UNIVERSITY OF CINCINNATI

Date:_____

hereby submit this work as part of the requirements for the degree of:

in:

It is entitled:

I,

This work and its defense approved by:

Chair: _____

Wear Resistance and Electrical Property of Infrared Processed Copper/Tungsten Carbide Composites

A thesis submitted to the Department of Chemical and Materials Engineering

College of Engineering Division of Graduate Education and Research University of Cincinnati

In partial fulfillment of the requirement for the degree of Doctorate of Philosophy 2006

> By Pranav K. Deshpande

B.E., Visvesvaraya Regional College of Engineering, India, 1999M.S., University of Cincinnati, Cincinnati, OH, 2002

Thesis Committee Chair: Prof. R.Y. Lin

Abstract

Copper matrix composites with 53 vol% of WC particle reinforcements have been prepared with an infrared infiltration technique. The process produced fully dense composite owing to excellent wetting between copper and WC. The microhardness values of completely infiltrated Cu/WC composites were in the range of 360-370 HV which is significantly higher than the microhardness of pure copper, 65 HV. The electric conductivity of these composites, as determined by a four-point-probe method, is similar to commercially available Cu/W composites containing 52 vol% of tungsten. The wear behavior of Cu/WC composites has been determined with a pin-on-disk technique against a sintered SiC abrasive disk. The wear rate as a function of a normal wear stress and composite porosity was investigated. Results have shown that up to a normal load of around 9 N (or 0.55 MPa pressure), the wear rate of fully dense Cu/ WC composites increases linearly with the applied pressure. Results also show that porosity in the Cu/WC composite increases wear. A model of wear, taking into account various wear mechanisms, was developed. This model successfully predicts the wear behavior of dense Cu/WC composites. Owing to its significantly better wear resistance, as compared to Cu/W composites, the composition of Cu/ 53 vol% WC composite was varied by an innovative technique to improve the electrical conductivity of these composites without much compensation on its wear resistance. The technique of composition variation also helped in overcoming the shortcomings of pressure-less infiltration technique.

Acknowledgement

I would like to take this opportunity to express my sincere appreciation for my PhD research advisor and thesis committee chair, Dr. Ray Y. Lin, for his constant support, encouragement, and able guidance throughout this study.

I am grateful to my thesis committee members, Dr. Relva Buchanan, Dr. Stephen Clarson and Dr. Rodney Roseman for their review and helpful criticism.

I would like to thank my lab co-worker and friend, Dr. Jason Li, for sharing his experience and providing valuable suggestions throughout this study. My other lab coworkers; Jin Seok, Yimin Wang and Pravahan Salunke also deserve a special mention for their help and suggestions. I would like to appreciate the CME staff; Dale, Ellen, Deena, Christa, Bhaskar and Phyllis for their help. I am also grateful to the CME department for extending all of its resources. My friends here have been a great support and I would like to thank them for making my stay here a nice experience.

I would like to thank Sherbrooke Metals, Inc, Willoughby, OH for providing test samples for comparison.

My special thanks are reserved for my parents, wife and sister for their love, sacrifice and belief in all my pursuits. It would have been impossible to complete my study without their contribution and support.

Table of Contents

List of Tables	iii
List of Figures	iv
List of Symbols	vi
1. Introduction	1
2. Background	3
2.1 Composite Materials	3
2.2 Metal Matrix Composites	5
2.3 Fabrication Methods	6
2.4 Wettability	8
2.5 Copper Composites	11
2.6 Patents	22
2.7 Tungsten Carbide vis-à-vis Tungsten	24
2.8 Infrared Heating	25
2.9 Electrical Contact Requisites	29
2.10 Wear Resistance of MMCs	30
3. Objectives and Approach	36
4. Experimental	37
4.1 Materials	37
4.2 Experimental Procedure	37
4.3 Characterization	39
4.3.1 Density Measurement	39
4.3.2 Microstructure	40
4.3.3 Electrical Resistivity Measurement	40
4.3.4 Microhardness Measurement	40
4.3.5 Wear Test	41
5. Results and Discussion	44
5.1 Density Measurement	44
5.2 Microstructure	48

5.3 Electrical Resistivity Measurement	49
5.4 Microhardness Measurement	52
5.5 Wear Test	56
5.5.1 Wear of Composites Containing Pores	56
5.5.2 Wear of Fully Dense Cu/WC Composites	61
6. Model: Wear Mechanism of MMCs	66
6.1 Composite Wear of the First Type: Abrasive Wear	67
6.2 Composite Wear of the Second Type: Particle Pull-Out	71
7. Composition Variation of Cu/WC Composite	95
7.1 Comparison of Cu/WC and Cu/W Composite	95
7.2 Composition Variation Techniques	97
8. Conclusions	104
9. Future Work	105
10. References	106

List of Tables

		Page
Table I	Resistivity of Cu/WC composites (in $\mu\Omega$ -cm)	54
Table II	Resistivity of Cu/W composites (in $\mu\Omega$ -cm)	54
Table III	Microhardness of Cu/WC composite (HV)	55
Table IV	The comparison of electrical and mechanical properties of Cu/WC composites, having varying amounts of WC reinforcement, with that of pure copper	103

List of Figures

		Page
Figure 2.1	Schematic of energy balance in a sessile drop	8
Figure 2.2	Phase Diagram of W-C	14
Figure 2.3	Flow-Chart of the Gusmano Process	15
Figure 2.4	Flow-Chart of the Johnson Process	17
Figure 2.5	Flow-Chart of the Jedamzik Process	19
Figure 2.6	Flow-Chart of the Process [23]	21
Figure 2.7	Schematic representation of typical heating and cooling cycles for (A) rapid infrared furnace, (B) induction furnace, (C) resistance / vacuum furnace	28
Figure 2.8	Wear test results of Al/SiC particle composites reported by Sahin and Acilar [48]	34
Figure 4.1	SEM micrograph of morphology of WC particles	38
Figure 4.2	Schematic of the experimental set-up	38
Figure 4.3	Schematic representation of a pin-on-disk wear tester	42
Figure 5.1	Density variation with infiltration time and temperature	46
Figure 5.2	Porosity variation with infiltration time and temperature	46
Figure 5.3	Optical micrographs of Cu/WC composites at various conditions of time and temperature	50
Figure 5.4	A high magnification optical micrograph of pore structure in Cu/WC (1250-4) composite	51
Figure 5.5	Optical micrographs of comparison of indentation sizes on the Cu/WC composite and the copper	55
Figure 5.6	Effect of porosity on the wear rate of Cu/WC composites	57
Figure 5.7	Effect of porosity on the wear rate of Cu/WC composites with the effective area compensation	57
Figure 5.8	The notch effect of porosity in the wear rate of Cu/WC composites	60
Figure 5.9	Wear rate of Cu/WC (fully dense) composite having 53vol% WC reinforcement	62
Figure 5.10	Comparison of wear rates of Cu/WC composite with pure copper	63
Figure 5.11	Surface optical micrographs of (a) Cu/WC (Fully Dense) composite and (b) Pure copper after wear at 4.27N and 500m sliding distance	63
Figure 6.1	A schematic drawing of a composite surface	68

Figure 6.2	Predicted wear rate as a function of the normal wear stress in the low stress region	70
Figure 6.3	A schematic drawing of partially worn particles on the composite surface	74
Figure 6.4	A schematic drawing of a partially worn particle with removed portion shown as by a dash line	74
Figure 6.5	Particle pullout conditions predicted by the pullout model	77
Figure 6.6	Predicted wear rate as a function of the normal wear stress over a wide range of the wear stress	86
Figure 6.7	SEM micrographs of Cu/WC composites showing the composite surfaces prior to wear (a) and after wear (b). The arrow in (b) shows the wear direction	91
Figure 6.8	Wear results of Al-4%Cu/TiB ₂ composites reported by Tjong and Lau [49]	92
Figure 6.9	Wear results of Al alloy/SiC composite reported by Modi et al [58]	93
Figure 6.10	Wear results of Al alloy/SiC whisker reinforced composite reported by Yu et al [59]	93
Figure 6.11	Wear rate comparison between Cu/WC composites having different average particle sizes of WC particles	94
Figure 7.1	Comparison of wear rates of Cu/WC composite with Cu/W composite	96
Figure 7.2	Optical micrographs of Cu/WC composites with varying copper content processed at 1250 °C-4 min.	99
Figure 7.3	Wear rate comparison of Cu/WC composites, having varying amount of WC reinforcement, with Cu/W composite	102

List of Symbols

D	Density
$\gamma_{\rm sv}$	Interface energy between solid and vapor
γ_{sl}	Interface energy between solid and liquid
γ_{lv}	Interface energy between liquid and vapor
θ	Contact angle
L	Metal front position
K	Permeability tensor of the preform
ΔP	Pressure drop at the infiltration front
Т	Time
μ	Viscosity of the liquid metal
Vs	Volume fraction of the reinforcements
Q	Heat flux
σ	Stefan-boltzmann constant
3	Emissivity of the heat source
T_1	Heat source temperature
T ₂	Specimen temperature
HV	Vickers hardness number
Р	Load
D	Length of diagonal of the square indentation
ρ	Resistivity
V	Voltage output
Ι	Input current
Х	Volume fraction of porosity
S_N	Normal wear stress
R _{AW}	Rate of abrasive wear
f_R	Reinforcement content in the composite
F _T	Transverse force
A _S	Surface area of the particle exposed to the opposing surface of wear

μ_{f}	Friction coefficient
F _H	Held down force
Ai	Matrix-reinforcement interface area
σ_i	Particle-matrix bond strength
η	Pull-out coefficient
h _{Pull}	Critical wear depth
V _{Wear}	Wear volume of particle
V_{Pull}	Pull-out volume of particle
PF	Pull-out function
A _{R,Ave}	Average cross section area of reinforcement particles
N _R	Reinforcement particle number concentration per unit area of composite
$f_{R,,Eff}$	Effective reinforcement on the wear surface after pullout

1. Introduction

Metal matrix composites are materials with metals as the base and distinct, typically ceramic phases added to improve the properties. Although it is desired that these phases remain distinct and separate, reactions do occur between them. If this is the case, it affects the processing and final properties of the composites, regardless of which type of reinforcement is used. Reinforcement types include laminations, continuous fibers, discontinuous fibers, whiskers and particles of different morphologies. Each of these reinforcements affects the base metal in different subtle ways, but composites generally show improvement over the monolithic metal in at least one of the following properties: yield strength, hardness, tensile strength, wear resistance, coefficient of thermal expansion. Properties that depend on the system include thermal and electrical conductivities.

While metal matrix composites show great potential in these areas, they have only found limited use in actual industrial applications. Continuous fiber composites have been especially restrained, finding use only in high value parts in the aerospace field. This is due to the difficulty in processing of the materials, forcing manufacturers to offer them at high cost. Discontinuous metal matrix composites, isotropic in nature, have more options and ease of preparation than continuously reinforced types, so that cost is lowered and acceptance is wider. However, even these materials are limited to a few industrial applications.

For particle reinforced copper matrix composites, main current commercial processing is done using the powder metallurgy technique of mixing, compacting and sintering. While this method has the advantage of controlling the volume ratio of the

1

constituents it also has many drawbacks. These include tendency to segregate due to the difference in the atomic weight, particles desire to clump with each other, shrinkage and increased void formation. These all lead to higher cost.

Many previous studies by this research group have shown the potential of infrared processing to produce continuous fiber reinforced composites as well particulate reinforced composites. Infrared processing has the advantages of short processing time, minimal reaction between the constituents, no time for reinforcement settling and no need for vacuum or pressure. This thesis shows that tungsten carbide particle reinforced copper matrix composites can be fabricated by the infrared pressure-less infiltration method. Due to the interest in use of tungsten carbide reinforced copper composites for electrical applications such as relays and switches, analysis of the resultant composites focuses primarily on density, porosity, microstructural examination, electrical resistivity, microhardness and wear resistance. The composition of these composites was varied from 53 vol% WC to 32 vol% WC using an innovative technique. The Cu/32vol% WC composite showed better electrical resistivity and higher wear resistance as compared to commercially available Cu/ 52vol% W composites.

2. Background

2.1 Composite Materials

The word 'composite' in composite materials means that two or more materials are combined together in a certain order on a macroscopic level to form a new material with different and attractive properties. The reason alloys are not considered in this category is because they are homogeneous on the macroscopic level.

Composite materials consist of a bulk material called the matrix, and a filler of some types such as fibers, whiskers or particles. Composite materials are conventionally classified into three categories viz. polymer matrix, metal matrix and ceramic matrix depending on the matrix employed. Furthermore, composites can be grouped on the type of reinforcement provided [1]. They are:

Dispersion strengthened: In this type of composite, fine hard particulates, uniformly distributed, ranging in size from 0.01μ m to 0.1μ m and in a volume percentage from 1 to 15% are used to increase the strength and hardness.

<u>**Particle reinforced:**</u> This is similar to the dispersion-strengthened category but the size of the particles is greater than $0.1\mu m$ and the volume percentages can be greater than 25%.

Fiber reinforced: This category includes all types of fibers, whiskers and filaments, continuous and non-continuous, over the whole range of concentration of the reinforcements.

Although the continuous-fiber-reinforced metal matrix composites (MMCs) have the best combination of mechanical properties, particulate-reinforced MMCs are superior from the viewpoint of cost-performance trade-off. Compared to fiber reinforced MMCs,

3

the particulate-reinforced MMCs possess improved ductility, reduced anisotropy of mechanical properties, as well as ease of secondary working with conventional metal working techniques. The availability of inexpensive particulates as reinforcements serves as an added advantage.

In particulate strengthened metal matrix composites, the strengthening is due to both the matrix as well as the dispersed phase. While the matrix provides strengthening by restricting the crack growth, thus avoiding the brittle failure, the dispersed phase acts as an impediment for dislocation movements. This type of strengthening is similar to precipitation hardening but for the fact that the strengthening effect is not as pronounced as with precipitation hardening. But because the particles that are dispersed into the matrix are inert, the strengthening is retained at elevated temperatures. Also, precipitation hardening is limited to the small amount of the dispersing phase. On the other hand, particulate reinforced composite can have significant percentage of the particulate and provide outstanding wear resistant properties. Composite of up to 80-90% particulate have been made.

The properties of a composite depend on the following

- Properties of constituent phases
- Relative amounts of constituents
- Geometry of the dispersed phase
 - Shape of particles
 - Particle size
 - Particle distribution
- Interfacial reactions between constituents

Several properties of the composites may be assessed by the rule of mixture (ROM), which states that the property of the composite is the sum of products of the property of an individual constituent and its volume fraction in the composite. For example:

Density:
$$D_c = D_r V_r + D_m V_m$$
 (1)

where, D stands for density and subscripts c, r and m stand for composite, reinforcement and matrix respectively. This theoretical calculation can be used to check whether the composite produced has the optimum properties. Modulus, Strength, Electrical properties may sometimes be estimated with ROM as the first approximation. Only particulate reinforced metal matrix composites will be dealt with here. Discussion on other types of composites is beyond the scope of this chapter.

2.2 Metal-Matrix Composites

Metal-matrix composites (MMCs) have, in the last two decades or so, come up in a big way primarily because of their superior mechanical properties compared to monolithic materials. The principal advantage MMCs enjoy over other materials lies in the improved strength and hardness on a unit weight basis. Metal-matrix composites were first developed for the application in aerospace industries. The expansion into the nonaerospace and non-military areas came about as the price of MMCs came down largely due to the availability of inexpensive particulates and development of low cost fibers.

Metal-matrix composites have several advantages over conventional structural materials. These advantages include a combination of the following properties [1]:

- High strength
- High modulus
- High toughness and impact properties
- Low sensitivity to temperature changes and thermal shock
- High surface durability and low sensitivity to surface flaws and
- High electrical and thermal conductivity.

Resistance to severe environments, toughness and retention of strength at elevated temperatures are some areas where metal-matrix composites perform better than other composites.

Metal-matrix composites are artificially produced by two or more materials having completely different properties. The constituent materials that often do not posses very good properties on their own, when combined, produce some very attractive propositions for materials design. Metal-matrix composites find applications in the manufacture of aircraft, automobile engines, electrical machinery, electrical and thermal conductors, bearing materials, missiles, spacecrafts, rocket launch vehicle structures and numerous other applications.

2.3 Fabrication Methods

Methods for fabricating MMCs vary from conventional powder metallurgy to newer ones such as in-situ making using laser technology and to specially adapted techniques of electroless plating and hot pressing, liquid metal infiltration [1]. These processes are described in brief as follows **Powder Metallurgy:** This process involves the mixing of two powders in the desired volume ratio followed by compaction. The compacts are then sintered to get the composite. The advantages in this process include the latitude in controlling the volume ratio of the constituents. However, if the difference in the atomic weight of the constituents is large then it is difficult to mix them for liquid phase sintering. Addition of transition metals is a common practice to aid the sintering behavior. This may or may not affect the properties of the resulting composite.

In-situ Processing: This process is similar to the powder metallurgy technique described above in that the powders of the required constituents are mixed in the desired volume ratio. The mixture is then laid in layers and compacted using the laser beam, which melts the constituent with lower melting point and the liquid metal in turn, binds the powder together. This process allows the production of complicated shapes with ease. The shortcoming of the process is that the resulting composite is not fully dense since the narrow laser beam does not cover the entire area effectively.

<u>Electroless plating and hot pressing</u>: The process involves electroless plating of the matrix phase on the reinforcements followed by hot pressing technique. The process is still in the developing stages and not much literature is available to comment on the advantages and disadvantages of the process.

Liquid metal infiltration: In this process the skeleton of the cold-pressed reinforcement is filled with the liquid metal. The liquid metal infiltration has been the area of prime

interest for developing MMCs. The major advantages include low cost, easy processing steps and dense product.

The processes also differ in terms of the heating media used. While vacuum furnaces find wide application in the industries, induction furnaces also has their share of users.

This study is based on infiltration process using infrared furnace. One of the most important factors in infiltration process is the degree of wetting between the constituents. Wettability between the molten matrix and the reinforcement governs the success of any infiltration process and, it is for this reason, we discuss it in the following section.

2.4 Wettability

The contact angle made by the molten metal on the substrate can be used to define the term wetting. If the contact angle is less than 90° , the metal wets the substrate; otherwise it does not. The following Young's equation (2) can be considered as the fundamental equation in calculating the degree of wetting.



Figure 2.1: Schematic of energy balance in a sessile drop

$$\gamma_{\rm sv} = \gamma_{\rm sl} + \gamma_{\rm lv} \cos{(\theta)} \tag{2}$$

where γ is the interface energy and subscripts l, s and v stand for liquid, solid and vapor respectively, θ is the contact angle. $\gamma_{lv} \sin(\theta)$, the vertical component is balanced by A, the work of adhesion.

The primary goal in synthesizing composites is to combine two or more physically and chemically dissimilar materials. The interfacing between the surfaces of different constituents is of vital importance [2-5]. Ideally, this interfacing may be achieved spontaneously if both the phases are physically and chemically compatible. This means that the reinforcing phase must make an intimate contact initially with the liquid metal and then finally with the solidified matrix. The initial contact with the liquid phase is established by replacing the solid-gas interface with an equivalent solid-liquid interface. The energetics of this interface substitution process is primarily governed by the wettability of the system.

To measure the value of the angle of contact, a sessile drop test is often done. The value of (θ) obtained is used to estimate the surface energy of the solid liquid interface.

Although, sessile drop test is a simple, precise and reliable way to calculate the wetting angle, several limitations arise in characterizing wetting during infiltration of fibers by a liquid metal. The data from sessile drop tests are often controlled by epiphenomenon such as the presence and tenacity of oxide layer covering the metal drop or the time of metal particle contact elapsed at the moment of measuring the angle [6]. These complications, along with the variations in test environments, invalidate direct applicability of sessile drop test data to liquid metal infiltration because the velocity of the three phase contact line will be slower in a sessile drop experiment than in processing

[6]. In addition, it does not model composite infiltration and wetting because (1) the interface will not be stationary and (2) surface roughness will rapidly change the apparent contact angle.

The limitations of the sessile drop test are immanent. However, it can still be used to make a rough estimate of the wettability behavior. Reduction of surface energy provides the driving force for wetting to occur. This is the mechanism that liquid metal infiltration uses to its advantage. With good enough wetting, the liquid will automatically cover all of the reinforcement and will pull in the remaining metal to engulf the preform.

So while the advantages of spontaneous liquid metal infiltration have been noted, especially in eliminating the need for vacuum or pressure systems, producers of these types of composites need to have properly accounted for wetting phenomenon.

Mortensen et al [7] studied the kinetics of infiltration. They found that the capillary pressure drop at the infiltration front could be estimated by the following equation:

$$L^{2} = 2.K.\Delta P.t / \mu (1-V_{s})$$
(3)

where, L is the metal front position, K is the permeability tensor of the preform, ΔP is the pressure drop at the infiltration front, μ is the viscosity of the liquid metal, V_s is the volume fraction of the reinforcement and t is the time. Wetting kinetics is generally very complicated [8, 9]. It includes reactions at the interface, solution of elements into one another, absorption of trace elements into the liquid and diffusion of elements through reaction zones, if at all there is any reaction. Roughness of the particle reinforcements also affects the wettability.

The importance of wettability during melt impregnation of preforms is best demonstrated by invoking equilibrium thermodynamic arguments to estimate a lower bound on energy (pressure) requirements for reversible infiltration of pores of various geometries that may form within ceramic preforms. The real process of infiltration, however, requires pressure far in excess of theoretical capillary pressure owing to several complicating factors [7]. Thus melt intrusion and flow in preform are complicated by the irreversible energy losses resulting from the fluid dynamic effects, the viscous shear of the melt moving in a gravitational field, the percolation and end effects near the entrance zone of the preform, the thixotropic dilation and rupture of the oxide membrane on the infiltration front and the possibilities of chemical reactions, solute segregation and liquidsolid phase change accompanying fluid flow.

In this study, the liquid metal infiltration is carried out without the application of any pressure on the liquid metal to force its way into the porous preform. The threshold pressure at the infiltration front is believed to have been overcome due to the excellent wetting characteristics between tungsten carbide and copper, the two constituents used in this study for the making of the composite.

2.5 Copper Composites

This study is based on the tungsten carbide reinforced copper composite. This family of composites benefit from the high electrical and thermal conductivity of copper and mechanical wear and electrical erosion resistance of tungsten carbide. These composites, thus, find applications as contact materials in relays and switches, electrical discharge machining (EDM) electrodes, arcing tips. These composites can match the thermal expansion coefficient of almost any ceramic substrate and can, therefore, be used as heat sinks [10].

Copper-based ceramic composites, in general, offer excellent wear and arc resistance accompanied by high electrical conductance. Application for such materials include welding electrodes, high performance switches and electrometers, metallic friction materials for high speed motors as well as actively cooled parts in gas turbine structures and plasma interactive components in fusion power systems [11].

Copper-based ceramic composites have the advantage of high thermal stability, high heat dissipation (heat sink), and high wear resistance at even elevated temperatures. Copper- based composites are currently manufactured by dry mixing the constituents, cold-pressing followed by high temperature sintering [11]. The conventional processes employ low heating and cooling rate and so application of high pressure during sintering is found necessary because the components expand during sintering at high temperature thus leading to porosity when cooled with the attendant weakening of the bond between the ceramic powder and the metal matrix. The need of pressure during processing limits the productivity and increases the total cost of production.

The reinforcements used in copper based composites depend on the need and requirements of the end application. In applications where high strength coupled with high electrical conductivity is desired, steel rods or wires have been used to reinforce the ductile copper matrix. Graphite reinforced copper composites are in vogue for the applications where the antifriction properties of graphite are desirable. Ceramic reinforced copper composites in which hard particles like tungsten, tungsten carbide, and

12

silicon carbide are reinforced into the soft copper matrix find application in wear resistance or abrasion resistance applications without any major compensation of electrical conductivity [8, 11].

This study is focused on one of the copper based composite systems i.e. tungsten carbide reinforced copper composite. It was a goal for this study to improve upon the widely studied and commercially utilized tungsten reinforced copper composite system. Since the tungsten carbide reinforced copper systems have not been developed, the following discussion highlights the trends in Cu/W system owing to distinct similarity between tungsten and its carbide.

Many methods have been devised to make tungsten-copper composites. Mixing of tungsten and copper powder in a desired volume ratio followed by compaction and sintering at high temperatures in protective environment is a popular manufacturing process [10-12]. Others include casting with addition of some activators to the powder mix to ameliorate the wetting behavior between the constituents [13]. However, the most common and widely used method is the liquid phase infiltration [11]. This involves presintering of tungsten preform followed by the infiltration of the liquid copper in protective environment.

It has been established that the solubility of tungsten in liquid copper is exceedingly small [14]. The C-W phase diagram, Figure 2.2, also suggests that the WC is stable from above 2600°C till the ambient temperature. Earlier data on the solubility of carbon in molten copper suggests that carbon does not diffuse through solid copper and that the solubility is exceedingly small [15, 16]. The success of the liquid phase infiltration process lies in the excellent wetting characteristics between tungsten carbide particles and copper and limited solubility of tungsten in copper (10^{-5} a/o at 1200°C) giving a composite rather than a solid solution [17].

In this section we will discuss in brief the approaches used for making of tungsten-copper composite by various researchers along with their advantages and disadvantages.



Figure 2.2: Phase Diagram of W-C

2.5.1 G. Gusmano et al [10] have reported the preparation of W/Cu composite powders by a wet process based on the reduction of selected copper precursors in ethylene glycol and in the presence of tungsten powders. Reactions were performed in different conditions of temperature, time and concentration of the copper precursor. Two different Cu compounds, Cu (AcO)₂. H₂O and CuO, and tungsten powders were used. The following flow-chart illustrates the processing conditions:



Figure 2.3: Flow-Chart of the Gusmano Process

The above-mentioned process has been able to achieve composites with varying volume ratios of the constituents. Dense bodies (up to 97% fractional densities) with highly homogeneous microstructure as well as high electrical conductivity (up to 41% IACS) were obtained for the composites sintered at 1350°C. However, the yield of the powder after mechanical mixing and heating step was in the range of 70-90 %. Since the starting powders are not pure tungsten and copper, synthesis of each powder requires different process conditions and in some cases particle coalescence might lead to

inhomogeneous powders, which would result in an inhomogeneous composite. The process also has the drawbacks of tedious processing steps and long sintering times.

Mechanically alloyed tungsten-copper composite powders display enhanced sinterability due to their highly refined microstructures, according to recent investigation of these materials. Based on this promising behavior, mechanically alloyed W-Cu powders have been explored as possible raw materials for the production of metal injection molded (MIM) parts by the researchers of Korea's Hangyang University. Despite, the beneficial sintering behavior, the researcher encountered problems in producing high quality MIM parts from the mechanically alloyed powders. They found that parts molded from the powders exhibited low green densities and thus were difficult to transport during further processing. Furthermore, porosity in the MIM green bodies resulted in difficulties in attaining full densification via liquid phase sintering at the relatively low sintering temperature. The low green densities were attributed to the agglomerated nature of the mechanically alloyed W-Cu powders. To minimize the internal porosity in the MIM green parts, the researchers subjected the mechanically alloyed W-Cu powders to a heat treatment in hydrogen at 600°C. Internal pores were largely removed and the specific surface area of the powders was found to increase. The MIM green part fabricated from the hydrogen reduced mechanically alloyed W-Cu composite powders exhibited improved shape stability and high sinterability relative to that prepared from the unannealed powders.

2.5.2 J. L. Johnson et al [12] proposed that for high tungsten contents, the liquid phase sintering method generally results in some final porosity due to the insolubility of

tungsten in liquid copper, which severally limits densification during the solutionreprecipitation stage of liquid phase sintering. Also, for tungsten contents above 65v/o, rearrangement processes alone cannot produce theoretical densities; however, the addition of sintering aids which have solubility for tungsten can greatly reduce the final porosity by promoting either grain shape accommodation or sintering of the tungsten skeleton. The following flow-chart illustrates the processing conditions.



Figure 2.4: Flow-Chart of the Johnson Process

The process has been able to improve the sintering behavior of W-10Cu with small amount of cobalt additions. The sintered densities were 98% of theoretical regardless of heating rate. Cobalt additions had a positive effect on the strength and ductility while the density and microhardness remained the same.

2.5.3 Seung-Ki Joo et al [18] applied a new process, fluidized bed reduction method, for fabrication of uniform W-Cu sintered material. The liquid phase sintering was carried out to obtain fully densified W-Cu composite, and the effect of cobalt addition on the

sintering behavior was investigated. It was found that fully densified material could not be obtained even after sintering at 1200° C for 4 hours in the case of 75W-25Cu, while more than 96 pct density could be obtained as soon as the sintering temperature reached 1200° C when 0.5 wt pct cobalt was added prior to the sintering. They found that the wetting angle of the liquid copper is reduced significantly by the addition of cobalt, and the formation reaction of Co₇W₆ intermetallic compound at the surface of the tungsten powder was mainly responsible for the enhancement of the densification process.

2.5.4 German et al [19] compared the effectiveness of Ni and Co as activators and the dependence of sintered density on initial homogeneity by preparing powders of W-10Cu and 0.5 Ni or Co by three different methods; mixing, milling and coating. Initial homogeneity was found to increase in the same sequence. The compacts were pressed and sintered at 1400°C for 1 hour. For Ni, the sintered density increased significantly with the increasing homogeneity but the density remained well below theoretical. For Co, the powder preparation method had less of an effect on sintered density because of the much greater effectiveness of Co as an activator.

The drawbacks of these processes include the need of lower heating rate to allow additional cobalt-activated solid state sintering to occur before liquid phase formation, thus lowering the production rate, and shrinkage was observed in all the samples due to the rearrangement of particles, which is typical of all liquid phase sintering processes. Gusmano G. et al [10] have reported that the presence of an amount of cobalt as small as 0.5 wt% can lead to a significant reduction of the electrical conductivity, which is detrimental for the electrical applications of these composites. Since the additions of sintering aids cause the deterioration of thermophysical properties such as thermal and electrical conductivity, Joo et al [18] have reported that the requirement for full densification of W-Cu powder could be fulfilled by using micro-homogeneous W-Cu composite powders. Near full density and homogeneous microstructure were achieved in the powder injection molded W-15wt%Cu nanocomposite powder.

2.5.5 R. Jedamzik et al [20] presented a novel processing route that is capable of manufacturing composites with continuous gradients in chemical compositions. This route is based on the electrochemical modification of porous preforms and subsequent infiltration steps. By adjusting the experimental parameters like current density, electrolyte type and conductivity or electrical charge passed through the material, different gradation profiles could be produced. The outline of the process is illustrated in the following flow-chart.



Figure 2.5: Flow-Chart of the Jedamzik Process

The advantages of the process are that the product with unique properties is obtained and it is a semi-automated process. The disadvantages include the requirement of precise control over the processing parameters and it is a tedious and expensive process.

2.5.6 Yoshiyasu et al [21] also developed a sintering and infiltration technique to manufacture functionally gradient materials. The technique consisted of two steps viz. making sintered tungsten with gradient pore distribution and infiltrating molten copper into the pores. In this technique, capsule-free HIP (hot isostatic pressing) treatment was effectively used for fully densifying the surface tungsten layer and for eliminating only closed pores in the other layers. Capsule HIP treatment was found effective to fully infiltrate molten copper into the open pores of the sintered tungsten. This gradient material is found to have excellent ability to reduce thermal stress and has good thermal conductivity from the tungsten layer to the copper.

2.5.7 Bin Yang et al [22] investigated the effects of tungsten particle size on shrinkage, relative density, hardness and microstructure after sintering. They reported that excellent sintered properties could be obtained by chemically depositing 15 wt% copper onto submicron tungsten powder and sintering in pure hydrogen at 1450°C for 90 min. The shrinkage value of 24%, relative density of about 99.6%, Vickers hardness of about 382 HV200 and superfine microstructure were reported. Regarding the tungsten particle size, they observed that finer the tungsten particle size, better the final sintering properties for W-Cu systems. For sintered W-Cu systems with lower copper content (Cu<27.7%), they suggested that full density or very high sintered density required the use of superfine or very fine tungsten particle size, good powder treatment techniques and high sintering temperature.

In one of the studies [23], in-situ tungsten-copper composite was prepared using laser beam sintering technique. The following flow-chart illustrates the process.



Figure 2.6: Flow-Chart of the Process [23]

The advantages of the process include latitude in composition control, in-situ production of complex shapes and automated nature of the process. However, the process is slow since narrow beam of laser is employed and there is a great deal of porosity in the final product.

From the above discussion on various ways of making the tungsten-copper family composites, it can be concluded that there are some desirable key issues in the making of the composite. They are listed as follows

- Minimum processing steps
- Higher production rates

- Homogeneous microstructure
- Low or no shrinkage
- Optimum mechanical and electrical properties.

In the following section we will take a brief overview of the patents related to this family of composite.

2.6 Patents

The commercial significance of W-Cu composites have led to various researchers registering patent for not only the process of producing this composite but also the process of making the starting powders and preforms for the making of this composite.

Byoung-Kee et al. [24] have received a U.S.A. patent for the process of producing high density and ultra fine W/Cu composite material by the mechano-chemical process. In the method of this invention, metal salts as start materials are spray dried under the condition of 250° C of container temperature, 11,000 rpm of nozzle rotation velocity and 20 ml/min of flow rate of aqueous solution thus producing W-Cu precursor powder having uniformly dispersed tungsten and copper components. The W-Cu precursor powder in turn is subjected to a desalting and dehydrating process at 750°C for 2 hours in the air atmosphere, thus preparing W-Cu oxide composite powder. Thereafter, the W-Cu oxide powder is formed into a green body and is then subjected to reduction and sintering at a temperature 50°C above the melting point of copper for 1 hour at a heating rate of 5° C/min under hydrogen atmosphere. The process was successful in producing W-30% Cu composites.

Dorfman et al. [25] obtained a U.S.A. patent for devising a method for making of tungsten-copper composite oxide. In this method an amount of an ammonium tungstate

and an amount of an oxide or hydroxide of copper are combined without milling to form a mixture. The unmilled mixture is then dehydrated and fired at a temperature and for a time sufficient to form the tungsten-copper composite oxide.

Schmidt et al. [26] have patented the method of making tungsten-copper pseudo alloys by a consumable electrode method. In this process, lower end of a consumable electrode, having a copper matrix with a plurality of tungsten strips embedded longitudinally therein, is subjected to direct current arc melting within an enclosed chamber containing an inert gas. The volume percent of tungsten is varied from 2-50%. During the arc melting, super atmospheric inert gas pressure is maintained in a chamber sufficiently above the vapor pressure of Cu at the liquidus temperature of the alloy being formed effectively to suppress boiling point of liquid copper. The melt of the electrode is cast into an ingot.

Dorfman et al. [25] patented the sintering technique of W-Cu pseudo alloy articles having homogeneous distribution of W and Cu phases without experiencing copper bleed-out. The tungsten-coated copper composite powder comprising individual particles having a tungsten phase and a copper phase wherein the tungsten phase substantially encapsulates the copper phase is compacted and then subjected to sintering. The sintering comprises of subjecting the compact to a temperature cycle comprising (1) increasing temperature from ambient temperature to a temperature sufficient (950°C to 1080°C) to cause solid state sintering, (2) slowly increasing the temperature at a rate of about 1°C/min to about 5°C/min until liquid phase sintering begins (1080°C to 1130°C), and (3) increasing the temperature to a temperature sufficient (1150°C to 1600°C) to complete densification of the compact.

Yoo et al. [27] have patented the tungsten skeleton fabrication method employed in application of copper infiltration. The fabrication method includes the steps of forming a source powder by coating the tungsten powder surface having purity of 99.9 weight percent with nickel by less than 0.06 weight percent, forming an injection molded admixture by admixing a source powder and a polymer binder, carrying out a powder injection molded with regard to the admixture, and obtaining tungsten skeleton structure by removing the polymer binder from the resultant injection molded body. The method prevents the molded body from being unevenly shrunken during a liquid phase sintering for thereby decreasing its production cost.

The various patented processes discussed above, though provide new dimensions to the art of making W-Cu family composites they still remain wanting as far as the productivity is concerned.

2.7 Tungsten Carbide vis-à-vis Tungsten

The tungsten-copper composites have been studied in details by various researchers. However, for electrical contacts and similar applications, a material having better electrical conductivity and wear resistance along with its chemical stability is desirable. The following properties of tungsten carbide make it a serious candidate for its viable use in copper based composites.

- Lower density (15.63 g/cc) as compared to tungsten (19.3 g/cc)
- Electrical conductivity of tungsten carbide is in the range of tool steel and carbon steel.
- Tungsten carbide retains its room temperature hardness up to 1400°C.
- Its wear resistance is better than wear-resistant tool steels.
- Tungsten carbide undergoes no phase changes during heating and cooling and retains its stability indefinitely.

Tungsten carbide has already been used as reinforcement for silver based composites for electrical contact applications [28]. However, the Cu/WC system has not been studied yet. This study employs the liquid metal infiltration technique for the production of tungsten carbide-copper composites. As we have discussed earlier, the success of this process lies in the excellent wetting characteristics between tungsten carbide particles and copper and limited solubility of tungsten in copper (10⁻⁵ a/o at 1200°C) giving a composite rather than a solid solution. The limited solubility of the constituents could have led to the porous composites but for the promoting factors such as high temperature and micron size particles which give the sintered density close to the theoretical density [17]. The need of higher temperatures is the shortcoming of the conventional liquid phase sintering/infiltration techniques in vogue due to slower heating and cooling rates. The present study is an effort to overcome this shortcoming using the infrared heating technology, producing composites having comparable, if not better, mechanical and electrical properties.

2.8 Infrared Heating

All bodies radiate energy as a function of their absolute temperature, as defined by Stefan-Boltzmann's Law [29]. No medium is required for the transfer of energy as it is transported by the electromagnetic wave propagating at the speed of light. The infrared rage is the portion of the electromagnetic spectrum with wavelength (λ) lying between 0.78 to 100 μ m. The actual emission spectrum of a given source depends on its absolute temperature. Higher the temperature, shorter is the average wavelength of the energy spectrum. The infrared electromagnetic spectrum can be divided into three divisions, short wave 0.78 - 2.0 μ m, medium wave 2.0 - 5.0 μ m, and the long wave 5.0 - 1000.0 μ m.

As defined by Bischoff [30], categories of infrared emitters can be classified into three categories:

- Short-wave 0.85 1.6 μm, peak wavelength 1.2 μm and maximum running temperature 2200°C, power density 60 - 600 kW/m², and 1 second response.
- (2). Medium-wave 2.1 2.75 μm, peak wavelength 2.6 μm and maximum running temperature 950°C, power density 30 40 kW/m², and response 30 90 seconds.
- (3). Long-wave 3.5 6.0 μm, peak wavelength 3.0 μm and maximum running temperature 800°C, power density 30 - 40 kW/m², and response 3.0 - 10 minutes.

The absorption of radiation heat is dependent on the wavelength. Certain materials absorb shorter wavelengths better while other materials are better absorbers of longer wavelengths. The factors on which the absorption is dependent on are color, material, surface condition, temperature and the absorptivity of the material.

There are three heat transfer mechanisms, conduction, convention, and radiation. Conduction and convention of transport rely on the existence of a material medium. For heat conduction to occur there must be temperature inequalities at neighboring points in the material medium. For heat convention to occur, there must be a fluid that is free to move and transport energy with it. The radiation heat transfer may be represented by equation (4)

$$q = \sigma \varepsilon (T_1^4 - T_2^4) \tag{4}$$

Where q is the heat flux, σ is the Stefan-Boltzmann constant of 5.670 × 10⁻⁸ Wm⁻²K⁻⁴, ε is the emissivity of the heat source, T₁ is the heat source temperature and T₂ is the specimen temperature both in Kelvin [31]. Radiation, and particularly infrared radiation, is much more rapid than the other two heat transfer mechanism. Infrared radiation is more effective for heat transfer because for most of the materials the atomic bonds are excitable by radiation for which the wavelength lies within the infrared radiation region.

Besides, infrared radiation for industrial application is typically produced by quartz type radiators, which ensure high power densities, maximum heat efficiency, flexible design parameters and easy control. The quartz type radiators can consist of a tungsten filament encapsulated in a quart envelope in which halogen is the atmosphere. The tungsten is heated as high as 3000°C, which results in shorter overall wavelength of energy and increased emissive power. According to equation (4), we can expect the heat flux from an infrared heat source to the absorber would be more than one order of magnitude higher than that from a resistance heat source.

Comparing with conventional resistance heating, infrared heating has many advantages. Infrared heating is a cold wall process, in which only the sample is heated to the desired temperature. This allows for fast heating and cooling, precise control of the temperature, instantaneous starting and stopping, and low operating cost. Heating rate on the order of 100°C/sec and cooling rates on the order of 20°C/sec can be archived during

infrared heating process. Typical heating and cooling curves for resistance, induction, and infrared joining process are shown in Figure 2.7.



Figure 2.7: Schematic representation of typical heating and cooling cycles for (A) rapid infrared furnace, (B) induction furnace, (C) resistance / vacuum furnace

Utilizing the heating and cooling rates produced by infrared, composite making can be accomplished in an inert gas atmosphere in minutes. However, conventional vacuum or resistance heating typically takes multiple hours [32].

The infrared processing has witnessed the success of joining of advanced materials such as titanium-matrix composites, titanium aluminide, iron aluminide, nickel aluminide, titanium alloys, nickel based superalloys, carbon-carbon composites and steels. Not only can joining be completed in seconds and vacuum requirements be eliminated, but the joining process has very little effect on the base material properties.

The process has also been used to fabricate SCS-6 and carbon-fiber-reinforced titanium and aluminum-matrix composites with well-controlled interfaces. Infrared composites showed very small interfacial reactions and possessed mechanical properties superior to currently available titanium- and aluminum-matrix composites [33-46].

In summary, the rapid infrared process provides a quick, simple, and economical method of joining and composite making. The process does not require any vacuum, has low investment and operating costs while producing no environmental wastes.

2.9 Electrical Contact Requisites

High electrical and thermal conductivity of copper are combined with the wearresistant and non-welding properties of tungsten or their carbides to form an extensive series of compositions each designed to give the best performance for a given particular application.

It is easy to think of electrical resistivity and wear resistance as the two most governing criteria in developing the electrical contact material. However, the importance of fully dense structure cannot be overstated since any presence of porosity in the materials will have an adverse effect on its wear resistance. The porosity in the composite acts as non-load bearing area and thus leads to an increased effective operating pressure. The resulting increased effective operating pressure can lead to increased wear rate of the composite and increased overhaul charges among other potential losses.

While the electrical conductivity increases with increase in copper content, the wear resistance dependence on the reinforcing tungsten carbide phase depends on various other factors. In the next section we will discuss various factors which govern the wear characteristics of composites.

2.10 Wear Resistance of MMCs

There are a few methods used for measuring the wear property of materials: hardness measurement, scratch test and wear test as demonstrated in the literature. Though microhardness of the composite provides, to a certain extent, a measure of wear resistance, it is indirect and reflects the composite property from a very small area seen by the indenter. The scratch test done by scratching a stylus over the wear surface is improper for composite materials owing to composite surface's alternating soft-hard nature. On the other hand, the wear test is a better representation of the wear resistance of the composite since it covers a relatively large area of the specimen being inspected and reflects the real wear against an opposing surface.

For wear of monolithic metal against abrasive counter surfaces, Richardson [47] suggested that wear was governed by factors such as the hardness of metal being tested (H_m) and the hardness of the abrasive counter surface (H_a) . The relative abrasive wear

rate of metal tends to decrease when H_m exceeds about 0.8 H_a . When $H_m < 0.8 H_a$, the abrasive particle will indent and penetrate into the metal surface. When $H_m > 0.8 H_a$ the abrasive particle will be strained and blunted. Experimental evidences had verified such differences.

For composite materials, the wear phenomena differ significantly from that of the monolithic metal due to the multiple phase nature of the composite. It is believed that during the initial stages of the abrasive wear test of MMCs, the abrasive particles from the counterface are capable of gouging the soft metal matrix from the polished composite surface, thus, protruding the reinforced particles to the composite surface. At this stage, the hard reinforced particles are in contact with the abrasive particles. The wear mechanism, from hereon, is governed by various intrinsic factors such as hardness difference between counter faces, hardness of the reinforcement and the matrix amount of reinforcement, the size and shape of reinforcement, hardness, distribution of reinforcement, bond strength between the reinforcement and the matrix, interfacial reaction between the reinforcement and the matrix, porosity and pore distribution.

The particle size of the reinforcement determines the load bearing capacity of the reinforcement and the surface area for bonding i.e. interfaces between the constituents of the composite. In their study of SiC particle reinforced aluminum alloy composites, Sahin et al. [48] observed that increasing the particle size of SiC resulted in increasing density of the composite, thus, resulting in decreasing wear rate. The decrease in the wear rate with increase in the particle size was also evident in the study of Al_2O_3 – reinforced aluminum composites by Yilmaz et al. [49]. The volume fraction of reinforcement governs the extent of exposure of the soft matrix phase to the abrasive counterface during

the wear test. Sahin et al. [50] observed that the wear rate of Al alloy / SiC composite decreased with the increase in volume fraction of SiC particles, Figure 2.8. A considerable reduction in wear was observed for the 10 vol% SiC particulate composite, compared to the unreinforced alloy. However, increase in the volume fraction beyond 10% produced only a small decrease in the wear rate. Tiong et al. [51] in their wear study of Al-4 wt% Cu/TiB₂ composites also observed a decreasing wear rate as the reinforcement content increased. The nature of interface between the constituents of the MMCs determines the ability of the matrix phase to hold the reinforcing particle and prevent its pull out during the wear test. Wang et al. [52] observed that Ti₅₀Ni₂₅Cu₂₅ particle reinforced aluminum matrix composite with interfacial reactions exhibits lower wear resistance than the composite without interfacial reactions. The effect of porosity on the wear behavior of composites, however, is not well documented. In the limited study that has been done on the effect of porosity on the wear resistance of composites, it has been observed that the presence of porosity can be very detrimental to the wear characteristics of composites [48, 50, 53, 54]. Gui et al. [54] considered the pores in the Al-6Cu-Mn/SiCp composite equivalent to crack sources which can be created when an external force is applied. The intrinsic factors described above could also have a combination effect on the wear resistance of the MMCs [48, 50, 54].

The wear resistance of composite can also be affected by extrinsic factors such as applied load/stress, test temperature, counterface material and counterface surface condition (as in dry or lubricated). The other significant extrinsic factor, often overlooked in various studies, is the cleaning of the wear debris from the wear track to avoid threebody wear. While all the extrinsic factors can have a significant individual or combined

effect on the wear resistance of the composite, most of the studies focused on the effect of applied load/stress [48-53]. It is imperative at this point to underline the significance of using applied stress, instead of applied load, while reporting the wear data. The knowledge of applied stress associated with a given wear rate value is of more practical importance with respect to understanding the true potential of the material.

In the studies related to effect of applied load/stress [48-51, 53], it was observed that the wear rate increased continuously with the increase in applied stress, Figure 2.8. The increase in applied stress leads to increase in wear of the load bearing reinforcement particles and also resurfacing of soft matrix phase to the abrading surface. The wear rate increases linearly with the increase in applied stress till a point after which it deviates from linearity and the wear rate is more pronounced with the further increase in applied stress. This deviation from linearity is due to change in wear mechanism at higher applied stress. As the applied stress increases beyond a certain value, defined by the intrinsic and extrinsic factors, the matrix is no longer able to hold some of the reinforcing particles leading to their pull-out from the wear surface. The particle pull-out is accompanied by instant loss of material and reduced effective reinforcement on the wear surface. Both factors lead to the deviation from linearity of the wear rate curve.



Figure 2.8: Wear test results of Al/SiC particle composites reported by Sahin and Acilar [48]

In the studies related to the effect of test temperature on the wear rate of composite [55-57], it was observed that increase in the test/sample temperature resulted in increased wear rate. The increase in test temperature leads to increase in coefficient of friction between the contacting surfaces which leads to increase in the wear rate. Also, the matrix starts to loose its ability to hold reinforcing particles with the increase in temperature leading to increased probability of particle pull-out phenomenon.

The significance of abrading surface material lies in the fact that this material should be harder than the wear surface and should provide an identical counterface during the entire duration of the test. This requires cleaning of the wear track during the entire duration of test to avoid any three-body wear mechanism. Muratoglu et al [55] observed that the presence of wear debris on the wear track can lead to significant increase in the wear rate of the composite. It was also observed in their study that presence of lubrication between the contacting surfaces can lead to decrease in wear rate of composite. The lubrication reduces coefficient of friction between the contacting surfaces and thus leads to a decreased wear rate as compared to wear under dry conditions.

The wear resistance of composite can be regulated by optimizing the intrinsic factors during design and fabrication of composite. However, assessing the wear properties of composite requires adequate control on the extrinsic factors. In this study, an attempt is done in addressing all the intrinsic and extrinsic factors during the design, fabrication and testing of Cu/WC composites.

3. Objectives and Approach

The Cu/W composite has been the subject of investigation of various studies dealing with the development of electrical contact material. However, an electrical contact material having comparable electrical resistance and an improved wear resistance can be an attractive substitution for widely used Cu/W composites.

Tungsten Carbide has been successfully used as reinforcement in silver matrix composites. The superior properties of tungsten carbide as compared to tungsten were the driving force for this study. The objective of this work was to develop fully dense Cu/WC composites as a potential candidate for electrical contact application by pressureless infiltration technique and comparing them with the commercially acceptable electrical contact materials with respect to their electrical and mechanical properties. The approach was to design a process for developing fully dense Cu/WC composite and subject these composites to relevant characterization techniques to assess their true potential. The scope of work also included developing a model to predict the wear mechanism of particulate reinforced MMCs and improving the electrical and mechanical properties of Cu/WC composites as compared to its commercial counterparts by employing an innovative composition variation technique.

4. Experimental

4.1 Materials

Tungsten carbide powder (Alfa product, 99.5% purity) having an average particle size of 1 μ m, Figure 4.1, was used to make preforms for infiltration. The agglomerations of powders, if any, were broken using sieving and the mortar and pestle grinder. In all experiments, 2-3 gm of powder was used. The weighed powder was then poured in a cylindrical die made of steel. The die was thoroughly cleaned with acetone, dried and lubricated with silicone lubricant to provide smooth surface for the powder to be compacted prior to loading the powder. The die, containing the powder, was then subjected to cold hand pressing followed by mechanical compaction. A compacting pressure of 34.5 MPa was used to obtain green preforms. Cold pressing at this pressure resulted in cylindrical preforms 9.6 mm in diameter and 3.8 mm in height with density values equal to 53 ±1% of the theoretical density (15.63 g/cm³).

A copper block weighing around 2.5 gm was cut from a 99.9% pure copper bar. The copper block was polished using SiC polishing paper to remove the oxide layer, if any. It was then cleaned ultrasonically with acetone and the deionized water before infiltration.

4.2 Experimental Procedures

For infiltration, a graphite crucible of 9.7 mm inner diameter was used to hold the preform and copper block, Figure 4.2. Graphite was chosen because a) it has excellent emissivity to convert IR radiation into heat, b) it is easily machined, c) it does not form compound with either copper or WC, and d) the solubility of graphite in copper is



Figure 4.1: SEM micrograph of morphology of WC particles



Figure 4.2: Schematic of the experimental set-up

exceedingly small (0.003 wt% at 1700 °C) [22]. The preform was loaded carefully in the graphite crucible to avoid any cracking. The copper block was placed on top of the preform. The whole assembly was then subjected to infrared heating. The sample temperature was monitored and controlled by using a Pt/Pt-10%Rh thermocouple, secured at the bottom of the graphite crucible. Infiltration was carried out at different combinations of time and temperatures under a flowing argon atmosphere to avoid oxidation. A typical thermal cycle consisted of heating the assembly to a preset processing temperature above the melting point of copper (1083 °C), holding for 2-8 minutes followed by rapid cooling down to room temperature. All heating cycles were completed in less than 30 min.

4.3 Characterization

The composite density, microstructure, electrical resistivity, hardness and wear resistance were determined immediately after the infiltration process. Prior to characterization, excess copper on the composite surface was removed with cutting and grinding.

4.3.1 Density Measurement

The infiltrated composite was cut into a rectangular block by high-speed saw (Buehler Isomet 2000, Lake Bluff, IL) using diamond blade. The densities of the sintered samples were measured by Archimedes principle of water displacement using the Mettler H54AR, Matawan, NJ suspension balance. The height and diameter of the composite were determined and compared to the initially measured height and diameter of the green preform for shrinkage determination. Using the measured density values, the porosity of each composite was calculated by comparing with the theoretical density, calculated by the rule of mixtures.

4.3.2 Microstructure

A part of the composite was cold mounted for the metallographic examination. The sample was polished down to 1 μ m with diamond paste. The micro-images were taken using an optical microscope (Buehler Versamet, Lake Bluff, IL).

4.3.3 Electrical Resistivity Measurement

The electrical conductivity was assessed by using C4S-64/5S four-point probe at a constant current of 2 Amp. The spacing between the probes (s) is 0.159cm (0.0625 inch). The resistivity was calculated using the following resistivity equation for the bulk specimen,

$$\rho = 2\pi s \cdot V / I. \tag{1}$$

Where, ρ is the resistivity (Ω -cm), V is the output voltage (V), I is the input current (Amp). At least 7 readings were taken for each sample and the average value was calculated after removing the highest and the lowest value.

4.3.4 Microhardness Measurement

Microhardness was measured using a Vickers hardness tester (LECO M-400-H1, St. Joseph, MI) at a constant load of 100 gm and dwelling time of 15 seconds. At least 7 measurements were done for each sample. The average value was taken after removing the highest and the lowest value. The hardness tester calculates the hardness value using the following formula.

$$HV = 1.72 \cdot P / d^2$$
 (2)

where, P is the load and d is the length of diagonal of the square indentation. The indent diagonals were measured with an optical microscope at a magnification of 400 times.

4.3.5 Wear Test

The wear test was carried out with a pin-on-disk tester as shown in Figure 4.3. The test set up was isolated from the environment, by keeping it enclosed in a glove box, to maintain constant temperature and humidity conditions. The temperature was monitored by using a thermometer while humidity was monitored by using a psychrometer, which operates on wet bulb-dry bulb method. The tests were carried out at room temperature. The temperature and relative humidity levels (55%) were found to be consistent during all the tests.

Each specimen was ground up to grade 1200 abrasive paper to ensure that the wear surface was in complete contact with the abrasive counterface. Rectangular specimens having contact area of 0.167 cm² were loaded against a disk, which rotated at 184 rpm. The disk carried an abrasive SiC cutting blade (180 Grit) (Metlab, NY). The applied normal loads used were 1.12N, 2.17N, 3.21N, and 4.27N except the fully dense composites, for which up to 22 N were used. Thus, the applied pressure was varied from 0.07 to 0.26 MPa. The sliding distance was kept constant at 500m for each sample.



Figure 4.3: Schematic representation of a pin-on-disk wear tester

Simple mechanical wiping of the debris, with a brush, from the SiC blade surface was employed during the entire test duration. The wear rates of the composite were calculated by dividing the difference in weight of the specimens measured before and after the tests (measured with an analytical balance Mettler AJ100, Hightstown, NJ of 0.1 mg precision) by the sliding distance. Copper, being a soft metal, undergoes plastic deformation during the test. Wear removed copper debris might be deformed to the side of the tested samples and still attached to the test bar. It is because of such observations, the wear loss of copper was determined by the length reduction of the sample after the test.

5. Results and Discussion

Composite samples were prepared at 1200, 1250, 1300, and 1350 °C with the holding time varying from 2 to 8 min. For samples processed at 1200 °C for 2, 4 and 6 min, only partial infiltration was observed. Samples prepared at 1250 °C and 1300 °C for 2 min also show partial infiltration. Only those samples with complete infiltration were further analyzed for their density, microstructure, electrical resistivity, microhardness and wear properties.

5.1 Density Measurement

Figure 5.1 shows the measured density of the composite samples prepared at different conditions of time and temperature. The reported density value for each condition is the average density value from two or more samples done under the same condition. It was found that there was only negligible density deviation for samples prepared under the same conditions.

The dimensions of the infiltrated composites were determined from polished composite cross sections. It was found that there was no detectable dimensional difference between the preform and the infiltrated composite. No expansion or shrinkage of preform occurred as a result of infiltration. This observation allows us to estimate the theoretical composite density based on the green density of the preform. Using the measured density values, the porosity of each composite can be calculated, when comparing with the theoretical density, by the equation derived as follows. Considering a composite with the WC volume fraction being V_{WC} , the density of the composite would be given as following

$$d_{c} = V_{WC} d_{WC} + (1 - V_{WC} - X) d_{Cu}$$
(1)

where, X is the volume fraction porosity; d_{WC} is the WC density; and d_{Cu} is the copper density. With zero porosity, the theoretical density of the composite, $d_{c,th}$, would be

$$d_{c,th} = V_{WC} d_{WC} + (1 - V_{WC}) d_{Cu}$$
(2)

Combining Equations (1) and (2), we have

$$X = \frac{d_{th} - d_c}{d_{Cu}}$$
(3)

where, $d_{c,th}$, d_c and d_{Cu} are the theoretical composite density, measured composite density and pure copper density, respectively. In this study, V_{WC} is 0.53 and the WC density and Cu density are 15.63 gm/cc and 8.9 gm/cc. The percent porosity, thus, will be 100 times the volume fraction porosity. Using the average WC preform green density, the calculated theoretical composite density, assuming no porosity, is 12.33 g/cm³. Meanwhile, the maximum measured composite density is 12.44 g/cm³ for the composite prepared at 1350 °C for 8 min. The fact that the maximum measured density is higher than the theoretically calculated density might indicate a slight shrinkage occurred during infiltration. Since, the difference is 0.89% reflecting a possible volumetric shrinkage, the corresponding linear shrinkage would be 0.3%. The 0.3% linear change is beyond the experimental limit of dimensional measurements from the cross section images of the as fabricated composites obtained in this study. The difference between the theoretical density and actual density of the composite processed under this condition being less than 1% suggests that the composite so prepared (at 1350 °C and 8 min) is fully dense and the porosity, if any, is negligible.

For porosity calculations in this study, 12.44 g/cm³ was used as the actual theoretical density to account for the potential shrinkage of composite during processing.



Figure 5.1: Density variation with infiltration time and temperature



Figure 5.2: Porosity variation with infiltration time and temperature

The variation of porosity with time and temperature, as shown in Figure 5.2, shows that all samples processed at 1350 °C and samples processed at other temperatures but with 8 min infiltration time, except for 1200 °C, have extremely low porosity.

It can be seen from Figure 5.1 that the composite density increases with increasing processing time and temperature toward the theoretical density. Correspondingly, the percent porosity variation with time and temperature, Figure 5.2, indicates rapid fall in the porosity levels with increasing temperature or increasing time at the same temperature. Increasing the temperature to 1350 °C allowed one to shorten the holding time to only 2 min and still give composites with near-theoretical density values. The ease in infiltration at high temperatures can be attributed to the fact that, since, the WC preform is porous and the WC has lower heat conductivity and higher heat capacity, as compared to the Copper, it requires longer time to reach the set point temperature and so the superheat of molten copper should be high enough to avoid any solidification at the Cu/WC preform interface. At lower temperatures, longer holding times are required to allow WC preform reach the set point temperature. Also, for cases of relatively high temperature infiltration, both viscosity [58] and superheat of copper factors are favorable for infiltration resulting in composite approaching theoretical density even at shorter holding times.

The increase in density, for a particular temperature, with increase in infiltration time can also be attributed to the fact that the air/gas entrapped in the preform gets longer time to diffuse out and let the molten copper fill in the fine pores to aid completion of the infiltration process. The decrease in viscosity with increase in temperature also favors

the diffusion phenomenon of the entrapped air/gas. Thus, the processing time can be reduced if high temperatures are used.

5.2 Microstructure

The micrographs of polished composite cross-sections were taken using the Buehler optical microscope and are shown in Figure 5.3. Three distinct regions can be identified: the white region representing the copper phase, the grey region representing the WC phase and the dark regions reflecting pores. The micrographs show uniform distribution of both the Cu and WC phases with no noticeable isolated areas containing only a single phase. The maximum pore size appears to be around 15 μ m, Figure 5.4, in diameter.

The effect of time and temperature on the porosity of the Cu/WC composites can also be observed from the micrographs. At low temperatures and short processing times, the samples showed evidences of pores (the dark regions). Under these conditions, the viscosity and the superheat of molten copper are not sufficient to fill in the fine pores before copper solidified. The voids in the micrographs could also be blind pores formed due to the agglomeration of sub-micron sized tungsten carbide particles. The sub-micron sized WC particles tend to form agglomerates during the cold-pressing step of preform preparation. Pores inside agglomerates were not easily accessible by the molten metal. Penetration of molten metal through the agglomerate shell requires excess time or temperature. It can be seen from the micrographs that as the processing temperature or the holding time for a particular temperature is increased, the porosity is reduced.

The potential cause for void formation which is due to thermal mismatches was not likely to have happened. The difference between the CTE values of copper (16.5 x $10^{-6}/^{\circ}$ C) and tungsten carbide (5.2 x $10^{-6}/^{\circ}$ C) makes it imperative to consider the CTE effect on the Cu/WC composites. The CTE difference might lead to generation of stress during the cooling cycle. When the value of this stress at the interface exceeded the critical stress value, de-bonding between the constituent phases might happen and lead to initiation of micro-voids. However, this is only true for the constituents having poor bonding between them and both constituents being rigid. In the Cu/WC composite, at the highest processing temperature, the strain developed in copper matrix ($\Delta\alpha\Delta T$) is higher than the yield strain of copper. Since the wetting characteristics between copper and WC are favorable, copper is believed to have yielded, avoiding de-bonding and micro-void generation and thus ruling out the CTE contribution to the presence of voids.

5.3 Electrical Resistivity Measurement

The resistivity of Cu/WC composites was determined with a four-point probe for electric resistivity. Table I lists results of all composites processed under different conditions in this study. The fact that all completely infiltrated composites show similar resistivity of around $3.3 \times 10^{-6} \Omega$ -cm or a conductivity of 52 %IACS (International Annealed Copper Standard) suggests that pores in the composite do not affect the electrical property of composites.

For comparison, the resistivity values of commercially available Cu/W composites are listed in Table II, in which S1WC, S3WC, S5WC, S10WC and S30WC are product identifications having compositions shown also in the Table II.

Comparing Table I and Table II, it can be observed that, for similar reinforcement content, the electrical resistivity value of Cu/WC composites is at par with that of Cu/W composites. The similar electrical resistivity values can be appreciated more by considering that, for a similar amount of copper content, the Cu/W composite has tungsten as a reinforcement which is much more conducting than that of the WC reinforcement used in the Cu/WC composites.

5.4 Microhardness Measurement

Microhardness of all the composites was determined with a Vickers hardness tester. The microhardness values of all completely infiltrated Cu/WC composites (Table 3) were in the range of 360-370 HV, Table III. As a reference, the microhardness value for pure copper is 65 HV. The effect of reinforcement on indentation during the hardness test can be visualized form the micro images of indented surfaces. Figure 5.5 shows the optical micrographs of indentation images of WC reinforced copper composite and pure copper under identical indentation conditions: 100g load and 15 seconds dwelling time.

It can be seen from Figure 5.5 that a significantly larger indent was made on pure copper than that on composites. Such indent size comparison suggests significant improvement in resistance against diamond stylus indentation under 100 gm load when 53 vol% WC particles were placed among the copper matrix.

Included in Table III is also the standard deviation of measured hardness data for each sample. For micro-hardness measurements of composites consisting two or more constituents, deviation in measured hardness values could come from presence of isolated phases, i.e. copper or WC in this study. This could lead to significantly lower or higher

hardness values than the average composite hardness value. In the samples prepared in this study, no significant hardness deviation was found. The consistent hardness values for Cu/WC composites processed at different conditions of time and temperature suggest that (a) the presence of porosity, even for the less dense composite, did not affect the hardness of the composite as a whole, and (b) there were little or no isolated WC or Cu phases in the composite, indicating homogeneous distribution of phases.

The hardness measurement was considered to be a measure of wear resistance of these composites. However, the hardness tester provides information about only a very small portion of the composite, seen by the indenter. The small size of the indenter and low load, 100 gm, employed during the hardness test are not able to gauge the porosity contribution to the hardness values. Since the presence of porosity has a significant effect on the wear resistance of any material, it was deemed crucial to assess the wear resistance of resistance of Cu/WC composites before proclaiming them as a potential candidate for electrical contact application.

Table I

Resistivity of Cu/WC composites (in $\mu\Omega$ -cm)

Time	Temperature					
(sec)	1200 °C	1250 °C	1300 °C	1350 °C		
120				3.4		
240		3.4	3.3	3.3		
360		3.3	3.4	3.4		
480	3.3	3.4	3.5	3.3		

Table II

Resistivity of Cu/W composites (in $\mu\Omega$ -cm)

Material Grade	Composit	tion (vol %)	Electrical Resistivity	
	Tungsten	Copper	(μΩ–cm)	
S1WC	37	63	2.68	
S3WC	49	51	3.06	
S5WC	52	48	3.18	
S10WC	58	42	3.58	
S30WC	65	35	4.10	

Table III

Time	Temperature					
(sec)	1200 °C	1250 °C	1300 °C	1350 °C		
120				359 (±3)		
240		367 (±12)	362 (± 14)	368 (±4)		
360		362 (±9)	361 (±8)	362 (±2)		
480	364 (±15)	365 (±4)	369 (±5)	367 (±5)		

Microhardness of Cu/WC composite (HV)



a) Cu/WC Composite at 1300⁰C-240 sec



b) Copper

Figure 5.5: Optical micrographs of comparison of indentation sizes on the Cu/WC composite and the copper

5.5 Wear Test

Wear resistance of Cu/WC composites was measured using a pin-on-disk method with a composite pin against a SiC disk. The SiC disk is a sintered SiC disk with the grain size of SiC particles ranging from sub-micron to more than 100 μ m.

5.5.1 Wear of Composites Containing Pores

The wear test was carried out for Cu/WC composites with different porosity: 0, 1, 5, 7 and 12%. Figure 5.6 shows the wear rate of these wear tested Cu/WC composites under identical testing conditions. All samples show an increase in the wear rate with the increase in applied load. The fully dense Cu/WC composite samples showed the least wear rate among these composite samples at all applied loads. The fully dense Cu/WC sample was prepared at 1300 °C for 8 min and has only negligible porosity, as can be seen from Figure 5.2. The Cu/WC sample with the highest porosity (12% porosity) was prepared at 1250 °C for 4 min and exhibited the highest wear rate of all samples at all applied loads. The 7% and 1.5% porosity Cu/WC samples were prepared at 1250 °C for 6 min and 1250 °C for 8 min, respectively, and showed intermediate wear rates. Data presented in Figure 5.6 also show that the porosity effect on the composite wear rate is more pronounced at high applied loads. In the following sections, we attempt to provide explanations of the porosity effect on the wear behavior of composites.

First of all, the porosity in the wear surface of composite effectively reduces the contacting surface area against the opposing abrasive surface and thus increases the net wear stress that the pin presses on the disk.



Figure 5.6: Effect of porosity on the wear rate of Cu/WC composites



Figure 5.7: Effect of porosity on the wear rate of Cu/WC composites with the effective area compensation

Having observed the composite wear rate increase with the increasing applied wear stress for fully dense composites, we expect an effect of porosity on the composite wear to be an increased wear rate from the increased effective wear stress. One may treat the wear data using the effective wear stress in place of the applied stress by using the true composite contact surface area for the stress calculation. Figure 5.7 shows the wear rate as a function of effective contact stress during wear. Comparing Figures 5.6 and 5.7, it can be seen that, indeed, the wear rates of composites with pores have shifted toward those of the fully dense composite after using the effective wear stress, but still do not completely coincide with the data of fully dense composites. Furthermore, the higher the composite porosity, the larger the deviation of the wear rate from those of fully dense composites. It suggests that using the effective wear stress only accounts for a part of the wear rate increase induced by porosity.

The excess wear rate increase induced by porosity brings forth the other implication of the porosity i.e. the notch effect. The irregular boundary of a pore as shown in Figure 5.4 suggests possible presence of sharp corners near the wear surface in composite around the pore. The stress intensity is particularly high at these sharp corners and thus, the pore acts as a source of crack when the normal compressive load is applied during the wear test causing a transverse shear force to be imposed on the arm around pore. Gui et al. [52] had reported this type of wear behavior with their sliding wear study on Al-6Cu-Mn/SiCp composite. The stress intensity at these corners increases with an increasing applied normal load. Because of that, the area surrounding the pore becomes increasingly failure-prone with the increase in the applied normal load. Since the fully dense Cu/WC sample represents the true wear behavior without pores, the degree of the

notch-effect of porosity can be estimated by showing the deviation of the wear rate at various wear stresses. Figure 5.8 presents the wear rate deviation of porous composite from the fully dense composite with the effective wear stress accounted.

The wear rate deviation reflects the excess wear over abrasively contributed wear. In the low wear stress region, there is essentially no excess wear. Noticeable excess wear starts at around 0.125 MPa in terms of the effective wear stress. For the Cu/WC composite, this is the onset wear stress for the "run away" wear resulted from the notch effect of the pores. Beyond such a wear stress level, the excess wear rate increase linearly with the effective wear stress. It is also interesting to observe that the highest porosity composite has the most rapid increase in the excess wear rate as the wear stress increases. However, the onset wear stress remains very close to 0.125 MPa. Since the excess wear rate is accounting for the portion of composite loss rate due to pore induced notches and tearing of sharp corners around pores immediately next to the wear surface, it is reasonable to have all onset wear stresses started near similar stresses if each pore is located around similar environments disregarding the porosity. It is also to be pointed out that the wear stress referred to in this study is the applied normal stress. The pore induced tearing of sharp corners, on the other hand, is from the transverse stress as a result of the normal stress and the friction coefficient. Detailed analysis of the tearing as a function of the transverse stress during wear requires a knowledge of the friction coefficient which is beyond the scope of the present study.



Figure 5.8: The notch effect of porosity in the wear rate of Cu/WC composites
5.5.2 Wear of Fully Dense Cu/WC Composites

Figure 5.9 shows the wear rate of fully dense Cu/WC composites with 53vol% WC particles having an average particle size of 1µm. The composite was prepared with infrared infiltration at 1300 °C for 8 min. The wear rate of composites under low wear stress (less than 0.6 MPa) can be approximated as linearly increasing with the wear stress. The linear relationship can be represented by the following equation.

Wear Rate
$$(mm^3/m) = 8.6 \times 10^{-3} S_N + 6.84 \times 10^{-5}$$

where, S_N is the normal wear stress in MPa. The linear relationship between the wear rate and the applied wear stress has been reported in the literature [50, 51] and was attributed to the abrasive nature of wear. As the applied wear stress increased to more than 0.6 MPa, the composite was worn faster than that predicted by the above straight line, suggesting that other factors governing composite wear also became significant under high wear stresses. One of the factors investigated was the composite wear surface temperature as a function of increasing load. It was observed that the temperature of the composite wear surface increased significantly with the increase in applied load. Thus, the wear phenomena of composites under high loads can be partly attributed to decrease in interfacial strength between the matrix and the reinforcement, due to increase in sample temperature, leading to the particle pull-out during wear. To compare the decrease in wear rate due to addition of WC particles, pure copper pins were tested using the pinon-disk wear test machine and the copper wear rate was compared with the fully dense composite, Figure 5.10.



Figure 5.9: Wear rate of Cu/WC (fully dense) composite having 53vol% WC reinforcement



Figure 5.10: Comparison of wear rates of Cu/WC composite with pure copper



Figure 5.11: Surface optical micrographs of (a) Cu/WC (Fully Dense) composite and (b) Pure copper after wear at 4.27N and 500m sliding distance

It can be seen that the wear rate of copper also increased with the increase in the applied load. The wear rate of copper is significantly higher than that of Cu/WC composites at all load conditions. At the applied load of 4 N, the wear rate of copper was found to be an order higher than that of the Cu/WC composite.

Figure 5.11 shows the wear surface morphology of the Cu/WC composite, 5.11(a) and copper, 5.11(b), tested under an applied load of 4.27N after a sliding distance of 500 m. The smooth polished surface with scratched appearance of Cu/WC composite suggests the presence of low stress two-body abrasive wear mechanism [59].

In accordance with the abrasive wear mechanism for MMCs, the soft copper matrix is gouged by the abrasive SiC particles of the counterface from the polished Cu/WC composite surface during the very early stage of wear, thus, protruding the reinforced WC particles to the composite surface. After that, the hard WC particles were in contact with the abrasive SiC particles. Since, the hardness of WC (2300 kg/mm²) is very close to the hardness of SiC (2600 kg/mm²); WC particles are able to strain and blunt the abrasive SiC particles [47]. This reduces the severity of microploughing action of the blunted abrasive SiC particles resulting in lower wear rate of the Cu/WC composite as compared to that for pure copper.

The increase in wear rate of Cu/WC composite with the increase in applied load is due to the increased wear of the WC particles in contact with the counterface followed by the re-appearance of new soft copper matrix phase to the abrasive counterface. Also, the better wear resistance of Cu/WC composite as compared to that of pure copper is due to better overall hardness of the Cu/WC composite (Table II) as compared to pure copper (65 HV_{100}).

Based on the observations of wear rate behavior of fully dense Cu/WC composite, a model was developed which could predict the wear behavior of fully dense Cu/WC composite. It is critical to note that the following model applies to the fully dense composite with essentially no porosity.

The porosity in the composite could have a four-fold effect on the wear resistance of composite. The presence of porosity on a wear surface leads to a decrease in effective reinforcement since pores act as non-load bearing areas, thus leading to increase in the wear rate. This constitutes the first contribution of porosity. Pores, in general, has characteristically an irregular shape which gives rise to sharp corners and edges (Figure 5.4). When the normal wear stress is applied during wear test, the stress concentration can be significantly higher at the sharp corners/edges leading to easy removal of material around these corners with increase in the normal wear stress. The removal of material not only leads to sudden volume loss but also leads to increase in the pore surface area. Both of these factors can lead to significant increase in the wear rate. This constitutes the second contribution of porosity. Any non-load bearing arm around a pore or a vertical arm in between two very closely located pores can be removed from the wear surface easily with practically a very little applied normal wear stress. Both these factors lead to sudden volume loss and corresponding increase in wear rate. This constitutes the third and fourth contribution of porosity. It is because of these aforementioned factors, the following model has been developed to address the wear behavior of fully dense composite with essentially no porosity.

6. Model: Wear Mechanism of MMCs

For composites reinforced with hard reinforcement, wear resistance comes primarily from the resistance to shear of the reinforcement against the shear stress imposed on the reinforcement from the opposing abrading surface. Abrasive wear of the reinforcement determines the wear rate of the entire composite when the composite is fully dense and the interfacial strength between the reinforcement and the matrix is strong enough to resist the reinforcement from being pulled out. This constitutes the first mechanism of the composite wear. As the normal force between the opposing surfaces of wear increases, the friction induced shear force on the reinforcement also increases. When the shear stress reaches a point that the interfacial strength is no longer strong enough to hold the reinforcement in place, pull out of the reinforcement from its surrounding matrix will occur. Wear of this specific reinforcement and the localized composite area around this reinforcement will experience significantly more rapid material removal than the abrasive wear. Such a pullout phenomenon constitutes the second type of composite wear and happens only under relatively high normal load during wear. A third wear mechanism of composite is a nature result of porosity. Pores cause the effective normal load of wear to increase depending on the extent of porosity. Assuming a homogeneous distribution of pores in the composite, the effective normal stress on the wear surface will increase since the pore area bears no load. Furthermore, the peninsular type arms around a pore will bear no load and can be torn apart as wear progresses. In fact, a vertical arm between two pores can fracture at the weak point near the root if the shear stress working on the arm is higher than the fracture strength of the

arm. One may treat the peninsular arms near pores and the vertical arms between two close pores as extra porosity and represent the aggregate of the real pores and these arms as the effective porosity, which depends on the effective normal wear stress. As it can be demonstrated, the effective porosity of a composite material during wear varies with the effective normal wear stress and can be significantly larger than the true composite porosity. Different composite wear mechanisms as described above may be illustrated in the schematic drawing shown in Figure 6.1. "A" represents the abrasive wear of the reinforcement. "B" represents pull out of the reinforcement. "C" represents the effective normal wear stress due to porosity. "D" represents non-load bearing arms around a pore. "E" represents premature fracture of vertical arms. An effective porosity as a function of the actual porosity and the wear normal stress may be deduced to represent the combination effect of "C", "D" and "E" shown in the diagram.

6.1 Composite Wear of the First Type: Abrasive Wear

Composite wear of the first type is the abrasive wear which occurs in the region of low normal wear stress. This is similar to the wear behavior of brittle material such as ceramics or refractory metals. The wear rate of such abrasive wear increases linearly with the normal wear stress and primarily reflects the wear rate of the reinforcement material. Under the low wear stress, the reinforcements are strongly held by the surrounding relatively soft matrix. The removal of the composite material is due to the shear stress acting on the composite as a result of friction between the opposing wear surfaces. Since the reinforcement material has a relatively high modulus and strength, the reinforcement material removal is slow and linearly proportional to the normal wear stress.



Figure 6.1: A schematic drawing of a composite surface

For the relatively soft matrix material, its removal requires very little effort from the opposing surface due to the relatively small shear strength of the matrix material.

Based on the principle of shear fracture of brittle materials, it is expected that the wear rate of this type increase linearly with the wear normal stress and decrease linearly with the reinforcement content. For composites with a fixed reinforcement content,

$$\mathbf{R}_{\mathrm{AW}} = \mathbf{C}_1 + \mathbf{C}_2 \, \mathbf{S}_{\mathrm{N}} \tag{1}$$

where R_{AW} is the rate of abrasive wear; C_1 and C_2 are constants; and S_N is the normal wear stress. Meanwhile under a fixed normal wear stress,

$$R_{AW} = C_3 (1 + C_4 f_R)$$
(2)

where C_3 and C_4 are constants; and f_R is the reinforcement content in the composite in volume fraction. Combining these two equations,

$$R_{AW} = (C_1 + C_2 S_N) (1 + C_4 f_R)$$
(3)

This equation can be represented by a graph shown in Figure 6.2, in which, the composite wear rate is plotted as a function of the wear stress for composites with different volume fraction of reinforcement.



Figure 6.2: Predicted wear rate as a function of the normal wear stress in the low stress region

The linear relationship between the composite wear rate and the wear stress exists over the low wear stress region. It is to be noted that the low wear stress region varies among different composite systems depending on the interfacial strength between the reinforcement and the matrix, along with the friction coefficient between the counter surfaces in wear. This will be discussed in detail below.

6.2 Composite Wear of the Second Type: Particle Pull-out

As the normal wear stress increases to a level that some reinforcement no long can be held down by the surrounding matrix, the friction induced transverse stress will remove the reinforcement and cause a sudden material loss both from the loosen reinforcement and its surrounding relatively soft matrix. The rate of material removal in this stage thus depends on the amount of reinforcement being pulled out on top of the abrasive wear of those areas without pull out. At this stage, the amount of reinforcement held down force. For easy derivation, we focus on a composite system containing one size spherical reinforcement particles. With spherical particle reinforcement, the friction induced transverse force working on the particle may be expressed as

$$F_{\rm T} = A_{\rm S} \,\mu_{\rm f} \,S_{\rm N} \,, \tag{4}$$

where F_T is the transverse force working on a specific particle, A_S is the surface area of the particle exposed to the opposing surface of wear and is a function of the extent of wear of this particle, μ_f is the friction coefficient of the particle against the opposing wear surface, and S_N is the wear normal stress. Since μ_f and S_N are constants during any specific wear process, F_T is only a function of A_S which can be calculated if the particle radius and the extent of particle wear are known.

The reinforcement held down force refers to the force that the matrix holds the reinforcement in the composite through the matrix-reinforcement interface and is a function of the particle-matrix bond strength and the interfacial area. The particle-matrix bond strength, in turn, is a function of the interface chemistry and can be modified during composite fabrication. The particle-matrix bond strength level may be determined with a fiber push-out test when fibers are the reinforcement used in the composite. Numerous investigations have been devoted to the particle-matrix bond strength determination over the past few decades and are not to be duplicated here. During a wear test, the particlematrix bond strength is a constant if the wear part remains at a constant temperature. However, due to friction, we often observe an increase in the wear part temperature which will reach a saturated plateau when the friction generated heat equals the heat dissipating to the surrounding of the wear part. During a wear test of Cu/WC composite with 53 vol% reinforcement against a SiC abrasive disk, the composite pin temperature increased to 92 °C from the room temperature within 5 min at 90 m/min disk linear speed. It is expected that a slight decrease in the particle-matrix bond strength may result as the wear part temperature increases. The interfacial area, on the other hand, decreases with the increase in the extent of wear for a specific particle. A simple geometric calculation can be used to determine the interfacial area. The held down force, F_H, thus can be expressed as

$$F_{\rm H} = A_{\rm i} \,\sigma_{\rm i} \tag{5}$$

where A_i is the matrix-reinforcement interface of the specific particle and σ_i is the particle-matrix bond strength.

Pull-out of the reinforcement will occur when

$$F_{\rm T} > F_{\rm H}.$$
 (6)

This condition is illustrated schematically in Figure 6.3, where two particles partially worn to different extents are embedded in the matrix.

In this schematic drawing, Particle A has been worn to a greater extent than Particle B. Once the Equation (6) condition is met Particle A will be pulled out when the composite is worn further while particle B will be still far away from been pulled out. Pullout of particle B will occur only when further wear has reduced its height to a point that the Equation (6) condition is met. Strictly speaking, F_H should refer to the horizontal component of the overall held down force integrated over the entire interfacial area between the matrix and the reinforcement. It can be seen that when S_N increases, there can be a point where the pull-out condition is met and the particle will be removed suddenly. Likewise, as the particle becomes smaller and smaller, there can be a point that the pull-out condition is met and the particle will be removed suddenly. Likewise, as the particle becomes smaller and smaller, there can be a point that the pull-out condition is met and the particle will be removed. As presented previously, once the reinforcement is removed the surrounding matrix will also be removed quickly since the matrix is significantly softer than the reinforcement. Since the reinforcement distribution in composite is random, at any composite surface, there will be roughly similar amount of particles worn to the same extent.



Figure 6.3: A schematic drawing of partially worn particles on the composite surface



Figure 6.4: A schematic drawing of a partially worn particle with removed portion shown as by a dash line

Therefore, the wear rate due to pull-out would be a constant if the wear normal stress is fixed and the composite maintains at a constant temperature.

Figure 6.4 shows the schematic of a composite surface region, in which a spherical particle has a depth of h removed due to wear. When h reaches h_{Pull} , the condition that a partially worn particle meets the pullout condition, it will be removed from the composite surface.

Assuming that all particles are spherical of the same radius, r, the surface area exposed to the opposing wear surface after a thickness of h being removed due to wear is

$$A_{\rm S} = \pi \left[r^2 - (r - h)^2 \right] = \pi h \left(2r - h \right)$$
(7)

The interfacial area between the matrix and the particle below the wear surface is

$$A_i = 2 \pi r (2r - h)$$
 (8)

The pull-out condition may be re-written as

$$A_{S,Pull} \ \mu_f \ S_N \! > \! A_{i,Pull} \ \sigma_i$$

Rearranging the terms, we can have

$$A_{S,Pull} \mu_f S_N / \sigma_i > A_{i,Pull}$$
(9)

Defining
$$\eta = \mu_f S_N / \sigma_i$$
, (10)

The pullout condition can be expressed as

$$\mathbf{A}_{\mathbf{S},\mathbf{Pull}} \,\,\boldsymbol{\eta} > \mathbf{A}_{\mathbf{i},\mathbf{Pull}} \tag{11}$$

 η can be termed as the pullout coefficient. Comparing Equations (7) and (8), it can be seen that η must be greater than one for Equation (11) to be met. $\eta = 1$ provides the limit condition that both sides of Equation (11) intercept at h = 2r. This is the condition when Equation (11) is satisfied, the wear depth reaches 2r and no particle remainder is left for pullout. Graphically the pullout condition can be represented by plotting both sides of this in-equality equation with the wear depth as the variable, Figure 6.5. The straight line in the graph is A_i. The series of curves represents the left hand side of Equation (11) with increasing η as the curve increases its height. The intercept of each curve with the A_i line represents the critical point of meeting Equation (11). The portion of the curve above Line A_i represents the region that particles having their h values in this region had been pulled out. Therefore, the h value corresponding to each intercept represents the critical wear depth for the particle under a certain η value (and, thus, a certain wear stress value) to be pulled out and is termed, h_{Pull} , the critical wear depth. Any particle with $h > h_{Pull}$ would have been pulled out and any particle with $h < h_{Pull}$ would have only been worn by the opposing wear surface.

Mathematically, if A_s and A_i at the intercept are represented by h_{Pull} and r, Equation (11) becomes

$$\pi h_{\text{Pull}} \left(2r - h_{\text{Pull}}\right) \mu_{\text{f}} S_{\text{N}} = 2 \pi r \left(2r - h_{\text{Pull}}\right) \sigma_{\text{i}} \tag{12}$$



Figure 6.5: Particle pullout conditions predicted by the pullout model

Solving h_{Pull}, we can have the critical wear depth of the particle at pullout,

$$h_{\text{Pull}} = 2 r \sigma_i / (\mu_f S_N) = 2r/\eta$$
(13)

This equation suggests that h_{Pull} , the critical wear depth of particle at pullout, is inversely proportional to S_N . As S_N increases, h_{Pull} reduces since r, σ_i , and μ_f are considered constants during wear. This means that the particle can be pulled out with a smaller amount of wear.

This equation also shows that, if σ_i is greater than ($\mu_f S_N$), h_{Pull} is greater than 2r and is impossible since the maximum value of h can only be 2r. It suggests that the particle will never be pulled out during wear since with the calculated h_{Pull} being larger than 2r, the particle would have to be worn completely before pullout occurs. It appears, then, the first pull out will occur at $h_{Pull} = 2r$ and a critical S_N can be defined as

$$S_{N, Critical} = \sigma_i / \mu_f \tag{14}$$

When the applied normal wear stress is below $S_{N, Critical}$, there is no particle pullout and linear abrasive wear prevails. As S_N exceeds $S_{N, Critical}$, particles will be pulled out before being completely worn out. From this equation it is interesting to see that the critical normal wear stress required to have particle pullout is independent of the particle size and is only the function of the interfacial strength between the matrix and the reinforcement and the friction coefficient. The higher the interfacial strength, the higher the critical normal wear stress for pull out. The efforts of modifying the interfacial strength through various treatments, such as heat treatments, coatings or altering interface chemistry, are effective to the wear property of the composite in changing the $S_{N, Critical}$ value. In the meantime, the higher the friction coefficient between the reinforcement particle and the opposing wear surface, the lower the critical normal wear stress. It is to be noted that this estimate must be modified to reflect the fact that the force balance is between the transverse frictional force and the horizontal part of the integrated interfacial force.

With the critical wear stress defined, the pullout coefficient can be re-written as

$$\eta = S_N / S_{N,Critical} \tag{15}$$

The pullout coefficient is effectively the ratio of the applied wear stress to the critical wear stress. When η is smaller than 1, no pullout will occur. When η is greater than 1, pullout will happen during wear. The higher the η value, the higher the extent of pullout wear. Equation (13) also suggests that h_{Pull} is proportional to r. It indicates that as the particle size reduces, the critical wear depth needed prior to pull out also reduces. In other words, smaller particles can be pulled out sooner (with less wear) than larger particles under identical normal wear stresses.

To reflect the wear rate when pull out occurs, one must take into account both abrasive wear and pullout loss of material. The pullout portion of wear is a sudden volume loss due to pullout of the particle having a wear depth of h_{Pull} . When the wear depth of a particle is h_{Pull} , the volume of the particle removed portion is

$$V_{\text{Wear}} = (\pi/3) h_{\text{Pull}}^{2} (3r - h_{\text{Pull}})$$
(16)

The volume of the remainder portion to be removed by the pullout process is

$$V_{Pull} = (\pi/3) (2r - h_{Pull})^2 (r + h_{Pull})$$
(17)

Substituting the h_{Pull} equation above and rearranging the terms, we have

$$V_{\text{Pull}} = (4/3)(\pi r^3) \left[1 - \sigma_i / (\mu_f S_N)\right]^2 \left[1 + 2\sigma_i / (\mu_f S_N)\right]$$
(18)

Substituting Equation (14) into this equation,

$$V_{Pull} = (4/3)(\pi r^3) (1 - S_{N, Critical}/S_N)^2 (1 + 2S_{N, Critical}/S_N)$$
(19)

This can also be represented with the pullout coefficient, η , as

$$V_{\text{Pull}} = (4/3)(\pi r^3) (1 - 1/\eta)^2 (1 + 2/\eta)$$
(20)

The first portion of Equation (20) is the volume of the reinforcement particle. The second portion occurs often in the pullout calculation and may be called the pullout function, PF. The pullout function is independent of the particle size and is only the function of the pullout coefficient, η , which in turn, is the ratio of the wear stress to the critical wear stress. The pullout function is defined as

$$PF = (1 - 1/\eta)^2 (1 + 2/\eta)$$
(21)

From Equation (20), it can be seen that the pull out function is effectively also the fraction of sphere that is pulled out all at once during wear. When a particle wears down to a volume of V_{Pull} , it will be pulled out and the composite will have a sudden volume loss of this amount. Such pullout volume loss contributes to the sudden wear rate increase. Estimating the number of particles having such a volume as a function of linear abrasive wear allows one to estimate the wear rate from the pull out process.

Assuming a composite reinforced with totally random distributed particles of a radius r, abrasive wear shows a linear wear rate of R_{AW} m/s when the normal wear stress is low. As the normal wear stress increase to greater than the critical normal wear stress, pullout of particles will occur. Since particles are randomly distributed in the composite, there will be $h_{Pull}/2r$ fraction of the particles with remainder volumes greater than V_{Pull} on any composite wear surface and will not be pulled out. In other words, the (1- $h_{Pull}/2r$) fraction of the particles on any surface will have been extracted from the surface already. Immediately the opposing wear surface will wear against a composite surface containing a smaller net effective reinforcement amount and the wear behavior will be altered to one with less reinforcement content. Furthermore, as wear continues, the remainder particles will have their wear depth increased at a rate of R_{AW} mm³/m. Thus, there will be (R_{AW}/Ao)/2r fraction more of total particles removed per unit time along with the same fraction of particles being newly exposed to the opposing wear surface. Ao is the total composite surface area being tested.

For a composite with randomly distributed reinforcements, at any composite surface, the surface fraction of reinforcement will be the same as the volume fraction of reinforcement in the composite, f_R . Considering a composite with the reinforcement

particles of only one size randomly distributed, all composite cross sections will have an identical distribution of particle cross sections and the total reinforcement area will sum up to f_R within each unit cross section area of composite, or

$$\Sigma \pi r_{R,i}^2 = f_R \tag{22}$$

where $r_{R,i}$ is the radius of the cross section of the ith reinforcement particle on a specific composite surface. The value of r_R varies from 0 to r. The average cross section area of reinforcement particles on any composite surface may be calculated to be,

$$A_{R,Ave} = (2/3) \pi r^2$$
(23)

The reinforcement particle number concentration per unit area of composite is therefore

$$N_{\rm R} = 3f_{\rm R}/(2\pi r^2)$$
 (24)

For example, for a 50 vol% particle reinforced composite, if the reinforcement particle is 1 μ m in diameter, N_R is 9.54 x 10⁷ particles/cm². Considering the wear surface of a composite, from previous wear and pullout discussions, among this particle count, any particle with an A_S smaller than A_{S,Pull} and A_i smaller than A_{i,Pull} would have been pulled out and could not be "seen" on the composite by the opposing wear surface. In other words, the opposing wear surface will wear against the composite with only (f_R - f_{R,Pull}) reinforcement, where

$$f_{R,Pull} = f_R (1 - 1/\eta)^2 (1 + 2/\eta) = f_R PF$$
 (25)

The effective reinforcement on the wear surface after pullout is thus

$$f_{R,Eff} = f_R \left[1 - (1 + 2/\eta) (1 - 1/\eta)^2 \right]$$
(26)

Using the pullout function, this can be simplified to

$$f_{R,Eff} = f_R (1 - PF)$$
(27)

It is interesting to observe that the effective reinforcement content on the composite wear surface is independent of the particle size and is only a function of the normal wear stress and the critical normal wear stress, as well as the initial reinforcement content in the composite. Because of the lower effective reinforcement content on the composite wear surface, the effective wear rate will increase accordingly. This constitutes the first effect of reinforcement pull out during wear. Equation (3) for the abrasive wear rate will have to be modified to

$$R_{AW} = (C_1 + C_2 S_N) (1 + C_4 f_{R,Eff})$$
(28)

Substituting Equation (27) for $f_{R,Eff}$, one will have

$$R_{AW} = (C_1 + C_2 S_N) [1 + C_4 f_R (1 - PF)]$$
(29)

This is the first effect of reinforcement pullout on the composite wear rate. As wear proceeds, more particles will be pulled out due to further wear of particles causing reduction in the held down force on the particle. With an abrasive wear rate being R_{AW} mm³/m, the particle wear depth will also increase at this rate. Assuming a total random distribution of particles in the composite, the number of particles within a dh thickness that meet the pullout requirement is

$$d N_R = [3 f_R/(4\pi r^3)] dh$$
 (30)

Since the remainder volume of the particle being pulled out is derived in Equation (20), the total volume of pullout particles, thus, the composite volume loss due to pullout within the dh depth is

$$dN_R V_{Pull} = f_R PF dh$$
(31)

With random distribution, this volume would evenly distribute over the entire per unit area of composite, and the pullout wear will be

$$dh_2 = f_R PF dh_1 \tag{32}$$

where dh_1 is from abrasive wear and dh_2 is from pullout wear. This equation indicates that abrasive wear trigger pullout wear and the pullout wear rate depend on the abrasive wear rate. The over all wear rate would be the sum of both

$$R_{\text{Overall}} = (dh_1 + dh_2)/dt \tag{33}$$

Combining Equations (29) and (32) and knowing that $dh_1/dt = R_{AW}/Ao$, we will have

$$R_{\text{Overall}} = (C_1 + C_2 S_N) [1 + C_4 f_R (1 - PF)] (1 + f_R PF)$$
(34)

It is to be noted that Equation (34) applies only in the region that $\eta > 1$ or $S_N > S_{N,Critical}$. For the region that $\eta < 1$ or $S_N < S_{N,Critical}$, the wear rate should follow Equation (3). To include both regions in the wear stress, Figure 6.2 can be expanded to Figure 6.6. This Figure closely mimics what was observed with wear of the fully dense Cu/WC particle composite. Considering that the WC particles were not all at one size and not spherical, the resemblance of Figure 6.6 and Figure 5.9 is extremely valuable in that the fully dense composite wear behavior indeed follows what was presented in the model above. The model presented above suggested that the particle pullout phenomenon is independent of the particle size. The pull out coefficient is only a function of the normal load and the friction coefficient. One may provide a geometric factor to account for the non-spherical simple geometry particles. But the basic concerns for pullout remain the same. It is to be noted also that the pullout model derived above assumed that the interfacial strength contribute to the hold down force as is. However, in the real force balance, it is the horizontal portion of the interfacial stress which acts to counter the pulling tangential

force resulting from friction. This oversimplified assumption can also be accounted for with another simple geometrical factor.



Figure 6.6: Predicted wear rate as a function of the normal wear stress over a wide range of the wear stress

Nonetheless, with all such assumptions, the actual wear data agrees very well with the theoretically predicted behavior as presented in Figures 6.6 and 5.9. The pullout effect on the composite surface during wear has also been identified from the SEM micrographs of the wear surface. Figure 6.7 shows the wear surface before and after wear. The wear direction is also included in Figure 6.7 (b). The dark regions in Figure 6.7(b) are voids after particles were pulled out.

Results reported in the literature on the wear properties of metal matrix composite systems also agree with that predicted with this model. Sahin et al. [50] observed that the wear rate of Al/SiC composite decreased with the increase in the volume fraction of SiC particulates. A considerable reduction in wear was observed when SiC particulates were incorporated in the matrix of aluminum alloy. Figure 2.8 shows data obtained by Sahin et al. Due to limited amounts of data reported, the critical wear stress can not be accurately resolved. However, the wear rate appeared to have increased drastically beyond 0.8 MPa. It is believed that the pullout effect has contributed to the sudden increase of the wear rate. Likewise, Tjong et al. [51] in their wear study of Al-4%Cu/TiB₂ composites showed decreases in wear rates as the amount of reinforcement increased (Figure 6.8). In their composite system, the linear region of wear appears to have extended to 2.7 MPa of the normal wear stress suggesting a strong interfacial bonding or a low friction force. They reported that bonding between Al-4% Cu and TiB₂ was significantly stronger than that between Al and SiC from their previous studies. Modi et al [60] in their wear study of Al alloy/SiC particulate composites observed that wear resistance of Al alloy increased with the addition of 10 vol% of reinforcing SiC phase. It was observed that the wear rate of the composites increased significantly after around 2 MPa of normal wear stress, a trend

similar to the one predicted by the model. The wear behavior of Al alloy/SiC particulate reinforced composite was attributed to the particle pull-out phenomenon. Yu et al [61], in their wear study of Al alloy/SiC whisker reinforced composite, observed that there was a critical load above which the wear rate increased rapidly as the applied load increased (Figure 6.10). Similar observations were done for Al alloy/SiC particulate reinforced composite. Due to the presence of limited data, the critical load could not be converted into critical applied stress. Though their study does not offer explanation for the critical load condition, the wear behavior corroborates the model presented in this study.

The wear model also suggests that the wear rate is independent of the size of the reinforcing particle. The particle size of the reinforcement is one of the intrinsic factors that could have an effect on the wear resistance besides other mechanical properties of a particulate reinforced metal matrix composite (PRMMC). The study of the literature based on reinforcement particle size effect on wear resistance of composite proves inconclusive. Zhou et al [62] in their study of Cu/W composite, with different W particle sizes, observed that the hardness of the composite increased with decrease in W particle size since decrease in particle size leads to decrease in particle mean free path. Similarly, Reihani et al [63] observed that the mechanical properties of Al6061 / 30 vol% SiC composite, such as hardness, elastic modulus, yield strength and tensile strength, improved with decrease in SiC particle size since the smaller particles provided greater surface area for the age hardening process. However, to establish any correlation between the reinforcing particle size in a composite and its wear resistance, it requires consideration of other intrinsic and extrinsic factors. These factors are interfacial strength between the constituents, microstructural homogeneity, and applied stress during the

wear test, accessibility of soft matrix phase by the abrading counterface which further depends on the particle size of the abrading surface. The researchers, studying various composite systems, have tried to establish a correlation between particle size of reinforcement in a PRMMC and its wear resistance. Kok [64], in the abrasive wear study of Al2024 / Al₂O₃ composite, observed that the composite made with finer Al₂O₃ particles led to poor interfacial bonding between the constituents, greater porosity and microstructural inhomogeneity, thus, leading to higher wear rate as compared to composites made with coarser Al_2O_3 particles. The decrease in wear resistance with decrease in reinforcing particle size was also observed by Desai et al [65] in their study of Co / Cr_7C_3 composites. The observation was attributed to the presence of microchips, of size greater than size of finer reinforcing particles, generated during the wear test which facilitated the removal of fine particles from the wear surface. The effect of abrasive particle size on wear rate of Al / SiC composite with different SiC particle sizes was studied by Rubaie et al [66]. They observed that the wear rate of composite increased with decrease in SiC particle size against finer abrading surface while the wear rate remained same with decrease in particle size against coarser abrading surface. Candan et al [67], however, in their study of effect of abrasive particle size on Al / SiC composite with different SiC particle sizes, observed that the wear rate of composite with fine SiC particles was higher against finer abrading surface and lower against coarser abrading surface as compared to wear rate of composite with coarse SiC particles. This was considered to be due to the nature of coarse SiC particles to undergo fracture against coarse abrading surface. Dogan et al [68], in their study of Ni / TiC composites, observed that the composite with finer TiC particles performed better at lower wear

stresses while the composite with coarser TiC particles performed better at higher wear stresses. This observation was attributed to different wear mechanisms operating at different wear stresses. Kennedy et al [69], in their study of Cu / SiC composites, observed that the wear rate of these composites initially increased with increase in SiC particle size and then decreased with further increase in SiC particle size. The hardness of these composite was found to vary with SiC particles in similar way, thus, the wear rate behavior was considered to be dependent on the hardness of the composite. Also, the initial increase in wear rate with increase in SiC particle size was attributed to decrease in interfacial area and increase in contact force per particle whereas, the subsequent decrease in wear rate with further increase in particle size was attributed to decreased accessibility of copper matrix due to presence of large protruding SiC particles.

The aforementioned discussion suggests that the correlation between composite wear rate and reinforcing particle size is a function of various other factors and that no definite relation exist between them. However, this study has made an attempt to investigate the reinforcing particle size effect on wear resistance by comparing two different average particle sizes of WC i.e. 1 µm and 10 µm. Figure 6.11 shows the wear rate comparison for the two different sizes of reinforcing WC particles. It can be seen from the figure that varying the WC particle size has not induced any change in wear rate of the Cu/WC composite, thus, supporting the reinforcing particle size independence claim made by the model. It is, however, important to state that increasing the WC particle size beyond 10 µm may or may not affect the wear resistance of Cu/WC composite. This is due to the fact that particle with larger size tend to have inherent micro cracks which can contribute adversely during wear of composite.



(a)



(b)

Figure 6.7: SEM micrographs of Cu/WC composites showing the composite surfaces prior to wear (a) and after wear (b). The pullout effect can be clearly observed. The arrow in (b) shows the wear direction



Figure 2.8: Wear test results of Al/SiC particle composites reported by Sahin and Acilar [50]



Figure 6.8: Wear results of Al-4%Cu/TiB₂ composites reported by Tjong and Lau [51].



Figure 6.9: Wear results of Al alloy/SiC composite reported by Modi et al [60]



Figure 6.10: Wear results of Al alloy/SiC whisker reinforced composite reported by Yu et al [61]



Figure 6.11: Wear rate comparison between Cu/WC composites having different average particle sizes of WC particles

7. Composition Variation of Cu/WC Composite

7.1 Comparison of Cu/WC and Cu/W Composites

The superior performance of Cu/WC composite in terms of, both, wear resistance and electrical resistivity provided an impetus to compare their performance with the commercially available Cu/W composite. One of the commercially available Cu/W composites, S5WC, supplied by Sherbrooke Metals, Willoughby, OH was tested for its wear resistance and electrical resistivity. The S5WC composite contains 52 vol% tungsten, which is close to the 53 vol% WC in our Cu/WC composites.

Figure 7.1 shows the wear rate comparison of Cu/W composite with that of Cu/WC composite. Wear resistance of metal matrix composites depends strongly on the porosity, the amount of reinforcements, the mechanical properties of reinforcements, the reinforcement particle size, which, in turn, determines the bonding strength between reinforcements and the matrix. Comparing Cu/WC composites and Cu/W composites, there is about 2% porosity in commercial Cu/W composites whereas essentially no porosity exists in Cu/WC (fully dense) composites. Porosity alone would play a very important role in the wear behavior of the composites. Furthermore, the amount of WC in the Cu/WC composite is 53 vol% which is essentially similar to the amount of W in the commercial Cu/W composite, 52 vol%. The comparable contents of reinforcements in these composites should mean that there wear behavior are similar if only the reinforcement amount is of the main concern. However, the hardness of W is 500 HV₁₀₀ whereas the WC hardness is 1730 HV₁₀₀ (Alfa Aesar, Ward Hill, MA).



Figure 7.1: Comparison of wear rates of Cu/WC composite with Cu/W composite
The higher hardness of WC means better resistance to the abrasive force of the SiC counterface resulting in lower wear rate for Cu/WC composite. Thus, the pull-out effect will be more pronounced on the Cu/W composite as compared to that on Cu/WC composite leading to higher wear rate of Cu/W composite. The better wear resistance of Cu/WC composite as compared to Cu/W composite is, thus, a cumulative effect of porosity, and reinforcement hardness.

The electrical resistivity measurements revealed that the electrical resistivity value of the Cu/W composite (3.18 $\mu\Omega$ -cm) is at par with that of Cu/WC composite (3.3 $\mu\Omega$ -cm).

A significantly higher wear resistance and comparable electrical conductivity of Cu/WC composites, as compared to commercial Cu/W composites, provided an opportunity to develop Cu/WC composites having higher volume fractions of copper, so that, while, its electrical resistivity is lowered, its wear resistance is still in an acceptable range. The advantages of increasing the copper content in Cu/WC composite and, with it, increasing its electrical conductivity are operational as well as economical. High electrical conductivity ensures less heating-up of the parts due to reduced current density and, thus, reduced probability of oxidation of the surface. Increase in volume fraction of copper can also help in making the parts lighter and cheaper. These advantages can sum up to save considerable amount of time and money by avoiding regular maintenance and any catastrophic failures.

The change in composition of Copper MMCs has been usually achieved through liquid phase sintering of compacts pressed from mixed powders [10, 12, 70-72]. The composition is varied by varying the weight fractions of the powders to be mixed.

97

However, the solubility of tungsten in liquid copper is exceedingly small $(1x10^{-5} \text{ a/o at } 1200 \text{ °C})$ [14]. Earlier data on solubility of carbon in molten copper suggests that their mutual solubility is also exceedingly small [15, 16]. Thus, the liquid phase sintering technique for Cu and WC can result in some final porosity as the mutual insolubility of the constituents can severely limit densification during the solution-reprecipitation stage of liquid phase sintering.

The change in composition of Cu/WC by infiltration route can be achieved by either adding organic binder to the starting WC powder followed by its burn-out prior to infiltration by copper or by changing the green density of the WC preform by varying the compaction pressure. The binder addition process, however, is a time consuming process due to an additional step of binder burn-out. Also, any residual binder in the preform after the burn-out process can affect the wettability of copper leading to poor composite properties. Changing the green density of WC preform by varying the compaction pressure is also not a viable process since the WC powder, due to its inherent high hardness, does not deform or undergo a significant change in its green density with the change in compaction pressure.

The shortcoming of all the aforementioned techniques of composition variation compelled to come up with an innovative technique of increasing the copper content of Cu/WC composites. The technique of composition variation is not discussed here for confidentiality purpose; however, Figure 7.2 shows the optical micrographs of the Cu/WC composites having varying copper contents.

98



(a) Cu/ 45 vol% WC Composite



(b) Cu/ 39 vol% WC Composite



(c) Cu/ 32 vol% WC Composite

Figure 7.2: Optical micrographs of Cu/WC composites with varying copper content processed at 1250 $^{\circ}$ C-4 min

At this stage it was considered important to analyze these composites for their hardness, electrical resistivity and wear resistance and, in process, assess the potential of this route of composition variation.

The theoretical calculation of the copper content in the Cu/WC composites revealed that the total copper content in the final composite varied from 55, 61 and 68 vol%, respectively, as compared to 47 vol% in the Cu/WC developed earlier.

Table IV summarizes the microhardness and electrical resistivity values of all the Cu/WC composites with varying copper content and compares them with that of pure copper. The comparison of microhardness values of Cu/WC composite having varying copper content indicates that by increasing the copper content i.e. decreasing the hard reinforcing WC content of the Cu/WC composite, the microhardness value has decreased only marginally. However, the increase in copper content has led to a significant decrease in the electrical resistivity of Cu/WC composites. The composition variation of Cu/WC composites has, thus, produced the desired results as far as the electrical resistivity is concerned. Though the hardness measurements did not show much variation with the decrease in hard reinforcing WC phase, they represent the information about a very small portion of the sample, seen by the indenter. The Cu/WC composites with varying copper content were, thus, tested for their wear resistance. The process of composition variation of Cu/WC composite could be deemed a potential one only if its wear resistance has not decreased, with the increase in copper content, as compared to commercial Cu/W composites.

Figure 7.6 compares the wear rate of Cu/WC composites having varying amounts of reinforcing WC phase with that of commercially available Cu/W composite. The

100

Cu/WC composite having the least amount of reinforcing WC phase (32 vol%) showed the highest wear rate of all the Cu/WC composites. However, even with only 32 vol% of WC reinforcement and some degree of porosity, it has a significantly higher wear resistance as compared to Cu/W composite.

Thus, the composition variation technique developed is capable of producing Cu/WC composite having significantly better electrical and wear properties as compared to the Cu/W composite that too with lesser amount of reinforcement.



Figure 7.5: Wear rate comparison of Cu/WC composites, having varying amount of WC reinforcement, with Cu/W composite

Table IV

The comparison of electrical and mechanical properties of Cu/WC composites, having varying amounts of WC reinforcement, with that of pure copper.

Sample	Copper Content Vol%	Microhardness (HV ₁₀₀)	Electrical Resistivity (μΩ-cm)
Cu/WC	47	367	3.33
Cu/WC	55	331	3.16
Cu/WC	61	325	2.94
Cu/WC	68	309	2.58
Copper	100	65	1.74

8. Conclusions

Fully dense Cu/WC composites were prepared by controlling various process parameters. Wear test of Cu/WC composite having porosity showed that wear rate of these composites increased with increasing porosity. For the fully-dense composites, the wear rate increased with increase in wear stress. However, the composite showed significant improvement in hardness as well as wear resistance as compared to pure copper due to presence of reinforcing WC phase. A model, based on wear rate behavior of fully dense Cu/WC composite, was developed and it successfully predicted the actual wear rate behavior of these composites. Cu/WC composites were compared with commercially available Cu/W composites for their electrical resistivity and wear resistance. The Cu/WC composites showed similar electrical resistivity but significantly higher wear resistance as compared to Cu/W composites having similar volume fraction of reinforcement. Better wear resistance and similar electrical resistivity of Cu/WC composites as compared to Cu/W composites provided an opportunity of varying the composition of Cu/WC composite from the initial, having 53vol% WC reinforcement. An innovative technique of composition variation was developed and successfully applied to Cu/WC composites. The composition was varied from 53vol% WC to 32vol% WC. The microhardness, wear and electrical resistivity measurements of Cu/WC, at all compositions, indicate that the resistivity of composites decreases with increasing copper content without affecting their hardness and wear resistance significantly. The Cu/WC with increased copper content performs significantly better than commercial Cu/W composites.

9. Future Work

The composition variation of Cu/WC composites by varying the green density of WC preform is not a viable option due to high hardness of WC. However, owing to the new technique of composition variation in this study, the green density of WC preform can be varied. This would provide a better control on the composition variation and can also lead to improved electrical and wear properties.

- To achieve composition variation in Cu/WC composite by varying the compaction pressure during preform preparation.
- To obtain fully dense composites at all compositions by controlling the processing parameters.
- To compare the electrical and mechanical properties of these composites with the commercial Cu/W composites as well as the composites developed in this study.

10. References

- 1. J.E. Schoutens and K. Tempo, Introduction to Metal Matrix Composite Materials, DOD metal matrix composite information analysis center, 1982.
- 2. A. Banerjee, P.K. Rohatgi and W. Reif, "Role of Wettability in the Preparation of Metal-Matrix Composites," Metallurgia, 38 (7), 1984, pp. 656-667.
- V. Laurent, D. Chatain and N. Eusthathopoulos, "Wettability of SiC by Aluminum and Al-Si Alloys", Journal of Materials Science, 22, 1987, pp.244-250.
- A. Munitz, M. Metzger and R. Mehrabian, "The Interface Phase in Al-Mg/Al₂O₃ Composites", Metallurgical Transactions, 10A, 1979, pp.1491-1497.
- R.J. Arsenault and C.P. Pande, "Interfaces in Metal Matrix Composites", Scripta Metallurgica, 18, Issue 12, 1984, pp. 1131-1134.
- A. Mortensen, "Interfacial Phenomena in the Solidification Processing of Metal Matrix Composites", Materials Science and Engineering, 135, 1991, pp. 1-11.
- A. Mortensen and T. Wong, "Infiltration of Fibrous Preforms by a Pure Metal III: Capillary Phenomena", Metallurgical Transactions 21A, 1990, pp. 2257-2263.
- 8. A. Mortensen, "Solidification of Metal Matrix Composites", P. Rohatgi (ed), TMS, 1990, pp. 1.
- A. Mortensen and J.A. Cornie, "On the Infiltration of Metal Matrix Composites", Metallurgical Transactions 18A, 1987, pp. 1160-1163.
- G.Gusmano, A. Bianco, R. Polini, "Chemical Synthesis and Sintering Behavior of Highly Dispersed W/Cu Composite Powders", Journal of Materials Science 36, 2001, pp. 901-907.
- W.F. Wang, "Effect of Particle Size and Copper Content on W-Cu Electrodes", Powder Metallurgy, vol. 40, no. 4, 1997, pp.295-300.
- John L. Johnson and Randall M. German, "Chemically Activated Liquid Phase Sintering of Tungsten-Copper", The International Journal of Powder Metallurgy, vol. 30, no. 1, 1994, pp. 91-102.
- T.H. Ihn, S. W. Lee and S.K. Joo, "Effect of Transition Metal Addition on Liquid Phase Sintering of W-Cu", Powder Metallurgy, vol. 37, no.4, 1994, pp. 283-288.
- L. Guillet, Rev. met., 3, 1906, 176; O. Rumschottel, Metal u Erz, 12, 1915, pp. 45-50; D. Kremer, Abhandl. Inst. Metallhutt. U. electromet. T. H. Aachen, 1(2), 1916, pp.10-11; K. schroter, Z. Metallkunde, 23, 1931, pp. 197.
- 15. M. B. Bever and C. F. Floe, Trans. AIME, 166, 1946, pp.128-141
- 16. W. Baukloh and F. Springorum, Z. anorg. Chem., 230, 1937, pp. 315-320.
- A. Upadhyaya and Randall M. German, "Densification and Dilation of Sintered W-Cu Alloys", The International Journal of Powder Metallurgy, vol. 34, no.2, 1998, pp. 43-55.

- Seung-Ki Joo, Seok-Woon Lee and Tae-Hyoung Ihn, "Effect of Cobalt Addition on the Liquid Phase Sintering of W-Cu Prepared by the Fluidized Bed Reduction Method", Metallurigical and Materials Transactions A, vol. 25A, 1994, pp. 1575-1578
- 19. R.M. German and J. L. Johnson, "Effect of Processing Variables on the Properties of Liquid Phase Sintered Tungsten-Copper Composites", Advances in Powder Metallurgy, vol. 1, 1991, pp. 391-405.
- R. Jedamzik, A. Neubrand, J. Rodel, "Functionally Graded Materials by Electrochemical Processing and Infiltration: Application to Tungsten/Copper Composites", Journal of Materials Science 35, 2000, pp. 477-486.
- 21. I. Yoshiyasu, M. Takahashi, H. Takano, "Design of tungsten/copper graded composite for high heat flux components", Fusion Engineering and Design, vol. 31, No. 4. 1996, pp. 279-289
- B. Yang and R. M. German, "The Effects of Tungsten Particle Size and Powder Treating Techniques on the Sintered Properties of W-15Cu. Advances in Powder Metallurgy and Particulate Materials, vol. 2, Metal Powder Industries Federation, Princeton, NJ, 1993, pp. 203-216.
- 23. P. Hasse, "Selective Laser Sintering of Powders", MS Thesis, University of Texas, 1989.
- K. Byoong, "Mechano-Chemical Process for Production of High Density and Ultrafine W/Cu Composite Material", US patent no. 5842108, 1998.
- 25. L. P. Dorfman, "Tungsten-Copper Composite Powder", US patent no. 6103392, 2000.
- F. A. Schimdt, "Molybdenum-Copper and Tungsten-Copper Alloys and Method of Making", US patent no. 4832738, 1989.
- M. K. Yoo, "Tungsten Skeleton Structure Fabrication Method Employed in Application of Copper Infiltration and W-Cu Composite Material Fabrication Method Thereof", US patent no. 5963773, 1999.
- Sam E. Allen and Eric Streicher, "The Effect of Microstructure on the Electrical Performance of Ag-WC-C Contact Materials", Proceedings of the 44th IEEE Holm conference on Electrical Contacts, 1998, pp. 276-285.
- N. C. Cox, and D. E. McGee, "Use of High Density IR for the Rapid Heating of Metals", 1989, Industrial Heating, Vol.4, pp. 46-48.
- 30. H. Bischof, "The Answer is Electrical Infrared", 1990, J. of Microwave Power and Electron Energy, Vol. 25, No. 1, pp 47-52.
- 31. R.B. Bird, W.E. Stewart, E.N. Lightfoot, "Transport Phenomena", 1960, pp. 426-437.
- E. Hoffman, R. Bird, and D. Dicus, "Effect of Braze Processing on the Microstructure and Mechanical Properties of SCS-6/β21S Titanium Matrix Composites", AIAA Fourth Int. Aeo. Planes Conf., pp.1-10, 1992.
- S.J. Lee, S.K. Wu and R.Y. Lin, "Infrared Joining of TiAl Intermetallics Using Ti-15Cu-15 Ni Foil, Part I: The Microstructural Evolution at High Temperature," Acta Mat., Vol. 46(4), 1297-1306, 1998.

- S. Annaji and R.Y. Lin, "Infrared Brazing of a TiAl-Base Alloy Using Ti and Al Foils and The Joint Microstructural Evolution," Structural Intermetallics 1997, Ed. M.V. Nathal et al., TMS Publ., Warrendale, PA, 1997, pp. 395-404.
- 35. S. Annaji, R.Y. Lin and S.K. Wu, "Joining of Titanium Aluminides Using Aluminum Foils," in Design Fundamentals of High Temperature Composites, Intermetallics, and Metal-Ceramics Systems, ed. R.Y. Lin et al., TMS Publ., Warrendale, PA, 1996, pp. 125-138.
- P. Deshpande, J. H. Li, R. Y. Lin, "Infrared Processed Cu/WC Composites", Materials Science and Engineering, B (Submitted on 02 / 08 / 2005)
- J. H. Li, P. Deshpande, R. Y. Lin, "Infrared Heat Treatment of Ti-6Al-4V with Electroplated Copper", Journal of Materials Engineering and Performance, vol. 13(4), pp. 445-450, 2004
- C.A. Blue, R.A. Blue, R.Y. Lin, J.-F. Lei and W.D. Williams, "Infrared Transient-Liquid-Phase Joining of SCS-6/b21S Titanium Matrix Composite," Proc. 1995 SEM Spring Conf. on Experimental Mechanics, SEM, Bethel, CN, 1995, pp. 669-676.
- C.A. Blue, R.A. Blue, R.Y. Lin, J.F. Lei and W.D. Williams, "Joining of Hastelloy X to Inconel 718 Using an Infrared Process", PAM, Vol. 5, pp. 31-37, 1995.
- C.A. Blue, R.A. Blue and R.Y. Lin, "Microstructural Evolution in Joining of TiAl with a Liquid Ti Alloy," Scr. Met. Mat., Vol. 32[1], pp. 127-132, 1995.
- 41. C.A. Blue, R.A. Blue and R.Y. Lin, "Infrared Joining of Titanium Aluminide," PAM, Vol. 4, pp. 141-147, 1994.
- C.A. Blue, R.A. Blue, R.Y. Lin, J.F. Lei and W.D. Williams, "Joining of a PdCr Resistance Strain Gauge to Inconel 718 Using an infrared Process," SAE Tech. Paper 941201, SAE, Warrendale PA, 1994, pp. 1-8.
- R.Y. Lin, et al., "The Infrared Infiltration and Joining of Advanced Materials," JOM, vol. 46[3], pp. 26-30, 1994.
- 44. C.A. Blue and R.Y. Lin, "Rapid Infrared Joining of Ti-6Al-4V," PAM, Vol. 4, pp. 21-28, 1994
- C.A. Blue, R.A. Blue, R.Y. Lin, J-F. Lei and W.D. Williams, "Joining of SCS-6/Beta 21S Titanium Composites," PAM, Vol. 4, pp. 105-110, 1994.
- C.A. Blue, R.A. Blue and R.Y. Lin, "Infrared Joining of Titanium Matrix Composites," Proc. Am. Soc. Comp., pp. 903-908, 1993.
- 47. R. Richardson, "The Wear of Metals by Relatively Soft Abrasives", Wear, vol. 11, 1968, pp. 245-275.
- Y. Sahin, "Preparation and Some Properties of SiCp-Reinforced Aluminum Alloy Composites", Materials and Design, vol. 24, 2003, pp. 671-679.
- O. Yilmaz, S. Buytoz, "Abrasive Wear of Al₂O₃-Reinforced Aluminum-Based MMCs", Composites Science and Technology, vol. 61, 2001, pp. 2381-2392.
- Y. Sahin, M. Acilar, "Production and Properties of SiCp-Reinforced Aluminum Alloy Composites", Composites: Part A, vol. 34, 2003, pp. 709-718.

- S. C. Tjong, K. C. Lau, "Properties and Abrasive Wear of TiB₂/Al-4%Cu Composites Produced by Hot Isostatic Pressing", Composites Science and Technology, vol. 59, 1999, pp. 2005-2013.
- G. Wang, P. Shi, M. Qi, J. J. Xu, F. X. Chen, D. Z. Yang, "Dry Sliding Wear of a Ti₅₀Ni₂₅Cu₂₅ Particulate Reinforced Aluminum Matrix Composite", Metallurgical and Materials Transactions A, vol. 29A, 1998, pp. 1741.
- P. Yih, D. D. L. Chung, "Titanium Diboride Copper-Matrix Composites", Journal of Materials Science, vol. 32, 1997, pp. 1703-1709.
- Manchang Gui, Suk Bong Kang, Jung Moo Lee, "Influence of Porosity on Dry Sliding Wear Behavior in Spray Deposited Al-6Cu-Mn/SiCp Composite", Materials Science and Engineering A, vol. 293, 2000, pp.146-156.
- M. Muratoglu, M. Aksoy, "The Effects of Temperature on Wear Behaviors of Al-Cu Alloy and Al-Cu/SiC Composite", Materials Science and Engineering A, vol. 282, 2000, pp. 91-99.
- 56. Szu Ying Yu, Hitoshi Ishii, Keiichiro Tohgo, Young Tae Cho, Dongfeng Diao, "Temperature Dependence of Sliding Wear Behavior in SiC Whisker or SiC Particulate Reinforced 6061 Aluminum Alloy Composite", Wear, vol. 213, 1997, pp. 21-28.
- A. Martin, M. A. Martinez, J. LLorca, "Wear of SiC-Reinforced Al-Matrix Composites in the Temperature Range 20-200 °C", Wear, vol. 193, 1996, pp. 169-179.
- 58. E.A. Brandes and G.B. Brook, General physical properties, Oxford; Boston: Butterworth-Heinemann, 1992, pp. 146-147.
- Norman A. Waterman, Michael Ashby, CRC-Elsevier Materials Selector, vol. 1, CRC press, Ann Arbor, Boston, 1991, pp. 383-390.
- O. P. Modi, B. K. Prasad, A. H. Yegneswaran, M. L. Vaidya, "Dry Sliding Wear Behavior of Squeeze Cast Aluminum Alloy-Silicon Carbide Composites", Materials Science and Engineering A, vol. 151, 1992, pp. 235-245
- Szu Ying Yu, Hitoshi Ishii, Keiichiro Tohgo, Young Tae Cho, Dongfeng Diao, "Temperature Dependence of Sliding Wear Behavior in SiC Whisker or SiC Particulate Reinforced 6061 Aluminum Alloy Composite", Wear, vol. 213, 1997, pp. 21-28
- 62. Z. J. Zhou, Y. S. Kwon, "Fabrication of W-Cu Composite by Resistance Sintering Under Ultra-High Pressure", Journal of Materials Processing Technology, vol. 168, 2005, pp. 107-111.
- S. M. Seyed Reihani, "Processing of Squeeze Cast Al6061-30vol% SiC Composites and their Characterization", Materials and Design, vol. 27, 2004, pp. 216-222
- 64. M. Kok, "Abrasive Wear of Al2O3 Particle Reinforced 2024 Aluminum Alloy Composites Fabricated by Vortex Method", Composites: Part A, In Press, 2005.
- V. M. Desai, C. M. Rao, T. H. Kosel, N. F. Fiore, "Effect of Carbide Size on the Abrasion of Cobalt-Base Powder Metallurgy Alloys", Wear, vol. 94, 1984, pp. 89-101.
- Kassim S. Al-Rubaie, Humberto N. Yoshimura, Jose Daniel Biasoli de Mello, "Two Body Abrasive Wear of Al-SiC Composites", Wear, vol. 233-235, 1999, pp. 444-454.

- 67. E. Candan, H. Ahlatci, H. Cimenoglu, "Abrasive Wear Behavior of Al-SiC Composites Produced by Pressure Infiltration Technique", Wear, vol. 247, 2001, pp. 133-138.
- O. N. Dogan, J. A. Hawk, J. H. Tylczak, R. D. Wilson, R. D. Govier, "Wear of Titanium Carbide Reinforced Metal Matrix Composites", Wear, vol. 225-229, 1999, pp. 758-769.
- F. E. Kennedy, A. C. Balbahadur, D. S. Lashmore, "The Friction and Wear of Cu-Based Silicon Carbide Particulate Metal Matrix Composites for Brake Applications", Wear, vol. 203-204, 1997, pp. 715-721.
- A. J. Stevens, "Powder-Metallurgy Solutions to Electrical-Contact Problems", Powder Metallurgy, vol. 17, 1974, pp. 331-337.
- A. K. Bhalla, J. D. Williams, "A Comparative Assessment of Explosive and Other Methods of Compaction in the Production of Tungsten-Copper Composites", Powder Metallurgy, vol. 19, 1976, pp. 31-36.
- 72. G. H. Gessinger, K. N. Melton, "Burn-Off Behavior of W-Cu Contact Materials in an Electric Arc", Powder Metallurgy Int., vol. 9, 1977, pp.67-71.