Carbon black pastes as coatings for improving thermal
gap-filling materials

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Abstract

Carbon black pastes were found to be effective as coatings for improving the performance of thermal gap-filling materials, including flexible graphite, aluminum and copper. The thermal contact conductance across copper mating surfaces was increased by up to 180%. A fluidic form of carbon black paste (based on polyethylene glycol) was more effective than a thixotropic form (based on polyol esters). The carbon black pastes were much more effective as coatings than a commercial silver paste. With a carbon black paste coating, aluminum foil (7 μm thick) was a superior gap-filling material compared to similarly coated flexible graphite (130 μm thick). However, without a coating, flexible graphite was superior to aluminum. Commercial silicone-based gap-filling materials were inferior to flexible graphite or aluminum (whether coated or not).

Keywords: Carbon black; Exfoliated graphite; Graphite; Carbon composites; Thermal conductivity

1. Introduction

Heat dissipation is the most critical problem that limits the performance, power, reliability and further miniaturization of microelectronics. The alleviation of this problem is mostly attained by the use of heat sinks, which are materials of high thermal conductivity (such as copper) for allowing the heat to flow by conduction from the heat source (e.g., the microprocessor of a computer). However, the effectiveness of this approach is limited by the thermal resistance associated with the interface between the heat sink and the heat source [1–5]. In order to diminish the thermal resistance, a thermal interface material is placed between the heat sink and the heat source. This material can be fluids, pastes and solders (solders being applied in the molten state) [6–15].

The heat sink may be in direct contact with the heat source at the asperities of either of the mating surfaces, due to the roughness associated with each surface. There may even be a gap between the two surfaces, due to the geometry of the surfaces, the degree of alignment of the surfaces, and/or the configuration of the assembly. The presence of a gap is actually quite common. Due to the thermally insulating nature of air, the use of a thermal interface material that fills the gap is needed.

The design of a thermal interface material for filling gaps differs from that of one for filling the valleys in the surface topography of the mating surfaces that are in contact. These valleys contain air which should be displaced by a thermal interface material that is highly conformable and that is very thin (ideally just thick enough to fill the valleys, as the thermal resistance increases with thickness) [12,13]. Thus, a thermal interface material for filling the valleys is typically a paste of low viscosity. (The higher the viscosity, the less is the conformability [10].) However, for gap filling, the thermal interface material must be thick enough to fill the gap and be able to maintain its geometry. Thus, a gap-filling material typically involves a thixotropic paste (such as silicone filled with thermally conductive particles [6–9]), which is in contrast to the fluidic pastes (such as polyethylene glycol filled with thermally conductive particles...
that are effective for filling the valleys in surfaces that are in contact. Another type of gap-filling material is a solid sheet such as a metal foil. Ideally the sheet exhibits resiliency and hence conformability. Metals are ductile but have low values of the elastic limit. Therefore, metals are limited in resiliency or conformability. In contrast, “flexible graphite” [16–19] is a graphite sheet that is flexible and is resilient in the direction perpendicular to the sheet. The resiliency is made possible by the microstructure, which involves the mechanical interlocking of exfoliated graphite in the absence of a binder [20]. In general, a gap-filling material in the form of a solid sheet may be made more effective by coating both sides of the sheet with a thermal paste. Thixotropic pastes have been used for this purpose. Due to the relatively large thickness of a gap-filling material, high thermal conductivity is a more important attribute for a gap-filling material than for a material for filling valleys in surfaces that are in contact.

This paper is aimed at the improvement of thermal gap-filling materials by the use of carbon black paste coatings [12–14] in both fluidic and thixotropic forms. The fluidic form uses polyethylene glycol as the vehicle, whereas the thixotropic form uses polyol esters as the vehicle. Both pastes have been shown to be highly effective for filling the valleys in surfaces (especially surfaces that are quite smooth) that are in contact [12–14]. The high effectiveness of carbon black pastes stems from the high compressibility (hence conformability) of carbon black, which is in the form of porous agglomerates consisting of particles of size 30 nm [12,13].

As shown in this work, the use of carbon black paste (particularly the fluidic type) to coat a thermal gap-filling sheet results in a composite material that exhibits high conformability (due to the carbon black paste) as well as the ability to provide a substantial thickness and to maintain the geometry associated with the gap. In particular, this paper addresses the use of carbon black paste to coat flexible graphite, aluminum foil and copper foil for thermal gap filling. Flexible graphite is attractive for its resiliency in the direction perpendicular to the sheet, whereas metal foils are attractive for their high thermal conductivity.

The mating surfaces used in this study for measurement of the thermal contact conductance are copper, due to the common use of copper for heat sinks. Furthermore, this study includes comparison of copper surfaces that are of different degrees of roughness, because different degrees of roughness are encountered in practice and both conformability and thickness of the paste in valleys depend on the roughness.

The objectives of this work are (i) to evaluate the effectiveness of carbon black pastes as coatings for improving thermal gap-filling materials, (ii) to compare the effectiveness of carbon black paste coatings in fluidic and thixotropic forms, (iii) to compare the effectiveness of carbon black paste coatings on various supporting sheets, including flexible graphite, aluminum foils and copper foils of various thicknesses, (iv) to compare the effectiveness of carbon black paste coatings for mating surfaces of different degrees of roughness, and (v) to provide a comparative study that includes commercial gap-filling materials.

2. Experimental methods

The formulation, ingredients, preparation method and testing method of the carbon black thermal paste of this work are identical to those in the prior work of these authors [12–14]. The carbon black was Vulcan XC72R GP-3820 from Cabot Corp., Billerica, MA. It was a powder with particle size 30 nm, a nitrogen specific surface area 254 m²/g, maximum ash content 0.2%, volatile content 1.07%, and density 1.7–1.9 g/cm³. The carbon black powder was mixed with a vehicle by hand stirring to form a uniform paste. The particle size (30 nm) of the carbon black is much less than those of the metal or ceramic particles used in commercial thermal pastes.

Polyethylene glycol (PEG, or HO(CH₂CH₂O)ₙH) was used as the organic vehicle for the fluidic type of thermal paste. It was PEG 400 from EM Science (Gibbstown, NJ). It had an average molecular weight of 400 amu; this average value corresponds to n ~ 8.68. It was a liquid at room temperature and contained ethyl cellulose (E8003, Sigma Chemical Co., St. Louis, MO) at 3 vol.%. The ethyl cellulose was a white powder that was dissolved in the vehicle. It served to improve the dispersion and suspension of the solids in the paste.

The vehicle used for the thixotropic type of thermal paste consists of polyol esters, which are attractive for their thixotropic behavior and ability to resist elevated temperatures. The polyol esters in the vehicle are pentaerythritol ester of linear and branched fatty acids and dipentaerythritol ester of linear and branched fatty acids. The polyol ester mixture is provided by Hato Corp., Fords, NJ. The specific gravity is 0.97.

The fluidic thermal paste was prepared by first dissolving ethyl cellulose (3 vol.%) in the vehicle PEG. The solution was performed at about 60 °C (with heat provided by a hot plate). The heating was applied to hasten the dissolution of ethyl cellulose. After this, carbon black (1.25 vol.%) was added. Mixing was conducted by using a ball mill and stainless steel balls for 30 min. After mixing, the paste was placed in a vacuum chamber (which involved a mechanical vacuum pump) without heating for the purpose of air bubble removal.

The thixotropic paste contained 2.4 vol.% carbon black. It was prepared by manual stirring of a mixture of carbon black and vehicle.

Conventional thermal gap-filling materials in the form of thin sheets were cut to size 1 × 1 in. (25 × 25 mm) in the plane of the sheet. Then the thermal paste was applied manually on both 1 × 1 in. (25 × 25 mm) surfaces of a gap-filling sheet, such that the thickness of the paste on either side was 25 μm or less. The conventional thermal gap-filling materials used were flexible graphite, copper foil (thickness = either 13 or 130 μm) and aluminum foil.
The flexible graphite was of thickness 130 μm, specific surface area 15 m²/g (as determined by nitrogen adsorption), ash content <5.0%, density 1.1 g/cm³, tensile strength in the plane of the sheet 5.2 MPa, compressive strength (10% reduction) perpendicular to the sheet 3.9 MPa, thermal conductivity at 1093 °C 43 W/m K in the plane of the sheet and 3 W/m K perpendicular to the sheet, and coefficient of thermal expansion (CTE) (21–1093 °C) – 0.4 × 10⁻⁶/°C in the plane of the sheet.

Various thermal gap-filling materials with and without thermal paste coating were sandwiched between the 1 × 1 in. (25 × 25 mm) surfaces of two copper blocks (both 1 × 1 in. surfaces of each block having a controlled degree of roughness). Each copper block had a height of 35 mm.

The thermal contact conductance between two 1 × 1 in. (25 × 25 mm) copper blocks with a thermal gap-filling material between them was measured using the guarded hot plate method, which is a steady-state method of heat flux measurement (ASTM Method D5470). The heat in this test was provided by a 3 × 3 in. (76 × 76 mm) copper block that had two embedded heating coils (top block in Fig. 1).

During the period of temperature rise, the heating rate was controlled at 3.2 °C/min by using a temperature controller. This copper block was in contact with one of the 1 × 1 in. copper blocks that sandwiched the thermal gap-filling material. The cooling in this test was provided by a second 3 × 3 in. copper block, which was cooled by running water that flowed into and out of the block (bottom block in Fig. 1). This block was in contact with the other of the two 1 × 1 in. copper blocks that sandwiched the thermal gap-filling material. The two mating surfaces of the two 1 × 1 in. copper blocks were either “rough” (15 μm roughness, as attained by mechanical polishing) or “smooth” (0.009 μm roughness and 0.040–0.116 μm flatness, as attained by diamond turning). Four thermocouples (Type T) were inserted in four holes (T₁, T₂, T₃ and T₄ in Fig. 1, each hole of diameter 2.4 mm). Two of the four holes were in each of the 1 × 1 in. copper blocks. The temperature gradient was determined from T₁ – T₂ and T₃ – T₄. These two quantities should be equal at equilibrium, which was attained after holding the temperature of the heater at the desired value for 30 min. Equilibrium was assumed when the temperature variation was within

![Fig. 1. Experimental set-up for the guarded hot plate method of thermal contact conductance measurement. T₁, T₂, T₃ and T₄ are holes of diameter 2.4 mm. A thermocouple (Type T) is inserted in each hole. All dimensions are in mm.](image-url)
±0.1 °C in a period of 15 min. At equilibrium, the temperature of the hot block was in the range 75–80 °C, that of the cold block was in the range 10–15 °C, while that of the thermal interface material was in the range 40–50 °C. The pressure in the direction perpendicular to the plane of the thermal interface was controlled by using a hydraulic press at pressures of 0.46, 0.69 and 0.92 MPa. The system was thermally insulated by wrapping laterally all the copper blocks with glass fiber cloth.

In accordance with ASTM Method D5470, the heat flow \( Q \) is given by

\[
Q = \frac{\dot{A}}{\partial A} \Delta T,
\]

where \( \Delta T = T_1 - T_2 = T_3 - T_4 \), \( \dot{A} \) is the thermal conductivity of copper, \( A \) is the area of the \( 1 \times 1 \) in. copper block, and \( d_A \) is the distance between thermocouples \( T_1 \) and \( T_2 \) (i.e., 25 mm).

The temperature at the top surface of the thermal interface material is \( T_A \), which is given by

\[
T_A = T_2 - \frac{d_B}{d_A} (T_1 - T_2),
\]

where \( d_B \) is the distance between thermocouple \( T_2 \) and the top surface of the thermal interface material (i.e., 5 mm). The temperature at the bottom surface of the thermal interface material is \( T_D \), which is given by

\[
T_D = T_3 + \frac{d_D}{d_C} (T_3 - T_4),
\]

where \( d_D \) is the distance between thermocouple \( T_3 \) and the bottom surface of the thermal interface material (i.e., 5 mm) and \( d_C \) is the distance between thermocouples \( T_3 \) and \( T_4 \) (i.e., 25 mm).

The thermal impedance \( \theta \) is given by

\[
\theta = (T_A - T_D) A \frac{1}{Q}.
\]

Note that insertion of Eq. (1) into Eq. (4) causes cancellation of the term \( A \), so that \( \theta \) is independent of \( A \). The thermal contact conductance is the reciprocal of \( \theta \).

Previous work by Leong and Chung on carbon black thermal pastes used the laser flash method (a transient method) for thermal contact conductance measurement [10,11]. The guarded hot plate method used in this paper gives results that are consistent with those given by the laser flash method, as shown by testing the same interface material and the same mating surfaces using the two methods.

The gap-filling materials tested in this work are listed in Table 1, where \( A \) is the flexible graphite of thickness 130 \( \mu \)m, \( B \) is copper foil (110 annealed) of thickness 13 \( \mu \)m, \( C \) is aluminum foil (1145) of thickness 7 \( \mu \)m, \( D \) is aluminum foil (1100) of thickness 130 \( \mu \)m, \( E \) is copper foil (110 annealed) of thickness 130 \( \mu \)m, \( F \) is Dow Corning heat path (silicone supported by a porous fiberglass sheet, TP 1070-B001-0250-0020) of thickness 200 \( \mu \)m, \( G \) is Chomerics Therm-A-Gap G580 (silicone filled with ceramic (mainly Al2O3) particles and supported by a porous fiberglass sheet) of thickness 510 \( \mu \)m, \( H \) is Chomerics Therm-A-Gap A580 (silicone filled with ceramic (mainly Al2O3) particles and supported by an aluminum sheet of thickness 76 \( \mu \)m; total thickness 510 \( \mu \)m) and \( I \) is Thermagon T-pli 210 (silicone pad filled with boron nitride particles, without a supporting sheet; thickness 250 \( \mu \)m). The thicknesses of

<table>
<thead>
<tr>
<th>Gap-filling material</th>
<th>Rough (MPa)</th>
<th>Smooth (MPa)</th>
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<tbody>
<tr>
<td></td>
<td>0.46</td>
<td>0.69</td>
</tr>
<tr>
<td>A (uncoated)</td>
<td>1.40 ± 0.09</td>
<td>1.72 ± 0.12</td>
</tr>
<tr>
<td>A (coated 1)</td>
<td>2.93 ± 0.09</td>
<td>3.16 ± 0.20</td>
</tr>
<tr>
<td>A (coated 2)</td>
<td>2.34 ± 0.16</td>
<td>2.60 ± 0.19</td>
</tr>
<tr>
<td>A (coated 3)</td>
<td>1.74 ± 0.15</td>
<td>1.88 ± 0.15</td>
</tr>
<tr>
<td>B (uncoated)</td>
<td>0.78 ± 0.05</td>
<td>0.96 ± 0.07</td>
</tr>
<tr>
<td>B (coated 1)</td>
<td>3.47 ± 0.17</td>
<td>3.73 ± 0.21</td>
</tr>
<tr>
<td>C (uncoated)</td>
<td>1.32 ± 0.06</td>
<td>1.81 ± 0.14</td>
</tr>
<tr>
<td>C (coated 1)</td>
<td>3.67 ± 0.31</td>
<td>4.52 ± 0.39</td>
</tr>
<tr>
<td>C (coated 2)</td>
<td>3.54 ± 0.30</td>
<td>3.85 ± 0.31</td>
</tr>
<tr>
<td>C (coated 3)</td>
<td>2.46 ± 0.18</td>
<td>2.92 ± 0.27</td>
</tr>
<tr>
<td>D (uncoated)</td>
<td>0.99 ± 0.07</td>
<td>1.34 ± 0.08</td>
</tr>
<tr>
<td>D (coated 1)</td>
<td>2.64 ± 0.19</td>
<td>3.09 ± 0.21</td>
</tr>
<tr>
<td>E (uncoated)</td>
<td>0.75 ± 0.06</td>
<td>0.93 ± 0.08</td>
</tr>
<tr>
<td>E (coated 1)</td>
<td>2.59 ± 0.23</td>
<td>2.94 ± 0.26</td>
</tr>
<tr>
<td>F (uncoated)</td>
<td>0.42 ± 0.02</td>
<td>0.44 ± 0.02</td>
</tr>
<tr>
<td>G (uncoated)</td>
<td>0.37 ± 0.02</td>
<td>0.40 ± 0.03</td>
</tr>
<tr>
<td>H (uncoated)</td>
<td>0.33 ± 0.02</td>
<td>0.35 ± 0.02</td>
</tr>
<tr>
<td>I (uncoated)</td>
<td>0.99 ± 0.04</td>
<td>1.09 ± 0.03</td>
</tr>
</tbody>
</table>

Note: \( A \) = flexible graphite (130 \( \mu \)m thick); \( B \) = copper foil (13 \( \mu \)m thick); \( C \) = aluminum foil (7 \( \mu \)m thick); \( D \) = aluminum foil (130 \( \mu \)m thick); \( E \) = copper foil (130 \( \mu \)m thick); \( F \) = Dow Corning heat path (200 \( \mu \)m thick); \( G \) = Chomerics Therm-A-Gap G580 (510 \( \mu \)m thick); \( H \) = Chomerics Therm-A-Gap A580 (510 \( \mu \)m thick); \( I \) = Thermagon T-pli 210 (250 \( \mu \)m thick); Coating 1 = fluidic carbon black paste; Coating 2 = thixotropic carbon black paste; Coating 3 = Arctic Silver 5 paste.
the various materials were chosen based on commercial availability. In addition, commercial gap-filling materials in the form of pastes were evaluated; they are Arctic Silver 5 (silver particle filled oils from Arctic Silver Inc., Visalia, CA) and Shin-Etsu X-23-7762 (aluminum particle filled silicone from Shin-Etsu MicroSi, Inc., Phoenix, AZ). All the copper and aluminum foils (not those in the commercial gap-filling materials) were obtained from All-foils, Inc., Brooklyn Heights, OH.

The coating labeled 1 was the carbon black thermal paste in fluidic form (based on polyethylene glycol, with 3 vol.% dissolved ethyl cellulose and 1.25 vol.% carbon black). The coating labeled 2 was the carbon black thermal paste in thixotropic form (based on polyol esters, with 2.4 vol.% carbon black). The coating labeled 3 was the Arctic Silver 5 thermal paste. All coatings were of thickness 25 µm or less. The cost is similar for coatings 1 and 2, but is much higher for coating 3. This is due to the high cost of silver compared to carbon black. Furthermore, the volume fraction of silver in coating 3 is much higher than the volume fraction of carbon black in coating 1 or 2.

Each type of gap-filling material was tested for at least three times. Each time involved measurement at these pressures (0.46, 0.69 and 0.92 MPa) that were in increasing order.

3. Results and discussion

Table 1 shows that, whether for rough or smooth surfaces, all without coating, flexible graphite (130 µm thick, without coating) is superior to thinner copper foil (13 µm thick, without coating) and is as effective as thinner aluminum foil (7 µm thick, without coating). This is due to the conformability of flexible graphite.

Whether for A, B, C, D or E, the coating enhances the effectiveness substantially. The enhancement is more dramatic for the smooth surfaces than the rough surfaces, though it is significant for both. The enhancement is due to the increased conformability provided by the coating, as the thermal conductivity of the carbon black coating is less than that of copper or aluminum.

Coating 1 is more effective than coating 2, which is in turn more effective than coating 3, as shown for both A and C. For both rough and smooth surfaces, coating 1 is more effective than coating 2. This is due to the superior conformability of coating 1 compared to coating 2 [14]. The superiority of coating 1 over coating 2 is more dramatic for smooth surfaces than rough surfaces. Both coatings 1 and 2 are much more effective than coating 3. This is due to the inferior conformability of coating 3, which is considerably higher in viscosity than coating 1 or 2.

Of all the materials tested, C (coated 1) is most effective, whether the surfaces are rough or smooth, due to the combination of small thickness (provided by the thin aluminum foil) and the high conformability (provided by coating 1).

Comparison of C (uncoated) and D (uncoated) and comparison of B (uncoated) and E (uncoated) show that a smaller thickness is associated with higher effectiveness, as expected due to the thermal resistance within the foil along its thickness.

Among A, D and E (all uncoated, all the same thickness), A gives the highest conductance and E gives the lowest conductance. Among A, D and E (all coated with coating 1), A gives the highest conductance, while D and E are similar. E (uncoated) is less effective than D (uncoated), in spite of the high thermal conductivity of copper (E) compared to aluminum (D) and the equal thickness of these two foils. This means that a high thermal conductivity within the gap-filling material does not necessarily result in a more effective gap-filling material. In contrast, in the presence of coating 1, D and E are similar, indicating the significant effect of the coating.

The commercial gap-filling materials F, G and H are the least effective of all the materials studied, in spite of their resiliency (which is due to the silicone). This is attributed partly to the thickness, which is larger than those of all the materials fabricated in this work. It is probably also due to the poor conformability of silicone. The commercial material I is superior to B (uncoated), E (uncoated), F, G and H. However, material I is inferior to most of the materials fabricated in this work.

For any of the materials studied, the use of smooth mating surfaces in place of rough ones increases the thermal contact conductance. This is consistent with previous results [12] and is due to the relatively small size of air pockets for the case of smooth surfaces. However, the case of rough surfaces is closer to the situation in microelectronics.

4. Conclusion

Carbon black pastes in fluidic and thixotropic forms, as obtained by dispersing carbon black in polyethylene glycol and polyol esters respectively, were found to be effective as coatings for improving the performance of thermal gap-filling materials, including flexible graphite, aluminum and copper. By coating flexible graphite (130 µm thick) on both sides (25 µm or less in coating thickness) the thermal contact conductance across copper mating surfaces was increased by up to 110%, 70% and 20% for coatings in the form of fluidic carbon black paste, thixotropic carbon black paste and commercial silver paste respectively. By similar coating of aluminum foil (7 µm thick), the conductance was increased by 180%, 170% and 90% respectively.

The improvement caused by a coating is due to the enhanced conformability. The fluidic form of carbon black paste is more effective than the thixotropic form. A commercial silver paste (Arctic Silver 5) is much less effective than either form of carbon black paste.

With the coating, aluminum foil (7 µm thick) is more effective than flexible graphite (130 µm thick). Without the coating, flexible graphite is more effective than aluminum or copper foils. Flexible graphite (130 µm thick) and aluminum (7 µm thick), whether coated or not, are more effective than commercial silicone-based gap-filling materials.
For a gap thickness of less than 100 µm, aluminum and copper foils (both coated with a carbon black paste) are recommended, such that the coated aluminum foil is most recommended. For a gap thickness of more than 100 µm, flexible graphite (coated with a carbon black paste) is recommended.

References