Diffusion Bonding of Bi-Layered Silver Graphite-Copper Electrical Contacts

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ABSTRACT

Due to economic considerations, companies that produce electrical contacts are shifting from single-layered to bi-layered electrical contacts. In this method, a thin layer of refractory based material (e.g. silver-graphite, silver-tungsten, silver-tungsten carbide) is bonded to a layer of pure copper (Cu) to create a bi-layered contact. Unfortunately, the traditional press, sinter, repress method has not been successful in producing bi-layered (clad) silver graphite (AgC)-Cu electrical contacts due to the presence of carbon (graphite) at the interface, as carbon is not diffusible into either silver or copper. This leaves a poor interface between the AgC section and the copper section decreasing the shear strength of the joint. This paper presents the results on the use of NiCr and Fe interlayers for diffusion bonding of bi-layered AgC-Cu electrical contacts.

INTRODUCTION

The high electrical and thermal conductivity of silver (Ag) and copper (Cu) compared to other metals (see Table 1), have made silver-based and copper-based composites an integral part of many thermal-electrical applications, from heat sinks in computers and microwave communication systems to electrical contacts. Beside the high conductivity of the base material, these composites are blended with refractory metals in order to withstand severe electrical and mechanical forces [1].

The two most common silver-based contacts are silver-graphite (Ag-C) and silver-tungsten (Ag-W) composites. Due to excellent anti-welding, low thermal expansion coefficient and lubricating properties of the graphite, the Ag-graphite contacts are known for their widespread applications in various low-voltage protective switchgears, such as low-voltage circuit breakers [1]. On the other hand, tungsten's high hardness, wear resistance, low coefficient of thermal expansion, and high melting temperature, have made Ag-W contacts not only suitable for high current circuit breakers, but also attractive for thermal management applications [1].

Table 1: Physical Properties of Copper, Silver, Graphite, and Tungsten [2]

Property	Copper (Cu)	Silver (Ag)	Tungsten (W)	Graphite (C)
Melting Point (K)	1356	1764	3653	3923
Specific Heat (J/kg-K) at 293K	385	233	134	708
Density (g/cm3) at 293K	8.94	10.43	19.3	2.25
Electrical Resistivity ($10^{-8}\Omega$m) at 293K	1.70	1.61	5.3	600
Thermal Conductivity (W/m-K) at 293K	393	429	167	24.0
Coefficient of Thermal Expansion (x 10^{-6} m/m-K) at 273-373 K	17.1	18	4.5	0.60 - 4.30

Most electrical contacts are produced by means of powder metallurgy (PM). Depending on the required application and/or composition, one of the following three processes is generally employed:
(i)   Press-Sinter-Infiltrate (PSI),
(ii)   Press-Sinter-Repress (PSR), or
(iii)   Press-Sinter (PS).

Due to the increase in silver and tungsten prices (Figure 1) over the last 30 years, companies that produce electrical contacts are developing new ways to reduce the cost of contacts. One of these ideas is the use of clad (bi-layered) contacts. In this cost saving method, a thin layer of refractory-based contact is bonded with a layer of pure copper (a backing layer) to create a bi-layered contact.
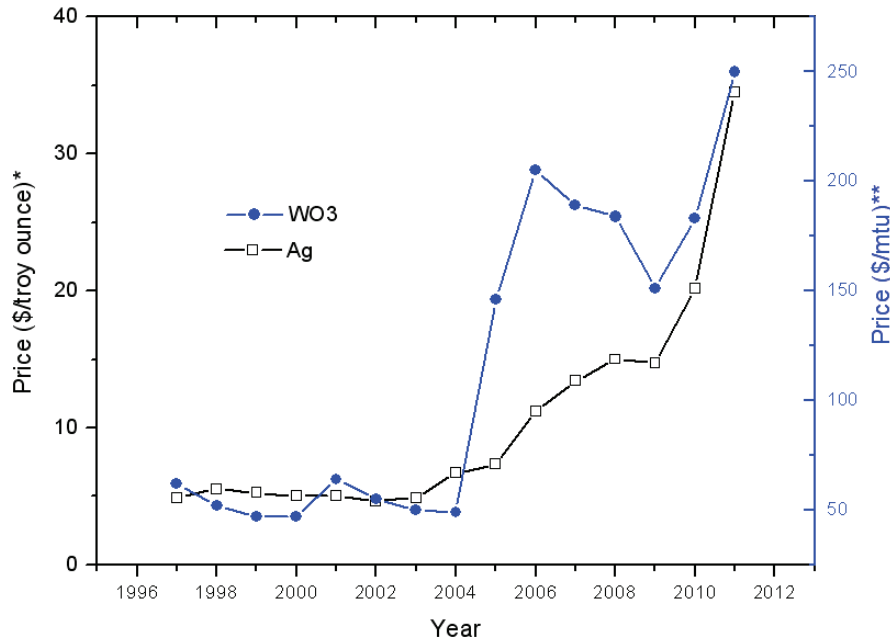

Figure 1: US Consumer Prices of Ag and W (Source: http://minerals.usgs.gov/minerals/pubs/commodity)
(* 1 metric ton =1,000 kilograms = 32,150.7 troy ounces)

While the PSR process has been successful in fabricating bi-layered make-break (MB) contacts of Cu-graphite (see Figure 2a), this process has shown significant interface break-up when employed to make sliding contacts (brushes) of Ag-graphite or Ag-W composites. Consequently, a hot-press method (Figure 2b) is used to fabricate these types of contacts. Unfortunately, hot pressed parts can only achieve a final density of about 80-85% theoretical density. This is not acceptable for MB contacts, where a 96% theoretical density is the minimum industrial standard. Nevertheless, the process is an expensive and time intensive batch processing method for mass production. From the economic point of view, millions of dollars will be saved if the sliding contacts (brushes) are fabricated by the PSR method instead of the hot press process.
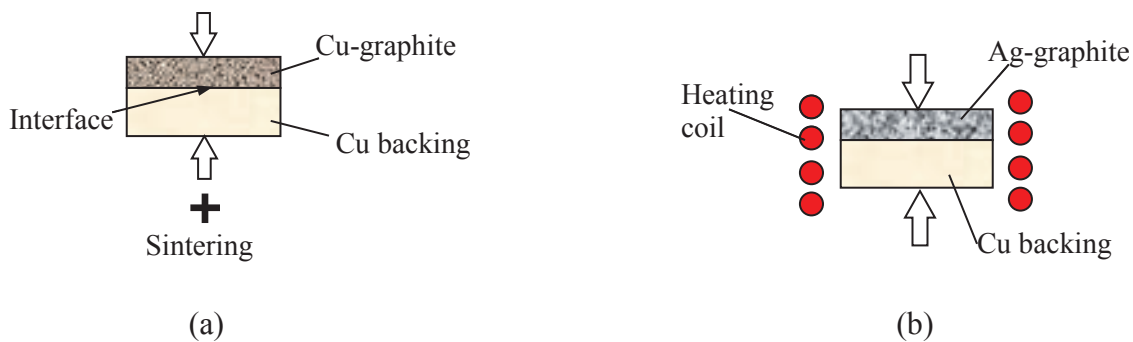

(a)   (b)

Figure 2: (a) PSR process for Cu-graphite (with Cu backing) MB contact and (b) hot press process for Ag-graphite (with Cu backing) sliding contact

This paper presents the results of collaborative efforts between Penn State DuBois and Contact Technologies Inc. (CTI)[1], in the investigation of AgC-Cu interface failures and viable diffusion bonding systems for economical fabrication of electrical contacts.

EXPERIMENTAL PROCEDURE

All materials for this study were supplied by CTI. The premixing of graphite in the silver, hot-pressing, and sintering were all done at CTI. Powder characterization was done using Malvern Mastersizer 2000 particle size analyzer, and interface characterization was carried out using optical microscope, scanning electron microscope (SEM), and energy dispersive X-ray spectroscopy (EDS). Dimensional changes during sintering was performed in situ using Anter 1161 dilatometer. Table 2 presents green compacts used for measuring dimensional changes.

Table 2: Green Compacts of Ag-C and Cu for dilatometric measurements

Material	Sample ID	Green Density (g/cm^3)	% Theoretical Density
Silver-graphite	Ag755	7.55	75
	Ag800	8.00	80
	Ag850	8.50	85
Copper	Cu720	7.20	80
	Cu765	7.65	85

RESULTS AND DISCUSSION

Analysis of the powder particle distribution (Figure 3) indicated that the average particle sizes of the AgC and copper powders were 6.5µm and 11.5µm, respectively.
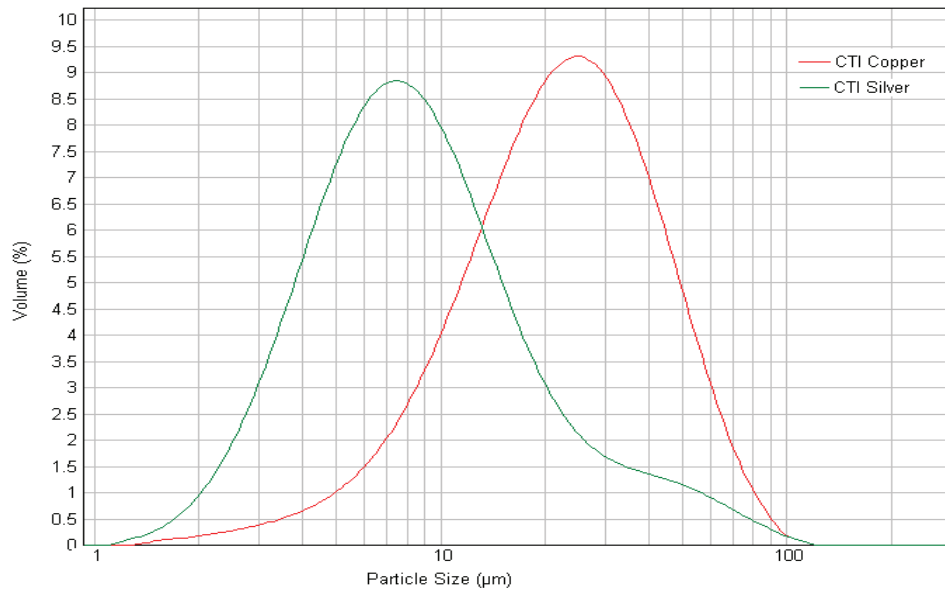

Figure 3: Particle size distribution for AgC and copper powders used for fabricating electrical contacts

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Figure 4 shows through-thickness SEM micrographs of the AgC-Cu contacts fabricated by the PSR method. The diffusion layer in Figure 4a unequivocally shows that there is a higher diffusivity of Ag into Cu than in the reverse direction. On the other hand, Figure 4b shows presence of graphite at the interface. For comparison purpose, Figure 5 presents cross sectional optical micrographs of the AgC-Cu contacts fabricated by the hot press (Figure 5a) and by the PSR process (Figure 5b). Evidently, Figure 5b shows the presence of graphite formed at the interface during sintering of the AgC-Cu contacts, whereas Figure 5a shows the absence of this detrimental feature in contacts made by the hot-press process.
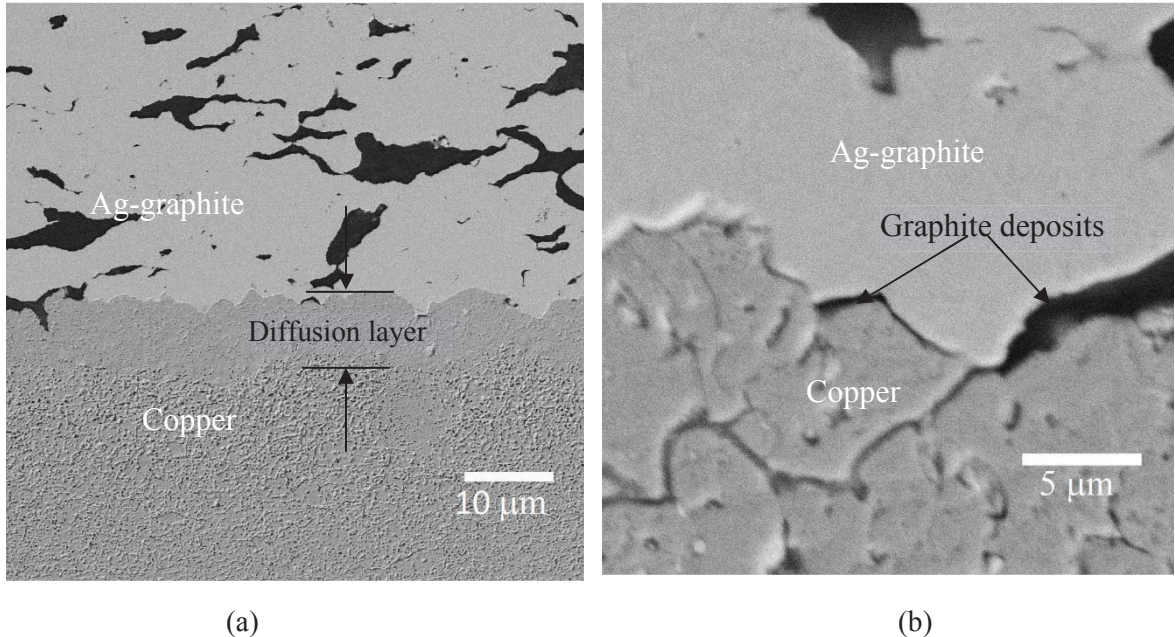

(a)   (b)

Figure 4: SEM micrographs of the AgC-Cu bilayer contacts fabricated by the PSR process showing (a) the diffusion layer and (b) graphite deposits at the interface.
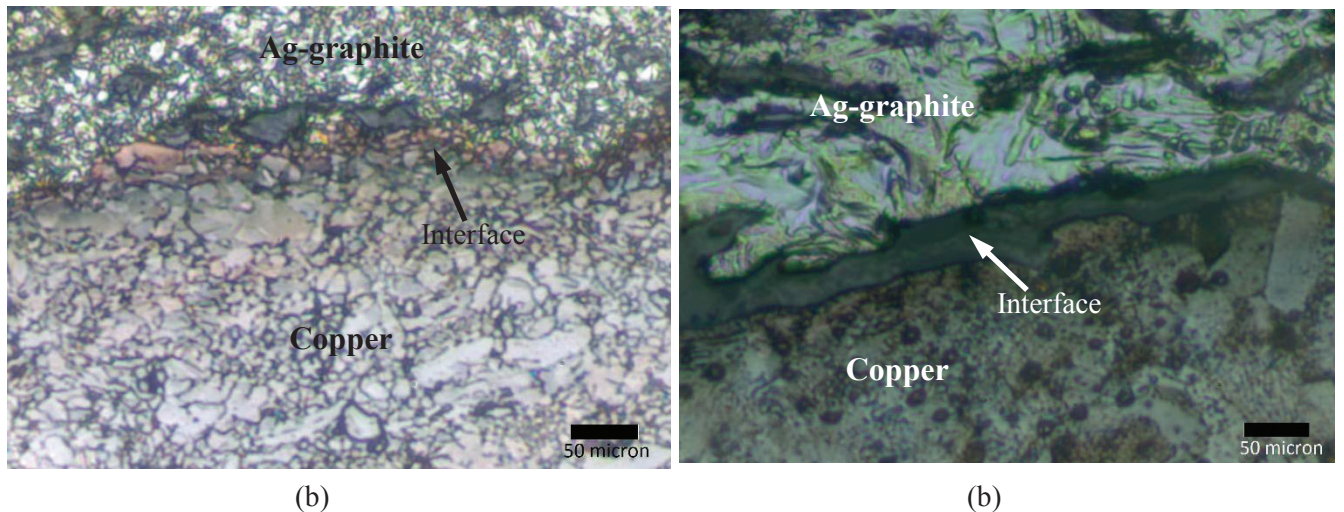

(b)   (b)

Figure 5: Through-thickness optical micrographs of the AgC-Cu bilayer contacts fabricated by (a) the hot press and (b) by the PSR process.

Additional characterization of the interface was done by the energy dispersive X-ray spectroscopy (EDS) analysis, using an X-ray line scan in a scanning electron microscope (SEM), as shown in Figure 6. Beside

the constituent elements of the bi-layered contact, the X-ray line scan shows a peak of C (graphite) at the interface (the white arrow in Figure 6). This high concentration of graphite is the main cause of a weak metallurgical bonding at the interface of the bi-layered contact. One possible explanation of the presence of graphite at the interface is the fact that Ag and graphite are immiscible in each other (Figure 7) whereas Cu and Ag have limited solubility (Figure 8). In that case, during sintering, Ag, having a higher diffusivity in Cu than Cu in Ag, will diffuse into Cu leaving the immiscible graphite (C) at the interface.
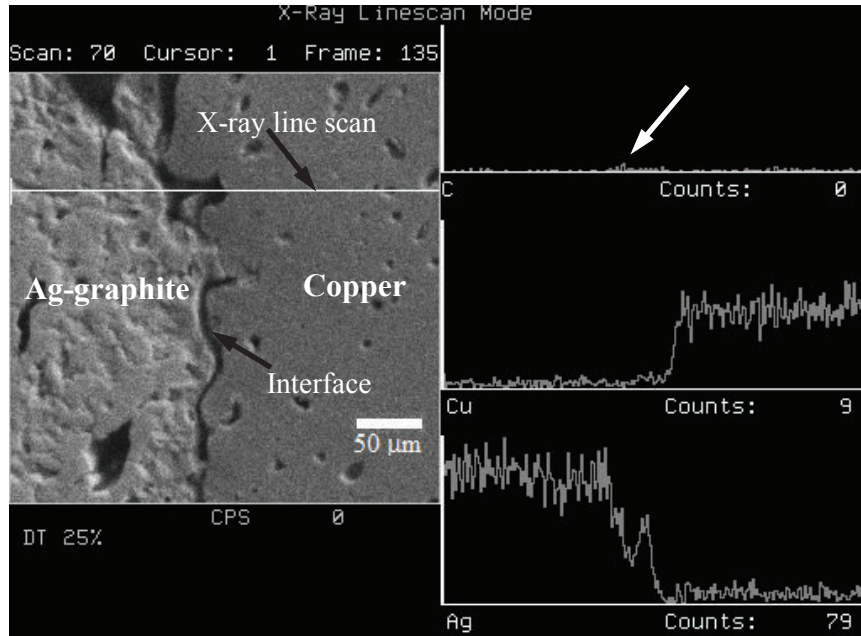

Figure 6: SEM micrograph of the AgC-Cu bilayer contact showing the X-ray line scan across the interface. The white arrow shows the peak of graphite.
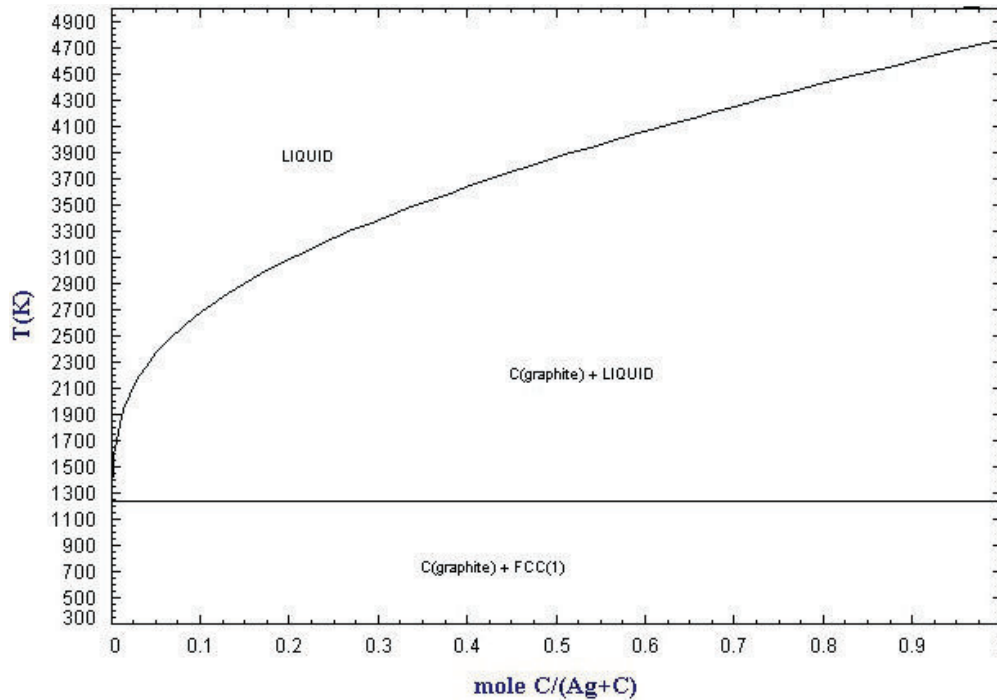

Figure 7: Phase diagrams of Ag-graphite binary system [3].
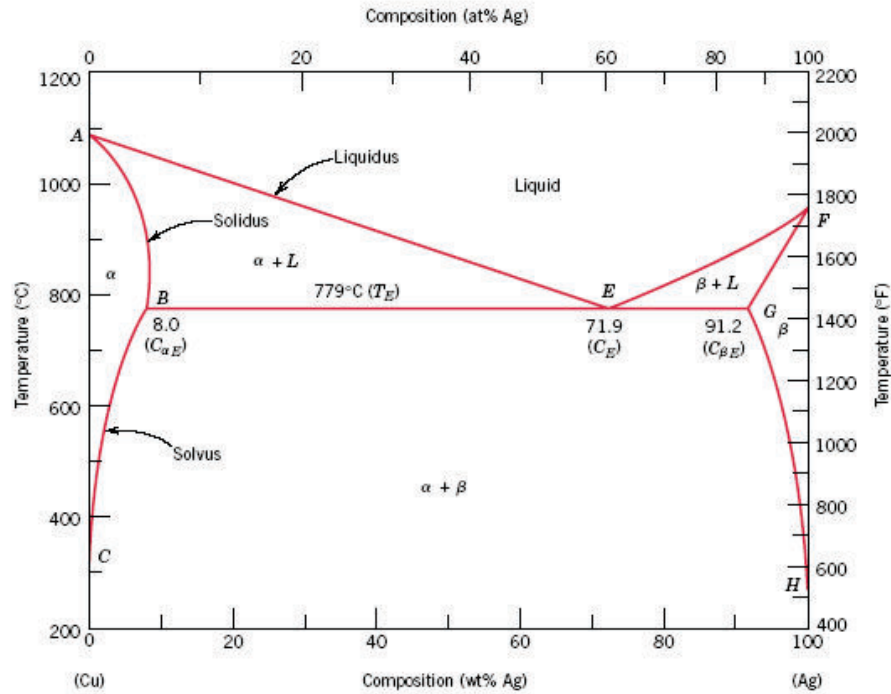
Figure 8: Phase diagrams of Cu-Ag binary system

It is apparent that the weak interface is due to lack of adhesion between copper and graphite, i.e. copper tends not to 'wet' the graphite [4]. Consequently, any distortion (strain field) due to dimensional changes during sintering will amplify this problem. Unfortunately the PM process does inherently produce density gradients in powder compacts. These density variations impact a difference in shrinkage strain from one region to another. The differential shrinkages produce densification stresses and distortions during sintering [5, 6]. For bilayer compacts such as AgC-Cu, density gradient is unavoidable due to differences in the compressibility between AgC and Cu. Beside differences in densities, the dimensional changes in the two layers during sintering is further magnified by the differences in the coefficient of thermal expansion (CTE). For this reason, dilatometric measurements were carried out to determine the effect of dimensional changes on the interfacial properties.

Figure 9 presents the dimensional changes in the AgC and Cu compacts sintered individually at 816°C (1500°F) for 4 minutes in ANTER 1161 dilatometer under 100% nitrogen atmosphere at a heating and cooling rate of 10°C/min. It can be deduced from Figure 9 that in order to avoid sintering stresses and distortion, the densities of the AgC and Cu layers should be about or above 85% theoretical density. Clearly, silver graphite and copper with 85% theoretical densities produced nearly identical dimensional changes during sintering.

An attempt was made to make a bilayer compact with these densities in order to observe their impact on the interface. Despite the minimal difference in the dimensional changes between AgC and Cu layers, the interface was still filled with graphite deposits after sintering. Figure 10 shows the AgC layer sintered as individual part and as a bilayer of AgC-Cu compact. Remarkably, the AgC layer sintered as individual part is clean devoid of any graphite deposit, whereas the AgC layer sintered as a bilayer of AgC-Cu compact has unmistakably graphite deposits on the interface side. A similar observation was noted on the Cu layer. This is a clear indication that dimensional change is not a major problem, but rather the inability

to 'wet' graphite is a critical limiting factor for proper diffusion bonding. This suggests that the use of an interlayer or additives that 'wet' graphite may be a solution.
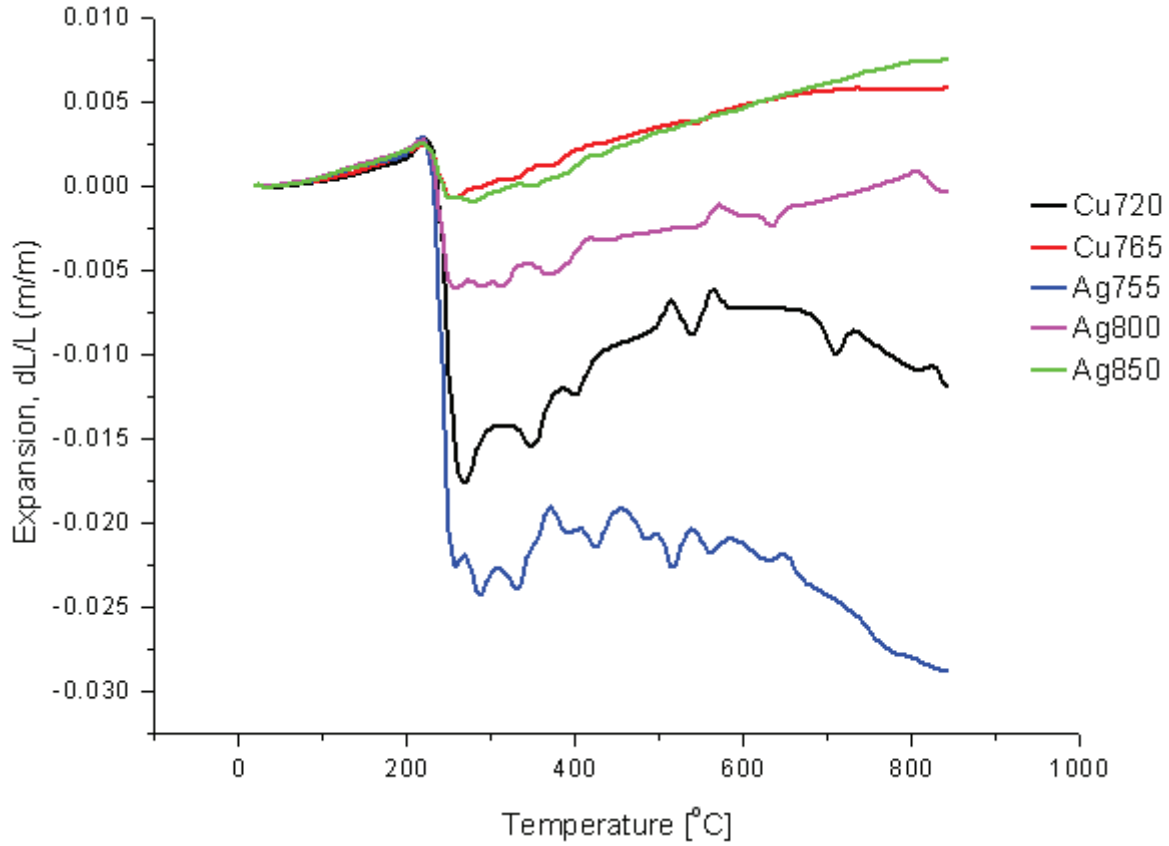

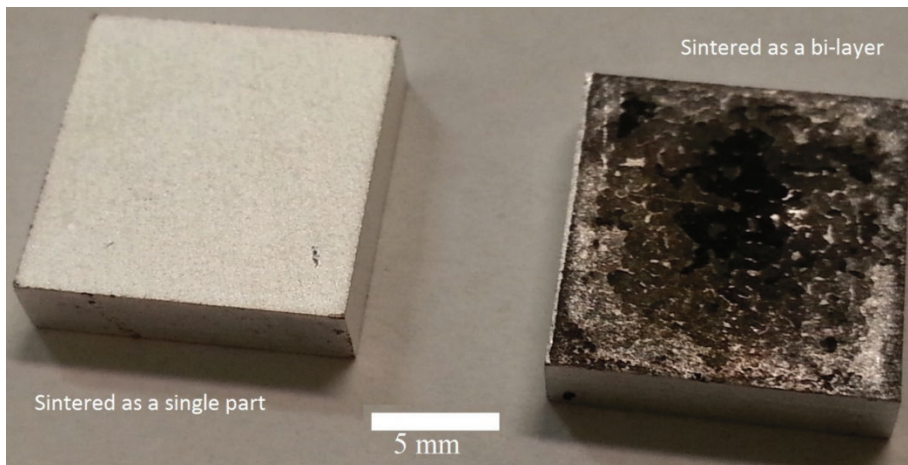**Figure 9:** Dimensional changes in the AgC and Cu compacts during sintering

Figure 10: AgC layer sintered as individual part and as a bilayer of AgC-Cu compact. The graphite deposit (black spots) is visible on the contact surface of the AgC bilayer.

Wetting can be improved by addition of additives (or a.k.a. activators) in the matrix. The role of the activator is to lower the process activation energy for diffusive transport [7]. The additive provides a high-mobility phase for rapid base-metal transfer [8, 9]. In the work by Mortimer and Nicholas, copper bonding to graphite was improved by alloying the copper with small amount of titanium and chromium [4]. These active metals were intended to segregate to the interface and produce carbide, thereby improving copper adhesion to the reaction layer. Nickel has also been reported to improve the erosion properties of the of Ag-W contacts. Tungsten is insoluble in Ag, and in order to obtain high densification, Ni doping is a common practice [10, 11].

Wetting can also be achieved by a process known as liquid phase sintering (LPS). LPS occurs when an additive forms a liquid during sintering. The surface tension associated with the liquid provides a capillary force which induces wetting between particles and grains, or particle rearrangement (or dissolution). The wetting promotes a faster rate of diffusion and rapid densification through solution dissolution (re-precipitation). In a nut shell, during LPS the liquid is supposed to quickly come to a local equilibrium with the surrounding solid, to remain homogeneous, and to change its volume (e.g., by melting some of the solid). In a later stage, the liquid and solid phases are assumed to maintain local equilibrium compositions, such that diffusion profiles are developed in the solid. A slow isothermal solidification ensues, controlled by the rate of solute diffusion in the solid phases, until the liquid is exhausted. A final stage involves the homogenization of the region, again by solid-state diffusion [12]. The liquid can either be formed by heating the mixture above the solidus temperature of the activator or by transient liquid phase sintering (TLPS), where a liquid phase (such as eutectic liquid) is formed by a chemical reaction between the base powder and the additive. Among the many investigations on this process, LPS of W has received considerable attention due to tungsten's slow sintering rate, high atomic bond strength (and hence high melting temperature), and high activation energy of diffusion [10]. Nickel (Ni), iron (Fe), palladium (Pd), and cobalt (Co) are common activators for sintering of W [11]. In the investigation of the sintering of compacts of tungsten spheres that had been infiltrated by liquid Ni, Yoon and Huppmann [13] showed evidence for the migration of nickel-rich liquid films into the pure tungsten, leaving in their wake an equilibrium solid solution of nickel in tungsten.

In this study, alloys of Fe, Cr, and Ni were used as sintering additives for improving the wetting of graphite. Figure 11 shows the AgC-Cu bilayer contacts with Fe as an additive pre-mixed with Cu. The figure shows virtually no diffusion; the graphite deposit is visible on the contact surfaces of both layers. The two layers separated without the use of a force.
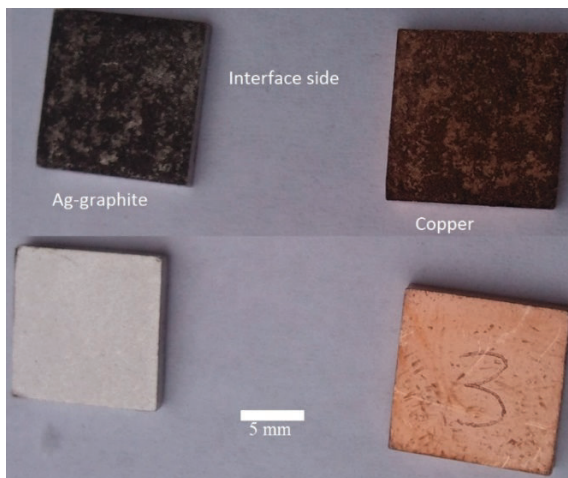

Figure 11: AgC-Cu bilayer contacts with Fe as an additive pre-mixed with Cu. The graphite deposit (black spots) is visible on the contact surfaces of both layers.

However, a close look of the microstructure showed heterogeneous sizes of Fe grains distributed within the Cu matrix (Figure 12a). Comparison of Figure 12b with Figure 5b shows some granular structure at the interface of Figure 12b that is absent in Figure 5b. This speculatively indicated that the use of active interlayer of Fe between AgC and Cu layers could potentially provide the wetting of graphite and improve diffusion bonding. Figure 13 shows a sintered AgC-Cu bilayer compact with Fe interlayer. Clearly, the interlayer provided a good diffusion bond with the two layers. This suggests that lack of bonding between AgC and Cu with Fe as pre-mixed additive is due to insufficient diffusion of the Fe in the copper reaching the interface. The use of the interlayer also reduces the likelihood of impacting electrical conductivity due to concentration of additives in the copper layer.
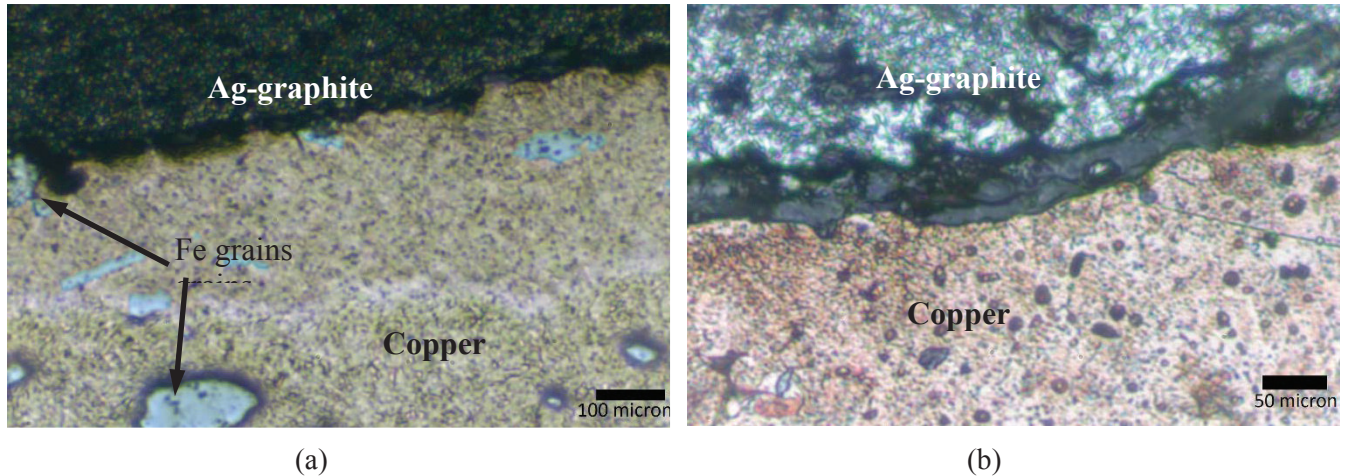

| (a) | (b) |

Figure 12: Through-thickness optical micrographs of the AgC-Cu (with Fe as additive) contacts fabricated by the PSR process. Magnifications at (a) 50x and (b) 100x.
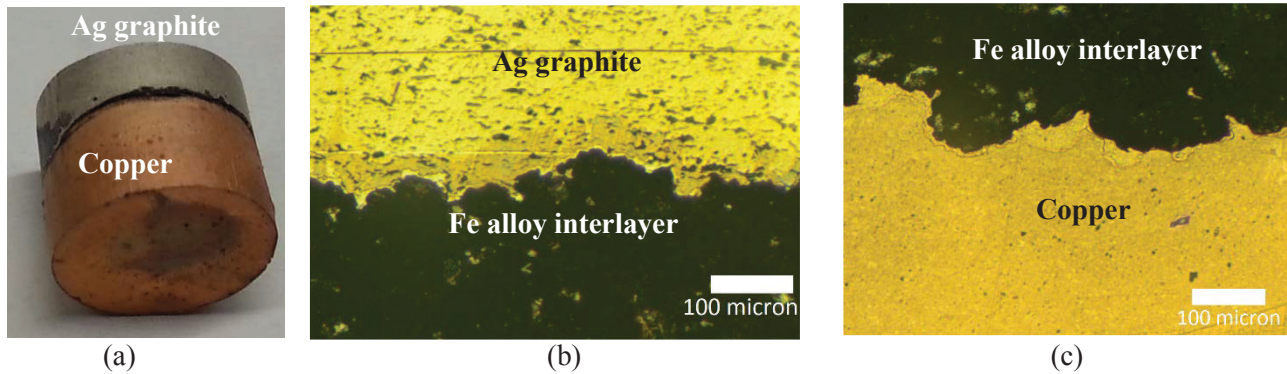

| (a) | (b) | (c) |

Figure 13: (a) Sintered AgC-Cu bilayer compact with Fe interlayer. The interlayer provided a good diffusion bond with Ag-graphite (b), as well as with copper (c).

Further investigations were done on the use of other interlayers such as NiCr, brass, bronze, and TiNiCu. Figure 14 shows a sintered AgC-Cu bilayer compact with NiCr interlayer (since the research is still under development, the actual amount and composition of NiCr is proprietary). Clearly, the NiCr interlayer enhanced the diffusion and eliminated the problem of graphite deposits at the interface.
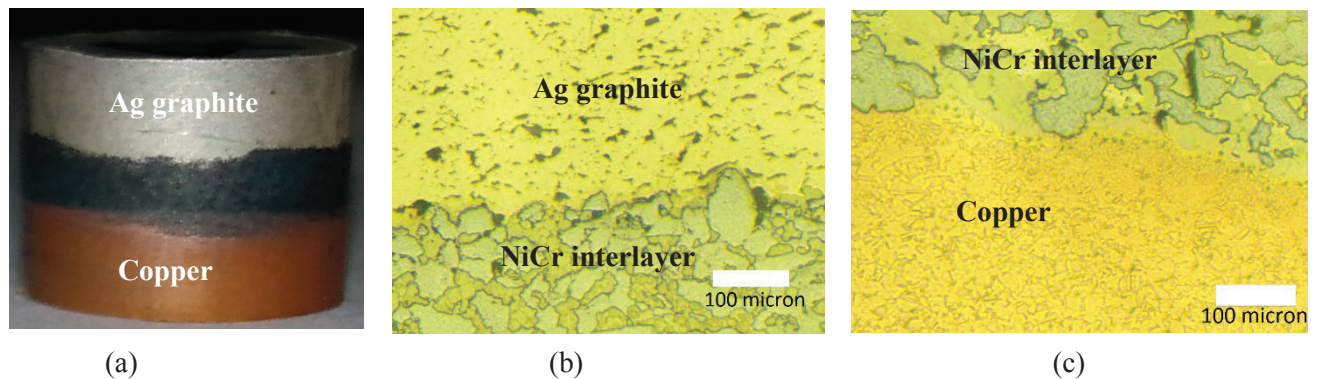
Figure 14: (a) Sintered AgC-Cu bilayer compact with NiCr interlayer. There is improved diffusion between the interlayer and Ag-graphite (b), as well as with copper (c).

CONCLUSIONS

This investigation has shown that the use of NiCr and Fe interlayers is a promising diffusion bonding method for fabricating the AgC-Cu bilayer electrical contacts. The application of these interlayers has successfully prevented graphite from depositing on the interface. Further characterization is, however, required to ascertain the effect of the interlayer on the electrical conductivity, shear strength of the bond, coefficient of thermal expansion, and the effect of the interlayer on the dimensional changes of the layers during sintering. There is also a strict industrial control on the thickness of the bilayer, hence further research is required to determine the minimum/optimal thickness of the interlayer that will provide the diffusion bonding and still maintain the required properties of the contacts.

ACKNOWLEDGEMENT

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