

## Research Article

# Effect of Liquid Phase Additions on Microstructure and Thermal Properties in Copper and Copper-Diamond Composites

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This study details a new approach to creating copper-diamond composite materials for thermal management applications by using a two-phase (solid-liquid) approach in powder metallurgy using Field Assisted Sintering Technology (FAST). Silver-copper alloyed powder at eutectic compositions was used as a nonreactive liquid phase while Cu<sub>3</sub>Si was used as a reactive liquid phase. Microstructure results are reported favorably comparing the additions of a small amount of liquid phase to pure solid state sintering. Additionally, EDX results indicate that the liquid phase material fills gaps at the interface of the matrix and diamond particle resulting in improved microstructure and density. Thermal conductivity results show that liquid phase additions improve the thermal conductivity of composites compared to composites without any liquid phase, but Si additions cause a severe drop in baseline conductivity.

## 1. Introduction

Thermal management is a critical issue in the development of high performance microelectronics such as computers, cell phones, and other electronics. Heat sink plates are used to dissipate the heat generated by the integrated circuit (IC). Two major properties are used to determine performance of heat sink plates—thermal conductivity and coefficient of thermal expansion (CTE). It is desirable to have as high thermal conductivity as possible to move heat away from the source and a CTE to match the CTE of the source (which is generally silicon) to prevent damages that can occur from a CTE mismatch. The problem is that one of these properties comes at the expense of the other in most traditional materials. Materials such as copper and aluminum with very high thermal conductivities tend to have a very high CTE value and vice versa. Materials such as diamond, carbon nanotubes (CNT), and pyrolytic carbon have excellent thermal conductivities coupled with low CTE values. However, diamonds are very expensive and often not feasible as a heat sink plate, and graphite/CNT lack mechanical rigidity.

A basic approach to overcoming these challenges is to create a composite material using a highly conductive metal (such as copper) as the matrix material and incorporate a highly conductive form of carbon to further enhance the thermal conductivity while lowering the CTE [1]. However, copper has zero wettability with carbon. This leads to porosity along the grain boundary when combining the materials into a composite. The presence of porosity leads to a poor interface between the matrix and diamond which is associated with a significant decrease in thermal conductivities, which reduces the effectiveness of diamond additions [2]. Improvements to the interface are possible either by changing the chemistry of the matrix through the addition of an alloying element that will chemically react with diamond (or CNT) or possibly by liquid phase sintering [3].

Limited research has been conducted in the area of encapsulating diamond by liquid phase sintering in an aluminum matrix [4] by using Al-eutectic alloys (such as Al-Mg, Al-Si). Any addition of impurities in Al matrix often results in reported reduction of its thermal conductivity. The loss of thermal conductivity was compensated by the large volume

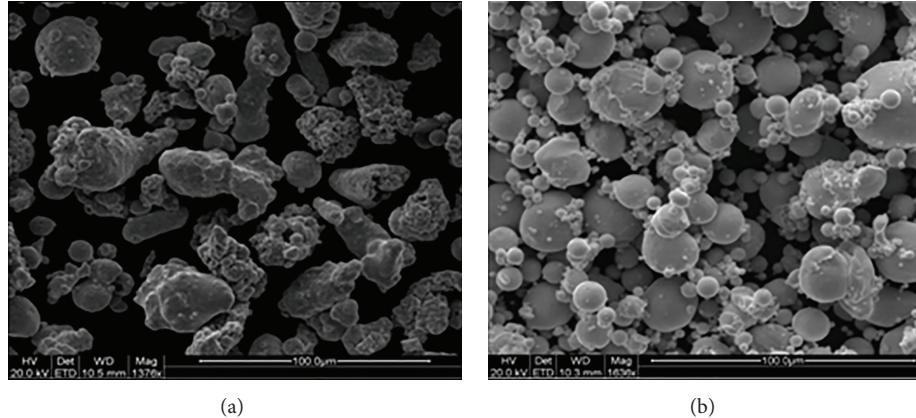


FIGURE 1: SEM images of the starting powders (a) Cu powder (b) 72 wt.% Ag-28 wt.% Cu powder.

fraction of diamond addition before seeing its benefit, that means require large volume fraction of diamond addition in the Al matrix. A similar approach was used by the same group using an aluminum-silicon eutectic composition as the liquid phase material in the silver matrix. An improvement in the thermal conductivity of Ag with diamond and Al-Si eutectic was reported over pure silver [5].

There were two primary objectives of this research. The first goal was to understand the behavior and impact of liquid phase additions to a solid copper powder system. The system would then be densified by FAST. A silver-copper alloy at the eutectic composition was selected as the material used to understand liquid phase behavior during FAST sintering because of its low melting temperature and elemental similarity to the copper matrix.

Diamond particles are added to the system once the sintering behavior of liquid containing systems and the optimum parameters are selected. Another liquid phase addition, copper silicide ( $\text{Cu}_5\text{Si}$ ), was also studied to determine if it was possible for the liquid phase to form a chemical reaction between the silicon with the diamond particles to form silicon carbide (SiC). The goal of the chemical reaction is to improve the interface between the matrix and diamond particle to improve the thermal properties of the materials. The resulting composite materials are studied to determine the effect of the liquid phase on the thermal conductivity of the sintered composite.

## 2. Materials and Methods

**2.1. 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 high density DC current. A very high, pulsed electric current allows for an extremely fast heating rate, which is combined with the pressure, and results in the rapid densification of powders [6, 7]. 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 provides conductive heat to the powder. Current can also flow through the powder which causes Joule heating instantly. The current flows through the powder along the contact points between the particles (which become the grain boundaries) because it is the path of least resistance. Any resistance between current paths can cause fast heating and lead to melting, vaporization, and/or plasma formation. 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 [8].

**2.2. Material Preparation.** Elemental copper powder (~325 mesh, ~40 μm, purity: 99.99% [American Element]) is shown in Figure 1(a). Silver-Copper (Ag72Cu) alloyed powder at the eutectic composition of 72 wt.% Ag and 32 wt.% Cu [Cimini and Associates] powder is shown in Figure 1(b). Copper Silicide ( $\text{Cu}_5\text{Si}$ ) [ESPI metals] was ground by mortar and pestle and screened through a -325 mesh sieve. Powders were weighed into cylindrical plastic containers with 5, 10, and 20 wt.% of the eutectic powder along with the copper powder. The powers were blended using a Resodyn acoustic mixer using a recipe of 50% intensity for 30 seconds.

Diamond particles (40–60 μm) were also added into the metal blends at up to 40 volume %. The blending recipe had to be modified to 100% intensity for 60 seconds for these blends due to drastic difference in particle density.

The mixed powders were placed into a 40 mm graphite die lined with graphite foil. The die was placed into the FAST system (FCT-HP D25, Germany) for densification. The samples that contained any of the Ag72Cu were heated to 825°C with 45 MPa determining the effect of sintering time on the liquid phase in the matrix. The  $\text{Cu}_5\text{Si}$  containing samples was heated to 900°C with 45 MPa of applied pressure. The temperature was measured by an optical pyrometer reading the graphite die 1 mm from the sample surface. Table 1 summarizes the starting powder compositions that were used

TABLE 1: Summary of starting powers and processing conditions.

Starting powder (10 vol% diamond is assumed)	Sintering temperature (°C)	Heating rate (°C min <sup>-1</sup> )	Sintering time (min)
Pure copper	825	50	20
	725		20
Ag72Cu	760	50	20
	825		Squeezed out
Copper + 10 wt.% Ag72Cu (with and without diamond)	825	10	n/a
		100	5
		400	20
			n/a
Copper + 20 wt.% Ag72Cu	825	100	20
Copper + 10 wt.% Cu <sub>5</sub> Si + Dia	900	50	20

and processing conditions each sample experienced in the study.

Sintered sample densities were determined using Archimedes' method. Cu and eutectic samples were then cut with an alumina cut-off wheel. The samples containing diamond were cut by wire EDM. The samples were polished with diamond suspensions to 1 μm and polished to 0.04 μm with a silica solution. Microstructural information was collected using both optical and scanning electron microscopes (Jeol 6700). Energy dispersive X-ray spectroscopy was used to determine concentration differences within the grain structure of sintered samples.

### 3. Results and Discussion

**3.1. Material Development and Characterization of Materials Containing Ag72Cu.** The Ag72Cu powder was sintered to understand its melting behavior when being subjected to FAST processing. The power was sintered to 99.8% theoretical density at 725°C with an applied load of 45 MPa for 15 minutes with a 50°C min<sup>-1</sup> heating rate. Figure 2 shows the microstructure of the sintered eutectic powder. Characteristic microstructure of melting was observed 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).

The Ag72Cu powder was then heated to various temperatures to determine its melting behavior in the FAST system. It was shown that the material underwent a phase transformation from solid to liquid at 780°C, which is the eutectic melting temperature for the material. This is evidenced by the rapid change in piston displacement as measured by the FAST unit. The piston's velocity changed rapidly as a result of the material melting and displacing itself from the die. Figure 3 shows two different FAST experiments under otherwise 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 amount of material melted at 780°C. The melting was further evidenced by the fact that material squeezed out of die/punch

combination and beaded up around the punch. SEM images of that beaded material are shown in Figures 2(c) and 2(d).

The Ag72Cu powder was blended with copper and heated to 825°C and 45 MPa with different heating rates and holding times 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 of 780°C. The amount of eutectic powder added was varied to determine the optimal amount that could be used in coordination with an addition of a highly conductive additive. Figure 4 shows SEM images of 10 and 20 wt.% eutectic powder additions to the copper powder. The material squeezed out of the die assembly when 20 wt.% of Ag72Cu was blended with the balance of copper powder. It is thought that this amount of liquid in the system left the structurally weak. Smaller amounts of Ag72Cu ( $\leq$ 10 wt.%) allow copper matrix to form a skeleton-like structure for which the liquid Ag72Cu can flow and fill porosity. The "squeezing out" effect can be observed by the general lacking of eutectic phase in 20 wt.% eutectic sintered samples. This can be explained by the scenario that when more eutectic powder is added a larger percentage of the total system becomes liquid. The result of this is that there is less solid structure to add rigidity to the system. The liquid metal is able to escape when external pressure is applied to the system.

The heating rate was varied from 20°C min<sup>-1</sup> to 400°C min<sup>-1</sup> to determine the effect on sintering and liquid behavior in the copper-Ag72Cu system. There is not an obvious difference in microstructure as different heating rates. However, the fact that 20 min hold times were used in each case may have erased any effect from the heating rates. Less Ag diffusion would be expected for the samples that experienced high heating rates but that would have been negated by long times at the maximum temperature where the diffusion could proceed.

The samples were held at their maximum temperature for 5 and 20 minutes to determine the effect of time at maximum temperature on the behavior of the liquid in the sample. The effect of the hold time is shown in Figure 5. It is clear that the shorter hold time allows more liquid to remain at the grain boundaries instead of diffusing into the copper grains.

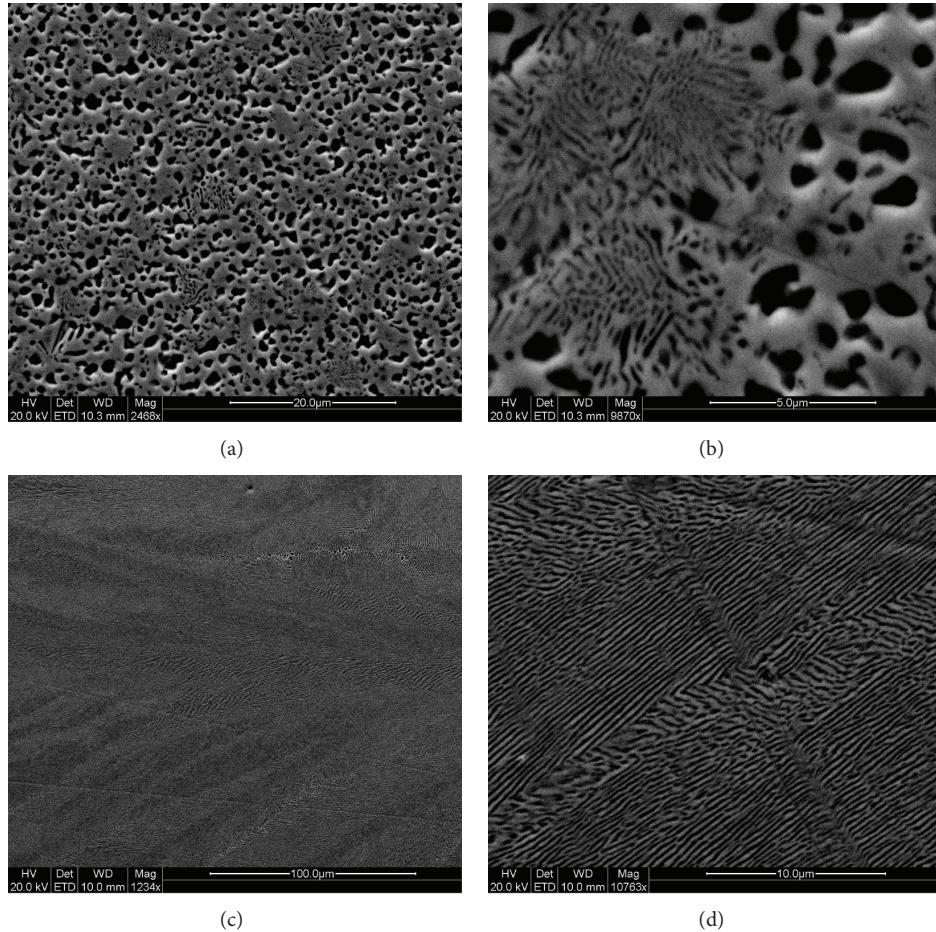


FIGURE 2: SEM images of sintered Ag72Cu powder at 725°C (a, b). Localized melting can be clearly observed. SEM images at 1200x and 10000x of the beaded material clearly showing the material was melted and squeezed out (c, d).

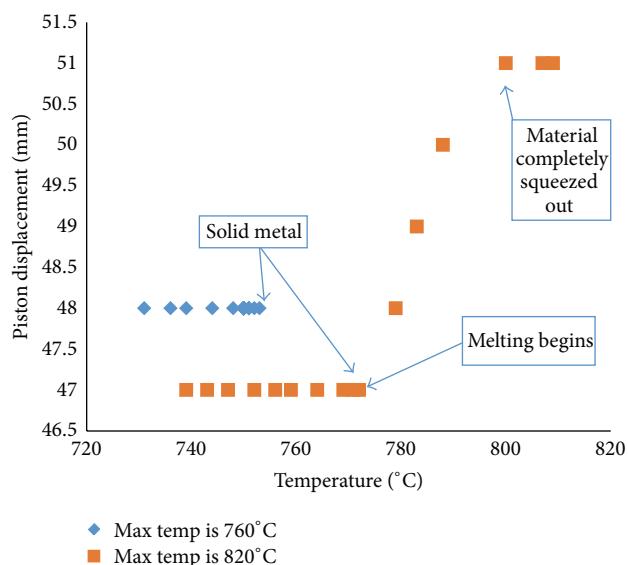


FIGURE 3: Graph of piston displacement of two different FAST experiments at temperatures 760°C and 825°C. Both runs were conducted at  $50^{\circ}\text{C min}^{-1}$  with a load of 45 MPa. It is evident from the plot that the material quickly changes from solid to liquid at 780°C.

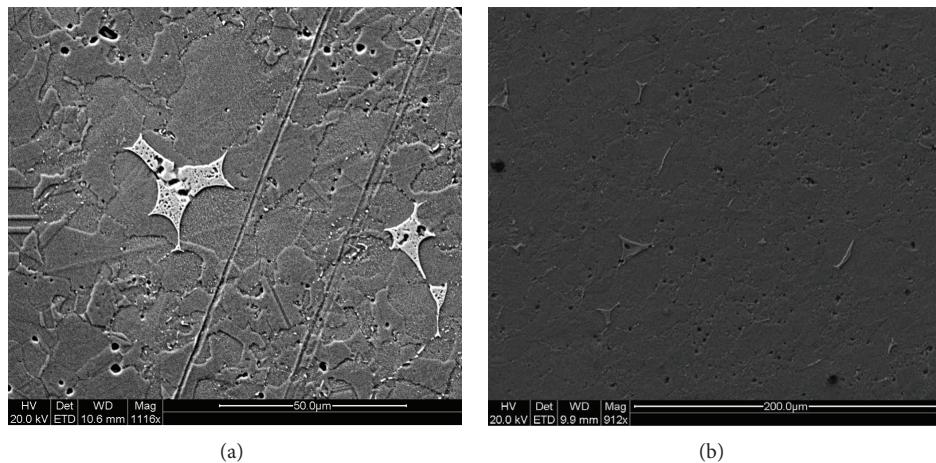


FIGURE 4: SEM images of: (a) Cu + 10 wt.%, (b) 20 wt.% Ag<sub>72</sub>Cu powder sintered at 825°C, 45 MPa, 100°C min<sup>-1</sup>, 20 min hold time.

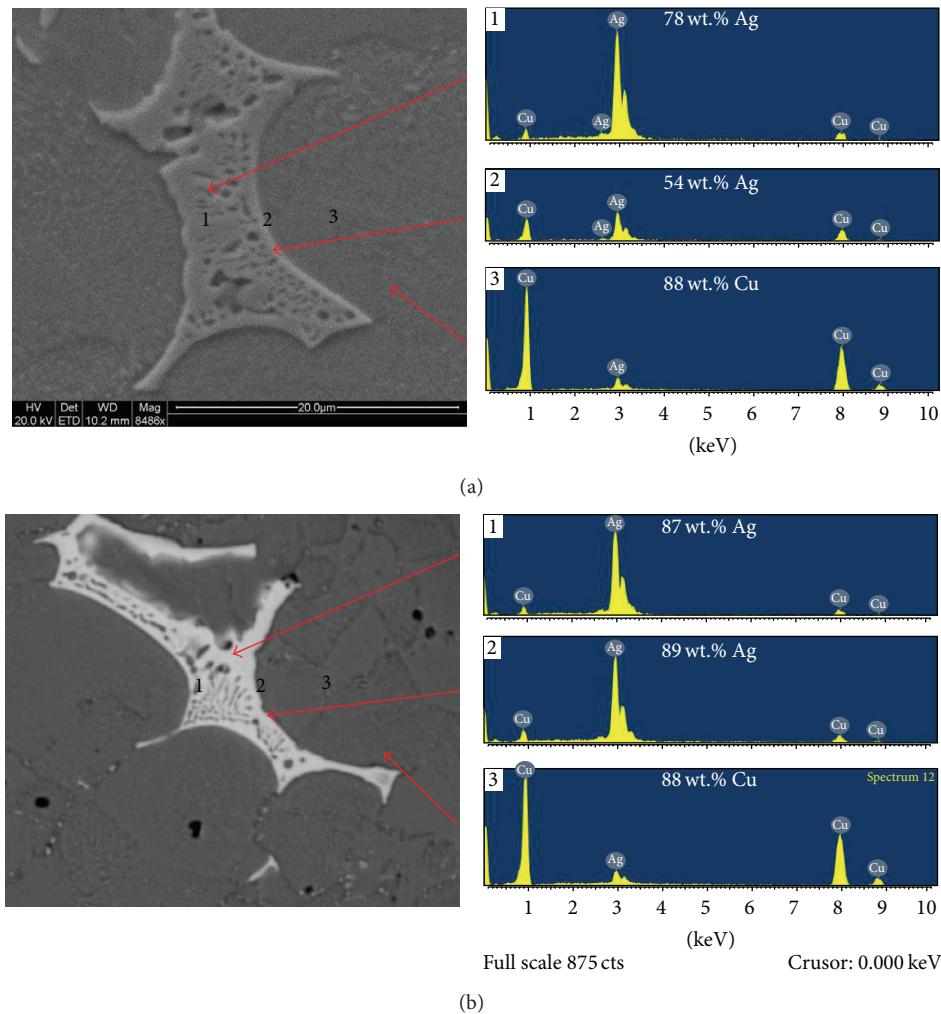


FIGURE 5: SEM image and EDX analysis of Cu + 10 wt.% eutectic held at 825°C for sintering time of (a) 5 minutes and (b) 20 minutes.

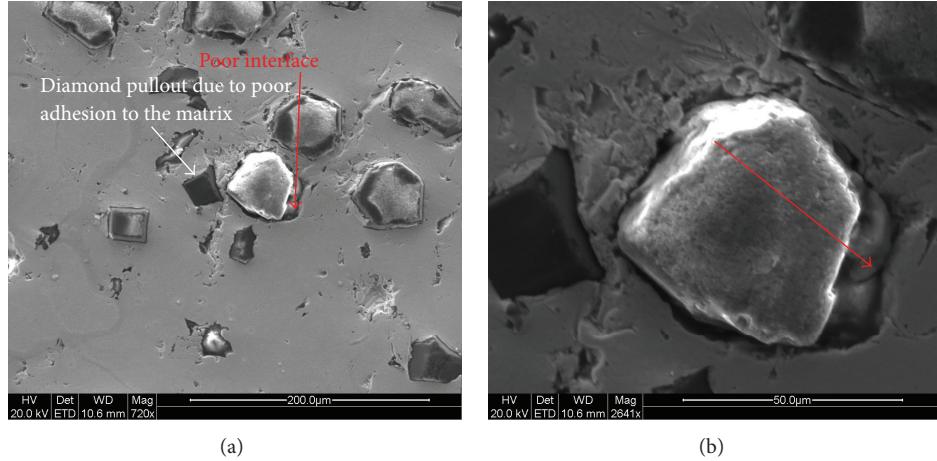


FIGURE 6: (a) Low and (b) high magnification SEM images clearly showing the poor interface that exists between the copper matrix and diamond particles.

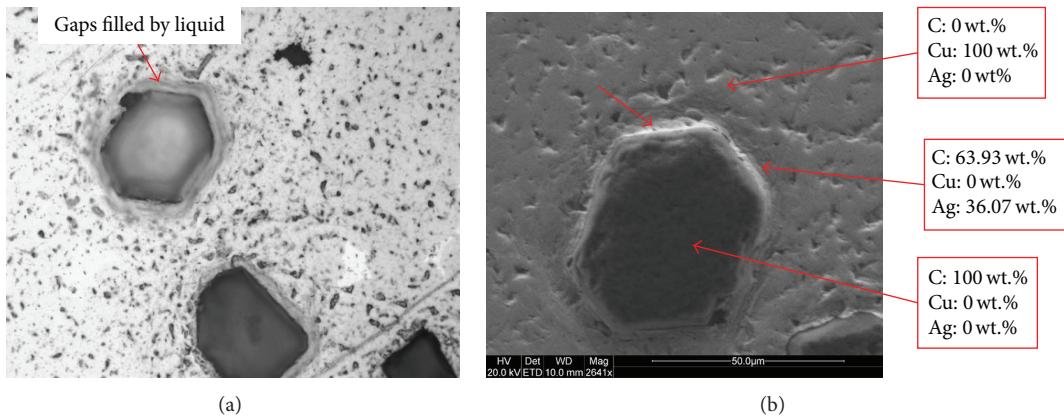


FIGURE 7: (a) Optical image and (b) SEM image including EDX spot analysis of Cu-10 wt.% Ag<sub>72</sub>Cu-10 vol.% diamond clearly showing the presence of liquid phase at the copper-diamond interface during sintering.

Holding the sample longer at maximum temperature allows for more diffusion of atoms from the liquid eutectic phase into the copper grains. As diffusion proceeds, atoms from the liquid eutectic phase migrate into the copper matrix and solidify, as they are no longer at the eutectic composition.

The diffusion behavior was probed using EDX for the Ag<sub>72</sub>Cu samples. Figure 5 shows an SEM image and EDX analysis of experiments held at the maximum temperature of 825°C for 5 minutes (Figure 5(a)) and 20 minutes (Figure 5(b)). 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 phase at the grain boundary. A small percentage of silver also diffuses into the copper matrix. There is an intermediate boundary layer in both cases of roughly equal composition. This suggests that the kinetics for copper self-diffusion is preferential to silver diffusion in copper in the FAST system under these processing conditions.

**3.2. Influence of Liquid Phase on Thermal Properties.** Pure copper powder was sintered with diamond particles to

highlight the porosity that can form at the interface between the materials when no measures are taken to mitigate the problem. The copper and diamond SEM images are shown in Figure 6. The poor interface is clearly visible and highlighted by arrows.

Figure 7 shows the optical and SEM microstructure of composites that were prepared using a pure copper matrix with additions of both 10 wt.% Ag<sub>72</sub>Cu and 10 vol.% diamond. The improvement of the interface due to the presence of the liquid phase at the grain boundaries is evident. The liquid phase appeared to move freely along the grain boundaries and fill voids, especially at the interfaces of the copper and diamond particles.

Figure 8 shows SEM images of Cu-10 wt.% Cu<sub>5</sub>Si-10% Dia. The microstructure similarly shows much more cohesive interfaces between the matrix 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 Cu<sub>5</sub>Si along the grain boundaries, which have negative implications on the thermal conductivity of the material.

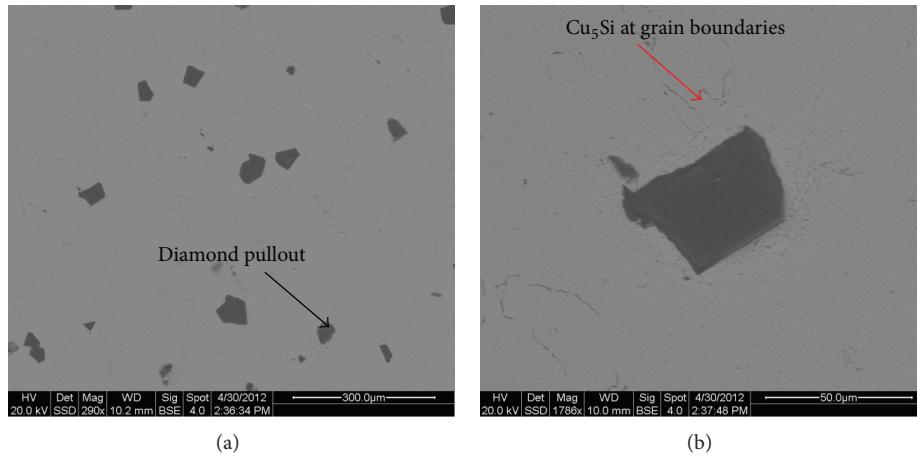


FIGURE 8: (a) Low and (b) high magnification SEM images of Cu-10 wt.% Cu<sub>5</sub>Si-10% Dia samples.

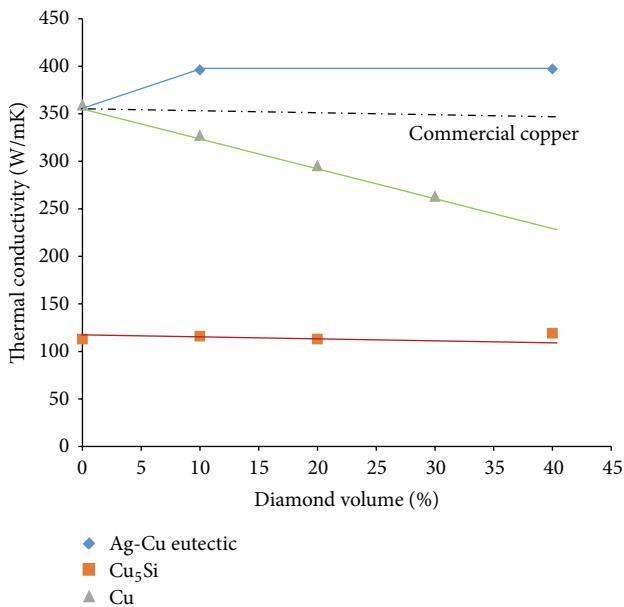


FIGURE 9: Thermal conductivities of Cu, Cu-Ag72Cu, and Cu-Cu<sub>5</sub>Si systems with diamond additions.

The thermal conductivity of both systems is shown in comparison with pure copper in Figure 9. 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 noneffect of thermal conductivity as opposed to a decline which is the case for pure copper. 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<sub>5</sub>Si additions dramatically drop the thermal conductivity of the baseline material, by almost 75% of pure copper. This means that Cu<sub>5</sub>Si cannot be considered a suitable additive 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. This is not completely unexpected as the reaction between Si and C for SiC does not have a strong propensity to occur compared to other carbide forming materials such as Ti and Zr.

#### 4. Conclusions

This experiment has shown that copper-silver alloyed powder of eutectic composition and copper silicide can be added to copper powder to form a two-phase, solid-liquid sintering process below the melting temperature of the copper matrix. Experiments have shown that the additional components melt in the FAST system very rapidly at the theoretical melting temperature of the material. The following conclusions can be drawn about the inclusion of liquid eutectic phase from the microstructure.

- (i) The liquid phase encapsulates diamond particles very effectively and significantly improves the interface between diamond particles and the matrix.
- (ii) The optimal amount of eutectic powder appeared to be 10% for the conditions examined in this study (pressure, temperature, heating rate, etc.).
- (iii) EDX analysis shows that copper diffusion from the eutectic material occurs relatively rapidly into the copper matrix leaving a high silver concentration at the interface.
- (iv) While Cu<sub>5</sub>Si is effective at encapsulating the diamond, it drops the baseline conductivity dramatically and cannot be considered as a thermal management material.
- (v) No chemical bonding occurs between either Ag72Cu or Si and diamond and so there is no improvement in the thermal conductivity as the volume fraction of diamond increases.

It is clear that the use of a two-phase approach to sintering can improve the interface between traditionally incompatible materials.

## Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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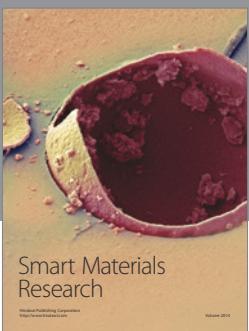
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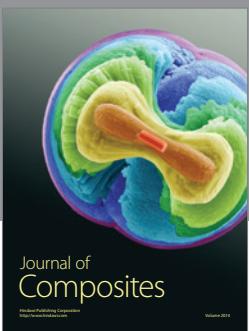
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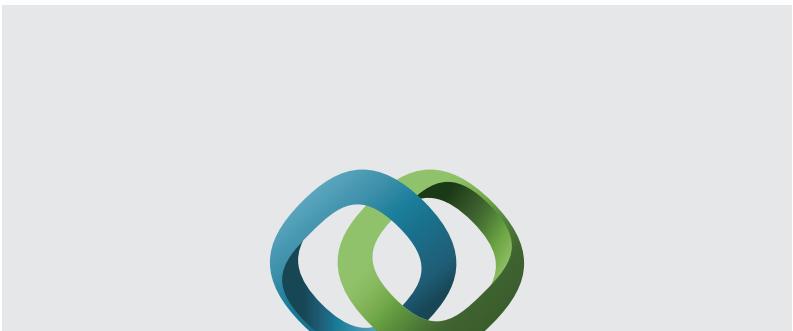
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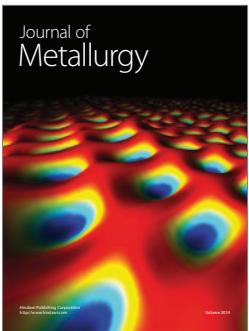


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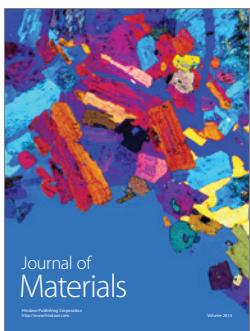
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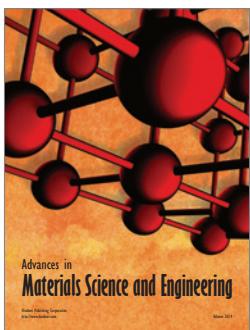
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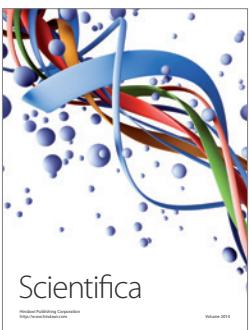
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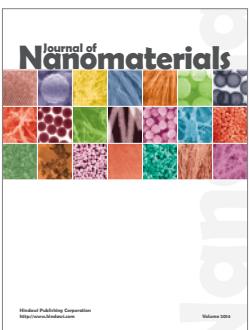
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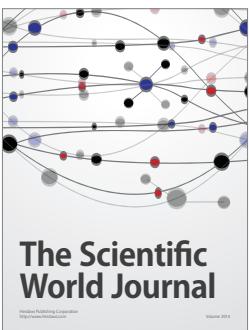
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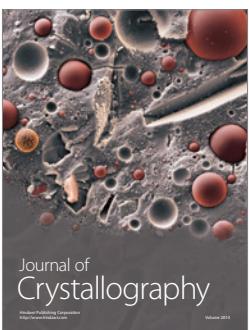
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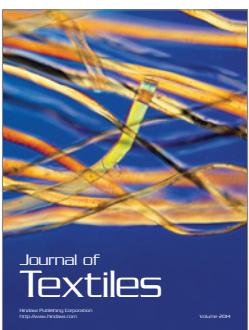
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