COPPER MATRIX COMPOSITES FABRICATED VIA FIELD
ASSISTED SINTERING TECHNOLOGY FOR THERMAL
MANAGEMENT APPLICATIONS

A Dissertation in
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by
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Abstract

This thesis provides significant evidence to support the hypothesis that Field Assisted Sintering Technology (FAST) can be used as an effective method to develop high performance thermal management materials. The work presented in the thesis can be divided into two parts:

1. The fabrication of composite material systems
2. The characterization of the composite material systems that have been developed.

The material development portion of the thesis focuses on developing copper based composite materials with the objective of improving a specific thermal property or properties. Copper-tungsten composites were developed to produce composite materials with relatively high thermal conductivity and low coefficient of thermal expansion (CTE). FAST proved to be effective in producing materials that had very high density.

Copper based material systems were combined with diamond particles were then developed to reduce CTE while improving thermal conductivity compared to the best known commonly used pure metal, copper. It was discovered that a pure copper matrix was not effective to develop quality composite systems due to the poor interface that existed between the matrix and diamond particle. Several approaches were taken to improve the interface. Incorporating low melting temperature materials that would become an in-situ liquid phase showed some effectiveness in improving the interface and thermal conductivity. Unfortunately, the thermal conductivity was not able to be improved due to the lack of chemical reaction between the diamond particles and the matrix. Copper alloys containing zirconium were found to be the best solution to improving the interface. Zr migrated to the interface from the matrix during the sintering process and formed a very thin layer of carbide. Finite element analysis (FEA) was employed to provide further insight into the composite materials. The analysis reveals that the thermal conductivity...
of the alloy matrix changes as a result of the Zr migration from the matrix to the interface.

The copper alloy approach was extended to include carbon nanotubes instead of diamond particles. While the Zr migration and carbide formation was also observed, the composites did not show good thermal properties because of agglomerations of the carbon nanotubes. The result was a composite material that had low density due to porosity within the pockets of nanotubes. The porosity was also severely detrimental to the thermal conductivity of the composites.

Composite materials made from a combination of pure metals and thermally annealed pyrolytic graphite (TPG) were fabricated as heat spreading materials. The results were characterized using a customized apparatus designed specifically to measure the thermal spreading capability of a material. The materials containing TPG showed a more uniform heat distribution and lower maximum temperature than their pure metal counterparts. Thermal modelling was carried out via FEA to determine the thermal interface resistance of the composite.
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My thesis committee has been very helpful and accommodating by proving support and advice through the process of completing this thesis. Thank you very much for your patience with me. A special thanks goes to Dr. Kulkarni for providing mentoring as a co-adviser on this thesis. His opinion and views are always welcomed as a view of the problem with a different lens.

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I must also thank my colleagues at Momentive for their support. Momentive's technology team is exceptionally talented and has provided me with amazing opportunities for continued learning and development as a critical thinker. They have reminded me that my learning will never be completed.

Finally I would like to thank my family and friends for always being there to
provide support in all of the ways I have needed it. I certainly would not be in a position to defend my thesis without the support they have given me.
Dedication

This thesis is dedicated to my family for all of the love and support they have offered me through the best and worst times of graduate school. I owe my parents tremendous thanks for inspiring me to pursue this highest honor. I also could not have done it without the (unspoken but very palpable, and mostly friendly) rivalry to keep me motivated. Finally, I dedicate this to my future wife who has supported and guided me toward the light at the end of the tunnel. I love you all very much.
Chapter 1  
Introduction

1.1 Challenges in Thermal Management

Thermal management is a critical issue in the development of high performance microelectronic chips that enable radar, satellites, and other power intensive electronics. Heat sink plates are attached to semiconductor chips to dissipate the heat that they generate. The major issues that face the development and inclusion of heat sink plates into electronic packages are heat dissipation and thermal stressing issues. Poor heat sink performance can limit the performance and lifetime of the device.

The trend in power electronics is to decrease the geometric size of the chip and simultaneously increase the power density. The combination of these factors leads to a significantly increased current density and higher heat generation. If the extra heat is not dissipated, it will limit the performance and/or lifetime of the semiconductor chip. Heat sink performance must be improved to accomplish the goal.

<table>
<thead>
<tr>
<th>Material</th>
<th>Thermal Conductivity (W/m K)</th>
<th>CTE ($10^{-6}/^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper (Cu)</td>
<td>400</td>
<td>17.5</td>
</tr>
<tr>
<td>Diamond</td>
<td>1000-2000</td>
<td>2.5</td>
</tr>
<tr>
<td>Tungsten (W)</td>
<td>175</td>
<td>4.5</td>
</tr>
<tr>
<td>Aluminum</td>
<td>180-230</td>
<td>23</td>
</tr>
</tbody>
</table>
The second issue limiting the performance of high power devices is thermal stressing. Thermal stressing occurs when there is a large CTE mismatch between the chip and the heat sink. Semiconductor devices are made from low CTE materials such as silicon (Si), gallium nitride (GaN), or gallium arsenide (GaAs) and have a CTE of around \(4 \times 10^{-6}/°C\). Materials with high thermal conductivities such as copper and aluminum are commonly used in heat sinks because of their superior ability to dissipate heat. Both materials have very high CTEs (Cu is \(17 \times 10^{-6}/°C\); Al is \(24 \times 10^{-6}/°C\)). Because of the large difference in CTE, there is differential expansion between device and heat sink when the device is operated. After numerous thermal cycles, stress builds up in the device and it will eventually fail. Conventional materials, such as ceramics and refractory metals, have a low CTE cannot be considered as heat sink materials because they do not possess thermal conductivities high enough to dissipate the heat adequately. Table 1.1 summarizes the relevant material properties of common thermal management materials [1] [2].

One common approach to solving this problem is to tailor the material composition of the heat sink to have more desirable properties by blending two or more different materials that have desirable properties. The current state of the art heat sink materials are composite materials made up of a high conductivity material (such as copper) and a low CTE material (such as tungsten). Adding a low CTE material, such as a refractory metal, significantly lowers the heat sink’s ability to dissipate heat. Another limitation of the current technology is that manufacturing processes require expensive and timely processing and limit the range of compositions [2].

### 1.2 Hypothesis

Given the challenges that face the high power electronics industry, it is clear that new material solutions must be developed to keep up with the increasing challenges that face the power electronics industry. The solution involves developing materials that are capable of performing to the standard required by higher power density electronics. The solution should also provide a path for producing the new materials in a way that provides an advantage over current processes to make the materials more readily available.
The hypothesis of this thesis is that high performance thermal management materials can be engineered and produced by using a powder metallurgy approach and sintering the samples using Field Assisted Sintering Technology (FAST).

Through material selection and process development, the thermal management composites investigated in this thesis will be able to be tailored to meet specific requirements set forth by designers. This thesis will demonstrate the feasibility of numerous composite systems as well as several processing conditions aimed at optimizing the properties of the final composite.

1.3 Approach

The approach taken in this thesis is to develop multiple pathways to develop a superior thermal management material. The ultimate goal of this thesis is to develop a fully customizable thermal management solution that can be altered based on the specifications dictated by semiconductor design. As such, the work in this thesis will be divided into several sections that can be used individually or in combination to provide a complete thermal management solution. As each section has a different set of materials, each chapter will contain a separate research background, experimental details, and results.

1. This chapter provides a fundamental basis for this research including sintering, FAST sintering, and thermal transport.

2. The second chapter will detail the sintering of copper powder. The goal of this chapter is to determine a baseline understanding for the sintering parameters of copper powder and the properties of the sintered material.

3. The third chapter will detail the sintering of copper-tungsten composites. The goal of this section is to develop and characterize fully tailorable thermal management materials composed of a full range of compositions between copper and tungsten with a primary focus of maintaining a low CTE.
4. The fourth chapter is focused on copper-diamond composites. The focus of this research is to develop materials that simultaneously possess high thermal conductivity and low CTE.

5. The fifth chapter uses carbon nanotubes as a means to improve thermal conductivity.

6. The sixth chapter describes the sintering and characterization of heat spreading materials containing thermally annealed pyrolitic graphite (TPG).

7. The final chapter will provide a brief summary of the results given in this thesis and present options for future studies that can build upon the current findings.
Bibliography


Chapter 2  |
Background

2.1 Fundamental Processes that Drive Sintering

Sintering is a thermal activation of mass transport mechanisms. It is a result of a thermodynamic driving force and a transport mechanism [1]. Sintering is accomplished by reducing the free energy in the system by reducing of surface or grain boundary energies. The three most common driving forces for sintering are particle curvature, externally applied pressure, and chemical reaction. In a powder compact of a single material, chemical reaction can be ignored as a driving force for sintering. Since the driving force for sintering from chemical reaction can be much higher than externally applied force and particle curvature, sintering can be less predictable leading to non-uniform microstructure [2].

At the atomic levels, the reduction of surface energy occurs as a result of a difference in particle curvature. A chemical potential difference exists between particles under flat and curved surfaces. This is described by the Gibbs-Thompson Equation:

\[
\Delta \mu = \mu_{\text{curve}} - \mu_{\text{flat}} = \frac{2 \gamma_{sv} \Omega}{r}
\]  

(2.1)

where \( \mu \) is the chemical potential, \( r \) is the particle radius, and \( \gamma \) is the solid-vapor surface energy. At equilibrium, the chemical potential difference can be written in terms of partial pressure.

\[
\Delta \mu = kT \ln \frac{P_{\text{curve}}}{P_{\text{flat}}}
\]  

(2.2)
Figure 2.1. Schematic diagram Grain Boundary Movement as a Result of particle Curvature [2]

The implication of this equation is that partial pressure above a convex surface is less than that above a flat surface. This idea can be extended to show that atoms are more tightly bound to a convex surface than to a concave surface. This pressure difference provides a driving force for atoms to move from convex to concave areas [2] [3]. Adding an external force can add to the chemical potential difference, and greatly enhance densification mechanisms [2] [3]. Equation 2.1 also implies that the vacancy concentration under a concave surface is greater than the vacancy concentration under a convex one. It can be rationalized that since atomic bonding is stronger under a concave surface, more energy is required to break a bond and create a vacancy. Since there is no bond involved with a vacancy, it is more thermodynamically favorable for a vacancy to exist under a concave surface than a convex surface [2].

Based on the curvature arguments from above, atoms migrate toward centers of curvature. This means that grains that are with interior angles of 120° are stable. Grains with larger angles will grow while grains with more acute angles will shrink. The consequence of this result is a phenomenon called coursening. Coursening refers to the behavior of larger grains growing at the expense of smaller grains [2]. This process can also be referred to as Ostwald ripening [3]. Figure 2.1 shows a schematic diagram of grains growing towards the center of curvature, and illustrates how larger grains will grow while smaller ones will shrink. It should be noted that
actual powder samples are not two dimensional objects, so this example is idealized.

There are six primary kinetic transport mechanisms that atoms can move as a result of the thermodynamic driving force. Surface diffusion, lattice diffusion from the surface, and vapor transport are all non-densifying mechanisms and contribute to grain growth. As the name implies, surface diffusion and lattice diffusion (from the surface) refer to atoms moving from the surface of the particle to the neck area where two particles are joined. Vapor transport involves the atoms changing to the vapor phase and then moving from the surface to the neck. Vapor transport plays a much less significant role than the other two non-densifying mechanisms. Grain boundary diffusion, lattice diffusion (from the grain boundary), and plastic flow are all mechanisms that promote densification and lead to shrinkage, or movement of particle centers towards each other [2]. Grain boundary diffusion is the most significant densifying mechanism. In this case, atoms move from the powder to the neck area along the grain boundary. If the grain boundary is thought of as a pore channel, grain boundary diffusion can happen very quickly. Lattice diffusion (from the grain boundary) involves atoms moving from the grain boundary to the neck area through the lattice. Plastic deformation generally plays a much smaller role.
Figure 2.3. Grain Size versus Density Plots Showing Typical Sintering Trajectories

in densification when compared to diffusion mechanisms. Figure 2.2 schematically summarizes the mechanisms of atomistic transport that occur during the sintering process.

Macroscopically, the reduction of surface energy can occur by two means. The first is by reducing the amount of existing solid-vapor interfaces that exist. This leads to the formation of grain boundaries between particles and ultimately densification. The other means is an increase in average particle size, which leads to grain growth. At elevated temperatures, both processes occur and are in active competition with each other. Generally, densification is desired while grain growth is not. Figure 2.3 shows a plot of grain size versus density, which is sometime referred to as sintering trajectory. It illustrates both grain growth and densification are at work during typical sintering processes [2] [3]. Adding an external force can add to the chemical potential difference, and greatly enhance densification mechanisms [2] [3].

The sintering process is commonly thought of in terms of a model proposed by Coble [4]. This model describes individual particles as fourteen sided polygons called tetrakaidecahedrons. The stages of sintering are shown schematically in Figure 2.4. In the initial stage of sintering, there is minimal contact area between particles. Systems in this stage are characterized by neck formation between the
Figure 2.4. Schematic Diagram of Sintering Stages [3]

particles. This neck growth is coupled with shrinkage between particles. The density of a system in the initial stage is roughly 60% and grain growth does not occur because the solid-vapor interface angle is less than 90°. These factors show that grain boundary migration would require an increase in surface energy. As neck formation progresses, the system enters the intermediate stage of sintering. This is characterized by a continuous network of cylindrical pore channels, which are intersected and bound by grain boundaries. Since the grain boundaries are in contact with pores, grain boundary migration is limited. The density increases in this stage from about 60% to about 90%. In intermediate sintering stages, boundary-pore junctions require more energy to migrate than not. This leads to a pinning of the grain boundaries in the early and intermediate stages of sintering. In this stage a pore will spread and reduce contact between grains, leading to mitigated grain growth. Sintering in the intermediate regime will allow grain boundary diffusion but hinder grain boundary migration [5] [6]. The final stage of sintering is reached when about 90% density is reached and the pore channels
become pinched off leaving isolated pores. The pores will continue to shrink in this stage until full densification is reached. Grain growth will start to dominate as grain boundaries become separate from pores [3] [4].

Sintering mechanism can be given by determining the sintering and grain growth exponents in the following equations:

\[ \epsilon^m = \frac{\Delta l}{l_0} = \frac{kt}{TG^n} \]  \hspace{1cm} (2.3)

where m is the densification exponent, n is the grain growth exponent, l is the linear shrinkage, t is time, T is a temperature, G is the grain size, and

\[ K = K_0 e^{-\frac{Q}{RT}} \]  \hspace{1cm} (2.4)

where Q is the activation energy. Assuming no grain growth (which is reasonable in early stage of sintering because of grain boundary pinning by pores), plotting ln\( \epsilon \) vs. lnT will yield a slope of \( 1/m \). Comparison to model data will give insight into the dominant sintering mechanisms. Similarly, the slope of a plot of \( \frac{1}{n} \ln k \) vs. \( \frac{1}{T} \), where \( k = \frac{\delta L}{t^\pi} \) will yield the activation energy for that densification process [7] [8].

2.2 Field Assisted Sintering Technology

Field Assisted Sintering Technology (FAST) is a relatively new sintering technique that utilizes the simultaneous application of high temperature, uniaxial pressure, and DC current. FAST is also commonly referred to in literature as spark plasma sintering (SPS), pulsed electric current sintering (PECS), and pulsed plasma sintering (PPS). A schematic of the FAST system is shown in Figure 2.5. A very high electric current allows for an extremely fast heating rate. The high heating rate is combined with the uniaxial pressure resulting in the rapid densification of powders [9]. The powder to be sintered is placed inside a graphite die between two graphite punches. The punches and die are separated from the powder with graphite foil. This prevents reaction with the graphite die at the temperatures used in this study. Pressure is applied to the punches and current is passed through them, as well as the die. The current through the die and heats the powder through conduction. In the case of metallic powders, current can also flow through powder sample. The result this process is joule heating at the powder contact points. The current flows
through the powder along the contact points between the particles (which become the grain boundaries) along the path of least resistance. Any resistance between current paths can cause rapid local heating and may lead to melting, vaporization, and/or plasma formation. The rapid local heating is a result of the reduced cross section at the particle/particle contact points. The comparison of FAST sintering
and hot pressing is highlighted in a schematic diagram, Figure 2.7. Under pressure, the particles rearrange and deform resulting in mechanical bonding as well as solid state joining through grain boundary diffusion. When the pressure is combined with high temperatures, the sintering rate is significantly improved. This process has the advantage over other methods of having significantly shorter sintering times and lower sintering temperatures [10]. A photograph of the FAST unit used for densification in these experiments is shown in Figure 2.6.

### 2.2.1 Current Effects

One of the unique features of the FAST sintering technique is the use of electric current as the heating source. The electric current can give rise to extremely fast heating rates, which will be discussed later. However, the presence of electric current can also effect mass transport of atoms during the sintering process. There
are many reports on the effect of current assisting in densification. This happens through assisted mass transport via electromigration, point defect generation, and enhanced defect mobility [1] [11] [12] [13] [14] [15] [16] [17] [18] [19]. The presence of current has been shown to increase the solubility in liquid metals, which has implications on the final microstructure. A study that looked at the effects of current on the reaction between molybdenum and silicon foils found that the reaction was greatly increased in the presence of current [20]. This result was attributed to a lowered activation energy and enhanced diffusion. A different study carried out on a copper-nickel system shows that the direction of the current plays a critical role on the diffusion properties in the material [21].

Another study examined the current enhanced effects include increased growth rates for reactions between transition metals and carbon. The study found that the presence of electric current enhances the reaction rates between Zr and C plates as well as Ti and C plates [22]. The result is a thicker carbide layer in both material systems when exposed to an electric field. The enhanced reaction rates between zirconium and carbon are specifically critical to the work in this thesis. The enhanced growth rate in these studies is attributed to electromigration. It is proposed that the electric current enhanced the defect mobility in the metal layers [22].
In an attempt to demonstrate the advantage of current in the sintering process, an experiment was conducted using copper spheres on a copper plate. A schematic of the setup is shown in Figure 2.8. Graphite foils were used to inhibit the current while maintaining a constant temperature. Figure 2.9 shows the effects of current on neck formation resulting from reaction between the Cu spheres and Cu plate after experiencing a sintering temperature of 900°C for 60 minutes and exposed to 0, 700A, 850A, and 1040A. The neck diameter that forms between spheres is much larger in the presence of electric current and increases with increasing electric current. The mechanism for the enhanced neck growth was found to be the reduction of activation energy for defect mobility. [1] [23].

A separate study investigates the impact of current on mass transport by comparing the reaction between molybdenum and silicon foils. A silicon wafer was sandwiched between two molybdenum foils. Aluminum oxide discs were placed on
top and bottom of the foils in one of the trials to force the current to only pass through the graphite die. This experiment was compared against a trial in which no die was used so all of the current was forced to flow through the sample. It was shown that the samples that were exposed to current underwent much more reaction than their non-current counterparts. The authors observed no difference in the activation energy between the samples. As a result, they concluded that the enhanced reaction is a result of enhanced mass transport due to enhanced vacancy mobility [20] [1].

Garay et. al. observed that the presence of current led to an increased reaction rate between nickel and titanium. Increased growth rates of intermetallic phases were attributed to reduced activation energy from the current. The effect was shown to increase with increasing current and has the strongest effect at low temperatures (650°C) [12].

Zhao et. al. studies the diffusion behavior for samples sintered with current increasing from 0-1000A/cm². The authors observe an increased diffusion distance as a result of increased current densities. The activation energy was calculated and was determined to be dependent upon copper concentration in the sample. Samples with low concentrations of copper showed no impact of current on activation energy. The presence of current reduced the activation energy in samples with higher concentrations of copper. The authors conclude that the reduction of activation energy is a result of the decreased activation energy for defect mobility. Lower concentrations of copper would have less defects (vacancies) so the presence of current will have less impact [24].

Rudinski et. al. examined the diffusion behavior between copper and nickel disks in the FAST system. The authors observe less interdiffusion in samples that were subjected to current. Diffusion coefficients were calculated and showed that samples without current exposure had diffusion coefficients 1 order of magnitude higher. The authors do observe a reduction in activation energy and conclude that this is a result of temperature gradients within the sample [21].

Electromigration is known to occur in conductive metals for current densities ranging from $10^3$ to $10^5$ A/cm² [25]. The samples sintered in this thesis were subjected to much lower current densities of approximately 250A/cm² (3kA, 4cm diameter sample). It can be expected that electromigration did not play a significant role in the densification of samples in this study.
Comparative studies between FAST and hot pressing (HP) have been carried out to further understand the effect of current on the sintering process. One particular study compared the sintering behavior of copper and nickel spheres, as well as copper and iron spheres. In this study, sintering temperature and hold time were held constant in both the FAST and hot-pressed samples. Diffusion coefficients were calculated from the \((x/R)\) ratio and are shown in Figure 2.10. It is clear from this data that the presence of current improves the sintering behavior. \[1\].

Yanagisawa et.al. studied the effect of electric current on copper spheres under pressure \[26\]. The authors are able to conclude that arcing occurs between the particles at the contact points. The amount of arcing was shown to increase with lower pressure and higher current densities. Higher pressures result in larger contact areas between the particles (less resistance). The authors conclude that the sparking results in very high localized temperatures that can lead to localized melting and/or vaporization. The localized temperature rises are shown to be the most critical factor in the formation of necks (compared to sparks). The results indicate that impurities (such that oxides) could be removed as a result of the high localized temperatures \[26\].

Nagae et. al. compares the sintering behavior of aluminum powders sintered
in both FAST and hot press. Sintering parameters were fixed in both systems to isolate the effect of the current. Full density was achieved in much shorter sintering time (300s vs. 1200s) for FAST sintering [27]. The Joule heat given at the contact points can be calculated by [27]:

$$Q_{Tot} = I^2 R_{Tot}$$

(2.5)

where $Q$ is the total heat, $I$ is the current through the particle, and $R$ is the total electrical resistance of a particle. The total resistance of the particle can be expressed as the sum of the particle resistance and a contact resistance:

$$R_{Tot} = R_{Particle} + R_{Contact}.$$ 

The contact resistance, $R_{Contact}$, can be defined as

$$R_{Contact} = \frac{\mu}{2N\pi a}$$

where $\mu$ is the relative resistance of Al, $N$ is the number of contact points, and $a$ is the radius of the contact point. The quantity of heat causes a rise in temperature according to:

$$Q = c_{Al} V \rho_{Al} \delta T$$

(2.6)

where $c_{Al}$ is the specific heat of aluminum, $V$ is the particle volume, and $\rho$ is the particle density. The current through an individual particle can be calculated if it is assumed that all of the heat was generated from Joule heating. Solving the equations lead to the conclusion that the particle surface is clean without the presence of oxide. Since aluminum is readily oxidized it can be assumed that the oxide layer has broken down as a result of the electric current. The current then can freely flow through the particles at the contact points. The temperature rise is calculated by

$$\Delta T = \nu t$$

where $\nu$ is the heating rate and $t$ is the pulse width. The equations allow the estimation that very large heat generation occurs at the particle contact points. The heat generation in turn leads to a local temperature rise of at least 1000°C [27].

Xie et al. also studied the behavior of sintering aluminum powders using FAST. The study uses TEM to characterize the particle to particle interfaces after sintering. The authors find two distinct types of contact:

1. direct metal/metal bonding
2. metal/oxide film layer/metal bonding

The authors find that both plastic deformation and nonuniform temperature
distribution are the important factors for the large number of metal/metal contact points. Compared to hot pressing, the breakdown of the oxide was enhanced when FAST sintering was used [28].

Olevsky et.al. developed a model for FAST that takes into account three driving forces: surface diffusion, external pressure, and thermal diffusion (due to temperature gradients). The results of the model show that the densification due to thermal diffusion is significant and can be the strongest driving force at certain conditions [29].

2.2.2 Pressure Effects

There are many reports of the benefits of applying pressure during sintering, including both hot press and FAST studies. It has been shown applied pressure leads to an increase in chemical potential:

\[
\mu_I = \mu^0_i - \sigma_n \Omega_I
\]  

(2.7)

where \( \mu_I \) is the chemical potential at a particle interface, \( \mu^0_i \) is the standard chemical potential, \( \sigma_n \) is the normal stress at the interface, and \( \Omega_I \) is the atomic volume of the diffusing species [30] [1]. Besides enhancing diffusion, pressure assists densification by improving viscous and plastic flow, as well as creep. Pressure also increases particle rearrangement, which allows particles to come in closer contact and reduces diffusion distances. Studies on ceramic powders show that density significantly increases when pressure is applied at lower temperatures. The effect of pressure can be demonstrated through:

\[
\frac{d\rho}{(1-\rho)dt} = B(g\frac{\gamma}{x} + P)
\]  

(2.8)

where \( \rho \) is the fractional density, \( B \) is a constant that includes the diffusion coefficient and temperature, \( g \) is a geometrical constant, \( \gamma \) is the surface energy, \( x \) represents the size scale related to the particle size, \( t \) is the time, and \( P \) is the effective pressure. The geometry is important because the effective pressure applied to pores depends on the geometry of the pores and stage of sintering. The first term on the right hand side of Equation 2.8 describes the driving force for normal sintering processes. At low temperatures, diffusion is relatively low so the role of
pressure is greatly enhanced. At higher temperatures when diffusion becomes more prolific the effect of pressure is less pronounced. Similarly, the effect of pressure is much greater for larger particles because there is less inherent driving force due to less curvature compared to smaller particles. [1] [31].

2.2.3 Effects of Heating Rate

One of the main differences between FAST and conventional sintering techniques is the heating rate. FAST can achieve heating rates of up to $600^\circ$C/min. High heating rates reduce the time that powders experience at elevated but below sintering temperatures. Grain growth mechanisms dominate generally dominate in the temperature region. Additionally, thermal gradients that result from high heating rates can provide additional driving forces for diffusion [32]. There has been no consensus in the literature on the effect of heating rates. In fact, conflicting reports exist even for studies involving the same material system. The most likely explanation is that the effects of heating rate is highly dependent upon the properties of the individual system including material electrical and thermal conductivities as well as particle shape and size [1].

2.3 Thermal Transport

2.3.1 Electron Transport

Heat can be transported in solid materials by either electron transport or phonon transport, or some combination of the two. Electron transport involves the transport of thermal energy by direct movement of electrons in the system. Phonon heat transfer refers to the transport of thermal energy through lattice waves. In many of the copper matrix composites under examination in this thesis, both of these mechanisms play a crucial role. Electron transport’s role in a material’s thermal conductivity can be described by using the free electron Fermi gas model. In this model, each ion contributes a given number of electrons that are free to move within the solid. The electron cloud is described as a gas because the electrons can move freely through the volume similar to the way atoms can move freely through a given volume in the gaseous state. In the ideal case, the only particle interactions that
are counted are electron-electron collisions. At low temperatures, these interactions are negligible. In this scenario, there are far more electron-nucleus collisions occurring than electron-electron collisions. However, at operational temperatures, electron scattering occurs by defects, grain boundaries, and surfaces in sintered systems [33] [34].

Since the electrons are assumed to be unbounded, the solution of the free particle Schroedinger Equation can be applied. The allowable wavevectors according to the solutions are

\[
\begin{align*}
    k_x &= \frac{2\pi n_x}{L} \\
    k_y &= \frac{2\pi n_y}{L} \\
    k_z &= \frac{2\pi n_z}{L}
\end{align*}
\]

(2.9)

where \( L \) is the length of each side of the crystal, and \( n_x, n_y, \) and \( n_z \) are integers.

The resulting allowable energy levels are defined by

\[
\epsilon_k = \frac{\hbar^2 k^2}{2m}
\]

(2.10)

where \( m \) is the effective mass of an electron and \( \hbar \) is Plank’s constant. As mentioned previously, each atom contributes a certain number of electrons to the total number of electrons to the total volume of the metal, \( N_e \). The Pauli Exclusion Principle states that electrons must occupy different energy states, starting with the lowest first. The highest level occupied at 0°K is the Fermi level. The energy level associated with this level is the Fermi Energy, denoted \( \epsilon_F \). There are two allowable energy levels for every wavevector, which stem from the fact that there are two spin states. This means that there is \( \frac{N_e}{2} \). The distance between each allowable wavevector is \( \frac{2\pi}{L} \). The volume of each is \( \left( \frac{2\pi}{L} \right)^3 \). The volume of the sphere can then be approximated by multiplying number of wavevectors by the volume taken up by each wavevector. This relationship allows the calculation of the Fermi wavevector.

\[
\frac{8\pi^3 N_e}{V} \cdot \frac{2}{2} = \frac{4}{3} \pi k_F^3
\]

(2.11)

This result can then be substituted into 2.10 to give a useful expression for the
Fermi Energy.

\[ \epsilon_F = \frac{k_F^2 k_F^3}{2m} = \frac{k_t^2}{2m} \left( \frac{3\pi^2 N_e}{V} \right)^{2/3} \]  

(2.12)

In the 0°K situation, all of the energy levels below the Fermi energy are full, and all states above it are empty. When the temperature is nonzero, the probability of a state being full is given by the Fermi-Dirac Distribution.

\[ f(\epsilon) = \frac{1}{e^{(\epsilon - \mu)/k_B T} + 1} \]  

(2.13)

where \( \mu \) is the thermodynamic potential and \( k_B \) is the Boltzmann constant. This indicates that the number of electrons free to conduct heat in a given material at a fixed temperature.

As previously stated, the thermal conductivity in metals is a result of electron movement within the metal. The thermal conductivity can be expressed as:

\[ k = \frac{l}{3} Cv \]  

(2.14)

where \( k \) is the thermal conductivity, \( C \) is the electron’s heat capacity, \( v \) is the average particle velocity, and \( l \) is the mean free path. As heat capacity is a function of temperature, \( C_e = \frac{\pi^2 k_B^2 n_e}{2\epsilon_F} T \), the thermal conductivity also is linearly dependent upon temperature. The Fermi Dirac Equation states that only electrons near the fermi energy withinin the metal can make transitions and transfer energy. This energy is purely kinetic and can be converted into a velocity. It is assumed that all electrons are at the Fermi Energy and therefore travel with a Fermi velocity [34] [35].

\[ v_F = \sqrt{\frac{2}{m} \epsilon_F} \]  

(2.15)

where \( v_F \) is the Fermi velocity, \( m \) is the particle mass, and \( \epsilon_F \) is the Fermi Energy. The mean free path is a function of the frequency of electron collisions. Collisions can occur between electrons and other electrons (ee), electrons and the lattice (ep), defects (d), grain boundaries (gb), and surfaces (s). The rate of collisions (\( \nu \)) is calculated as the sum of all of these collisions [34].

\[ \nu_{tot} = \nu_{ee} + \nu_{ep} + \nu_{d} + \nu_{gb} + \nu_{s} \]  

(2.16)

The temperature dependence on the electron collision rate is critical. Electron-
grain boundary, electron-defect, and electron-lattice collision all scale linearly with temperature, while electron-electron collisions scale with the square of temperature. At low temperatures, lattice interactions dominate. Electron interactions dominate at higher temperatures. The difference in temperature dependance allows for isolation of mechanisms of thermal conductivity [34] [35] [33].

2.3.2 Phonon Transport

Thermal energy can also be transported through a solid by acoustic lattice interactions between atoms within a lattice. This is the very dominant heat transport mechanism in ceramic materials without freely moving electrons. Lattice vibrational energy is quantized into units called phonons. The lattice thermal conductivity is defined by the same equation that defines electron thermal conductivity, Equation 2.14. The difference is that now the heat capacity, velocity, and mean free path apply to the phonon instead of the electron [34] [35] [33].

The lattice vibrations have a defined frequency range, $\omega_m$. At the lower end of the frequency range the waves can be treated as elastic waves. At the upper end of the range, the wavelength is comparable to the atomic spacing. The position of each atom can be expressed as the sum of its Bravais lattice site and its displacement.

$$r(\vec{R}) = R + \mu(\vec{R})$$  \hspace{1cm} (2.17)

The atoms in the lattice can be thought of as being connected by springs, with spring constant $K$. Figure 2.11 shows this, schematically, in one dimension. As shown in the diagram the displacement, $\mu_n$ of each atom from the lattice is relative to the $n$th lattice site. The equation of motion for the atoms is given by

$$M\frac{d^2\mu_n}{dt^2} = K(\mu_{n+1} - 2\mu_n + \mu_{n-1})$$  \hspace{1cm} (2.18)

where $M$ is the mass of an individual atom. The frequency of the atomic movements can be calculated by:

$$\omega(k) = \sqrt{\frac{4K}{M}} \left| \sin \frac{1}{2} ka \right|$$  \hspace{1cm} (2.19)

When $k > \frac{\pi}{a}$ the waves correspond to wavelengths less than the interatomic
Figure 2.11. Schematic diagram of a 1-D chain of atoms connected by springs [34].

spacing. While this scenario only represents a one dimensional case, it can be modified to represent a two-dimension scenario by using a situation where each atom has the same mass, M, and alternating springs, $K_1$ and $K_2$. This case bears similarly to the case of diamond. Diamond is an FCC structure with a two point basis and all atoms are identical. However, the carbon atoms in the diamond lattice have different interatomic spacing. The different spacings result in different interatomic forces, which are represented by different spring constants. The two-dimensional equations of motion are

\[
M \frac{d^2 u_n}{dt^2} = -K_1(u_n - v_n) - K_2(u_n - v_{n-1})
\]

\[
M \frac{d^2 v_n}{dt^2} = -K_1(v_n - u_n) - K_2(v_n - u_{n+1})
\]

(2.20)

where $u_n$ and $v_n$ represent the first and second atom displacement, respectively. Just as before, the frequency as a function of wavevector can be expressed as

\[
\omega^2 = \frac{K_1 + K_2}{M} = \pm \frac{1}{M} \sqrt{K_1^2 + K_2^2 + 2K_1K_2\cos k a}
\]

(2.21)

This relation is known as the dispersion relation. The rate of energy transport can be derived from the dispersion relation. The group velocity, as it is called, is given by:

\[
v_g = \frac{\partial \omega}{\partial k}
\]

(2.22)
The dispersion relation is shown in Figure 2.12. It can be seen that for small values of \( k \) the group velocity is essentially constant and goes to zero at the edge of the Brillouin zone. Waves with small \( k \) values have long wave lengths and heavily contribute to energy transport in the material. These values are represented on the lower acoustic branch of the dispersion relation. The name is given because small values of \( K \) obey a linear relation, \( \omega = ck \) where \( c \) is the speed of sound (acoustic velocity). The optical branch of the dispersion curve is associated with higher frequencies and interactions with the visible or near-visible spectrum. The group velocity is generally much lower than that of the acoustic branch and often considered negligible when talking about energy transport properties.

Three dimensional dispersion relations are very similar to one dimensional ones except there are transverse modes, which arise due to the sheer waves that propagate in a 3-D crystal. These modes travel slower than the standard longitudinal acoustic mode but still contribute to the transport properties. The optical branch can also exhibit transverse modes, but they do not contribute to transport properties because of low group velocities.

Phonons describe a quanta of energy of lattice vibration. It is analogous to
photons for electromagnetic energy.

\[ U_1 = \sum_{k,s} [n_s(k) + \frac{1}{2}] \hbar \omega(k, s) \]  

(2.23)

This equation describes a crystal as a series of 3N simple harmonic oscillators, where N is the total number of atoms. There are both transverse(2) and longitudinal(1) modes within the lattice. The allowable energy levels for a harmonic oscillator are given in the summation of 2.23. The levels are summed over all allowable wavevectors and the three modes. The integer quantity \( n_s(k) \) is the mean number of phonons with energy \( \hbar \omega(k, s) \). The number of phonons at a given frequency represents the amplitude which excites that particular vibrational mode. Phonons are dictated by the Bose-Einstein distribution. Phonons behave in similar manners to photons, since they both obey Bose-Einstein statistics. Calculations can be done by integrating over allowable energy states. The specific internal energy of the lattice is given by

\[ u_l = \sum \int D_s(\omega)n_s(\omega)\hbar \omega_s \partial \omega_s \]  

(2.24)

where \( D_s(\omega) \) is the phonon density of states. The phonon density of states is the number of phonon states with frequency between \( \omega \) and \( \omega + d\omega \). The phonon density of states must be calculated from the dispersion relation but approximations are often used to produce accurate predictions.

As previously mentioned, phonon thermal conductivity is due almost exclusively to acoustic phonons. For the rest of this discussion, phonons will be treated as particles, like photons. The group velocity of these phonons will be assumed to be constant and equal to the speed of sound (temperature independent). Equation 2.14 can also be used to describe phonon heat transport. This is applicable if phonons scatter with phonons, defects, and grain boundaries - the same as electron scattering modes. This is the case in bulk materials. Phonons travel through the system like waves which are scattered at points in the material where the elastic properties change - such as defects and grain boundaries [34].
2.3.3 Interfacial Improvement

Much of this thesis is focused on combining separate material systems with different properties to yield a composite with properties superior to those of the individual materials. Good interfacial bonding between the materials may play an important role in taking advantage of the high thermal conductivity of diamonds. One of the most promising ideas that has been proposed is to add secondary elements to act as a coupling agent between the diamond particle and metal [Cu] matrix. The success of this approach is often attributed to the formation of a thin carbide layer at the interface. This fact makes it critical to understand the properties that contribute to the formation of carbide phases at the interface [36].

Tillmann et. al. completed a study to examine the reactivity of diamond particles in Cu, Cr, Ni, Fe, and Co matrices. The samples were densified using a hot press at temperatures relative to the melting temperature of the matrix metal for 3-4 hours. Once the samples were densified, the diamond particles were removed by mechanical processes to be characterized. The particles were characterized for both carbide and graphite formation. The study uses XRD to observe that carbide phases only exist when the diamond particles are sintered in Cr matrix. The author observed evidence of both $Cr_2C_3$ and $Cr_3C_7$. There is no evidence of graphitization in the presence of Cr or Cu. However, there is no carbide formation when diamonds are sintered in a copper matrix. There was no evidence of carbide formation, but high levels of graphitization of the diamond particles was observed when they were sintered in Co, Fe, and Ni matrices [37].

The Gibbs Free Energy of formation for different carbide formation elements is shown in Figure 2.13. From the image, it becomes clear as to why Cr shows the formation of a carbide while the other elements do not. Studies that use elements as carbide formers to improve the interface generally use elements that have low free energy of carbide formation such as Cr, Ti, W, and Zr. This allows the sintering time to be shorter and results in less graphitization of diamond [38].

Diamond is a metastable phase of carbon. At low temperatures, diamond doesn’t have enough energy to transform into the more stable graphite phase. However, graphitization of diamond particles also becomes a concern when they are exposed
Shao et al. conducted a study to investigate the extent of graphitization. The authors sintered Cu-Dia composites at temperatures ranging from 875-950°C with 300MPa of pressure applied in an argon atmosphere. The authors used XRD and TEM to determine the extent of graphitization, but were unable to observe any graphitization. The authors conclude that any graphitization that may occur would be less than 1% and would not have any significant impact on the composite properties [39].

Figure 2.13. Gibbs free energy of formation for carbide forming elements [38]
Bibliography


Chapter 3  
FAST Sintering and Characterization of Copper

3.1 Objectives

The work in this thesis is based upon the FAST sintering of copper based composites. A baseline understanding of how FAST parameters affect the sintered copper part must first be understood before any of the composite sintering can be undertaken. A simple parametric study to examine the affects of sintering temperature, sintering time, and pressure on the microstructure of copper was conducted to develop a starting point for future studies on copper based composites.

3.2 Previous Research on Copper Sintering

There is limited research published on the sintering of copper powders. Copper is readily available in all forms and is easily machinable so there is no motivation to develop sintering processes for copper. The motivation for the work in this thesis is to provide a baseline for further experimentation. Sule et. al. sintered pure copper powder at 650 and 700°C to densities ranging from 95-99% of theoretical density. The author measured the oxygen content of the powder and found that the density was heavily dependent upon the oxygen content of the powder. The author found the the grain size was smaller for samples sintered at higher temperatures. The proposed rationale for this is that pores restrict grain growth. It was observed that the thermal conductivity of the sintered sample is 390
W/mK, which is attributed to the very low oxygen content and high density [1]. Another study sinters copper to compare the sintering of cryo-milled powders compared to atomized powders. The authors find that cryo-milled powders have a lower sintering temperature when sintered at 550-650°C [2]. Vincent et. al. studies the effect that thermal conductivity has on thermal conductivity. The authors find that the thermal conductivity decreases linearly as the porosity increases in the sample. The interesting finding is that the decrease doesn’t begin until the porosity level is near 5 vol % [3].

3.3 Experimental Details

Elemental copper powder of > 99% purity was purchased from Acupowder (NJ). The size of the powder was -325 mesh, which is approximately equal to 40-45 µm. The powder was placed into a graphite die between 2 graphite punches. The powder was separated from direct contact with the punches by graphite foil. The setup was placed into the FAST system and sintered under vacuum. The specific recipes for sintering are described in the results section.

3.4 Results

Initial batches of powder was densified in the FAST system with the conditions of 800°C for 20 minutes, 36MPa applied pressure, and a 50°C/min. Figure 3.1 shows the sintering conditions of copper powder that was sintered under these conditions. Grain growth is minimal in this scenario. The final microstructure of a cross section of the pure copper sample is shown in Figures 3.2 and 3.3. The final relative density was 99.3%. It is shown that porosity exists both along grain boundaries and within the copper grains. When the sintering temperature is increased to 900°C, the grain growth is much more pronounced - from 40µm to 100µm. This is evident when comparing Figures 3.2 and 3.4. The measured density is 99.0% for the sample sintered at 900°C, but the microstructure, shows much smaller pores. There was no significant difference in the density of the samples.

At 800°C, when the sintering time is increased to 30 minutes, the grain size increases modestly, as shown in Figure 3.5. Again, there is no effective change in final density.
Figure 3.1. FAST run plot showing the sintering parameters for copper powder that was sintered at 800°C with 36MPa for 20 minutes.

Figure 3.2. Low magnification optical microscope image of 99.3% dense copper sintered at 800°C with 36 MPa for 20 minutes showing many small pores.

The effect that external pressure had on sintering was also studied. Pressure was increased from 36 to 50MPa while sintering at 800°C for 20 minutes. No observable effects are reported when the applied pressure is increased to 50MPa with the same sintering conditions. The microstructure of the sample sintered with 50MPa applied pressure is shown in Figure 3.6. This data suggests that 800°C is sufficient
Figure 3.3. High magnification optical microscope image of 99.3% dense copper sintered at 800°C with 36 MPa for 20 minutes showing size of pores ranging from <1 to 5 µm.

Figure 3.4. Optical microscope images of the microstructure of pure copper powder sintered at 900°C with 36 MPa for 20 minutes. The sample density was 99.0% theoretical density.

to achieve nearly full density in sintering pure copper. Increasing the temperature gives no further benefit in densification but increases the grain size. However, larger grain size may actually provide a benefit to the thermal conductivity of the sintered samples as grain boundaries are scattering site for electrons.
Figure 3.5. Optical microscope images showing the microstructure of densified copper powder with density of 99.3% sintered at 800°C with 36MPa pressure for 30 minutes.

Figure 3.6. Optical microscope images highlighting the microstructure of copper powder sintered at 800°C for 20 minutes with 50MPa of externally applied pressure. The sample had a recorded density of 99.3%.
3.5 Conclusions

It has been shown that the most important FAST sintering condition for the pure copper system is temperature. Increasing the temperature from 800°C to 900°C shows an increase in grain size from approximately 40 $\mu$m to larger than 100 $\mu$m. It has also been shown that neither applied pressure nor sintering time make a significant impact on the density or microstructure of the sintered sample when the samples were sintered at 800°C. The sample density was reported to be 99.3% for each of the samples that were sintered at 800°C.

For the rest of the work presented in this thesis, the standard baseline recipe of 900°C, 36MPa of applied pressure, 20 minute sintering time will be used as the starting point for the sintering of copper composite systems. Parameters may be altered to achieve high densities and/or specific features for individual composite systems.
Bibliography


Chapter 4  
Fabrication and Characterization of Copper-Tungsten Composites

4.1 Objective

This work investigated the effectiveness of fabricating Copper-Tungsten composites via FAST. The goal of this research was to develop a composite material of tungsten and copper to match the CTE of high power semiconductor dies. Tungsten was used to reduce the CTE while copper was used so that the composite could maintain as high of a thermal conductivity as possible.

The second goal of using FAST would be to reduce the processing time, and processing cost as a result, compared to conventional processing methods. The current commercial approach to produce Cu-W composites is by the liquid infiltration method. In this method, tungsten powder is sintered into a porous skeleton at high temperature. Then copper is melted and the resulting liquid is introduced to the tungsten skeleton under pressure. The liquid fills the voids to form the composite material. The resulting composite is then generally hot or cold rolled to eliminate porosity and increase density. This process produces composites that are fully dense but have thermal performance that is highly variable [1]. The process has several drawbacks:

1. The multiple step process takes longer to arrive at the final composite
2. Very high temperatures are needed to sinter the tungsten skeleton
3. Both of the previously stated facts lead to a more costly process
4.2 Previous Research on Copper Tungsten Composites for Thermal Management Applications

Several studies have been done previously in the area of Cu-W composites. Powder metallurgy was used as a way to produce a W-Cu sample with a gradually increasing W composition. The study produced samples with three distinct regions with W compositions of 25, 50, and 75\% W. The samples were sintered at temperatures up to 1050°C. The highest reported density in this study was 96\%. The density and thermal conductivity both increased as a function of sintering temperature [2].

One study conducted by Quixin has examined the properties of Cu-W systems with 85wt.\% W using densified field assisted sintering technology. Powders in this study were mechanically alloyed via ball milling in acetone for 48h and then subjected to FAST processing at temperatures ranging from 1230-1300°C. The highest density reported was 99.6 \%. The corresponding thermal conductivity value was 196W/mK. This study was fundamentally different than the work presented in this thesis because the high temperatures used for densification. The temperatures used in the study would have melted the copper powder giving rise to a liquid sintering system [3].

Cu-W composites with 50 and 75wt. \% Cu were sintered to densities up to 98.6\% and 98.5\%, respectively using the pulse plasma sintering technique. Increasing sintering temperatures corresponded to higher densities. These composites showed strong influence of the W on the composite CTE, as expected. The CTE of W-50 wt.\% Cu was observed to be $7 \times 10^{-6} \degree \text{C}$ while 75 wt. \% Cu exhibited a CTE of $15 \times 10^{-6} / \degree \text{C}$ [4].

One other method of producing copper-tungsten composites is by using a fabricated composite powder. An alternative method has been done in which tungsten trioxide (WO3) and cupric oxide (CuO) were mixed in a ball mill and then reduced in a hydrogen atmosphere to achieve a composite agglomerate powder consisting of copper particles surrounded by tungsten particles as a starting point for sintering. Unlike liquid phase sintering, this method allows for any desired ratio of Cu and W to be used. The method of reducing oxides exhibited higher densities up to 98\% in the 80\% W sintered samples. However, the downside to this process
is that it is a multi-step process that requires longer time [5].

4.3 Experimental Details

Elemental tungsten (.6-.9µm) and copper (43µm) powder were weighed into a Nalgene bottle to the predetermined composition percentages and placed in a three-dimensional mixer to distribute the powders. Tungsten balls (2.5mm) were added as the milling media at a ratio of 5:1 (balls: powder). The bottle was filled with Ar and placed on rollers at a speed of 250rpm for 20 hours.

The blended powder was then compacted into a 40mm diameter cylindrical graphite die with graphite punches on both top and bottom if the die. Graphite foil was used as a barrier between the sample and the die/punches. The graphite foil prevented the powders from chemically reacting with the die making it easier to remove and prevents damage to the die. The die and punch setup was placed into the FAST unit for densification. All powders underwent a reduction process in the FAST unit under an H\textsubscript{2} environment ranging in time from 20 minutes to an hour at 700°C to remove any possible oxide that may have formed on the copper and tungsten powders. Temperature and pressure were varied between runs to determine optimal parameters for maximum densification. Figure 4.1 shows a FAST sintering plot containing the major sintering parameters. The plot shown is for Cu-70 wt.% W but is representative to the sintering data for each of the plots.

Sample densities were measured using the Archimedes method. Samples were then cut with a diamond saw and ground with SiC paper to 800 grit. The samples were then wet-polished using diamond suspensions containing diamond particles as small as 1 µm. The final polishing step was carried out using 0.04 µ colloidial silica. Optical and Scanning Electron Microscopes were used to characterize the microstructure of sintered samples. Thermal performance was measured by measuring both thermal conductivity and coefficient of thermal expansion for the full range of compositions for the sintered samples.

CTE measurements were taken on a small section of the sample (5 x 5 x 5 mm) in the range of 25-250°C using a TMA 2950 from TA Instruments. The system included a quartz rod positioned verically. The sample was placed under the rod
Figure 4.1. FAST run plot showing the sintering parameters for copper powder that was sintered at 975°C with 65 MPa for 20 minutes with a heating rate of 100°C.

Figure 4.2. Densities of Cu-W composites fabricated by the FAST method. Samples with 0, 10, and 20 wt. % W were sintered at 900°C with 36 MPa of applied pressure for 20 minutes. The sample containing 50 wt. % was sintered at 975°C with 45MPa of applied pressure for 20 minutes. The sample containing 70 wt. % W was sintered at 975 with 75MPa for 20 minutes. All of the samples were subjected to a 1 hour hydrogen treatment at 700°C inside the FAST chamber.

and the position was set to the zero point. The chamber containing the sample was flushed with nitrogen gas to protect the sample from oxidation. The CTE was measured by the displacement of the quartz rod as the temperature of the chamber increased.
4.4 Results

4.4.1 FAST Parametric Study

Figure 4.3 shows the maximum densities accomplished for the Cu-W system with 10, 20, 50, and 70 wt. % W. The trend is that the density of the composites is decreasing with increasing percentage of tungsten. Densities of at least 99% were achieved in each of the different tungsten compositions except for 70wt. % W. This can be partially attributed to the fact that the sintering temperature used in these experiments (975°C) are very low compared to the temperature that pure tungsten is sintered at (1800°C) [6].

![Figure 4.3. Densities of Cu-W composites fabricated by the FAST method. Samples with 0, 10, and 20 wt. % W were sintered at 900°C with 36 MPa of applied pressure for 20 minutes. The sample containing 50 wt. % was sintered at 975°C with 45MPa of applied pressure for 20 minutes. The sample containing 70 wt. % W was sintered at 975 with 75MPa for 20 minutes. All of the samples were subjected to a 1 hour hydrogen treatment at 700°C inside the FAST chamber.](image)

Temperature, pressure and heating rate were also explored as possibly having an effect in the final density of the product. As expected, higher pressure led to an increase in the final density of the sample. This was observed in both Cu-50 and 70wt.%W. The effects of temperature is shown in Figure 4.4. The sintered samples contained 10 wt. % W and were sintered with 36MPa of applied pressure for 20 minutes with a heating rate of 50 °C/min. It is not surprising that the density
increases with increasing sintering temperature due to increased driving force for mass transport.

The pressure effect on Cu-70 % W is shown in Figure 4.5. The samples were sintered at 975°C for 20 minutes with a heating rate of 50°C. Higher applied pressure increases particle rearrangement (which can lead to greater neck formation), hot deformation, and also increases the driving force for sintering. This ultimately leads to higher density in the final sample.

The heating rate was varied in Cu-70 wt.% W from 25°C/min to 100°C/min and showed no effect on the final density of the sample. The result is presented in Figure 4.6. This outcome was the somewhat expected. The objective of using high heating rates is to reach the final sintering temperature as quickly as possible to avoid particle coursening. In the situation with less coursening, the driving force for sintering is higher. However, the present experiment subjected samples to a $H_2$ pretreatment at 700° for 20 minutes. Any reduction in coursening that might have occurred as a result of faster heating rates may have been negated by the extended duration at elevated temperatures.
Figure 4.5. Measured density for sintered Cu-70 wt.% W samples that were sintered at 975°C for 20 minutes with a heating rate of 50°C and different sintering pressures.

Figure 4.6. Measured density for Cu-70 wt.% W samples sintered with different heating rates at 975 °C with 65 MPa

4.4.2 Microstructure Analysis

The sintered samples were cross sectioned and polished so that micrographs could be captured by both optical and SEM microscopes. Figures 4.7 and 4.8 show the optical and SEM images, respectively, of the sintered Cu-10 wt.%W samples. Both
images show that the W particles are agglomerated. Figures 4.9 and 4.10 are optical and field emission SEM images of 20 wt.% W samples, respectively. Again, these images show that the W particles are agglomerated. The W starting powder had a much smaller powder size ((0.6 to .9 µm) ) than the copper powder (43 µm) giving it a tendency to agglomerate. The FESEM resolution provides high magnification of one of the W particle agglomerations revealing very small amounts of porosity within the clusters.

Figure 4.7. Optical Image of Cross Section of Cu-10 wt.%W sintered at 900°C with 36 MPa of applied pressure for 20 minutes.

As the amount of W content in the sample increases it becomes more difficult to sinter to a high density. The cause is twofold. More W content increases the number of W agglomerations in the sample. It has been shown that there is a small amount of porosity contained in the agglomerations. As a result, there is more porosity because of increased W content. Secondly, the increasing W content increases the probability of W-W contact. In this case, to achieve high densitites, W particles must experience grain boundary diffusion. The temperatures used in the experiment aren’t sufficient for any significant mass transport of W atoms. As a result, minimal densification occurs between W particles. For samples with lower percentages of W, copper can deform to surround much of the W powder during
Figure 4.8. SEM Image of Cu-10 wt. %W sintered at 900°C with 36 MPa of applied pressure for 20 minutes.

Figure 4.9. Optical Image of Cross Section of Cu-20 wt.%W sintered at 900°C with 36 MPa of applied pressure for 20 minutes.

the ball milling process as well as from particle rearrangement during the sintering process. As a result, the sintering pressure must be increased to achieve high density for samples containing 50 wt.% W. Figures 4.11 and 4.12 show optical and SEM
images of Cu-50 wt.% W. It is very noticeable that the copper grains have elongated as a result of the increased pressure. Also, the copper was able to penetrate into the small areas between the W particles as a result of the combination of high temperature and high pressure.

Full density was not achieved in the Cu-W composite with 70 wt.% W. 75MPa of pressure was applied to maximize the amount of driving force for sintering from applied pressure. The maximum force that the graphite die is able to withstand without breaking is 75MPa. Figures 4.13 and 4.14 show an optical and SEM image, respectively of Cu-70 wt.% W. The optical image shows that the W particles are fairly well distributed thought the composite and a few pockets where large amounts of copper exist. The SEM image shows that there is noticeable porosity in areas where tungsten particles are in contact with each other. This is highlighted by arrows in Figure 4.14. This supports the idea that the sintering temperature is not high enough to eliminate porosity in areas where tungsten particles are in contact with other tungsten particles.
Figure 4.11. Optical Image of Cross Section of Cu-50 wt.%W sintered at 975° C with 45MPa of applied pressure for 20 minutes.

Figure 4.12. SEM image of Cu-50 wt.%W sintered at 975° C with 45MPa of applied pressure for 20 minutes showing the relatively uniform distribution of W particles.
**Figure 4.13.** Optical image of Cu-70 wt. %W showing W distribution in the composite

**Figure 4.14.** SEM Image of Cross Section of Cu-70 wt.%W
4.4.3 Thermal Performance Characterization

Figure 4.15 shows the value of the coefficient of thermal expansion for each of the different compositions of Cu-W. As expected, adding more W in the composite decreases the overall CTE of the composite. The value of CTE for 70wt% W is in agreement with previous work [7].

Since there is no chemical bonding between tungsten and copper, the CTE of the composite must be mechanically restricted by the tungsten particles. There is little restraint offered to the composite in the cases where the W content is low. The samples with low weight percentages of W show that there is no change in the composite’s CTE. Copper expands naturally since there isn’t enough tungsten in the composite to restrict the expansion. The composite CTE begins to decrease once the wt. % of W is increased to a point where it can sufficiently restrict the expansion of copper. The composite CTE for the range of compositions is given in Figure 4.15. The observed data is compared to the predicted value of the composite CTE given by the equation:

\[
\alpha_{\text{composite}} = \frac{\alpha_W V_W E_W + \alpha_{Cu} V_{Cu} E_{Cu}}{V_W E_W + V_{Cu} E_{Cu}}
\]  

where \( \alpha \) is the linear coefficient of thermal expansion, V is the volume fraction, and E is the Young’s Modulus. The CTE values for the CTE of commercially available Cu-W composites are also shown on the plot [1]. The values for the sintered samples fall on the same line as the commercially available copper-tungsten composites. The major difference is that the commercially available samples are produced by the infiltration method that limits the composition range to a minimum of 65 wt. % W. Both fabrication methods lead to composite CTEs slightly higher than the predicted value.

Figure 4.16 shows the thermal conductivity values of Cu samples with varying amounts of W. The advertised thermal conductivity of commercially available, infiltrated Cu-W samples are included as well as the predicted value for the composite material [1]. The predicted value was calculated using the Maxwell model [8], which is the most common theoretical model for thermal conductivity in composite materials. The predicted value is given by the equation
Figure 4.15. Coefficient of thermal expansion of copper-tungsten samples measures from 25-250 °C; compared to the theoretical value and commercially available composites [1]

$$\frac{k_{\text{composite}}}{k_{Cu}} = \frac{V_W + \frac{k_W}{k_{Cu}} + 2}{V_W(1 - \frac{k_{Cu}}{k_W} + \frac{k_W}{k_{Cu}})}$$  (4.2)

where \( k \) is the thermal conductivity and \( V \) is the volume fraction of each component. As expected, increasing the amount of W reduces the overall thermal conductivity of the composite. This is expected because tungsten has a low thermal conductivity. It is clear than increasing its content should reduce the overall thermal conductivity. The thermal conductivity of tungsten is approximately half that of copper. The value for pure W is the theoretical value, and was not directly measured [9]. While the thermal conductivity values are in agreement with the theoretical model for the all samples except pure copper and Cu-70 wt.%W sample which is 25% higher than the predicted value given by the Maxwell model. The sintered pure copper sample exhibits lower thermal conductivity values of 360W/m K because of small levels of impurities as well as low levels of porosity. Both impurities and pores act as electron scattering sites and reduce the thermal conductivity in the metal. Since the Maxwell model assumes no interaction between the particle additions, it may not be completely accurate for 70 wt. % W. At 70 wt. %, tungsten occupies 52% of the composite’s volume. There is almost certainly
interaction between $W$ particles at loading, so the model may not accurately describe the conditions.

## 4.5 Conclusions

High density samples Cu-W composite samples were sintered via FAST. In compositions containing 50 wt% or less tungsten, near full density was achieved. Full density was not able to be reached in compositions with larger percentages of $W$. The main cause of this is an incomplete blending of the particles and a mismatch of particle size. Had the copper particles been smaller, they may have blended more evenly with the tungsten and reduced the amount of volume of tungsten-tungsten contact.

The thermal performance was characterized by measuring the CTE and thermal conductivity of the sintered composites. Both properties are well aligned with the theoretical models and commercially available Cu-W composites.
There are some key advantages to sintering via FAST opposed to other fabrication methods. These reasons make the process developed in this thesis favorable to the current production methods. First, using FAST allows Cu-W composites to be produced in a very short, single step process compared to a lengthy two step process. The second advantage is that using FAST allows the composition, and thus properties, to be engineered to fit the thermal requirements for the whole range of compositions instead of just a fraction. This advantage is even stronger given that the composition can be functionally graded so the the composition can be further engineered to yield specific properties required by the application.
Bibliography


5.1 Objective

The goal of this work is to develop a superior material and fabrication process to produce superior performing thermal management products. The rationale of fabricating composite materials by blending copper (and copper alloy) powder and diamond particles and then sintering by FAST is to provide a composite material with ideal thermal properties in a short manufacturing time. The diamond particles have superior thermal conductivity of up to 2000W/mK (depending on quality), low CTE of $1 \times 10^{-6}$/°C, and low density (3.5g/cm$^2$). Using a copper matrix ensures that the composite can have as high of thermal conductivity as possible because of its own high thermal conductivity of 400W/mK.

A second objective of this work is to use thermal simulations to develop a model to accurately describe the experimental results given in this work and predict thermal performance based upon given parameters such as the base alloy composition and the volume percent of diamond particles used in the composite. The models were built to describe the (near) fully dense systems in this thesis. The objective of the models are to create a set of boundary conditions and material properties to accurately match the experimental results. Once the results match,
information can be extracted from the input boundary conditions that increase the fundamental understanding of the composite system.

5.2 Previous Research Copper-Diamond Composites

Numerous studies have been done on copper-diamond composite materials. All studies conclude that the interface between the copper matrix and diamond particles is critical to the performance of the composite. Several approaches have been taken to attempt to improve the interface. All of the approaches involve using an additional element to act as a coupler between diamond and matrix. Many of the studies involve coating the diamond particles as a method of introducing the additional element to the interface.

The thermal conductivity of diamond can vary greatly depending on the impurity levels. The most common impurity found in diamond particles is nitrogen. Ultimately, the thermal conductivity of the copper-diamond composite depends upon the thermal conductivity of the diamond particle. However, it is extremely difficult to measure the thermal conductivity of diamond particles. Most studies assume a thermal conductivity of 1500 W/mK for the diamond particles.

5.2.1 Coated Particles

Zhang et. al. used titanium coated diamond particles to create composites with 45-60 vol.% diamond in a copper matrix. The particles used in this investigation were approximately 75μm. The diamond particles were mixed with elemental Ti powder mixed with chloride salts. The mixture was heated to 800°C for 90 minutes. The resulting coating was measured to be 285nm. Figure 5.1 shows the XRD pattern as well as an SEM image of the Ti-coated diamond particles. The samples were then combined with copper powder and densified using FAST at 970°C under a pressure of 45MPa for 10 minutes. The authors use XRD to show the presence of TiC on the pre-sintered diamond particles that forms as a result of coating process. The sintered composite exhibited thermal conductivity of 493W/mK compared to 200W/mK for uncoated diamond particle composites. However, the thermal conductivity does not increase with increasing volume of diamond particles. This is because the interface between the matrix and diamond is not sufficient to promote
efficient heat transfer [1].

**Figure 5.1.** SEM image and corresponding XRD pattern of titanium coated diamond showing the existence of TiC [1]

Niazi et al. performed two separate studies using Cr-coated diamond powders. The particles were coated via an electroless plating process. The samples were densified via FAST processing. The samples were sintered at temperatures ranging from 800-1100 °C with 40MPa for 15 minutes with a heating rate of 100 °C/min. XRD was used to show that $Cr_2C_3$ existed at the interface between the diamond particle and copper matrix. Samples with 70 vol. % diamond particles exhibited thermal conductivity of 400 W/mK. The thermal conductivity was shown to increase as sintering temperature rose from 900 to 1100°C. This was attributed to reduced porosity as a result of increased sintering temperature. A very low CTE of $1.2 - 1.6x10^{-6}/°C$ was reported for the sintered composite. However, there was
no clear trend linking the CTE of the composite to the temperature that it was sintered at [3] [4].

Chu et al. also investigated the effectiveness of using Cr coated diamond particles. 100µm diamond particles were combined with copper powder in volume fractions ranging from 40-65%. The samples were sintered via FAST for 5 minutes with temperatures ranging from 820-940°C. Unlike other published studies, thermal conductivity of the sintered composite decreases as volume fractions of diamond particles is increased. The thermal conductivity of the coated diamond composites follow the same downward trend as the uncoated diamond composites, but exhibit higher baseline in thermal conductivity. The results can be seen in Figure 5.2. The highest reported value of thermal conductivity is 284 W/mK. The study also shows that the highest thermal conductivity are exhibited by samples sintered at temperatures over 920°C [2].

Figure 5.3. Diamond particle pretreated by B powder [5]

Bai introduced a surface metallization technique to use before FAST sintering. This method involves coating the diamond particles in B and W and then growing nanostructures on the coating to increase surface area between the coating and the matrix. Figure 5.3 shows an SEM image of the diamond particle after pretreatment. 200 µm sized diamonds were used for the study. The study used 44 vol.% diamond particles. The study uses XRD to report the existence of WC at the interface. The highest reported thermal conductivity is 660 W/mK for boron coated diamond particles [5]. A second study by Bai studies the effect of diamond particle size. The diamond particles were coated with W by the previously described process. Diamond particles of 100, 200, and 300 µm were used in this study. The highest reported thermal conductivity of 670 W/mK was observed in samples with 300µm
diamond particles [6]

5.2.2 Alloying Additions in Powders

One study by Schubert used hot press to densify samples with a variety of elemental additions added to the matrix with the goal of improving the interface between the copper matrix and the diamond particle additions. The samples were hot pressed at 950°C for one hour. The study shows the optimal elements added to the matrix are boron and chromium at 0.3 wt.% and 0.8 wt %, respectively. Other elements investigated included Al, Ti, and Zr. All additions except Al showed improvements in thermal conductivity compared to no additions. These results can be seen graphically in Figure 5.4. The sintering parameters were optimized for the Cu-Cr powders which allowed the authors to achieve a thermal conductivity of 639W/mK. A second study was an extension of this study focused on the optimum boron additions to add to the matrix as well as the effect of diamond particle size. The first interesting result from this work is that larger diamond particles (195µm) have higher thermal conductivities than smaller diamond particles (110µm) when all other conditions are the same. The study found that 1.1-1.2 wt.% B gave the best thermal conductivity. The study also examined the effects that thermal cycling had on the composite thermal conductivity.
thermal conductivity dropped by 5 % after 100 cycles and 10 % after 1000 cycles [7].

Sinha et al. used Cu-0.8 wt. % Cr alloyed to form a diamond composite by hot pressing. Composites were fabricated including up to 20 vol. % diamond particles. The authors used 196µm and 40µm sized diamond particles at a ratio of 3:1. The samples were sintered for 30 minutes at 950°C. The presence of a carbide layer is observed by electron probe microanalysis. The thickness of the carbide layer ranged from 294µm when 20 vol. % diamonds were present to 149µm when 60 vol. % diamond particles were included. As more diamond particles are added, less Cr available to react with each diamond particle. The thickness of the carbide layer is reduced as a result. The thermal conductivity values for the composite samples were 478, 591, and 601 W/mK for 20, 40, and 60 vol.% respectively. The CTE values were reported to be 12.66, 9.57, and 7.06 x10−6/°C for the same samples [8].

![Figure 5.5. TEM images of CuCr-diamond interface [9]](image)

Rosinski et al. examined the effectiveness of using an alloyed powder to improve the matrix-diamond interface. The study compared Cu and Cu-.8 wt.%Cr (CuCr) powders when they were blended with 180µm diamond particles. The study focuses on the microstructure and clearly finds that the CuCr powder improves dramatically by eliminating interfacial gaps that exist around the diamond particles. The study also uses the high angle annular dark field (HAADF) STEM image with EDX to capture a high resolution image of the interface. The HAADF STEM image and corresponding EDX images can be seen in Figure 5.5. The authors fail to prove
the existence of $Cr_3C_2$ using XRD. The authors conclude that the thickness of carbide layers is greater in other studies allowing it to be detected by XRD. The additional thickness is attributed to the diamond particles being pre-coating with Cr as opposed to the Cr initially being alloyed into the powder [9].

Mankowski et. al. used FAST to densify an alloy composed of Cu-6.5 wt.% Cr along with 50 vol. % diamond particles (180-250µm) and achieved a thermal conductivity of 658 W/mK. The authors also used the same alloy blended with 60 vol. % diamond particles but observed a decrease in thermal conductivity [10].

One final work was published examining the optimum amount of zirconium additions to add to the matrix in a hot press setup [11]. This powder metallurgy approach is similar to the approaches used in this thesis work. The study used 45 vol.% diamond particles with particle size of 100µm. The samples were sintered at 980°C with uniaxial pressure of 42MPa for 20 minutes. This study achieves the maximum thermal conductivity of 615 W/mK in samples that included 1.2 wt. % Zr. EDX scans were executed again to confirm the presence of Zr at the interface. Each of the samples (0.8, 1.4, 2.4 wt. % Zr) exhibited a much better thermal thermal conductivity over pure copper [11].

### 5.2.3 Miscellaneous Fabrication Methods

Several other studies have been conducted to fabricate copper-diamond composite materials. A variety of approaches have been taken, and it is difficult to place them into a single category.

One common approach that is used to fabricate copper-diamond composites is to use liquid infiltrationsimilar to the approach used to manufacture copper-tungsten composites. These works have limited relevance to the work in this thesis since the temperatures used to fabricate these composites are much higher. Furthermore, the matrix conductivity of these samples is much higher do to their porosity free nature from being cast.

Abyzov et. al. performed a study that investigates the effectiveness of tungsten coating on diamond particles. Approximately 60 vol.% diamond particles with particle sizes of 130 and 180 µm were used. The tungsten coatings were measured to be 190nm thick. The sample was fabricated by capillary liquid infiltration method. The coated diamond particles were pressed into a dense green body and subjected
to liquid copper at 1130°C. CTE values of $6 \times 10^{-6}/°C$ and thermal conductivities up to 800 W/mK [12] were reported for the final composite.

Kang et. al. use a molten salt method to coat diamond particles with both $Mo_2C$ and $Cr_7C_3$. The authors report thermal conductivities of 596 W/mK when 60 vol. % diamond particles are coated in $Mo_2C$ and 562 W/mK when 65 vol. % diamond particles are coated in $Cr_7C_3$ [13] [14] [15]. Weber finds that using alloys containing .001 atomic % Cr and .01 atomic % B yield a thermal conductivities of 600 W/mK and 700W/mK, respectively, for 60 vol. % diamond(200 µm) [16].

Sun and Ital used shock waves to consolidate samples with 10-70 vol. % diamond content in a copper matrix. The diamond particle size ranged from 54-80µm. The densities for the samples ranged from 93.1 to 98% theoretical density. The samples were heat treated to relieve thermal stresses from the shock wave consolidation and CTE was measured. The CTE values ranged from $10 - 13 \times 10^{-6}/°C$ [17].

### 5.2.4 Thermal Simulations

Numerous studies have been done on copper-diamond composite materials to improve the copper-diamond interface, which has been shown to be critical in the thermal performance of the composite. These approaches involve using an additional element to act as a coupler between diamond and matrix. The coupler material is either added as coating on the diamond particles or as an alloying element in the matrix. Several studies use diamond particles coated with a carbide forming element as the starting point to create a strong interface. Another approach is to use an alloy containing the carbide forming element. In both cases, the carbide forming element can react with the diamond to create a better interface for more efficient heat transfer [1] [7] [3] [4] [2] [8] [11].

Limited research has been completed on thermal simulations of these composite materials. One of these studies uses a diffuse mismatch model (DMM) as a theoretical model for the thermal conductivity of the composite material. The DMM model is based on thermal resistances that are calculated from phonon velocities, j phases and absolute temperature. The thermal resistance is calculated by
\[ R = \frac{4}{\rho_mC_m\nu_m\alpha} \]  

where \( \rho \) is the density, \( C \) is the specific heat, \( \nu \) is the phonon velocity, and \( \alpha \) is the phonon transmission probability. The model gives results that are accurate for cases where there is more than 1 wt\% Zr in the matrix. The authors assume that the thermal conductivity of the matrix is 330 W/m K [11]. This value is significantly higher than the values that were experimentally determined in previous research [18].

The other relevant work used finite element analysis (FEA) to simulate aluminum-diamond composites. The authors model the diamond particles as tetrakaidecahedrons. The authors determined that the quality of the interface between the aluminum matrix and the diamond particle is the most important factor in the thermal conductivity of the composite [19].

### 5.3 Experimental Details

#### 5.3.1 Sample Fabrications and Preparation Methods

Composite samples with a pure copper matrix and diamond particles were fabricated as a baseline for future studies. Elemental copper powder was supplied by American Elements. The powder, which was -325 mesh, 42 \( \mu \)m, is shown in Figure 5.6. Industrial grade diamonds from Diamond Innovations (Columbus, OH) of size 40-60 \( \mu \)m were used for this study. The thermal conductivity of the diamond particles are not controlled by the manufacturer since they are primarily used for industrial grinding and cutting applications. As a result, the particles have a high nitrogen inclusion rate and thermal conductivity much lower than the perfect diamond thermal conductivity of 2000 W/m K.

Silver-Comper alloy powder with eutectic composition (72 wt.%Ag-28 wt.%Cu)
was obtained from Cimini & Associates (Westerly, RI). SEM images of the powder and a corresponding EDX analysis are shown in Figure 5.7 and Figure 5.8, respectively. Powders were weighed into plastic jars with 5, 10, and 20 wt.% of the eutectic powder along with the copper powder. After determining the optimal amount of eutectic powder in the copper matrix, 10 vol.% diamond particles were added to the copper/10wt.%eutectic blend.

Copper silicide ($Cu_5Si$) pieces were purchased from ESPIMetals. The pieces were ground by hand with mortar and pestel so that the passed through a -325 mesh sieve. SEM images of the ground pieces is shown in Figure 5.9. As seen in the image, the final powder size is less than 45$\mu$m. The powder was weighed and combined with pure copper powder of the same size (American Elements). The copper silicide was added to the copper powder to equal 10 wt.% of the total composition. This combination was then combined with 10, 20, and 40 vol.% of diamond particles with a particle size range between 40-60$\mu$m. The powder-diamond combinations were blended in a Resodyne mixer for 60 seconds at 100% intensity. Particular attention was necessary to ensure blending uniformity between the powder and diamond particles. The powder combinations were sintered via FAST at 900$^\circ$C for 20 minutes with a 50$^\circ$C/min and 45MPa of applied pressure.
Figure 5.7. SEM Image of Starting Eutectic Powder of Composition 72 wt. %Silver-28 wt. %Copper Powder

Figure 5.8. EDX Spectrum of the Alloyed Powder of Silver-Copper Eutectic Composition

Two separate alloyed copper powders were obtained from NASA - Glenn Research Center (Cleveland, OH). They were fabricated by a conventional melt-spray process. The first alloy had a composition of 98.4 wt. % copper, 1 wt.% chromium, 0.6 wt.% zirconium (CuCrZr). The second powder had a composition of 96 wt.% copper, 3.5 wt.% silver, 0.5 wt. % zirconium (CuAgZr). The compositions of each alloy are outlined in Table 5.1. SEM images of the powders are shown in Figures 5.10 and 5.11, respectively. In both cases, there is a range in the particle size of the starting powder size from a few microns to about 40µm.
Figure 5.9. SEM image of the Cu$_5$Si powder that has been ground by hand and sieved through a -325 mesh sieve to give a final powder size less than 45µm.

<table>
<thead>
<tr>
<th>Table 5.1. Compositions of Alloyed Powders</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy Name</td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>CuCrZr</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>CuAgZr</td>
</tr>
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</table>

The powders were blended with diamond particles by using a Resodyne acoustic mixer in each of the composite systems. The samples were subjected to 85 times the gravitational acceleration (Gs) for 1 minute. Careful attention was again paid in blending the powder to avoid any settling between the less dense diamond powder and the heavier copper powder. The blended samples were places into the typical FAST sintering setup of graphite die/punch assembly lined with graphite foil immediately after blending. The assembly was held together with minimum pressure while transporting the sample from the blender to the FAST unit. This procedure greatly reduced the amount of separation that occurred during transportation. The samples were then sintered in the FAST system. Table 5.2 lists the sintering conditions required to reach full density for each copper-diamond subsystem. Different conditions were required to reach full density of each system because of the slightly modified chemistry.
Figure 5.10. SEM images of the alloyed CuCrZr powder

Figure 5.11. SEM images of the alloyed CuAgZr powder

Table 5.2. Sintering Parameters for Copper-Diamond Composites

<table>
<thead>
<tr>
<th>Matrix Material</th>
<th>Temperature(°C)</th>
<th>Pressure (MPa)</th>
<th>Sintering Time (min)</th>
<th>Heating Rate(°C)/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>850</td>
<td>36</td>
<td>20</td>
<td>50</td>
</tr>
<tr>
<td>Cu-AgCu</td>
<td>850</td>
<td>45</td>
<td>10</td>
<td>50</td>
</tr>
<tr>
<td>Cu-Cu₅Si</td>
<td>900</td>
<td>45</td>
<td>20</td>
<td>50</td>
</tr>
<tr>
<td>CuCrZr</td>
<td>920</td>
<td>65</td>
<td>20</td>
<td>50</td>
</tr>
<tr>
<td>CuAgZr</td>
<td>975</td>
<td>65</td>
<td>20</td>
<td>50</td>
</tr>
</tbody>
</table>
Cross sections were cut by wire EDM. The cross sections of the samples were then prepared first by grinding the surface of the sample to achieve relative flatness with 320 grit followed by 800 grit SiC sandpaper by hand while being flushed with water. The samples were then lapped on an automatic polishing machine with 0.9µm diamond slurry for 5 minutes. The samples were then polished with 0.6µm diamond slurry for 2.5 minutes before the final polishing step of 0.04µm silica solution for 1 minute.

5.3.2 Thermal Simulations

Solid models for the copper and copper alloy-diamond composite systems were built in Solidworks CAD software package. The experimental sections of this thesis have shown that the interface region where the diamond particles meet the matrix is of critical importance. As such, it was very important to use the correct shape of the diamond particle to achieve the appropriate surface area to volume ratio for the diamond particle. As a result, the diamond particles were assumed to take the shape of a tetrakaidecahedron. Figure 5.12 shows a 3-dimensional image of the diamond particle modelled as a tetrakaidecahedron. The diamond particle was created to be 50µm to align with the experimental particle size that ranged from 40-60µm. A model with identical geometry to that of the diamond particle was built around the diamond in the same shape to represent the interface layer. Finally, the diamond/interface assembly was surrounded by a cube to represent the copper alloy matrix. The size of the cube was chosen so that the diamond particle would occupy 10, 20, and 40 vol. % of the total volume. The cubes had sides that were 85.5, 67.8, and 54µm for 10, 20, and 40 vol. % diamond particles, respectively. Figure 5.12 shows the model being used. The figure shows the diamond model as well as half of the encapsulating block. The other half of the block is hidden so that the diamond model is visible. The interface layer is too small to be visible at full scale.

The geometric model was imported into the Ansys Mechanical Heat Transfer Module for thermal simulation. Ansys is a finite element analysis (FEA) software package. FEA analysis involves breaking the model into very small segments and calculating the interactions between each small element. Ansys uses Fourier’s Law of conduction, Equation 5.2, to calculate interactions in which elements have defined
conduction as the primary heat flow mechanism. In this case, $k$ is the thermal conductivity, $T$ is temperature, and $\frac{\partial T}{\partial n}$ is the thermal gradient.

\[ q = -k \frac{\partial T}{\partial n} \quad (5.2) \]

Static boundary conditions were chosen and applied to each model so that the thermal conductivity of each assembly could be calculated. A 1 watt heat load was applied to one face of the cube. The opposite face of the cube was set to a fixed temperature of 22 deg C. The other four surfaces of the cube were set to 0 Watt barrier to represent perfect insulation. This condition was set to ensure that the flow could be treated as a one dimensional case. Figure 5.13 shows a schematic diagram of the block and the boundary conditions that were used in the experiment. Material constants were determined from the experimental section (Chapter 4), where applicable, and are listed in Table 5.3. Figure 5.14 shows a the mesh that was used in the simulations. The mesh was created by a tetrahedron method. The mesh size was initially set at $2.37 \times 10^{-7}$ m. The mesh size was then reduced to $1 \times 10^{-8}$ m as a check to ensure that the results were not a consequence of mesh size.

\[ R_\theta = \frac{\Delta T}{Q} \quad (5.3) \]
Figure 5.13. Schematic diagram showing boundary conditions that were used in the experiment.

Figure 5.14. Image of the composite assembly model showing the mesh that was used for calculations.

\[ R_\theta = \frac{x}{Ak} \] (5.4)

The output of the model was a maximum temperature and temperature distribution profile (isotherms). Assemblies that possess higher thermal conductivities
Table 5.3. Material properties used as input parameters in the thermal models

<table>
<thead>
<tr>
<th>Material</th>
<th>Thermal Conductivity (W/m K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu (sintered)</td>
<td>360±36</td>
</tr>
<tr>
<td>Diamond</td>
<td>1200*</td>
</tr>
<tr>
<td>CuCrZr</td>
<td>245±25</td>
</tr>
<tr>
<td>CuAgZr</td>
<td>315±31</td>
</tr>
<tr>
<td>ZrC</td>
<td>20*</td>
</tr>
<tr>
<td>Air</td>
<td>.026*</td>
</tr>
</tbody>
</table>

*Thermal conductivity not measured. Theoretical value was used.

will exhibit lower temperatures because of more efficient cooling and vice versa. The maximum temperature for the model was then used to calculate the composite thermal conductivity. The thermal conductivity for the entire assembly was then calculated using a one dimensional thermal resistance model. Thermal resistance can defined in by 5.3 and 5.4, where $R_\theta$ is the thermal resistance, $x$ is the distance between measurement points, $A$ is the cross sectional area, and $k$ is the material thermal conductivity. Combining equation 5.3 and 5.4 yields Equation 5.5 used to solve for the thermal conductivity of the composite based on the simulation input parameters.

\[
k = \frac{Qx}{A\Delta T}\quad (5.5)
\]

The model was tested by assigning 400 W/mK (for pure copper) to each part of the geometric model. Figure 5.15 shows the simulation output for the pure copper calibration case. When the maximum temperature from the copper case is added 5.5, the resulting thermal conductivity for the composite was 399.6W/mK. Once the model was verified, the initial boundary conditions were varied so that the thermal conductivity of the model matched that of the experiment. As such, the void thickness and matrix conductivity were varied independently to determine the significance of these on the thermal conductivity of the composite material. The goal of modifying these parameters was to develop a model that accurately described the experimental composite system.
5.4 Results

5.4.1 Copper-Diamond

5.4.2 Microstructure Evaluation

Copper-diamond composites were sintered via FAST at 800°C with 36MPa for 20 minutes. Figures 5.16, 5.17, and 5.18 show optical microscope images of copper-10, 20, and 30 volume % diamond, respectively. In the cases of 10 and 20 vol. % diamond particles, the diamond particles maintain a uniform distribution within the copper matrix. Very little diamond particle agglomeration is observed in the sintered composites. However, some agglomeration begins to occur when the diamond particle content is increased to 30 vol.%. Additionally, diamond pullout is clearly observed by the remaining voids in the matrix. As the diamonds were freed from the matrix, they were able to damage the polishing surface.

Figures 5.19 and 5.20 show low and high magnification SEM images of copper-30 volume % diamond composites. The low magnification image again confirms that the diamond particles are fairly well distributed within the copper matrix. SEM images again highlight that there are some areas in which the diamond particles pulled out of the matrix during the polishing process. This phenomena is indicative of poor adherence between the copper matrix and diamond particles. The
Figure 5.16. Optical microscope image of sintered Cu-10 volume% diamond sample sintered at 800°C with 36MPa for 20 minutes

Figure 5.17. Optical microscope image of sintered Cu-20 volume% diamond sample sintered at 800°C with 36MPa for 20 minutes

high magnification image, Figure 5.20, confirms that the interface between the two is defined by gaps and voids (shown by arrow) which effectively separates the two materials, which is associated with large CTE differences.
Figure 5.18. Optical microscope image of sintered Cu-30 volume% diamond sample sintered at 800°C with 36MPa for 20 minutes

Figure 5.19. Low magnification SEM image of sintered Cu-30 volume% diamond sample sintered at 800°C with 36MPa for 20 minutes
5.4.3 Thermal Properties

The thermal conductivity of the copper-diamond composites were measured as a baseline for future studies. The results can be seen in Figure 5.21. Relative to pure copper samples, the thermal conductivity decreases as increasing volumes diamond particles. This is counterintuitive because the thermal conductivity of diamond is more than double than that of pure copper (> 1000 W/mK). However, due to the poor interface between the matrix and the diamond particles, the heat is transferred very inefficiently and lowers the overall thermal conductivity. It becomes very clear the the interface is critical for copper-diamond composites to have superior thermal conductivity. The thermal energy must be transferred efficiently from the copper matrix to the diamond particles, and vice versa in order to take advantage of the high thermal conductivity of diamond. It would also be expected that introducing diamond particles to the composite would reduce the overall CTE of the sintered composite. This is not the observed result, as shown in Figure 5.22. Since the interface is very poor, the diamond particles do little to restrict the expansion of copper.

5.4.4 Copper with Silver-Copper Eutectic Additives to Improve Matrix-Diamond Interface by Surface Wetting Improvement
Figure 5.21. Thermal conductivity for copper-diamond composites with increasing volume fractions of 40-60µm diamond particles
Figure 5.22. Thermal conductivity for copper-diamond composites with increasing volume fractions of 40-60$\mu$m diamond particles
5.4.5 Microstructure Evaluation

The Ag-Cu powder of eutectic composition (72 wt. % Ag - 28 wt.% Cu) was sintered alone to understand its behavior when being subjected to FAST processing. The powder was sintered to 99.8% theoretical density at 725°C with an applied load of 65 MPa for 15 minutes with a 50°C/min heating rate. Figures 5.23 and 5.24 show the microstructure of the sintered eutectic composition at low and high magnification, respectively. Most of the area shows clear separation between the silver and copper. However, there were areas that show characteristic microstructure of melting in the sintered sample showing that there was localized melting of the eutectic powder well below the theoretical melting point of the material (780°C). This is shown very clearly in Figure 5.24.

![SEM Image](image)

**Figure 5.23.** SEM Image of Eutectic Powdersintered at 725°C shown at 5,000X to show localized melting occurs below the alloy melting temperature

The powder was then heated to various temperatures to determine melting behavior withinin the FAST system. It was shown that a rapid phase transition from solid to liquid occurs in the eutectic powder at 780°C. This is evidenced by the rapid change in piston displacement as measured by the FAST unit. Figure 5.25 shows two different FAST experiments under identical conditions heated to 760°C and 825°C. It is clear from lack of change in piston displacement that no
bulk melting occurred at 760°C while the entire sample melted at 780°C. Once the powder was converted into liquid, there was no force to restrain the pistons from collapsing on each other. The liquid was able to squeeze from the side of the die. The material that escaped the die/punch combination formed beads around the punch was examined as well. SEM images of that beaded material are shown in Figure 5.26. The entirety of the beads exhibited the characteristic microstructure of eutectic cooling.

After determining the behavior of the Ag-Cu eutectic powder alone, it was blended with copper in various amounts. The objective of this work was to produce a small amount of liquid phase within the structure of a pure copper matrix. As such, the samples were heated to 825°C with 45MPa. Heating rates and hold times were varied in order to develop an understanding of the behavior of the liquid in the system. This temperature was chosen to ensure the eutectic powder would be above its established melting temperature. The amount of eutectic powder added was varied to determine the ideal amount of liquid phase to fill voids in the matrix. Figures 5.27 and 5.28 show SEM images of 10 and 20 wt. % eutectic powder additions to the copper powder, respectively, sintered for 20 minutes at 825°C with 45MPa. A diagram showing the sintering parameters is shown in Figure
Figure 5.25. Graph of piston displacement of 2 different FAST experiments at temperatures 760°C and 825°C. Both runs were conducted at 50°C/min with an applied pressure of 45MPa. It is clear that the material quickly changes from solid to liquid at 780°C.

5.29. When 20 wt. % was added to the copper, it proved to be too high volume fraction of liquid in the mixture and significant amounts squeezed out of the die. Smaller amounts of eutectic (10 wt. %) are able to migrate into existing porosity and along the grain boundaries in the copper matrix but 20 wt.% occupies too much of the volume and causes a significant loss of structure in the sample. The result is that the structure collapses and liquid escapes under applied pressure. An SEM image is shown in Figure 5.30 of the bead of melted material. As expected, it clearly exhibits a eutectic microstructure. Figure 5.29 shows a FAST run plot for Cu-AgCu eutectic alloy for the sintering conditions described above.

Heating rate was varied from 10°C/min to 400°C/min to determining sintering and liquid behavior in the copper-eutectic system. Figures 5.31 and 5.32 show SEM images of copper mixed with 10 wt.% eutectic powder at 10°C/min and 400°C/min, respectively. Figure 5.27 was used as the baseline, having a standard heating rate of 50°C/min. There is no difference in microstructure at different heating rates probably because all of these samples experienced a long 20 minute hold time.
Figure 5.26. SEM image of material that melted and escaped the die/punch setup and formed beads

Figure 5.27. SEM image showing 10 wt. % eutectic powder sintered at 825°C, 45MPa, 10°C/min, 20 min sintering time
Figure 5.28. SEM image showing 20 wt. % eutectic powder sintered at 825°C, 45MPa, 10°C/min, 20 min sintering time.

Figure 5.29. FAST run plot showing the sintering parameters for Cu-10 wt. %AgCu eutectic alloy that were sintered at 825°C with 45MPa for 5 minutes.

Holding the sample this long at temperature allows for much diffusion of the liquid eutectic phase into the copper grains. The effect of the hold time is shown in Figures 5.33 and 5.34. It is clear that the shorter hold time allows more liquid to remain at the grain boundaries instead of diffusing into the copper grains.

The diffusion behavior was studied by using the EDX feature on the SEM.
**Figure 5.30.** SEM image of melted material that squeezed out of the die and formed a bead on top of the die assembly

**Figure 5.31.** SEM Image of copper powder with 10 wt. % eutectic sintered at 825°C, 45MPa, 10°C/min, 20 min sintering time
Figure 5.32. SEM Image of copper powder with 10 wt. % eutectic sintered at 825°C, 45MPa, 400°C/min, 20 min sintering time

Figure 5.33. SEM image of copper with 10 wt. % eutectic Powder sintered at 825°C, 45MPa, 100°C/min, 5 min sintering time

Figures 5.35 and 5.36 shows an SEM image and EDX analysis of both an experiment held at maximum temperature for 5 minutes and 20 minutes. The diffusion profiles show that regardless of the sintering time, copper diffuses from the liquid phase into copper matrix rapidly leaving behind a silver rich solid precipitate in the grain boundary area. A small percentage of silver also diffuses into the copper matrix since roughly 10% exists within the copper matrix away from the silver rich areas.
Figure 5.34. SEM image of copper with 10 wt. % eutectic Powder sintered at 825°C, 45MPa, 100°C/min, 20 min sintering time

There is an intermediate boundary layer in both case of roughly equal composition.

Figure 5.35. SEM image with corresponding EDX analysis of copper with 10 wt. % eutectic powder sintered at 825°C, 45MPa, 100°C/min for 5 minutes

With the ideal sintering parameters for the copper-eutectic system determined, diamond particles were added to the system to form a composite. The goal of adding diamond particles to the copper-eutectic system is to use the liquid phase to fill the voids that existed at the interface between the pure copper and diamond.
Figures 5.37 and 5.38 show the optical and SEM microstructure of the Cu-10 wt. % Eutectic-10 vol. % diamond sample. The improvement of the interface over the sample with pure copper matrix is very clear due to the presence of the liquid phase at the diamond interface. The liquid phase freely moves along the grain boundaries and fills voids, especially at the interface of the copper and diamond particles. EDX analysis of this composition is shown in Figure 5.39 to further underline the existence of the liquid phase around the diamond particles. Similar diffusion behavior was exhibited as copper from the eutectic diffused into the copper matrix leaving behind a silver-rich composition at the interface.

5.4.6 Interface Improvement by Reactive Liquid Phase
**Figure 5.37.** Optical Microscope Image of Copper with 10 wt. % eutectic material that shows the presence of a liquid phase present at the matrix-diamond interface during sintering.

**Figure 5.38.** SEM Image of Copper with 10 wt. % eutectic material that shows a clean interface with no noticable porosity.
5.4.7 Microstructure Evaluation

As a follow up to the limited success of the previous experiment, another similar experiment was designed. The goal of the follow-up study was to use a liquid phase material that possessed the potential ability to undergo a chemical reaction with the diamond particles and form a stronger interface while still filling the voids at the interface. \( \text{Cu}_5\text{Si} \) was selected based on low melting temperature relative to copper and the potential reactivity of silicon with carbon. \( \text{Cu}_5\text{Si} \) is an intermetallic phase that contains 8 wt.% Si. The \( \text{Cu}_5\text{Si} \) powder was blended into the copper-diamond composite with the same weight ratio as the eutectic powder to maintain a constant amount of liquid-10 wt.% \( \text{Cu}_5\text{Si} \) and 0, 10, and 20 vol. % diamond. Figures 5.40 and 5.41 show SEM images of sintered Cu-10 wt. % \( \text{Cu}_5\text{Si} \)-10 vol. % diamond. Similar to the copper-eutectic-diamond system, the microstructure shows cleaner interfaces between the copper and diamond. The low magnification image shows signs of diamond pullout indicating the lack of chemical bonding between the diamond and silicon. The high magnification images show pockets of \( \text{Cu}_5\text{Si} \) along the grain boundaries, which have negative implications on the thermal conductivity of the material.
Figure 5.40. SEM image of the copper silicide powder blended with 10 vol. % diamond and sintered at 900°C for 20 minutes.

Figure 5.41. SEM image of Cu-10 wt. % Cu₅Si-10 vol. % Dia
5.4.8 Thermal Properties

The thermal conductivity of both liquid systems are shown in comparison with pure copper in Figure 5.42. The presence of liquid phase in the matrix allows the diamond particles to be encapsulated, which improves the interface over a pure copper matrix. The interface improvement leads to a stabilization of thermal conductivity as the volume fraction of diamond increases. In the case of the eutectic system, all of the components have a high thermal conductivity and so the conductivity of the baseline material is not affected. However, $Cu_5Si$ additions dramatically drop the thermal conductivity of the baseline material, by almost 75% of pure copper. This means that $Cu_5Si$ cannot be a suitable additive candidate for thermal management materials. The unchanged thermal conductivity also implies that the Si did not have any form of reaction with the diamond to promote bonding at the interface. Si has a low reactivity with carbon when compared to transition metals such as Cr, Ti, or Cr. The implication is that the reactive metals would make better candidate materials to promote a strong interface between the copper diamond. The ideal candidate material will also only minimally reduce, if at all, the thermal conductivity of the metal alloy.

![Figure 5.42](image_url). Thermal conductivity of the Cu-$Cu_5Si$-diamond composites copared to copper-eutectic-diamond system and copper-diamond
5.4.9 The Use of Alloyed Powders for Interface Improvement between Copper matrix and Diamond Particles

The previous sections and published literature have shown that the interface between the matrix and diamond particles is critical to the performance of the composite material. It has also been demonstrated that composites composed of copper and diamond alone have voids at the interface which reduce the thermal performance of the composite. It has been shown that the interface can be improved by adding a small amount of liquid phase to the system. The liquid phase melts at elevated temperatures and has the ability to fill gaps that form at the interface. This method showed improvement over pure copper-diamond composites in thermal conductivity. However, the improvement does not fully realize the potential of copper-diamond composite materials. The interface must be further improved by forming a chemical bond at the interface. The chemical bond will act as a coupling agent between the copper matrix and diamond particles and allow more efficient heat transfer between the two materials, which possess different heat transport mechanisms.

The approach is to create a good interface by adding small amounts of alloying elements to the copper matrix. This study focuses on two elements with high affinity for reaction with carbon that can alloy with copper - chromium and zirconium. Chromium was chosen because of its extensive usage in previous literature. Zirconium was selected because of its extremely high affinity for reaction with carbon and availability within a copper-based alloy.

CuCrZr (Cu 1 wt.% Cr .6 wt.%Zr) was sintered at 920°C for 20 minutes with 50MPa and CuAgZr (Cu 3.5 wt.% Ag 0.5 wt.%Zr) was sintered at 975°C for 20 minutes with 50MPa. The alloy composites were sintered with different sintering parameters as dictated by requirements to achieve full density. Both composites were sintered with heating rates of 50°C/min. Figures 5.43 and 5.44 show FAST sintering plots for CuCrZr and CuAgZr composite materials, respectively.
Figure 5.43. FAST run plot showing the sintering parameters for CuCrZr composites that were sintered at 920°C with 65MPa for 20 minutes.

Figure 5.44. FAST run plot showing the sintering parameters for CuAgZr composites that were sintered at 920°C with 65MPa for 20 minutes.

5.4.10 Microstructure Evaluation

Figures 5.45 and 5.46 show low magnification SEM images for CuCrZr and CuAgZr composites, respectively, sintered with 20 volume % diamond particles. The CuCrZr image shows small black spots that are leftover debris from polishing. These images clearly show that the diamonds are very evenly distributed within the matrix. Figures 5.47 and 5.48 show higher magnification SEM images that focusing on the interface between the diamond particles and the matrix. It is clear in both cases that the interface is much improved compared to the pure copper-diamond
Figure 5.45. Low magnification image highlighting distribution of diamond particles in CuCrZr matrix

Figure 5.46. Low magnification SEM image highlighting distribution of diamond particles in CuAgZr matrix
composites. The interface is void free and clean for both of the alloy systems. EDX mapping of this phenomenon is shown for the CuAgZr system in Figure 5.50, highlighting constituent elements in the sample. The mapping results clearly show that the zirconium is highly concentrated at the diamond-matrix interface. The zirconium is expected to react with the diamond and form a thin carbide layer. Although the amount of zirconium is small (0.5%), relatively large concentrations were found at the copper-diamond interface. It was assumed that zirconium was uniformly distributed in the matrix before sintering. It is clear that Zr migrated to the interfaces of the alloy and diamond particles. Zr diffused towards the diamond due to its high affinity for reaction with carbon (diamond). The Zr can act as a bonding agent between the diamond particles and matrix and allows for a much more efficient coupling of matrix to the diamond particles.

![Figure 5.47. High magnification SEM image highlighting the interface diamond particles and CuCrZr matrix](image)

The EDX maps for the CuCrZr-60 vol. % diamond samples show high concentrations of both Cr and Zr at the interface. This is shown in Figure 5.51. This indicates that both Cr and Zr contribute to interface improvement during the sintering process. However, the results are quite interesting when a comparison of EDX spectra is carried out between samples containing 10 and 60 vol.% diamond is considered. This comparison can be seen in Figure 5.52. The EDX spectra for composite containing 10 vol. % diamond clearly shows the presence of Zr at the interface but shows no evidence of Cr at the interface. This suggests that Zr is the
Figure 5.48. High Magnification Image Highlighting Interface between Diamond Particles and CuAgZr Matrix

Figure 5.49. Composite SEM image of CuAgZr-diamond composite for comparison with elemental EDX maps
Figure 5.50. Elemental EDX map of the sintered CuAgZr - diamond composite sample again showing the role that Zr plays at the interface.

Figure 5.51. SEM image of CuCrZr-60 vol. % diamond composite with corresponding elemental EDX maps showing the role of both Zr and Cr at the interface.
dominant reactive element when the volume percentage of diamond is low due to its more reactive nature. The amount of Zr in the alloy was not enough to react with all of the interface when large volumes of diamond are introduced to the system. The Cr can then migrate and react with the interface in a similar manner to Zr as a secondary reaction.

Figure 5.52. Comparison of EDX spectra for CuCrZr samples containing 10 (left) and 60 (right) volume percent diamond

5.4.11 Interface Characterization

Much of the work in this chapter focuses on the interface improvement to result in the improved thermal performance of copper-diamond samples. The commonly stated conclusion is that the interface is improved as a result of reaction product between alloying elements and diamond to create a thin carbide layer at the interface. This result has yet to be definitively demonstrated experimentally. X-ray photoelectron spectroscopy (XPS) of the CuAgZr samples has been used to verify, qualitatively, the presence of carbide formation at the interface.

XPS data was able to verify the presence of ZrC at the interface of CuAgZr-diamond. Unfortunately, the results could not be quantified due to the difficulty in preparing a perfectly flat sample. Figures 5.53, 5.54, 5.56, 5.55 show the XPS results for CuAgZr- 10 and 20 vol. % diamond. Figures 5.53 and 5.54 show the C 1s and Zr 3d oxidation peaks, respectively, for the polished sample. No ZrC peak is large enough to be detectable above the system noise for the C 1s
spectrum. A peak is present in both CuAgZr-diamond samples where one would expect a peak for ZrC for the Zr 3d spectrum. The fact that that the peak is higher in the 20% is also rational because there is more interface area in the sample in the case of 20 vol. % diamond when compared to the 10 vol. % diamond sample. More carbide would be expected as a result of more surface area. The minor peak shift from lower to higher binding energy indicates the presence of ZrO [20].

Figures 5.55 and 5.56 replicate the XPS analysis of the C 1s and Zr 3d peaks, respectively, on fracture surfaces of 20 vol. % CuAgZr-diamond samples. ZrC peaks appear in both C 1s and Zr 3d spectra on the fracture surface sample. This qualitatively shows the presence of ZrC at the interface of the sample. The peaks are slightly shifted from the expected position to higher energy peaks suggesting the presence of ZrO as well as ZrC.

![Figure 5.53. XPS data showing the C 1s peak of CuCrZr-diamond (10 and 20 vol. %) samples.](image)
Figure 5.54. XPS data showing the Zr 3d peak of CuCrZr-diamond (10 and 20 vol. %) samples.

Figure 5.55. XPS data showing the Zr 3d peak of the fracture surface of CuCrZr-diamond samples compared to the cut and polished CuAgZr-diamond.
5.4.12 Thermal Properties

The interface in copper diamond composites has been shown to play a crucial role in the material properties of the composite. The alloying elements in the matrix can react with the diamond and form a thin carbide layer at the interface. Small amounts of alloying elements to the matrix clearly show an increasing thermal conductivity trend. The reported thermal conductivities are shown in Figure 5.57. Both powder compositions the same amount of Zr was added. The same slope of the thermal conductivity was observed in both systems, also. This further implies that Zr is the dominant bonding element and that Cr does not play a primary role in bonding. The highest thermal conductivity in CuCrZr matrix was achieved with 40 vol. % diamond and was 430 W/m K. The high diamond content was required to compensate for the large decrease in thermal conductivity in the CuCrZr relative to pure Cu and to get back above the thermal conductivity of baseline copper. The highest thermal conductivity value achieved with CuAgZr was 533 W/m K with and was also accomplished by adding 40 vol. % diamond.
One issue that significantly impacts the thermal conductivity of the composite is the impact that alloying elements have on the thermal conductivity of the alloy itself. Although adding alloying elements improves the interface, their addition immediately drops the thermal conductivity of the baseline material from that of copper. Any (non-silver) alloying addition to the copper powder will drop the thermal conductivity. The thermal conductivity of copper is 385 W/ m K, Ag is 429 W/ m K, Cr is 93.9 W/ m K, and Zr is 22.7 W/ m K. Additions of Ag have no detrimental effect on the thermal conductivity because of its high inherent thermal conductivity and its ability to form substitutional solid solution with copper. In the case of CuCrZr, the baseline conductivity drops by 32% from 360 W/mK to 245 W/mK. The same phenomenon is observed for CuAgZr but to a lesser extent. The

Figure 5.57. Thermal conductivity data for copper-diamond composite materials showing a drop with increasing diamond content in a pure copper matrix, and increasing conductivity when added to an alloyed matrix
baseline drops by a modest 12.5% to 315 W/m K, making it easier to overcome by adding smaller volume fractions of diamond particles. It is difficult to compare the drop in baseline thermal conductivity between the two compositions because they have different alloying additions, with different individual thermal conductivities. It is clear in both cases that the alloying elements positively impact the thermal conductivity of the composite. The thermal conductivity increases linearly increasing volume percentages of diamonds. This trend is clearly different and opposite compared to pure copper diamond samples. It is also interesting to note that the slope of the increase is very similar for both alloy systems and that both alloy systems have roughly the same Zr content. This lends further credibility to the theory that Zr is dominating the contribution to the thermal conductivity.

The CTE of the composite is of nearly equal importance to the thermal conductivity. Figure 5.58 shows the CTE of the CuAgZr-diamond composite system. In contrast with the pure copper-diamond system, the CTE declines as the volume percentage of diamond increases. This is also a result of the improved interface. The copper is free to expand unrestricted if the interface is poor because the volume fraction of diamond is low. However, with the improved interface, the copper is anchored to the diamond particles. The result is that CTE of the composite is greatly reduced when compared to the pure copper system.

One aspect of copper diamond samples that is frequently scrutinized is long term reliability. This refers to the results will be maintained after the material has been exposed to the temperature cycles of real world applications. To examine this, the CuAgZr-diamond samples were subjected to thermal cycling testing. The thermal cycling tests were performed in accordance with the military packaging specification MIL-STD-883E - Method 1010.7; conditions B, C, D. Each cycling regimen consisted of 50 cycles with a ten minute dwell time at each temperature. Cycle 1 ranged in temperature from -55-125°C. Cycle 2 ranged in temperature from -55-155°C. Cycle 3 ranged in temperature from -55-200°C. Figure 5.59 shows the thermal conductivity of the samples after being exposed to each of the heat cycles. Since the thermal conductivity was unchanged by the heat cycles, it is evident that the interface between the diamond particles and matrix is very robust.
Figure 5.58. Coefficient of thermal expansion for CuAgZr-diamond composite system showing the reduction of CTE with increasing diamond content

Figure 5.59. Thermal conductivity results of CuAgZr-diamond samples after being exposed to cycles of 1. -55-125°C 2. -55-125°C 3. -55-200°C
5.4.13 Thermal Simulations

The input parameters were combined with the resulting temperature difference calculated by Ansys to calculate the thermal conductivity of the composite. The copper matrix was defined as having thermal conductivity of 360 W/mK, which was the empirical value of sintered copper. The void was modeled as an air gap surrounding the entire volume of the diamond particle. The simulation results very closely matched the experimental results when the absolute thermal resistance was set to 17.7 K/W. The resulting comparison can be seen in Figure 5.60. This result indicates that the width of the gap is not so much the critical issue degrading the performance composites as the lack of robust interface to ensure efficient heat transfer from the matrix to diamond particle and vice versa.

Figure 5.60. Comparison between the simulation and experimental thermal conductivity of copper-diamond composites

It was theorized in the previous section that incorporating an in situ liquid phase into the composite fills the gaps that exist between the copper diamond
interface. The hypothesis led to an improvement in thermal conductivity compared
to the pure copper-diamond composites. Simulations were done to provide further
analysis. The model was designed so that the absolute thermal resistance was
reduced to 5.27 K/W, and the matrix thermal conductivity was 400 W/mK, in
accordance with empirical data. The simulation results are compared with the
experimental results and shown in Figure 5.61.

![Figure 5.61. Comparison between the simulation and experimental thermal conductivity of copper-diamond composites with AgCu liquid phase additions](image)

The simulation was then repeated for the CuCrZr-diamond alloy system. The
thermal conductivity increased as the volume fraction of diamond increased in
the composite. However, the rate of increase was less than was observed in the
experimental results, as shown in Figure 5.62. One possible explanation for the
difference was that the thermal conductivity of the matrix increased as the Zr
migrated out of the matrix and to the diamond interface. The model matches
the experimentally observed data very well when the matrix thermal conductivity
increases by 5% for every 10 vol. % of diamonds added to the composite. Figures
5.63 and 5.65 show the FEA solutions for the CuCrZr systems with modified matrix
conductivity. Figure 5.64 shows the comparison of the updated FEA model and
the experimental results. The input parameters were placed into the DMM model
and added for comparison also, as a reference.

The same model was applied to the CuAgZr-diamond composite system. The
matrix thermal conductivity also had to be increased by 5% for every 10 vol. % diamond to match the experimental results. Figures 5.67, 5.68, and 5.69 show the FEA results for the 10, 20, and 40 vol. % diamond-CuAgZr compositions, respectively. The thermal conductivities of both CuAgZr-diamond models and experimental data can be seen in Figure 5.66. Compared to CuCrZr where Cr remains in the matrix inhibiting its thermal conductivity, CuAgZr becomes closer to pure alloy as Zr migrates to the interface. Figure 5.70 shows the comparison of the FEA model and the experimental results. Again, the input parameters were placed into the DMM model and added for comparison, as a reference.
Figure 5.63. Simulation results of CuCrZr with 20 volume % diamond with 1 watt of applied heat, fixed temperature of 22°C on the opposite side, and the other four faces perfectly insulated.

Figure 5.64. Comparison of simulation and experimental data for CuCrZr-diamond composite system.
Figure 5.65. Simulation results of CuCrZr with 40 volume % diamond with 1 watt of applied heat, fixed temperature of 22°C on the oppose side, and the other four faces perfectly insulated
Figure 5.66. Plot of the thermal conductivities of the CuAgZr-diamond system showing the different trend that exists between the model and experimental results.
5.4.14 Amount of Present at the Interface

The amount of Zr lost to the carbide layer is increased as more diamonds are added to the composite. This is because more diamonds translates to more surface area to react with the Zr. Eventually all of the Zr from the matrix will have migrated to the interface which would cause some of the interface area to be unreacted and yield voids and a lower than optimal thermal conductivity. An equation can be constructed using the conservation of mass to predict the final Zr percentage in the CuAgZr matrix.

The diamond particle is assumed to be a 14 sided tetrakaidecahedron with a side length of 17.5\(\mu\)m (which corresponds to \(17.52\times10^{-6}\)m). The surface area of such a particle is 8.02nm. The total volume of the interface per diamond particle would be 8.02x10\(^{-16}\)m if the interface region is assumed to be 100nm thick. The total number of diamond particles was determined from the total sample volume to be 8.58, 17.52, and 34.3 x10\(^6\) for 10, 20, and 40 vol. % diamond in the composite.

The interface can be assumed to be ZrC, which has a density of 6.7 g/cm\(^3\). 88% of that is due to the zirconium based on the the atomic and molecular weights of Zr and ZrC (91.224 and 103.23 g/mol, respectively). The mass of the interface can be calculated by multiplying the total interface volume by the density of ZrC. The mass of Zr at the interface can then be determined by multiplying the total mass of the interface by the 88% that is due to the zirconium.

The total mass of Zr required to form a full interface layer around the diamond particles for a 40mm diameter sample with 4mm thickness is then determined to be 0.04, 0.08, and 0.16g for 10, 20 and 40 vol. %, respectively. The total mass of alloy in each of the systems is 32.5, 31, and 27g (10, 20, and 40 vol. %). The CuAgZr alloy was made up of 0.5 wt.% Zr. The mass of Zr that was available to form an interface in each of the systems is The percentage of Zr used in each composite system can then be determined to be 0.15, 0.3, and 0.6 % of the total alloy weight.

The calculation can be repeated for chromium. The carbide that forms at the interface is \(Cr_3C_2\). The proportion of molecular weight of Cr in \(Cr_3C_2\) is approximately the same as the proportion of Zr in ZrC. As a result, the same amount of Cr and Zr are required for complete bonding at the interface.

This information can be used to determine the final amount of Zr remaining in the matrix and the amount of Zr that has migrated from the matrix to the interface.
The calculation is summarized in Equations 5.6 and 5.7.

\[ Wt.\%(Zr)_{\text{final}} = \frac{M_{Zr,\text{orig}} - M_{Zr,\text{lost}}}{M_{\text{total},\text{orig}} - M_{Zr,\text{lost}}} \]  

(5.6)

\[ M_{Zr,\text{lost}} = \rho_{ZrC} V_{ZrC} (1 - A\%_{\text{void}}) \frac{MW_{Zr}}{MW_{ZrC}} \]  

(5.7)

where \( Wt.\%(Zr)_{\text{final}} \) is the final Zr weight percentage of the CuAgZr matrix, \( V_{ZrC} \) is the total volume of the carbide layer on all diamond particles, \( MW \) is the molecular weight and \( M \) is the mass of the corresponding component of the matrix such as \( \text{orig} \) for the original composition before carbide formation and \( \text{total} \) for the entire matrix weight. These variables can be easily calculated from weight percentages and component dimensions and will vary for each case.

A linear relationship can be created that can predict the optimum amount of Zr to use in the matrix based on the volume percent of diamond one wants to use in the composite. Equation 5.8 shows the formula that can be used to predict the amount of Zr that should be used in the matrix for CuAgZr-diamond systems with a diamond diameter of 50\( \mu \)m.

\[ Wt.\%(Zr)_{\text{optimal}} = 0.0131 V\%_{\text{Dia}} \]  

(5.8)

The thermal conductivity of the matrix was then calculated as a function of the percentage of Zr lost from the matrix. Figure 5.71 shows the both thermal conductivity of the matrix as well as the wt. % of Zr remaining in the matrix as a function of the the volume percentage of diamond added to the composite. The Zr lost was determined by calculating the amount of Zr that would be required to form a 100nm thick layer of Zr around a 50\( \mu \)m diamond particle. An approximate equation for the matrix conductivity can be extracted by method of least squares and is expressed in Equation 5.9, for the case of a 100nm thick ZrC layer around a 50\( \mu \)m diamond particle.

\[ k_{\text{matrix}} = 119.59[W/mK]Zr_{\text{lost}} + 315[W/mK] \]  

(5.9)

This equation applies over a wt. % Zr range of at least 0 – 0.6. This calculation also shows that 40 volume % diamond addition will consume 0.6 weight % of the total sample of Zr. This agrees with the model assumption of 378 W/mK.
for the case where 40 volume % diamond was used. This is slightly higher than the experimentally determined thermal conductivity for sintered pure copper, 360 W/mK. The small amount of Ag additions provides this slight increase in thermal conductivity.

![Figure 5.67. Simulation results of CuAgZr with 10 volume % diamond with 1 watt of applied heat, fixed temperature of 22°C on the opposite side, and the other four faces perfectly insulated](image1)

![Figure 5.68. Simulation results of CuAgZr with 20 volume % diamond with 1 watt of applied heat, fixed temperature of 22°C on the opposite side, and the other four faces perfectly insulated](image2)

The model in which the matrix conductivity increases matched the experimental data extremely well, in both cases. A calculation of the amount of Zr necessary to fill a 100nm interface layer around every diamond particle shows that .6 wt.% is required to completely fill each layer. This means that the matrix would be
Figure 5.69. Simulation results of CuAgZr with 10 volume % diamond with 1 watt of applied heat, fixed temperature of 22°C on the oppose side, and the other four faces perfectly insulated.

![Simulation Results](image)

Figure 5.70. Comparison of simulation and experimental data for CuAgZr-diamond composite system depleted of all zirconium. This gives more credence to the theory that the thermal conductivity of the matrix increases as the Zr migrates to the interface.
5.5 Conclusion

This section details studies about the fabrication of copper-diamond composites. In has been established in this research, as well as other research, that composites fabricated with pure copper and diamond particles have poor thermal conductivity. The poor thermal conductivity is a result of a poor interface between the copper and diamond. The conductivity of the composite decreases as the volume percentage of diamond increases in the composite.

This research details several approaches taken to improve the interface between the diamond and copper matrix. The research shows that adding a small weight percentage of non reactive liquid phase to the copper matrix can improve the thermal conductivity compared to the pure copper matrix. The composite thermal conductivity is unchanged as larger volume fractions of diamonds are added to the composite instead of the decreasing with increasing amounts of diamond additions.

The thermal conductivity of the copper-diamond composite was able to be improved when a small amount of Zr was used as an alloy with the starting matrix. Two copper alloys containing a small amount of Zr showed improvement in thermal conductivity when the diamond particles are added. The Zr is able to migrate from the matrix to the interface and reacts to form a thin carbide layer during the sintering process. The thin carbide layer gives rise to the improved interface between
the matrix and diamond particles so that the composite thermal conductivity can
improve as the volume fraction of diamonds increases. In addition to improved
thermal conductivity, the coefficient of thermal expansion is greatly reduced from
that of pure copper. The samples were also exposed to various aggressive thermal
cycles with no degradation in thermal conductivity indicating the nature of the
interface is very robust.

The thermal simulations of the copper-diamond systems confirm the experimental
findings that the interface between the matrix and the diamond composite are criti-
cally important. The study shows that a small interfacial gap of 3.7nm can cause a
decrease in thermal conductivity as a function of diamond volume in the composite.
Using a liquid phase to reduce the gap thickness results in a thermal conductivity
is unaffected by the addition of diamond particles. Improved conductivity can be
realized when intimate contact between the matrix and diamond is assumed. The
thermal model matched the experimental data when the matrix conductivity was
increased as a result of Zr migrating from the matrix to the interface.

Previous reports have used the DMM methods to explain experimental data [11]
in copper-diamond systems. However, the thermal conductivity of the matrix
material in these experiments is not experimentally determined. Despite having
higher amounts of Zr in the matrix, the assumed matrix thermal conductivities
are higher than those determined experimentally in previous work [18]. Using
the higher matrix thermal conductivity values gives good matching between the
experimental and theoretical results, however additive migration expands on these
works and better describes the results seen throughout similar experimental work.

The work presented in this chapter has shown that Zr can be used to achieve
thermal conductivity 35% higher than that of pure copper. The CTE is reduced
by 35% compared to pure copper in the same composite. This work is the first to
report the existence of a carbide when using an alloyed powder composition. This
carbide is the reason for the improvement in thermal conductivity. The study
observed one highest reported thermal conductivities. This is even more true when
considering that the current experiments use less volume % diamonds and smaller
diameter diamond particles than other studies.
Bibliography


Chapter 6  
Material Development and Characterization of CuAgZr-Carbon Nanotube Composites

6.1 Objective

The objective of this research was to use the positive results from the previously reported CuAgZr-diamond results and apply them to a different material system to develop a composite system with superior thermal properties. The previous chapter of this thesis reports that using a copper alloy containing 3.5 wt. % Ag and 0.5 wt. % in combination with diamond particles allows the thermal conductivity of the composite to increase as the vol. fraction of diamond increases. The reason for this phenomenon is the interfacial improvement.

The goal of this work is to use the CuAgZr alloy system in combination with carbon nanotubes (CNT) in an attempt to achieve a high thermal conductivity composite material. Carbon nanotubes are one dimensional structures with thermal conductivity of up to 2,000 W/m K. The single wall variety is a graphene layer rolled into a tube. Multi-wall carbon nanotubes (MWCNT) are simply tubes that are several graphene layers thick. Due to their small size, it is very difficult to align the CNTs. It will be assumed that the nanotubes are randomly oriented so that the composite materials can be treated as isotropic.
6.2 Previous Work

Several studies have been done investigating the potential benefits of adding copper nanotubes to a copper matrix. Studies that use a pure copper matrix generally show that the composite density decreases as a result of increasing CNT volume percentages. The studies that use pure copper matrices are all sintered well below the sintering temperature used in this study. Cho et al. fabricated copper-CNT composites including up to 3 vol. % CNT. The samples were sintered at 50°C for 1 min with 50MPa of applied pressure by a heating rate of 50°C/min. The study results in densities ranging from 96.8-99.0% theoretical density. The thermal conductivity was reported to be 359W/mK, which was 10 W/mK higher than the reported value for pure copper sintered under the same conditions [1]. Chu et al. used a pure copper matrix and carbon nanotubes to create samples at 600 °C for 5 minutes with external pressure of 50MPa and a heating rate of 100°C/min. The study reports densities of 98.8, 98.4, 98.6, and 96.1 % theoretical for pure copper, 5, 10, and 15 vol. % SWCNT, respectively. The thermal conductivity in these samples remains unchanged within experimental error relative to the pure copper sample (331W/mK). The thermal conductivity of the sample decreases dramatically to 250W/mK when 15 % CNT is added to the matrix. The trend for thermal conductivity mirrors that of the trend for density [2]. Sule found that the thermal conductivity dropped from 362 to 273W/mK when 1 vol. % CNT was added to the pure copper matrix. These samples were sintered at at 650 °C under pressure of 50MPa for 5 minutes. The drop in thermal conductivities is a result of a poor interface between the matrix and CNT. [3].

Studies have also investigated the use of alloyed matrices incorporating carbon nanotubes. Chu sintered Cu-.73 wt. % Cr - CNT composites at 750 °C for 15 minutes with 40MPa of pressure and a heating rate of 50°C/min. The study finds that adding more than 10 vol. % CNT are not able to be dispersed in the matrix and lead to agglomerations in the composite [4]. Chu furthered his studies by using a Cu-.85 wt. % Ti to fabricate composites with carbon nanotubes. The samples were sintered at 780°C for 15 minutes with 40MPa of applied pressure. The study reports high densities of greater than 99% theoretical for 0, 5, and 10 vol. % CNT additions. The reported thermal conductivities are 315, 348, and
362 W/mK, respectively [5]. One final study uses Mo-coated CNTs and a pure copper matrix to form composites. Samples containing 2.5, 5, 10, and 15 vol. % CNT were densified at 850°C (100°C/min heating rate) for 5 minutes with 40 MPa of applied pressure. Sample densities were reported to be 98.5, 98.4, 97.5 and 94.6 % theoretical for the 2.5, 5, 10, and 15 vol. % CNT samples, respectively. The study shows a modest improvement in thermal conductivity of 340 W/mK over the sintered matrix (330 W/mK) for 2.5 and 5 vol. % CNT additions. The thermal conductivities compared favorably to the uncoated CNT equivalents in all cases [6].

6.3 Experimental Details

CuAgZr powders were combined with MWCNT volume fractions ranging from 1-20 % were received from NASA-Glenn Research Center (GRC) where they were ball milled for 30, 60, and 120 minutes. 2mm stainless steels were used at a 7.5:1 (ball:powder) ratio for the milling process. Figures 6.1 and 6.2 show the CuAgZr-10 vol. % CNT powder at low and high magnifications, respectively, after being exposed to the ball milling process for 30 minutes. The ball milling process deforms the CuAgZr into flat platelets from the original spherical shapes. It is clear from the higher magnification image that the CNT are intact and embedded into the matrix particles. Figure 6.3 shows the CuAgZr alloy ball milled with CNTs for 60 minutes. Increasing the ball milling time from 30 to 60 minutes shows little effect on the structure of the powder. Further increasing the ball milling time to 120 minutes destroys the integrity of the carbon nanotubes. This can be seen in Figure 6.4. It can be seen in all of the high magnification images that the CNTs are agglomerated and not evenly distributed in the matrix.

The samples were sintered at 950°C with 50 MPa of applied pressure, 50°C/min for 20 minutes. The sintering parameters were adopted from the previous CuAgZr-diamond results. Sintered samples were cut with an alumina cut off wheel, polished, and examined with a combination of SEM, FESEM, EDX, and TEM to determine microstructural characteristics of the samples. Thermal performance was measured by dilatometer (CTE) and laser flash (thermal conductivity).
Figure 6.1. Low Magnification SEM Image of CuAgZr ball milled with 10 vol.% CNT for 30 minutes

Figure 6.2. High Magnification SEM Image of CuAgZr ball milled with 10 vol.% CNT for 30 minutes
Figure 6.3. High Magnification SEM image CuAgZr ball milled with 10 vol.% CNT for 120 minutes

Figure 6.4. High Magnification SEM image CuAgZr ball milled with 10 vol.% CNT for 120 minutes
6.4 Results

6.4.1 Density

Samples were densified in the FAST system at 950°C with 50MPa of applied pressure for 20 minutes. The exception is the sample where 10 volume % CNT was used. This sample was densified into a 40mm diameter sample as opposed to the 60mm diameter sample that was used for all other CuAgZr-CNT samples. 50MPa is the maximum amount of pressure that can be applied to a 60mm sample due to limitations of the FAST system. However, the same applied force equals a higher applied pressure for a smaller diameter sample. As expected, the density is higher as a result. The CuAgZr with carbon nanotube sample density is summarized in Figure 6.5.

Upon sintering, densities above 92 % theoretical density were unable to be achieved in samples containing 20 vol.% CNT. As a result, these samples were not further characterized. The main reason for the low density is the lack of distribution of the carbon nanotubes. The nanotubes showed high levels of agglomeration and high levels of porosity within each CNT cluster. The high levels of porosity will

![Figure 6.5](image)

**Figure 6.5.** Densities of sintered CuAgZr samples with various amounts of carbon nanotubes sintered at 950°C with 50MPa for 20 minutes. (The 10 vol. % sample experienced 65Mpa of applied pressure)
Figure 6.6. SEM image of CuAgZr composite sintered with 5 vol. % CNT at 975°C with 65Mpa pressure for 20 minutes showing the distribution of CNT within the composite certainly destroy the thermal conductivity of the composite.

6.4.2 Microstructure

Figure 6.6 shows a low magnification SEM image of the cross section of the CuAgZr-5 vol. % CNT showing the distribution of CNT in the sample. It is apparent that the CNTs form clusters in the sample along the grain boundaries of the matrix particles. Figure 6.7 shows a high magnification of the CNT loaded area. The figure shows very clearly that the CNTs exist in the composite after sintering is completed. The figure also shows that there is some level of porosity that exists within the CNT agglomeration areas.

Figures 6.8 and 6.9 show SEM images of sintered CuAgZr sintered with 5 vol.% CNT with EDX spectra corresponding to the matrix (Figure 6.8) and CNT loaded area (Figures 6.9), respectively. As expected, there is no trace of carbon in the matrix that can be detected by EDX. The CNT loaded area contains EDX peaks for both copper and carbon. This is expected as the EDX spot size is much larger than the nanotube and cannot be focused on a single nanotube alone.

Figure 6.10 shows a high resolution image of the carbon nanotube. The image shows that the nanotube has a diameter of approximately 100nm, which is common for MWCNT. The nanotubes have also remained much longer (greater than 10X) than the diameter. The porosity between the nanotubes also becomes obvious.
Figure 6.7. FESEM Image of CuAgZr with 5 vol.% CNT sintered at 975°C with 65Mpa pressure for 20 minutes showing the high magnification of an area loaded with carbon nanotubes.

Figure 6.8. SEM and EDX image with corresponding EDX spectra of the CNT area of CuAgZr composite including 5 vol. % CNT sintered at 975°C with 65Mpa pressure for 20 minutes.

at very high magnifications.

Figures 6.11 and 6.12 show low and high magnification FESEM images of CuAgZr -10 vol. % CNT composites. The low magnification image shows that the CNT agglomerations exist in the same manner that they did in the CuAgZr-5 vol.% CNT composites. The high magnification image shows the structure of the nanotube after sintering as well as the porosity that exists between the agglomerations.
Figure 6.9. SEM and EDX image with corresponding EDX spectra of the CNT area of CuAgZr composite with 5 vol. % CNT sintered at 975°C with 65Mpa pressure for 20 minutes.

Figure 6.10. TEM Image of CuAgZr-5 vol. % MWCNT sintered at 975°C with 65Mpa pressure for 20 minutes highlighting individual nanotubes

CNT distribution was the most challenging barrier to achieving high density because of the porosity that exists between the CNT agglomerations. Samples with 1 and 2 vol. % MWCNT in an attempt to improve the distribution within the matrix. Figure 6.13 shows an SEM image of the 2 vol. %MWCNT along with the corresponding EDX map. The EDX map shows the presence of Zr in the areas with CNTs. Zr was initially present randomly in the powder matrix as a solid solution. This is consistent with the finding from the diamond work that Zr migrates to areas of high carbon concentration. However, the SEM cannot achieve the resolution to
determine the precise location of the Zr. Due to the resolution of the SEM, it cannot be determined if Zr in the exact areas of CNT interface.

XPS analysis was conducted to conclusively show that ZrC forms at the interface. The results are shown in Figure 6.14. The results confirm that ZrC is indeed present in the sample. The 3d spectrum (identified in 6.14 [left]) shows peaks indicating the presence of ZrC, ZrO, as well as Zr in solution in the sample. The carbon 1s spectrum shows a peak exactly where it is expected for carbon-carbon bonding. This spectrum also shows a small peak (identified in 6.14 [right] by arrows) located at slightly lower binding energy which is indicative of ZrC.

### 6.4.3 Thermal Conductivity Results

The thermal conductivity was measured for the sintered CuAgZr-CNT samples. The results for the thermal conductivity given Figure 6.15. Contrary to the initial expectation, the thermal conductivity of the composite did not increase with increasing amounts of CNTs. The main reason for this result is the nanotubes were extremely prone to agglomeration and were not able to be evenly distributed within the matrix. The size of the copper powder was approximately 500X the diameter of the nanotubes. As more nanotubes are added, the clusters of agglomerations
Figure 6.12. High magnification FESEM image of high CNT concentration areas showing CNT structure and porosity between the agglomerations.

Figure 6.13. SEM image and corresponding EDX Map of CuAgZr with 2 vol. % MWCNT sintered at 975°C with 65Mpa pressure for 20 minutes.
became more numerous. This phenomenon gave rise to more porosity in the composite and ultimately led to a reduction in thermal conductivity.

The secondary reason for the decrease in thermal conductivity was that there was not enough Zr in the composite system to interact with all of the surface area of the CNT. A large amount of Zr is needed to react with the nanotubes since the CNTs have an extremely high surface area to volume ratio.

6.4.4 Conclusion

This section describes the fabrication and characterization of copper based composites with additions of carbon nanotubes. High densities were able to be achieved with low volume fractions of carbon nanotubes. It proved very difficult to achieve a uniform distribution of carbon nanotubes when high volume fractions were added due to agglomerations of the nanotubes.

The thermal conductivity of the CuAgZr-carbon nanotube composite samples followed the same trend as the pure copper-diamond samples. As the volume fractions of nanotubes was increased, the thermal conductivity dropped. It is hypothesized that the Zr content in the matrix was not sufficient to bond with all
Figure 6.15. Thermal conductivity data for CuAgZr-MWCNT composite materials showing the decrease in thermal conductivity as the volume of CNT increases of the surface area of the nanotubes.

X-ray photoelectron spectroscopy was used to show that Zr from the matrix reacts with the carbon nanotubes to form a carbide layer at the interface. The carbide interface is suspected to be the mechanism for the improvement of thermal conductivity.
Bibliography


Chapter 7
The Design and Characterization of Heat Spreaders with Thermally Annealed Pyrolytic Graphite

7.1 Objective
The following work was designed to fabricate composite materials using Thermally Annealed Pyrolytic Graphite (TPG) as a heat spreading core encapsulated in a metal shell. Atomically, TPG is composed of $sp^2$ bonded carbon atoms in sheets, very similar to that of graphene. The layers are held together only by van der Waals forces. This gives rise to anisotropic properties in the material, which make it highly effective as a heat spreader. TPG has in-plane thermal conductivity of $>1500\text{W/mK}$ and through-plane thermal conductivity of 7.5 W/mK. TPG can be encapsulated in a metal shell, such as aluminum or copper, to add structural stability. Since TPG is a bulk material, there is lower surface area and less interface that must be overcame to achieve optimal thermal properties in the composite compared to other composite systems that have been presented in this thesis.

7.2 Previous Research Conducted on TPG Composite Materials
Very little academic work has been to investigate composites with pyrolytic graphite. The available research on TPG based composites comes from the commercial source
of the TPG. One TPG based composite is an aluminum encapsulated composite based on diffusion bonding technology. The resulting composite has extremely high thermal conductivity in the xy plane. It has been shown to be extremely effective at reducing the maximum temperature of hot spots by spreading the heat to a larger surface area to be dissipated [1] [2]. TPG can also be encapsulated by brazing process to create a high performance thermal management composite. The target application of the brazed composites are chip level cooling as opposed to head spreading applications [3].

7.3 Experimental Details

7.3.1 Composite Fabrication

The metal powders were placed into a 60mm graphite punch and die setup. The following procedure was followed for samples where TPG was included in the composite:

1. 1/3 of the powder was placed into the bottom of the punch and die assembly and then vibrated so that the powder would be allowed to settle until it was flat.

2. A 54mm diameter TPG disk with 2mm thickness was placed in the center of the assembly on top of the settled powder.

3. The remaining 2/3 of the powder was poured around and on top of the TPG disk to ensure complete encapsulation.

A schematic diagram of the assembly procedure is shown in Figure 7.1. Samples were prepared by the FAST process based on parameters that were determined in previous experiments. Table 7.1 summarizes the sintering parameters and relative densities achieved by sintering the composites.

7.3.2 Thermal Measurements

The ability to spread heat is not a fundamental material property. An experiment needed to be designed in order to determine the performance of TPG-encapsulated
composite materials compared to their pure metal counterparts. An experimental apparatus was designed to characterize the thermal spreading ability of sintered disks made of Al, Al-TPG, Cu, Cu-TPG, and CuAgZr-TPG. A schematic diagram of the setup is shown in Table 7.2. The experimental setup was based on the use of a thermal imaging infrared camera to measure the heat spreading capability by each sample. The thermal imaging camera used in this experiment had a quoted accuracy of ±2°C. The IR camera was mounted on the top of a stainless steel vessel. Heat was applied to each disk by applying current through a pyrolytic boron nitride coated graphite heater. The graphite works as a resistive heater to generate 24W of power. A 12.7mm stainless steel button was placed at the top of the heating element to be used to transfer the thermal energy from the heating element to the sample as a quasi-point source. Fiberglass wool insulation was placed around the button to ensure that the sample was only heated through the button. A thin layer of thermally conductive paste (Artic Silver) was applied to the top of the
stainless steel button before placing the sample to reduce interface resistance and ensure good heat transfer into the sample. Two fans were placed on each side of the setup to increase the convective cooling of the sample and amplify the temperature gradients across the sample. Samples were coated with graphite to eliminate any reflection of radiation that could interfere with the camera. The temperature of the room proved to be a variable and was recorded as such. Figure 7.3 shows a photograph of the experimental setup. Once the power was applied to the sample, it was allowed to settle at its equilibrium temperature. The equilibrium temperature was determined by monitoring the temperature change over time at 3 spots on the sample. The sample was determined to be at equilibrium once the temperature fluctuation for each spot was less than 0.25°C over the course of a minute.

7.3.3 Thermal Simulations

The sintered metal samples were characterized in the heat spreading apparatus. Thermal FEA models were completed to add additional insight to the heat spreading

Figure 7.2. Schematic diagram of the apparatus that was built to measure the performance of heat spreading (not to scale)
Figure 7.3. Photograph of the apparatus that was built to measure the performance of heat spreading performance. Convection played the major role in heat transfer in this system because of the fan cooling mechanism. The convection calculations are computed using Newton’s Law of Cooling where the heat flow rate per given area between surface and fluid is given by Equation 7.1, where $h$ is the convective film transfer coefficient, $T_S$ is the surface temperature, and $T_B$ is the bulk fluid temperature. Radiation is also used and defined by Stephan-Boltzmann Law, Equation 7.2, where $\sigma$ is the Stefan-Boltzmann constant, $\epsilon$ is the emissivity, $A_j$ is the area of surface j, $F_{ij}$ is the form factor from surface i to surface j, $T_i$ is the absolute temperature of surface i, and $T_j$ is the absolute temperature of surface j. However, radiation plays a secondary role in heat transfer at low temperatures.

$$q = h(T_S - T_B) \quad (7.1)$$

$$Q = \sigma \epsilon A_i F_{ij}(T_i^4 - T_j^4) \quad (7.2)$$

The FEA convection coefficient boundary condition was modified to match the experimental results. The 24 W heat load was applied to a 12.7 mm diameter stainless steel button in the center of one face of the sample. Convection was
imposed on the face opposite of the heat source. Three separate convection zones were set up so that the model would be compatible with experimental results. The three zones were radially symmetric around the center axis of the sample.

### 7.4 Results

Figures 7.4 and 7.5 show the thermal images for the pure copper and aluminum samples, respectively. Since the ambient room temperatures were 21°C and 23°C for Cu and Al, respectively, the absolute minimum and maximum temperatures cannot be used for analysis. The temperature difference from maximum temperature to minimum temperature can be analyzed, though. The data was repeated for the copper system a total of 5 repetitions, all with data matching within experimental error ($\pm 2\%$). From the images, the $\Delta T$ for Cu is 4.5°C, while $\Delta T$ for Al is 4.6°C. There is no significant difference in temperature gradient between aluminum and copper. In both cases, the path of least resistance for the thermal energy is through the thickness of the sample where it is dissipated into the air as opposed to conducting both vertically through the sample as well as along the direction of the diameter to maximize the convection efficiency.

The preferred thermal path changes once TPG is encapsulated into the material. Because of the very high thermal conductivity in-plane and low thermal conductivity through-plane, the thermal energy preferentially moves laterally through the sample and spreads the heat across the entire surface of the sample. The low through-plane thermal conductivity actually acts as a barrier to thermal transport through the center. The result of the TPG insert is a reduction in maximum temperature and more uniform temperature distribution across the sample diameter. The thermal images of Cu - TPG, Al - TPG, and CuAgZr - TPG are shown in Figures 7.6, 7.7, and ??, respectively. The $\Delta T$ from the hottest to closest spot on each sample were .9, 1.2, and .3 °C, respectively.

Figures 7.8 and 7.9 show the comparison of copper and aluminum samples with and without TPG encapsulation. It is clear in both cases that the TPG leads to a reduction of the maximum temperature experienced by the sample as well as a more uniform heat distribution. This is a result of the TPG efficiently spreading the heat to the entire surface area of the sample so that it can be dissipated into the atmosphere by convection.
Figure 7.4. Thermal image of pure copper sample at thermal equilibrium under heat load of 24W and fan cooling

Figure 7.5. Thermal image of pure aluminum sample at thermal equilibrium under heat load of 24W and fan cooling
Figure 7.6. Thermal image of copper-TPG sample at thermal equilibrium under heat load of 24W and fan cooling
Figure 7.7. Thermal image of aluminum-TPG sample at thermal equilibrium under heat load of 24W and fan cooling
Figure 7.8. Comparison of the maximum sample temperature in aluminum and copper with and without TPG encapsulation

Figure 7.9. Comparison of the temperature difference in aluminum and copper with and without TPG encapsulation
7.5 Thermal Simulations of Heat Spreaders

7.6 Results

Figures 7.10 and 7.11 show the finite element models of copper, copper-TPG, respectively. Adding TPG to both copper based systems dramatically improves the temperature difference across the sample. This is to be expected because of the very high thermal conductivity of TPG.

Figures 7.12 and 7.13 show the FEA thermal simulations for the pure aluminum and aluminum-encapsulated TPG samples, respectively.

Comparing the experimental results with the FEA thermal simulations, Figures 7.14 and 7.15 show reasonable agreement in all cases indicating that the boundary conditions and assumptions are reasonable and are good predictors of thermal performance in the experimental setup. The simulation can be a valuable tool in predicting the performance of composite samples of different material systems that have yet to be developed.

The models were then used to make predictions of the performance in scenarios that could not be measured given limitations of the experimental setups. Figure 7.16 shows the effect of TPG encapsulation in cases where the power input was increased from 24 watts to 50, 100, and 200 watts. The simulation shows that the temperature gradient across the surface of the sample is negligible in both samples that have encapsulated TPG compared to their pure metal counterparts. These results suggest that TPG dominate the heat spreading more than the encapsulating metal.

Figure 7.10. FEA Model of heat spreading experiment for pure copper sample
Figure 7.11. FEA Model of heat spreading experiment for the copper sample with TPG encapsulated

Figure 7.12. FEA Model of heat spreading experiment for an aluminum sample

Figure 7.13. FEA Model of heat spreading experiment for an aluminum sample with TPG encapsulated
Figure 7.14. Comparison of the temperature difference across the top of the sample between the experimental results and the FEA simulation.

Figure 7.15. Comparison of the maximum temperature of the sample between the experimental results and the FEA simulation. The left figure shows the data at full scale. The right hand figure shows the reduced temperature range to magnify the results of the study.

The sample diameter was also increased in the model to predict the influence of TPG in larger samples. Figure 7.17 shows the simulation results when the sample diameter was increased from 60 to 150 and 300mm. The benefit of TPG is again significant for larger diameter samples for both aluminum and copper samples. Again, the high thermal conductivity of TPG dominates the heat spreading.
7.7 Conclusion

This section specifies the fabrication and characterization of composites made from thermally annealed pyrolitic graphite encapsulated in both copper, CuAgZr, and aluminum. The objective of this research was to show that encapsulating TPG in metal by sintering via FAST improves its heat spreading ability. An apparatus was created to demonstrate the thermal spreading capabilities of the samples.

Thermal simulations were carried out and showed good compatibility with the experimental results. The addition of TPG shows clear improvement in temperature gradient and reduction of the maximum temperature. The benefit is exaggerated by increasing the power input and increasing the sample diameter. This indicated that encapsulating TPG in metal by FAST is a strong approach to solving thermal challenges, especially in large sample geometries.
Bibliography


Chapter 8  |  Conclusion

8.1 Overview

The importance of thermal performance is of critical importance for the future of the electronics industry. Power density is increasing rapidly as electronic devices continue to miniaturize without sacrificing any power output. Better thermal management materials are required to allow the continuation of this trend. The objective of the research in this thesis was to develop a superior thermal management material and corresponding processing technology to lead to the improvement in understanding of thermal management materials.

The research undertaken was focused on two primary thermal performance objectives while simultaneously developing a streamline fabrication method that allows the materials to be manufactured by an efficient method:

1. Improving the performance of the heat sink by matching the coefficient of thermal expansion (CTE) of the thermal management composite to the CTE of the semiconductor die. CTE mismatch leads to stress cracking due to differential expansion between the semiconductor and heat sink. The consequence is a reduction of lifetime. Closely matching the CTE of the heat sink to the semiconductor allows improved lifetime of the semiconductor.

2. Improving the thermal conductivity of the heat sink to allow improved heat
dissipation from the semiconductor device. Improving heat dissipation provides either longer lifetime by reducing the operating temperature, or allows improved performance by enabling higher power output to achieved by the device.

The research presented in this thesis focused on the material and manufacturing development of three main composite systems for improved thermal management properties. Field Assisted Sintering Technology (FAST) was used to fabricate each of the composite samples because of its ability to quickly produce near net-shaped samples.

### 8.2 Copper-Tungsten Composite Materials for Improved CTE Matching

Copper-tungsten composites ranging from 10 - 70 wt. % W were produced at near full density. The composite materials showed an even distribution of tungsten particles within the copper matrix despite the presence of W agglomerates. The agglomerates issue is attributed to a mismatch in particle size between the copper (42 µm) and tungsten (0.6-0.9 µm) particles. The smaller particles tend to agglomerate and were difficult to break despite rigorous mechanical mixing methods.

The thermal performance of copper-tungsten composites was evaluated. The primary objective of producing the composites was to enable the customization of CTE and thermal conductivity by adjusting the ratio of copper to tungsten in the composite. As expected, both the CTE and thermal conductivity decreased as the amount of tungsten in the composite increased. By adjusting the amount of tungsten in the composite, the CTE ranged from 17.5x10^{-6} /°C) with additions of 10 wt. % W to 10x10^{-6}/°C) when the composite was made up of 70 wt. % W. The thermal conductivities ranges from 360 W/m K to 250 W/m K for 10 and 70 wt. % W composites, respectively. Values of thermal conductivity and CTE both show agreement with theoretical values as well as commercially available products.

This work is significant in that it shows that composites can be fabricated from an entire range of copper and tungsten. Previous research has been limited to specific compositions. Additionally, this work provides a detailed study of sintering
parameters and their effect on final density of the composite. Complete thermal characterization was also shown for the entire range of compositions to show the materials created in this work compare very well with the commercially available materials.

8.3 Copper-Diamond Composites for Improved Thermal Dissipation and CTE Matching

Copper-diamond composites containing up to 40 volume % diamond particles. The objective was to take advantage of the high thermal conductivity and low CTE of the diamond particles without the high cost of large diamond heat sinks. After fabricating composite materials with diamond particles in a pure copper matrix it became clear that the interface between the copper matrix and diamond particles would be the major challenge in creating a composite with superior thermal conductivity. The thermal conductivity of copper-diamond samples decreased with increasing volume percentages of diamond particles.

One technique that was used to improve the interface between the matrix and diamond particle was to introduce small amounts of secondary additions to the copper matrix. The additions possessed melting temperatures lower than that of the composite sintering temperature. Two systems, Ag(72 wt.%)Cu and Cu$_5$Si, were added to the system to improve the wetting between the matrix and diamond particles. AgCu additions gave rise to a mobile liquid phase that could fill porosity around the diamond particles. The resulting thermal conductivity of these composites did not decrease with increasing volume percentages of diamonds, but remained unchanged with respect to the matrix. Copper-diamond samples with additions of Cu$_5$Si showed the same trend of constant thermal conductivity regardless of diamond volume. However, the Cu$_5$Si additions acted as impurities in the matrix and reduced the thermal conductivity of the matrix.

Alloyed powder systems proved to be the most promising option for developing copper-diamond composite materials with superior thermal conductivity. Two copper based alloy systems were investigated using Cu 1.5 wt.% Cr .6% Zr
(CuCrZr) and Cu 4 wt.% Ag .5wt.% (CuAgZr). The thermal conductivities of both systems increased with increasing diamond volume. The maximum thermal conductivities reported were 430 and 533 W/m K for the CuCrZr and CuAgZr samples, respectively, with 40 vol. % diamond particles. Energy dispersive electron spectroscopy reveals high concentrations of Zr at the interface between the matrix and diamond particles. The combination of the EDX results with x-ray photoelectron spectroscopy results suggest that the reason for improved thermal conductivity is the presence of a thin carbide layer at the interface. The theory of the existence of a carbide layer is also supported by the reduced CTE exhibited by the CuAgZr-diamond samples. The CTE was reduced from $18 \times 10^{-6}/^\circ\text{C}$ for the CuAgZr alloy to $11.6 \times 10^{-6}/^\circ\text{C}$ when 40 vol. % was added to the system. The CuAgZr-diamond composite proved to be quite robust by experiencing no change in thermal conductivity after 100 temperature cycles from -55 - 200° C.

Finite element thermal analysis was used to provide additional insight into the mechanism of improved thermal conductivity of the diamond containing samples. The analysis shows that a 3.5 nm void layer between the diamond and pure copper matrix can explain the decrease in thermal conductivity of the Cu-diamond composite materials. Reducing the gap to 1 nm for the composite systems with liquid phase additions shows very good agreement with experimental results. The alloy systems show good agreement when the interface gap is eliminated and the matrix conductivity improves over the baseline alloy as Zr migrates out of the matrix to the interface.

Much of the work presented in this thesis is very significant to the advancement of the field of copper diamond composites and the thermal management community as a whole. The work in this thesis was the first report that zirconium is an excellent choice of carbide forming element to improve the copper-diamond interface. It is also the only work to show the existence of carbide at the interface for studies where the carbide forming element was originally alloyed in the matrix. This is the first study to report positive results on the thermal conductivity after thermal cycling.

Additionally, this work is the first to offer in depth thermal modelling to provide insight into the interface. This work is the first to report that the thermal
conductivity of an alloyed matrix improves as a result of the migration of the carbide forming element to the interface. This theory can be used to explain the thermal conductivities reported in this work as well as other works.

8.4 Material Development and Characterization of CuAgZr-Carbon Nanotube Composites

The work detailed in this thesis describes the sintering and characterization of CuAgZr-CNT composite materials. It was shown that due to large agglomerations between the CNT that the thermal performance was not as expected. A secondary reason for the lack of thermal performance was the lack of Zr to react with all of the surface area of CNT. This study is the only study to use XPS to characterize the interface and provide proof of a carbide at the interface between the matrix and copper nanotubes.

8.5 TPG Encapsulated Composites for Improved Heat Spreading Performance

Thermally Annealed Pyrolytic Graphite was encapsulated in Cu, Al, and CuAgZr by FAST sintering and characterized for thermal spreading performance. An experimental apparatus with convective cooling mechanisms as well as an infrared thermal camera was designed to characterize the sintered samples along with comparable similar baseline samples of pure copper and aluminum. The TPG-encapsulated versions of each sample showed significant improvement in temperature difference between the hottest and coldest spots on the sample.

FEA models were used to validate the experimental results and provide insight to the experimental setup. The FEA model matched the experimental results when a variable convection was applied to the top surface of the sample. The variable convection is consistent with laminar and turbulent air flows.

This is the only academic work to develop and characterize heat spreaders using pyrolytic graphite. Furthermore, this is the only known work that uses a powder metallurgy approach to fabricate these composites. The thermal modelling that
accompanies the experimental observations can be used to predict the thermal performance of such heat spreaders based on the power input and sample diameter, as well as the chosen materials.

8.6 Future Work

The work in this thesis provides a starting point for further research into the development of high performance thermal management materials. There are several research projects that can be undertaken to further the knowledge established in this thesis.

8.6.1 Copper-Molybdenum Composites

This this provides a detailed analysis on the development of copper-tungsten alloys for CTE matching. While Cu-W is of interest for CTE matching, tungsten is an expensive material. The same benefits of low CTE can also be realized by using copper-molybdenum composites in some cases. Molybdenum is a much cheaper raw material. One advantage that Cu-Mo composites have over Cu-W is that they are lower density materials.

Developing a range of compositions of Cu-Mo composites will be very useful for applications where CTE, thermal conductivity, and weight are all important. Another possibility is to combine the knowledge from Cu-W and Cu-Mo to create functionally graded materials. The functionally graded materials can have a tremendous benefit in allowing further tailorability of CTE, thermal conductivity, weight, and cost.

8.6.2 Alloy Optimization

The work in this thesis shows that using Zr as a alloying element in the copper matrix improves the interface and enables high thermal conductivity of copper-diamond composites. Both of the alloys studied in this thesis cocused on 0.5-0.6 wt. % Zr in the copper matrix. A study could be done to determine the optimum amount of alloying element that can be added to the matrix to ensure proper interfacial bonding without reducing the thermal conductivity of the matrix more
than necessary.

A second possible study would be to investigate the use of different carbide forming elements in the FAST sintering process. Many commercial materials use titanium additions to ensure good reactions in joining applications. It may also be possible that chromium acts more effectively as an interface material without the presence of Zr to dominate the reactions.

8.6.3 Diamond Particle Optimization

The work in this thesis that involved copper diamond composites used only a single type of diamond particles. The diamond particles in this study were industrial grade diamonds that had a particle size distribution of 40-60µm. It is possible to improve the thermal conductivity of the copper diamond composite materials by obtaining higher quality diamond particles that possess higher thermal conductivity due to less impurities. It may also be possible to improve the thermal conductivity of the composite by increasing the volume percentages of diamonds that are included in the composite materials. There is some development work required in order to blending the powder effectively to make this achievable. The third study that could be done is to use larger diamond particles. Using larger diamond particles reduces the number of interfaces in the composite and should raise the thermal conductivity of the composite.

8.6.4 Diffusion Behavior

This research shows that Zr migrates from the matrix to the diamond interface during the sintering process. The behavior of these studies can be extended to provide a better understanding. A set of experiments could be performed where an alloyed powder sample can be sintered with varying lengths of time to study how rapidly the migration to the interface occurs. A high degree of control can be exercised in the experiments since FAST has the ability to heat and cool rapidly. This study would be very interesting for alloys containing Zr only as well as alloys containing both Zr and Cr. This study could be repeated at several sintering temperatures to determine the effect of the temperature on the diffusion rate. The experiments could also be repeated using larger current (and current densities) to
determine the effect that electromigration could have on the diffusion rates of the alloying elements.

Additionally, the amount of each alloying element could be modified to prove the theory that Zr is dominating the interface reactions. Reducing the amount of Zr compared to Cr in the alloy should allow both Cr and Zr to migrate to the interface at lower volume percentages of diamonds. The work in this thesis has provided a better understanding to allow the prediction of the amount of each element to use in the alloy for each volume percentage of diamond.

8.6.5 Additional TPG Configurations

In this thesis, TPG was encapsulated and intended as a heat spreader. It is possible to use encapsulate TPG in other configurations to achieve different goals. For example, TPG could be rotated so that the anisotropy dictates the high thermal conductivity directions are through-plane as well as one of the in-plane directions. Through-plane conductivity has many applications including chip level cooling where it is critical to remove heat from the semiconductor junction to improve performance and extend the lifetime.

8.6.6 Aluminum-Matrix Composites

Many of the concepts developed in this thesis are applicable to aluminum based matrix systems. Aluminum matrix materials are very important in aerospace applications where both thermal conductivity and weight are critical.

8.6.7 Aluminum Silicon and Aluminum Silicon Carbide

The analogous aluminum matrix composites to Cu-W are aluminum-silicon carbide (AlSiC) and aluminum-silicon (AlSi). Both of these materials offer relatively high thermal conductivity and reduced CTE compared to aluminum. The key to these materials is their very light weight. Much like copper tungsten, the aluminum matrix provides a relatively high thermal conductivity while the Si or SiC provide reduction in CTE.
8.6.8 Aluminum-Diamond Composites

Aluminum diamond composite materials are of very high interest due to their promise of high thermal conductivity, low CTE, and extremely low density. These materials are again interesting to the aerospace community. The challenges that face aluminum diamond composites are the same challenges that face the development of copper-diamond composite materials. The additional difficulty arises aluminum-diamond composite materials because of aluminum’s low melting temperature. Much of the diffusion that happens occurs at temperatures above the melting temperature of aluminum.

8.7 Summary

Composite materials were fabricated via FAST that exhibited superior thermal performance compared to any composite material available. The composites were fabricated using a powder metallurgy approach and sintered to near net shape in a single step making the manufacturing process simple and economical. The composite thermal performance was characterized by measuring thermal conductivity, CTE, and thermal cycling. All of these metrics showed an advantage of the samples fabricated in these thesis over existing thermal management materials. Additional characterization such as SEM, EDX, and XPS have given evidence that the reason for improvement in thermal properties is due to an improvement of the interface between the matrix and diamond particles.

Given the information in this thesis, it is possible to tailor the the material properties of the heat sink to optimize the performance by selecting a specific set of materials and adjusting the ratios of those materials to achieve the desired thermal properties. Finite element analysis has also been established as an exceptional tool that can be used to predict thermal properties and performance of material systems in different environments.
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