Thermal Conductivity Enhancement of Soft Polymer Composites through Magnetically Induced Percolation and Particle–Particle Contact Engineering

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Despite major advancements in the performance of thermal interface materials (TIMs), contact resistance between components persists as a major thermal bottleneck in electronics packaging. In this work, the thermal performance of composite TIMs is enhanced through a synergistic coupling of magnetic alignment and engineered particle coatings that reduce the thermal resistance between particles. By itself, magnetically induced percolation of nickel particles within a cross-linked silicone matrix doubles the thermal conductivity of the composite. This process significantly increases contact between particles, making the interfacial particle–particle resistance a major contributor to the composites thermal performance. The resistance at these interfaces can be reduced by introducing soft metal (silver) or liquid metal coatings onto the nickel particles. Compressing powder beds of these hybrid particles reveals that, dependent on coating thickness, the contact engineering approach provides multifold increases in thermal conductivity at mild pressures. When dispersed in a polymer matrix and magnetically aligned, the coated particles provide a threefold increase in composite thermal conductivity, as compared to unaligned samples (up to nearly 6 W m\(^{-1}\) K\(^{-1}\) with volumetric fill fraction of 0.5). For equivalent coating thicknesses, silver coatings achieve better performance than liquid metal coatings.

1. Introduction

Thermal interface materials (TIMs) significantly enhance the heat removal from integrated circuits (ICs) by filling in the air gaps that result from geometrical imperfections at mating component surfaces. This greatly reduces the thermal contact resistance (\(R_c\)) between electronic components and enables better heat transfer.\(^{[1,2]}\) TIMs are typically composites that consist of a base material in which thermally conductive particles are added. The base material is generally a cross-linked polymer matrix (i.e., a TIM “pad”) or grease. The resulting composite thermal conductivity (\(k_c\)) of the TIM is typically up to an order of magnitude higher than the base material (e.g., up to 2 W m\(^{-1}\) K\(^{-1}\) vs 0.2 W m\(^{-1}\) K\(^{-1}\)). However, as transistor density has increased over the last decade, TIMs persist as a major thermal bottleneck in the thermal management of modern ICs.\(^{[3,4]}\) Consequently, considerable research effort is dedicated to improving thermal performance of TIMs.

The thermal conductivity of TIM composites is traditionally improved by increasing the particle thermal conductivity (\(k_p\)) and the overall particle volumetric fraction (\(\phi\)).\(^{[5-8]}\) The most significant improvements to \(k_c\) are achieved by increasing \(\phi\) to well above the percolation threshold (\(\phi_p\), typically around \(\phi_p = 0.3\) for spheroidal particles).\(^{[9-11]}\) Unfortunately, increasing the particle volume fraction to \(\phi \geq 0.5\) in TIM pads, where significant \(k_c\) enhancements are made, also stiffens the composite.\(^{[12]}\) This produces undesirable effects for microelectronics packaging applications, including increasing \(R_c\) at the surface of the TIM.\(^{[2]}\) Recent advances have shown that using liquid metal inclusions in a polymer matrix can prevent composite stiffening, however, very high \(\phi\) along with additional processing that elongates the inclusions is required to achieve notable thermal conductivity.\(^{[12-15]}\)

Percolation can be enforced at \(\phi \ll \phi_p\) by imposing a magnetic field on an uncured polymer composite with magnetically permeable fill particles. This simple and cost-effective process creates composites with highly anisotropic electrical and thermal conductivities that are significantly enhanced along the direction in which the particles are aligned.\(^{[15-20]}\) For example, magnetically aligning spherical nickel particles in a polymer matrix provides a twofold improvement for \(k_c\) in the direction of particle alignment.\(^{[22-28]}\) Furthermore, aligning particles with higher aspect ratios provides an even higher enhancement to \(k_c\)—up to three- and fourfold for particles with aspect ratios between 7 and 20.\(^{[24-27]}\)

The direct contact between particles in these percolating networks decreases the interfacial thermal boundary resistance...
2. Results and Discussion

2.1. Microscale Structure of Soft Composites with Magnetically Aligned Nickel Particles

Alignment of nickel and nickel-core particles is achieved by placing magnets on the top and bottom of a TIM mold prior to curing the polymer matrix. This results in a magnetic field across the TIM pad, producing forces that align the filler particles into columns. The induced dipole moment in the particles creates an inter-particle attraction that causes them to aggregate together as shown in the schematic in Figure 1a and as described by Borbatch et al. Liquid metal can also lower R_{pp} by “soldering” particles together and improving the contact at the particle–particle interfaces.

In this work, we aim to significantly enhance the thermal performance of composite TIM pads with \( \phi \leq 0.5 \) through the synergistic coupling of magnetically induced percolation and reduction of \( R_{pp} \) with particle–particle contact engineering. To enable the combination of these two approaches, we use nickel particles with two types of coatings: silver and liquid metal. To provide insight into the performance of these coatings, we first study the thermal resistance of bare nickel and coated nickel particle beds during compression. Next, we fabricate polymer matrix composites with a wide range of process parameters and quantify thermal conductivity enhancements that can be achieved through magnetic alignment and particle coating. Through additional characterization, we then relate these enhancements to the percolated structure of the composite and to the individual particle–particle interfaces.

Figure 1. a) Illustration showing how, (I) when a magnetic field is applied, the particles go from (II) a random dispersion in the polymer matrix to (III) being aligned and (IV) forming columnar structures; and b) side view optical microscope images of the aligned (top) and unaligned (bottom) composites with (from left to right) 0.05, 0.15, 0.25, 0.35, and 0.45 volumetric fractions (\( \phi \)) of nickel particles with 350 nm silver shells. Analogous optical microscope images of aligned and unaligned composites with bare Ni particles and liquid metal-coated Ni particles are available in Figures S1 and S2 in the Supporting Information.
2.2. Contact Engineering with Silver Coatings on Nickel Particles

In this section, the soft and nearly oxide-free silver–silver interface characteristics are used to improve thermal transport in particle beds. Nickel particles as well as silver-coated nickel particles (8, 18, and 23 wt% Ag) were acquired from Potters Beads LLC. The base nickel particles on which the silver coatings are deposited are randomly shaped with an aspect ratio near 1 (Figure 2a). The 8, 18, and 23 wt% Ag particles correspond to calculated volume fractions of Ag to Ni, $\chi_{Ag}$, of 0.07, 0.16, and 0.20, each having an average shell thickness of 350, 750, and 850 nm, respectively (Figure 2b–d). We also compare the thermal performance of pure silver (Figure 2e) and pure nickel (Figure 2a) as reference points using particles of similar size to that of the silver-coated nickel particles. Since the shells are relatively thin, the particle size distributions are similar for the uncoated and silver-coated nickel particles with a mean particle size of around 20 µm and a standard deviation of 10 µm (see the Supporting Information for further details).

The silver-coated nickel particles show a significant decrease in thermal resistance compared to the bare nickel particles when compressing loose particle powder beds (1 mm thick) in our stepped-bar apparatus (SBA). The thermal resistance and sample thickness of the particle beds are measured as a function of the applied compressive force. The thickness of the compressed samples is normalized in Figure 2f by their estimated thickness at the estimated first point of contact with the SBA reference bars (this is where compression of the sample—and not just removal of the air above it—begins).

Comparing the three thicknesses of silver coatings on nickel particles to the bare nickel shows a dramatic decrease in thermal resistance, even at pressures as low as 300 kPa (Figure 2g). Specifically, all three silver coatings provide less than a quarter of the thermal resistance of the bare nickel particles at a moderate pressure of 500 kPa. Nevertheless, as the pressure increases up to 1 MPa and beyond, the thicker silver coatings do show even lower resistances, with pure silver particles exhibiting the lowest resistance of all. It is worth noting that, near the maximum pressure tested, the bare nickel bed can only be compressed by about 25%. At this point, it has a thermal resistance lower than the coated particle beds with the same normalized thickness (see Figure 2f). However, the plot in Figure 2g reveals that the pressure required to compress the coated particle beds to this normalized thickness is an order of magnitude lower than the bare nickel particle beds (around 250 kPa) and is well below the 1 MPa maximum for most TIM applications.

To confirm that the decrease in the overall thermal resistance stems from the deformation of the silver coatings, we image the various samples before and after compression. Imaging of the nickel particles after compressing them under more than 2 MPa shows no sign of surface deformations and they remain a loose powder. Conversely, the silver-coated nickel particles press into a cake under only 500 kPa that is easily handled and cross-sectioned without breaking apart (Figure 3a,b). Figure 3c clearly shows that the silver shell deforms under minor pressure, leading to better thermal contact and reduced resistance between particles, as illustrated in Figure 3d,e. This deformation also explains why
coated particle beds can be compressed significantly more than uncoated particle beds under the same applied pressure.

Compression of pure silver particles increases the thermal conductivity of the particle beds by eightfold—as compared to the bare nickel particles. However, pure silver is not affected by an applied magnetic field, preventing sufficient thermal performance in the polymer composite at reduced filler content through magnetically induced percolation. Furthermore, the pure silver particles used in this study are 30 times more expensive than the silver-coated nickel (see Figure S3, Supporting Information). This makes the silver-coated nickel particles a much more cost-effective way to reduce \( R_{th} \) and enhance the thermal conductivity of particle beds. The LM-coated nickel mixtures are pressed between the copper reference bars of the SBA and the thermal properties measured with increasing pressure. Figure 4e,f shows energy-dispersive X-ray spectroscopy (EDS) maps and corresponding Scanning electron microscopy (SEM) images of the mixed LM-coated nickel particles for the volume fractions of LM, \( \chi_{LM} \), of 0.1, 0.2, 0.3, 0.4, and 0.5, before and after the compression experiments (additional EDS images, as well as optical images, are provided in Figures S4 and S5, Supporting Information). The images reveal that as the content of LM increases, so does the number of LM “bridges” that connect the nickel particles together. Ultimately, at \( \chi_{LM} = 0.5 \), the LM almost completely fills in the gaps between nickel particles as the sample is compressed. These LM-bridges thermally connect the nickel particles and significantly enhance the thermal conductivity of the pressed particle powders, as evidenced in Figure 4a,b. The increase in \( \chi_{LM} \) from 0.1 to 0.5 steadily lowers the thermal resistance and at 500 kPa, the resistance of \( \chi_{LM} = 0.5 \) is an order of magnitude lower than bare Ni. Beyond 500 kPa, all samples decrease in \( R_{th} \) at roughly the same rate. The increase in thermal conductivity shows a similar trend with increasing \( \chi_{LM} \), but with a much larger jump between \( \chi_{LM} = 0.4 \) and 0.5. At 2 MPa, \( k \) doubles from 5 to 10 W m\(^{-1}\) K\(^{-1}\) at \( \chi_{LM} = 0.4 \) and 0.5, respectively.

With thick enough LM coatings, high powder bed thermal conductivities can be achieved. However, thin Ag coatings are still more effective. For example, at 2 MPa, \( \chi_{Ag} \) of 0.07 and 0.2 reach 2.5 and 5 W m\(^{-1}\) K\(^{-1}\), respectively, yet it requires \( \chi_{LM} \) of 0.2 and 0.4 to reach similar \( k \) values. This effect most likely stems from the presence of gallium oxide, which naturally forms when LM is exposed to air.\(^{[45]}\) This elastic, few nanometers thin oxide layer is prone to nanoscale and microscale wrinkling.\(^{[46,47]}\) Thus, we postulate that the oxide layer on the LM provides inferior contact between particles relative to the silver coatings. To test this hypothesis, we coat the silver-coated nickel particles with a secondary LM film. The thermal resistance of this powder shows similar thermal properties to the LM-coated nickel – suggesting the superior silver-silver interface is lost under the LM and its oxide shell. In addition to being present at the interfaces, some gallium oxide flakes are also likely to be incorporated into the bulk of the LM during processing, providing another mechanism for the reduction in thermal conductivity.

Both the silver and LM coatings reduce \( R_{th} \) and enhance the thermal conductivity of the nickel particle beds in an air environment. However, for application in TIMs pads, the particle coatings need to be effective in a polymer matrix. In the next section, we explore whether these engineered contacts also produce substantial increases in thermal performance within soft, cross-linked polymer matrices.

### 2.3. Contact Engineering with Liquid Metal Coating of Nickel Particles

In this section, eutectic GaInSn is used as a coating on the nickel particles. The liquid nature of this material facilitates the “gluing” of the nickel particles together and the subsequent decrease of the interfacial thermal boundary resistance between them. This leads to meaningful increases in the thermal conductivity of particle beds. The LM-coated nickel mixtures are pressed between the copper reference bars of the SBA and the thermal properties measured with increasing pressure. Figure 3a,b shows SEM images of the cross-section of the silver-coated nickel powder showing how the silver coating allows the particles to fuse together; d) illustration showing the small interface area between two nickel particles compared to e) the larger interface of the deformed/fused silver–silver interface.

![Figure 3. a) photo of the pressed silver-coated nickel powder; b) SEM image of the pressed silver-coated nickel powder; c) SEM of the cross-section of the silver-coated nickel powder showing how the silver coating allows the particles to fuse together; d) illustration showing the small interface area between two nickel particles compared to e) the larger interface of the deformed/fused silver–silver interface.](Image)

### 2.4. Thermal Conductivity Enhancement of Polymer Composites with Magnetically Aligned Silver- or LM-Coated Nickel Particles

Here, we evaluate the composite thermal conductivity enhancements that can be obtained through the synergistic
effects of magnetically induced percolation and reduction of particle-particle boundary resistance by silver or LM particle coatings. Specifically, particles are incorporated in a soft silicone matrix, cast in the form of a TIM-pad, and cured in an applied magnetic field. Composite cross-sections of magnetically aligned LM-coated nickel particles at $\phi = 0.3$ with $\chi_{LM}$ ranging from 0.1 to 0.5 are presented in Figure 5a. These images demonstrate that the LM coatings remain intact during magnetic alignment and the curing process. As expected, the magnetic alignment enforces percolation and induces contact between many particles, again making the effect of particle coatings (i.e., $R_{pp}$ reduction) more pronounced.

The enhancement of the powder thermal conductivity achieved through silver and LM coating of nickel particles demonstrated in the preceding sections is also evident in the powder dispersed in the polymer matrix. Figure 5c presents the thermal conductivity of the elastomer composites at various $\phi$.

Comparing the thickness of the silver coatings in Figure 5b reveals no significant increase in $k_c$ with increasing silver shell thickness. This is in contrast to the results from the powder bed measurements (compare to Figure 2h) where the thicker silver shells provided further enhancement to thermal performance. In these polymer composites, $\phi$ is only 0.3 whereas in the powder beds it is closer to 0.6—the maximum packing factor for random spheres.[48] Therefore, the number of particles in good contact with one another would be larger in the particle beds. Another important consideration is the difference in applied pressure during thermal transport measurements.
for the polymer composites versus the powder beds. The polymer composites in Figure 5b were only tested up to a pressure of 150 kPa whereas the powder beds were tested up to 2 MPa. Consequently, the Ag-coatings in the powder beds likely experienced much more deformation and fusion than in the polymer composites. Thus, thicker shells provide less benefit in these polymer composites. Testing on the polymer composites was limited to 150 kPa in order to maintain a compressive strain of 5% across all the samples to minimize contact resistance yet prevent negative thermal effects from aligned column buckling.

The effects of the various LM coatings are also evaluated at $\phi = 0.3$ (Figure 5d). Increasing the LM content increases $k_c$ for aligned particles, but not as drastically as in the compressed LM-coated Ni powders (compare to Figure 4b). There are only minor increases in $k_c$ from increasing the thickness of the LM coating (a 5% increase in $k_c$ for every 10% increase in $\chi_{LM}$) until $\chi_{LM} > 0.4$, where it jumps by 50% to near 4 W m$^{-1}$ K$^{-1}$ at $\chi_{LM} = 0.5$. We note that samples with $\chi_{LM} = 0.5$ had a visible decrease in mechanical stability when handling the composites and so we focused the majority of our studies on $\chi_{LM} = 0.4$ (Figure 5c).

We note that in order to obtain these meaningful enhancements in composite thermal conductivity using liquid metal coatings, it is important to combine the liquid metal–nickel particle mixture into the polymer in a particular manner. More specifically, aggressive mixing of the liquid metal–nickel mixture into the polymer results in independent nickel particles and liquid metal inclusions dispersed in the polymer matrix. It is more advantageous to preserve liquid metal–nickel aggregates (i.e., multiple nickel particles in a liquid metal droplet as opposed to single nickel particles in a liquid metal droplet). The LM must connect several nickel particles inside its oxide skin. Otherwise, the polymer matrix will wet the self-passivating Ga oxide[49] that covers the coated particles and no decrease in thermal resistance will be evident between nickel particles. The importance of these material processing characteristics is described in our prior work, in which we used LM-coated copper particles in a three-phase polymer composite and leveraged the unique, rapid alloying of copper and gallium to enhance percolation through the polymer matrix.[29] The use of magnetic alignment allows for achieving percolation at much lower filler volume ratios and significantly increases repeatability of the results. In addition, it is important to note that the aligned composites are electrically conducting under compression at high $\phi$.

The largest enhancement from the magnetic alignment of the particles is at $\phi = 0.4$. Magnetic alignment of the bare nickel particle composites increases $k_c$ by a factor of 1.6 (from 1.3 to 2.1 W m$^{-1}$ K$^{-1}$), while the alignment of the LM- and Ag-coated particle composites increases $k_c$ by a factor of 2.2 and 2.6 (from
1.4 to 3.1 and 3.7 \, \text{W m}^{-1} \, \text{K}^{-1}\), respectively. This means that the LM and Ag coatings themselves increase $k$ by 50% and 75%, respectively, over the aligned bare nickel particle composites at $\phi = 0.4$. These enhancements are of similar or greater magnitude than those previously achieved using other methods that increase conductance between filler particles in a polymer matrix such as bridging Ni particles with carbon nanotubes.\(^{[50,51]}\)

3. Conclusions

Magnetic alignment of nickel particles in a polymer composite enforces percolation of the high $k$ particles through the low $k$ polymer matrix, increasing the thermal conductivity of the composite by around 150%. It also increases the particle-particle interactions, making the thermal boundary resistance at the particle-particle interfaces a dominant thermal resistance. Thus, modifying the particle interfaces to lower $R_{pp}$ has a large impact when particles are magnetically aligned in the composite.

Leveraging the soft, nearly oxide-free silver surfaces as a coating on the nickel particles in a dry powder bed provides a fivefold decrease in thermal resistance with only 500 kPa of applied pressure. Similarly, the fluid nature of GaInSn is leveraged as a coating and bonding agent between nickel particles to cut the thermal resistance of the pressed particle beds in half with $\chi_{\text{LM}} = 0.1$ and a full order of magnitude with $\chi_{\text{LM}} = 0.5$. Both coatings reduce $R_{pp}$ and increase the thermal performance of the nickel particles, but the Ag coatings provide more benefit than LM coatings at an equivalent coating thickness.

Combining these engineered interfaces with magnetic alignment in a polymer composite results in significant enhancements in $k$. Nickel particles with silver shells of only 350 nm show a 175% increase in $k$ over the bare Ni in the aligned polymer composites, achieving 3.7 \, \text{W m}^{-1} \, \text{K}^{-1} at $\phi = 0.4$. Similarly, $\chi_{\text{LM}} = 0.4$ particles show a 150% increase over the aligned Ni composites, achieving 3.1 \, \text{W m}^{-1} \, \text{K}^{-1}. This work provides significant insight into surface engineering and materials processing methodology that lead to improvements in soft, thermally conductive composites. Future work will investigate how to minimize the negative thermal effects of LM oxide–LM oxide interfaces to enable greater enhancements with less LM to bridge the thermal gap between high $k$ fill particles.

4. Experimental Section

Materials: The polymer matrix used in this work for all the composites is Smooth-On EcoFlex 00-20, a soft, platinum cured silicone elastomer with a thermal conductivity of 0.3 ± 0.03 \, \text{W m}^{-1} \, \text{K}^{-1} (95% uncertainty). The nickel particles (Ni325, 325 mesh nickel powder), as well as the silver-coated nickel particles (SN40P08, SN40P18, SN325P25-ALT1), were all purchased from Potters Beads LLC. Size distributions of the nickel and silver-coated nickel particles, measured with Image J from SEM images, are provided in Figure S6 in the Supporting Information. The silver particles (325 mesh, supplier ID 327107-10G) were purchased from Sigma Aldrich. The GaInSn eutectic mixture, Galinstan, was purchased from Rotometals.

Material densities used in this work were 6.44 \, \text{g mL}^{-1} for Galinstan, 10.50 \, \text{g mL}^{-1} for silver, and 8.91 \, \text{g mL}^{-1} for nickel. The densities of the silver-coated nickel were calculated by multiplying the densities of each constituent by the weight percent of that constituent, then adding the two partial densities together. For example, the density of the 8 wt% Ag particles is calculated as

$$
\text{Ag: } 10.5 \, \text{g mL}^{-1} \times 0.08 = 0.84 \, \text{g mL}^{-1}
$$

$$
\text{Ni: } 8.91 \, \text{g mL}^{-1} \times 0.92 = 8.20 \, \text{g mL}^{-1}
$$

$$
9.04 \, \text{g mL}^{-1}
$$

Densities for the 18 and 23 wt% Ag particles are calculated as 9.20 and 9.28 \, \text{g mL}^{-1}, respectively.

Composite Fabrication: The particles were weighed out and mixed into the polymer matrix by hand with a mortar and pestle. For the composites with LM on the solid particles, the LM and solid fill were mixed in the mortar and pestle prior to adding the polymer and stirring the mixture lightly with a stir rod until somewhat homogenous, but without breaking up the LM-solid particle agglomerations. Since the oxidation of the LM has been shown to aid in wetting other metals, we mix the nickel powder with various amounts of LM in an air environment.\(^{[52,53]}\) The uncured composite was vacuum degassed to remove air bubbles prior to pouring into rectangular acrylic molds with dimensions of 1.5 \, \times \, 12.7 \, \times \, 12.7 \, \text{mm}. An acrylic top was placed on the mold and magnets (BY0Y02, 2” \times \, 2” \times \, 1/8”, NdFeB, Grade N42) purchased from K&J Magnetics, Inc. were placed on top and bottom of the acrylic mold for the magneto aligned samples, which positioned the magnets 2.25 mm above and below the center of the sample. Borbath et al.\(^{[41]}\) observed that a maximum column thickness was formed with a magnetic field strength of 110 kA m\(^{-1}\), similar to the magnetic field strength applied in our fabrication procedure. For the unaligned sample, a weight was placed on top of the mold during cure. The composites were cured at room temperature for 3 h.

Microscopy: Optical microscopy was conducted with Zeiss Axio Zoom.V16 with an objective lens of 2.3 \, \times \, 0.57 \, \text{FWD} and 10.6 \, \text{mm} focal length Zeiss PlanNeofluar Z. SEM of the particles were conducted using an Amray 1910 with field emission gun and was conducted at 20 kV and a working distance of between 8 and 12 mm. The cross-sectioning and imaging of the silver-coated nickel particles were done using a focused ion beam (FIB) instrument (FEI Nova Nanolab 200 FIB/SEM) using typical procedure.\(^{[44]}\)

Thermal Measurements: Thermal resistances ($R_{th}$) were measured in line with the aligned particles using an SBA.\(^{[42,43]}\) A linear encoder installed on the SBA measured the distance between the copper reference bars, thus providing a good estimate of the compressed sample thickness ($t_{c}$). A load cell integrated with the SBA provided concurrent load measurements. Thermal conductivity was calculated as

$$
k = \frac{t_c}{R_{th}}
$$

where $t_{c}$ is in meters and $R_{th}$ is in m\(^2\) \, \text{K} \, \text{W}^{-1}. The average sample temperature during thermal measurements was 55 °C. A thin layer of Galinstan was applied on top and bottom of the samples to minimize contact resistance at the sample-reference bar interface. The copper reference bars are not affected by gallium within the short timeframe of the measurements.\(^{[18]}\)

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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