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Assessment of Diffusion Bonding of Silver-graphite-copper Composite with Varying Atmospheres

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Abstract

Electrical contacts are an important component in the electrical motor industry. Having an electrical contact with excellent conductivity at an affordable price may help enhance this industry financially, and to help save precious metal. The best electrical contact material, silver, has electrical conductivity of $6.30 \times 10^7 \, \sigma/(S \cdot m)$ at $20^\circ C$, but is very expensive. A more affordable material, copper, has the 2nd most electrical conductivity of $5.98 \times 10^7 \, \sigma/(S \cdot m)$, but is more likely to become oxidized. A proper method for making and sintering an electrical contact is necessary. To make an affordable contact, an alternative method to using silver alone is to use bi-layering with copper. This method uses diffusion bonding at the interfaces of the two pressed metals during sintering. Unfortunately, this method has shown to be challenging process due to the immiscibility of graphite in copper and silver. During sintering of silver graphite-copper compacts, silver diffuses into copper leaving a trace of graphite at the interface. This creates a poor interface between the mating surfaces, thereby decreasing the shear strength of the joint.

This project focuses on the affects of different atmospheres with the different copper-based interlayers. Scanning electron microscope (SEM) is the major piece of machinery used in assessing data for this research.
Introduction

The goal of this project is to find a successful method of diffusion bonding of bi-layered silver-graphite-copper composite. This means a layer of silver graphite is pressed and sintered with a layer of copper. This is to help make a more affordable alternative to that of solely silver graphite in electrical contacts. Silver, which is the best conducting metal, is also a very expensive material [1]. Electrical contact manufacturers wish to use copper as a supplemental material in electrical contacts to decrease cost. This is because copper is the second-best conducting material.

Something to keep in mind when ordering materials is using the correct composition. Many silver powders used in electrical contact also consist of carbon graphite. This is used to prevent wear of the silver [2]. Unfortunately, this causes problems during the diffusion process. The melting temperature of carbon is much greater than that of silver or copper [3], even at very low concentrations (Figure 1). Table 1 shows the immiscibility of graphite in silver. This inability of graphite to diffuse in silver during sintering causes and accumulation of graphite at the interface of the copper and silver, producing a poorly diffused sample (Figure 2). A feasible method to solve this dilemma is the use of a copper-based interlayer with a low-melting temperature (below the sintering temperature) in order to create a liquid-phase sintering. This will hopefully prevent accumulation of graphite at the interfaces, and promote a stronger diffusion bond.

Figure 1: Silver - Graphite Phase Diagram
Table 1 – Thermal Properties of Copper, Silver and Graphite [4]

<table>
<thead>
<tr>
<th>Thermal Property</th>
<th>Copper (K)</th>
<th>Silver (K)</th>
<th>Graphite (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting Point</td>
<td>1356</td>
<td>1764</td>
<td>3923</td>
</tr>
<tr>
<td>Thermal Conductivity at 293K</td>
<td>393</td>
<td>429</td>
<td>24.0</td>
</tr>
</tbody>
</table>

![Figure 2: SEM Micrograph of Interface without Interlayer](image)

**Methodology**

The control sample was pressed to make a two-layer compact consisting of 2 grams of silver-graphite (97% silver + 3% graphite) and 2 grams of pure copper. The sample was pressed to a pressure of 345 MPa. Experimental samples were pressed with varying interlayer mass, less than that of the outer layers. Most masses were tested at 0.250 grams, 0.500 grams, and 0.750 grams. Making the layer as thin as possible is favored to help decrease the cost.

Three different atmospheric conditions were tested, all at approximately 820 °C (1500 °F) for ten minutes (Figure 3). The atmospheres were 95% N\textsubscript{2} + 5% H\textsubscript{2}, 100% H\textsubscript{2}, and a vacuum.
After sintering, samples were simply tested with a drop test several times, to ensure they would not simply break and were worthy of further testing. Unsuccessful interlayer materials, regardless of mass, included silver nano particles (< 150 nanometers), a mixture of 37.5% silver-graphite + 62.5% copper and vice versa, brass, bronze, a mixture of 2% copper + 48% nickel + 50% titanium, ball-milled nickel titanium powder, a mixture of 50% nickel + 50% chromium, and ball milled nickel chromium powder. Some materials were ball milled to change the surface structure of the particles to see if there was any affect on bonding. There appeared to be little or no change between samples sintered in different atmospheres.

Samples that survived the drop test and could not be pried apart were ball-milled copper powder (milled for either 24 or 48 hours), and a mixture of one-part silver-copper alloy + two-parts pure copper powder. Table 2 shows the well bonded samples, balled milled copper samples 1 and 2 (MC481, MC482) and the alloy (AC41).

**Table 2:** Interlayer Material with Sintering Atmosphere

<table>
<thead>
<tr>
<th>Interlayer material</th>
<th>Mass (grams)</th>
<th>*ID</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vac</td>
<td>95-5</td>
<td>100</td>
</tr>
<tr>
<td>Ball-milled copper</td>
<td>0.759*</td>
<td>MC482</td>
</tr>
<tr>
<td></td>
<td>0.508*</td>
<td>MC481</td>
</tr>
<tr>
<td>Ag-Cu alloy</td>
<td>0.208</td>
<td>0.208*</td>
</tr>
</tbody>
</table>

It is important to note that a second Ag-Cu alloy sample was made with a mass of approximately 0.250, however the exact mass is unknown, so it was not included in the table. This sample was marked as AC41 modified.
Results and Discussion

As mentioned previously, the most well bonded samples were that of pure ball milled copper powder, milled for 48 hours, and silver-copper alloy mixed with pure copper, labeled MC481, MC482, and AC41, respectively. The MC48 specimens were only sintered in 95% N₂ + 5% H₂ and was found to be well bonded. AC41 was sintered in all three conditions, with the 95% N₂ + 5% H₂ being most favorably bonded. AC41 modified was also sintered in the 95% N₂ + 5% H₂ atmosphere.

The MC48 specimens were found to be well bonded at both interfaces but showed obvious signs of porosity due to oxidation during ball milling [5], especially at the interface with silver-graphite (Figure 4). This oxidation is undesirable, as it could limit the electrical properties of the contact. Removal or prevention of this oxidation layer may enhance the bonding at the silver-graphite interface further, as well as improve the conductive properties. As a possible solution, the ball milled copper was cleaned using stirring in either vinegar and table salt, or 0.6 M acetic acid for approximately 45 minutes. The dried powders showed some, but little improvement. Oxygen removal during ball milling may be a necessary method to prevent porosity.
Figure 4: (a) SEM micrograph of sintered MC482 with corresponding EDS maps of (b) silver and interlayer map, (c) silver map, (d) copper map, (e) graphite map, and (f) oxygen map.

The AC41 and AC41 modified were both found to have successfully bonded at both interfaces. Unfortunately, the AC41 had a significant gap along the center of the interlayer, possibly due to an insufficient interlayer mass (Figure 5). The AC41 modified was produced with a larger interlayer to test if this could solve the problem (Figure 6). Indeed, the modified version had a much more cohesive state with well-bonded interfaces.

Figure 5: (a) SEM micrograph of AC41, (b) EDS map, (c) EDS maps of individual elements.
Figure 6: (a) SEM micrograph of sintered AC41 modified (b) backscatter electron map, (c) EDS map, (d) map of graphite.

Conclusions

The most successful interlayer materials were found to be that of the milled copper, milled for 48 hours with a mass of approximately 0.75 grams, and a copper-silver alloy with mass of approximately 0.250 grams.

To improve the development of ball milled copper, a method of oxidation prevention or removal is required. This is important in order to reduce porosity, as this oxidation layer may decrease the conductive properties of the material. Potential prevention method for oxidation is to remove the oxygen during ball milling, or to fill the atmosphere with either nitrogen or argon gas. Additionally, measuring the electrical properties of ball milled copper after a solution has been found to reduce porosity will be required to ensure that it is an acceptable electrical contact. As for the copper-silver alloy, samples with greater mass will be sintered to see if this will allow for cohesive bonding at both interlayers, and the mass itself.

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Future Research Direction

Currently, I am working on another project that has yielded promising results that may be used for an interlayer. This research involves electroless deposition of copper powder on silver powder, and vice versa. Exploring a method of coating silver onto copper powder, and vice versa, through electroless deposition could provide a cost-effective solution to this issue. Through our investigation, we successfully utilized electroless deposition of both silver onto copper and copper onto silver. Some of these modified powders were then compacted and sintered in controlled atmosphere to investigate if they could successfully bond. Other powder samples were characterized using X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and Metallography techniques. We have reason to believe that by further optimizing the methodology of preparing samples and sintering them, they may be used in electrical contacts as an improved composite material.

In this project, the objective is to find a way to coat copper onto silver, or silver onto copper, in this way using copper as a supplemental material to help decrease the overall cost of materials. The experimental coating procedure involves:

- To coat silver onto copper, 3g of copper was dissolved into 1M ammonium hydroxide. Then 5 grams of silver nitrate was separately dissolved into ammonium hydroxide then added to the dissolved copper. Sulfuric acid was used to adjust the pH to 9.
- To coat copper onto silver using a basic bath, 0.5g of copper sulfate, 0.5g of sodium citrate, and 0.5g of formaldehyde was dissolved in water. 4g of potassium hydroxide and 1.2g of silver graphite was dissolved in the solution at a pH of 13.
- To coat copper onto silver using an acidic bath, 2g of copper sulfate and 2.2g of sodium citrate was dissolved in water. 1M of sulfuric acid was added until a pH of 3 was achieved. Then 1.2g of silver graphite was added.
- All solutions were washed, filtered, and left to dry for at least 2 days. Samples were then compacted and sintered at approximately 1550 °F (~820 °C) for 10 minutes.

All baths turned a shade of blue, varying slightly between the different procedures. Attempts to use an acidic bath yielded flaky, clumpy particles with varying shades of grey, suggesting a poor mixture. Basic baths for the most part yielded finer, consistently colored particles. SEM and EDS mappings were used to examine the individual particles of the composite (Figure 7). Figure 7a showed some detection of copper (red) on the surfaces of particles. To determine the composition of the coating, EDS line-scan mapping was used (Figure 8). These line-scans revealed that as the amount of silver decreased, the amount of copper increased, and vice versa, suggesting there was some coating.
Figure 7: (a) EDS mapping of copper on silver, and (b) location of line scans.

Figure 8: EDS Line scans of (a) line 1, (b) line 2, and (c) line 3. Red, green, and yellow curves are for copper, silver, and graphite, respectively.

It is clear that a basic bath using the original recipe for copper on silver appeared to have the best coating. Prospective copper coated silver powders with masses ranging from 0.250 grams to 0.750 grams will be sintered at different atmospheres and tested for diffusion bonding with a silver-graphite layer. After a proper interlayer has been identified with the tested atmospheres, temperature affects will be tested.

The results from this research will be presented at the WorldPM2020, World Congress on Powder Metallurgy and Particulate Materials, Montreal, Canada, June 27 – July 1, 2020.
References