Tohgo and Weng, 1994).

The second is dispersion strengthened composites. In dispersion strengthened composites, small particles on the order of 10^{-5} mm to 2.5 x 10^{-4} mm in diameter are added to the matrix material. The strengthening mechanism involves interactions between the particles and dislocations within the matrix, as with precipitation hardening but dispersion strengthening effect is not as pronounced as with precipitation hardening. It is because the strengthening is retained at elevated temperature and for extended time periods because the dispersed particles are chosen to be unreactive with the matrix phase. While for precipitation hardening alloys, the increase in strength may disappear upon heat treatment as a consequence of precipitate growth or dissolution of the precipitate phase (Callister, 2003). Traditionally, dispersion strengthening of copper has produced by several processing route such as powder metallurgy, spray deposition, mechanical alloying and casting techniques (Zuhailawati *et al.*, 2008).

2.2.1 Fabrication methods of MMC

There are various methods employed in fabricating MMC. These are solid state, liquid state, *in situ* and semi-solid processing. Solid state commonly involves bringing the particles or foil into close contact with the reinforcement. Sometimes, solid phase processes yield better mechanical properties. Although there are a lot of problems concerning the distribution of the reinforcement and in obtaining a uniform matrix microstructure, it is necessary to use certain blending routes in order to get a homogenous distribution of reinforcement. For example, the study by Baikalova and Lomovsky (2000) on solid state synthesis of tungsten carbide in an inert copper matrix showed the uniformly distributed grains of tungsten carbide in the copper matrix.

Liquid state methods included electroplating, stir casting, squeezed casting, spray deposition and reactive processing. A majority of the commercially viable applications are now produced by liquid state processing because of inherent advantages of this processing technique over solid state techniques. Using liquid metal, the composite material can be produced in a wide variety of shapes and generally less expensive and easier to handle than the powders.

2.3 Copper Matrix Composites

Copper composites are widely used where high electrical or thermal conductivity is required. It is used extensively as an electrical and thermal conductor (Hussain and Mahani, 2009). Copper is a soft metal and have good thermal conductivity near to 0.55 W/mK at low temperature. In addition, at temperature of around 263 ˚C, the electrical conductivity of copper was about 150 x 10^6 $(\text{ohm.cm})^{-1}$ (Berman and MacDonald, 1952). However, the mechanical properties of such materials are relatively low, especially at temperatures above 200˚C. Several investigations have been carried out related to strengthening by the dispersion of particles in copper alloys, essentially with ceramics (Ellis *et al.,* 1990; Groza and Gibeling 1993).

A copper matrix composite with high strength and high electrical conductivity is very useful for the lead frame in semiconductor, conductive coil in hybrid magnet for nuclear fusion furnace, or a spot welding electrode and the like. Moreover, demand for its mechanical and electrical properties is increasing by the year.

The search for new uses of copper has justified the development and study of new copper-based alloys via powder metallurgy and mechanical alloying using ceramic as strengtheners. As a way to improve the mechanical properties at low temperatures, the matrix must be strengthened with very low-solubility particles, which have a low diffusivity in copper, by means of mechanical alloying maintaining equilibrium with the electrical properties obtained. These particles must be stable and if they form a phase with Cu, they should not be brittle nor alter the electrical conductivity.

Copper matrix reinforced with various sizes and amount of Al_2O_3 was produced by Rajkovic *et al.* (2008) by internal oxidation and high energy ball milling. In their study, milling of Cu-1wt% Al pre-alloyed powder promoted formation of fine dispersed particles (1.9wt% Al_2O_3, approximately 100 nm in size) by internal oxidation. While milling of Cu-3wt% commercial Al_2O_3 powder gives a uniform distribution of commercial Al_2O_3 particles in Cu matrix. Cu-1wt% Al_2O_3 has higher microhardness value compared to Cu-3wt% Al_2O_3 due to the nano-sized Al_2O_3 particles that have stronger reinforcement. However, electrical conductivity of Cu-3wt% Al_2O_3 is higher than Cu-1wt% Al_2O_3 because nano-sized Al_2O_3 particles reduce the conductivity of Cu more than larger Al_2O_3 particles due to the higher electron scatter caused by nano-sized particles.

In another work, Marques *et al.* (2005) synthesised *in situ* and at room temperature a composite material consisting of 5, 10 and 20 vol% of nanocrystalline NbC particles dispersed in a nanostructured copper matrix. The strengthening was observed in Cu by increase the volume percent of NbC and reflecting the thermal stability of the synthesised nanocomposites up to 600 ˚C without major coarsening of both Cu and NbC crystallite. The microhardness of Cu-20 vol% NbC powders increase to 4.8 GPa after annealing at 600 ˚C due to the completion of the reaction between C and Nb.

Formation of Cu–5 vol.% TiC alloy synthesized by reaction mechanical alloying in a high-energy mill and consolidated by hot extrusion was reported by Palma *et al.* (2005). The better performance of Cu–5 vol.% TiC than that of electrolytic Cu electrodes is explained by considering the homogeneous distribution of nanometric TiC dispersoids in the alloy Cu matrix.

Liang *et al.* (2008) reported the evolution process of the synthesis of TiC in the Cu-Ti-C system using differential thermal analysis (DTA) and x-ray diffraction (XRD). The results shows that the Ti_xCu_y compounds (Ti_2Cu, TiCu, Ti_3Cu_4 and $TiCu_4$) formed initially via solid-state diffusion reactions between Cu and Ti particles; and then Ti_2Cu and TiCu formed a Cu–Ti eutectic liquids at about 1233 K. The unreacted Ti and C particles were dissolved into the Cu–Ti liquids and led to the formation of Cu–Ti–C ternary liquids; subsequently, TiC particulates precipitated out of the saturated liquids. At the same time, the formation of Ti_2Cu occurred at the interface between the Cu–Ti liquids and the unreacted Ti particles. As the temperature increased further, the Ti_2Cu melted and more Cu–Ti liquids were formed; and then C particles continuously were dissolved into the Cu–Ti–C liquids and TiC particulates gradually precipitated out of the saturated liquids. The finding obtained has been explained to understanding the mechanism of self-propagating high-temperature synthesis (SHS) process in the Cu–Ti–C system.

2.4 Copper Based Composite Properties

2.4.1 Microhardness

Hardness is the measure of a material’s resistance to localised plastic deformation. Hardness of copper composite can be measured either in macro-, micro- or nano- scale according to the forces applied and the displacement obtained. Microhardness may be determined by forcing an indenter such as a Vickers or Knoop indenter into the surface of the material.

Introducing the reinforcement promotes an increase in hardness, stiffness, resistance to scratching, abrasion and cutting. Such properties are achieved because the reinforcement phases usually are hard and have high melting point that overcome the soft and low melting point of metal matrix. Generally, the reinforcement with 25%vol satisfies other properties such as ductile strength and electrical conductivity. Hardness is an easily measurable property that has a strong correlation with tensile properties. For example the presence of fine dispersion of Al_2O_3 particles in a copper matrix improves the hardness of this material at room and at higher temperatures.

2.4.2 Electrical conductivity

Particulate copper matrix composite offers high electrical conductivity due to copper itself as it shows excellent performance in electrical application. The addition of reinforcement such as ceramic particles somehow increased mechanical properties of the composite. Furthermore, the incorporation of particulates is not associated with severe deterioration of thermal and electrical conductivity of copper, which the copper alloys do. The excellent advantages exhibited by particulate copper-based composite can extend the application of copper markedly. Almost all metals have extremely good electrical conductivity. The term electrical conductivity, σ, commonly used to characterise the electrical properties of particular material as shown in Eq. 2.1:

$$\sigma = \frac{1}{\rho} \qquad \text{(Equation 2.1)}$$

where ρ is presented as resistivity, the unit measurement of σ is reciprocal ohm-meters ($(\Omega m)^{-1}$). Since conductivity is reciprocal of resistivity, it is necessary to provide enough information regarding the resistance behaviour. Increasing the number of crystal defect actually raised the resistivity values. Total resistivity of a metal is given as the sum of thermal vibrations, impurities, and plastic deformation. This may be presented in mathematical form (Eq. 2.2) as:

$$\rho = \rho_t + \rho_i + \rho_d \qquad \text{(Equation 2.2)}$$

where ρ_t, ρ_i and ρ_d are individual thermal, impurity, and deformation resistivity contributions, respectively. Thermal vibration and lattice irregularities are generated due to increase in temperature in the particular metal. The atoms are not in its equilibrium and spread the electrons. As the mean path decreases, the mobility of the electrons also decreases while the resistivity is increased. The temperature dependence on resistivity is shown in Eq. 2.3:

$$\rho = \rho_0 + a\Delta T \qquad \text{(Equation 2.3)}$$

where ρ_0 and a are constants for a particular metal. The influence of impurity is commonly related to concentration C_i in terms of atom fraction (Eq. 2.4):

$$\rho_i = AC_i(1 - C_i) \qquad \text{(Equation 2.4)}$$

The volume fraction of reinforcement needs to be controlled as they may increase the resistivity value of metal composite (Callister, 2003).

2.5 Copper Composites Reinforced by Transition Metal Compound

Applications such as spot welding electrode, high performance switch, rotating source neutron target, combustion chamber liners and nozzle liners demand materials with high strength, good wear and long term thermal stability. Composite reinforced by transition metal carbides are prime candidates for applications as above.

Transition metal compounds of the type of MX, where M denotes a transition metal element and X denotes one of the non-metallic elements C, N or O, are generally very hard materials and they often crystallise in the rock salt (NaCl) structure. These compounds have great scientific and technological interest. The titanium, tungsten and iron compounds belong to the class of the so-called refractory metal compounds. Furthermore, they have high melting points and extreme hardness, properties which are typically found in covalent crystals. It is interesting that properties associated with covalent bonding are found in a set of systems that display a crystal structure normally associated with ionic bonding (Ahuja, 1995).

In transition metal compounds, chemical bond and cohesion energy relate to mechanical properties, like Young's modulus and hardness. High cohesion energy and high hardness values normally correlate with a covalent character of the bonding. For example, in several transition metal carbides and nitrides group IV and V, maximum hardness value are found at an 'average number of valence electron' (ANVE) (anion s, p+cation s, p, d) of 4.1 - 4.3. Electron band structure schemes provide a more quantitative understanding of the cohesive and bonding properties, which depend on the distribution of valence electrons in the bonding state (Levy *et al.*, 1999).

Tungsten carbide (WC) and titanium carbide (TiC) are most commonly used for fabrication as 'cemented carbide' tools for cutting steel, in which the carbide is bonded in a metal matrix, usually cobalt or nickel. However, in the case of carbide particle reinforcements, little information is available in the literature concerning the fabrication and properties of WC and TiC particles reinforced copper-base composites. In the present work, synthesis of WC and TiC particles reinforced copper using elemental tungsten or titanium and graphite in copper matrix by mechanical alloying technique for high electrical conductivity and strength properties was produced.

2.6 Fabrication of *In situ* WC and TiC Reinforced Copper Composite

In situ MMC means the reinforcements are synthesised in a metallic matrix by chemical reactions between elements or between element and compound during composite fabrication (Hussain *et al.*, 2008). In *in situ* processing, however, reinforcement of metallic matrix by a chemical reaction during mixing and subsequent processing can be achieved. For the chemical reaction to occur, a minimum amount of energy must be introduced such as hot isostatic pressing with thermal energy, after extrusion with thermal treatment or high kinetic energy by mechanical alloying (MA) (Zuhailawati and Mahani, 2009). As a result, uniform distribution of fine particle and thermodynamically stable phase of reinforcement of the composite is produced (Wang *et al.*, 1997). The advantage of *in situ* processing is that it has the ability to develop nanostructured materials. Such materials have recently attracted a great deal of attention due to their unique properties as compared to bulk materials. Baikalova and Lomovsky (2000) have succeeded in producing Cu-W-C composite by mechanical alloying with annealing at 940 ˚C for 5 h. They reported that, a decrease of tungsten content in mixture up to $Cu_{94}W_3C_3$ led to the significant enhancement of WC synthesis. Tungsten content highly affects the content of WC and W_2C formation. Lu *et al.* (2000) studied the *in situ* formation of TiC in copper matrix by mechanical alloyed Cu-Ti-C for 2 h, and then used the powder mixture in the selective laser melting (SLM). X-ray diffraction results showed formation of *in situ* TiC ceramic after SLM process. *In situ* Cu-based composites can be synthesised via the reaction between elemental Ti and C powders in Cu by using a CO_2 laser. Cu can be melted with the help of Ti and the reaction heat of formation of TiC.

2.7 Powder Metallurgy

Powder metallurgy (PM) is the most widely used technique in solid state processing. It requires blending, compacting and sintering (Lenel, 1980). In powder metallurgy, metal powder; metals in finely divided form rather than molten metal, are the starting material. The powders are consolidated into products with a given shape. The basic steps in powder metallurgy are, therefore, powder production and powder consolidation. The most common sequence in powder consolidation is pressing the powder in a die into a compact and sintering the compact, which means heating it to a temperature below the melting point of the metal or alloy to give it to the desired physical, mechanical and chemical properties. Moustafa *et al.* (2002) investigated the copper composite reinforced with SiC or Al_2O_3 by powder metallurgy technique. It was shown that copper composite fabricated by coated powders of SiC or Al_2O_3 gave higher shrinkage rate during sintering.

The advantage of powder metallurgy compared to casting technique is cost consumption. The cost of producing a part of a given shape to the required dimensional tolerances by powder metallurgy is considered low for reactive and refractory metals which melting is not practical (Moustafa *et al.*, 2002). Powder metallurgy technique are attractive since all of the processing can be performed in the solid state.

Many applications also rely on the economical production of complex parts. Component for the automotive industry represent good examples of this area and their production is a large PM activity. Within the area of economical parts production come concerns with productivity, tolerances and automation. Both the precision and cost are very attractive, while with casting there are problems associated with segregation, machining and maintaining final tolerances. Prealloyed powders allow fabrication below the melting temperature. This eliminates segregation and other defects associated with casting (Randall, 1984).

There are many applications based on the unusual properties of the materials obtained by powder metallurgy. They range from fabricating metals with high melting points to applications where high wear resistance is needed, to porous materials, to products with special frictional, magnetic and electrical properties and many others.

2.7.1 Metal powder production

General classification of the approaches to produce metal powders to powder metallurgy application may be divided into three categories; physical methods, chemical methods and mechanical methods.

Physical method of powder production is designated by the rather misleading term “atomisation”. In mist atomising process a stream of liquid, usually water, or of gas impinges upon the liquid metal stream to break it into droplets. A stream of molten metal is broken up into droplets which freeze into metal powder particles (Lawley, 1977).

Chemical methods of powder production are those in which a metal powder is produced by chemical decomposition of a compound of the metal. This includes the large group of reduction reactions. Oxides in the form of finely divided solid powder particles may be reduced, as in the reduction of tungsten oxide to tungsten powder and of copper oxide to copper powder with hydrogen or of iron powder with carbon monoxide.

Certain powders may be produced by mechanical comminution process generally used for brittle materials, such as ores. The comminution plays only a minor role in metal powder production because comminuted brittle powder cannot be cold compacted as such (Lenel, 1980). Mechanical alloying (Suryanarayana, 2004) is the most common process to produce powder metal via mechanical methods.

2.7.2 Powder consolidation

Consolidation of metal powders at room temperature by application of pressure is a necessary step in the fabrication of the majority of powder metallurgy products. It is most often done in rigid dies made of tool steel or cemented carbides. Pressures in the range from 70-700 MPa are used. The compacts so produced, called “green compacts”, are strong enough so that they can be ejected from the die and handled. The green compacts are porous and have a lower density than cast and wrought parts of the same metal. When powders are pressed into compacts at room temperature, or are shaped by powder rolling or extrusion, the resultant products have insufficient strength and ductility for most applications. In order to make them useful they have to be sintered.

The processes occurring when a column of loose powder is compacted in a die have been described qualitatively by Seelig and Wulff (1946), who postulated a series of stages. The first stage is restacking of the powder particles in the column, so called packing, in which the bridging that always occurs in a randomly arranged stack of particles is at least partially eliminated. The second stage involves elastic and plastic deformation of the particles. Elastic deformation plays only a minor role, while plastic deformation depends on the ductility of the metal and may be of minor significance in very hard powders such as tungsten or tungsten carbide. In most metals, plastic deformation causes work hardening, which diminishes the amount of further deformation under stress. It may eventually lead to the third stage in which the particles fracture under the applied load and form smaller fragments. This third stage is more important during compacting of non-metallic powders. Lubricant must be provided when parts are pressed in rigid dies to reduce friction between the compact and the die wall (Lenel, 1980).

The most important commercial application of powder metallurgy is to control dimensions of structural parts closely. Methods of consolidating metal powders include cold isostatic pressing, powder rolling, extrusion, injection moulding.

2.7.3 Sintering

Sintering is a bonding process to improve strength and other engineering properties of the compacted material. This process involves consolidation of powder grains by heating the compacted materials to a high temperature below the melting point of the ‘green’ compact. The effects of temperature and soaking time to mechanical and physical properties have to be considered during sintering processing. Liang *et al.* (2008) studied the evolution process of the synthesis of TiC in the Cu-Ti-C system by using differential thermal analysis (DTA). The result shows that the initial temperature of the reaction of TiC formation was at about 960 ˚C in the 20wt% Cu-Ti-C system.

Another research (Upadhyaya *et al.,* 1995) reported on the effect of sintering of copper-alumina composite by blending and mechanical alloying and powder metallurgy routes. Densification kinetics was faster for mechanical alloyed powder compacts compared to blend compacts. Dong *et al.* (2002) indicated that a crystallite of size less than 50 nm could be attainable for ceria and YSZ at sintering temperatures below 900 ˚C. The grain size in YSZ and ceria film increased slowly with temperature at or below 900 ˚C. However, they showed that the grain size increased abruptly at temperatures in the range of 1000 -1200 ˚C.

Syed Nasimul Alam (2006) reported that the as-milled elemental W and W-10wt%Cu showed almost no growth in crystallite size during heat treatment. Due to the high impacts during milling a large amount of dislocation is introduced in the tungsten lattice and this hinders the growth of tungsten crystallite during heat treatment. Similar kind of results indicating slow grain growth in the nanocrystalline ferrite region was observed instead of recrystallisation in the annealing behaviour of nanocrystalline ferrite in Fe-0.89C spheroidite steel produced by ball milling (Xu *et al.*, 2002).

There are three types of sintering methods available, namely solid state, liquid state and hot consolidation metal powder which combining compacting and sintering.

2.7.3.1 Solid state sintering

Sintering forms solid bonds between particles when they are heated. It is possible to reduce pore volume which leads to compact shrinkage with extended heating, although in many sintering systems dimensional change is undesirable. Maneshian *et al*. (2008), in their research reported the effect of solid state sintering of

W-20 wt.% Cu mixture powder by mechanical alloying. At constant sintering temperature, higher density is achieved when more prolonged milling time is afforded. It was also shown that the high density of W-Cu composite synthesised by mechanical alloying and solid state sintering gave high conductivity and hardness values.

Zheng and Reed (2005) conducted work on alumina compacts fabricated with different green densities and different pores size distributions. They characterised and studied the changes of the pore characteristics during solid state sintering. A critical ratio of pore size to mean particle size for pore shrinkage was determined. They classified porosity in the compact into two classes: the first class contains pores smaller than the critical ratio, and the second class contains pores larger than the critical ratio. According to them, pores belonging to a different class of porosity behaved differently during sintering. Pores larger than the critical ratio were not totally eliminated during sintering. The first class of porosity controlled the ultimate sintering shrinkage, and the second class of porosity controlled the final sintered density.

2.7.3.2 Mechanism of sintering process

There are three basics stages in sintering process that refer to geometric categories. The geometrical changes are of concern primarily in the study of mechanism of sintering rather than changes in physical and mechanical properties.

The first stage is the expansion of small contact area (necks) between powder particles. This also involves changes in shape of the pores that become rounded. Simultaneously, the powder aggregate begins to densify, where there is a decrease in total void volume and a decrease in the centre to centre distance between particles. In spite of neck growth and initial shrinkage the particles in the original powder aggregate are still distinguishable. Fig. 2.4 shows a chain of three spherical copper particles approximately 50 µm in diameter sintered for 1 min, 2 h and 50 h near the copper melting point. During the sintering, the chain of particles stretched and the angle between the lines connecting the centre of the particles became larger.

In the second or intermediate stage, the pore channels in the powder aggregate gradually pinch off and close, which means the particles can no longer be distinguished. In this stage migration of the grain boundaries between the original particles by grain growth becomes possible. On the other hand, the pores continue to form a more or less connected continuous phase throughout the aggregate (Lenel, 1980). In the third stage, the pores become isolated and are no longer interconnected. The angle between the particles, initially larger than 90 ˚C, increase with increasing sintering time.

Fig. 2.5 shows the change in angle effect the planar array of spherical copper powder particle when it was sintered for 2 to 12 h at 1020 ˚C. It can be seen that the area of small pore decrease but the large pore grows steadily. This shrinkage is partially compensated by the opening of large pores.