

IBM Research Report

Drainage-Induced Structural Degradation of Thermal Greases

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I. Introduction

In flip-chip microelectronics packages, heat removal from the backside of the chip is important for device thermal management. This is commonly achieved by applying a thermal interface material between the chip and heat dissipating component, which can be a heat spreader or heat sink. [In packages that contain both a heat spreader and heat sink, a thermal interface material is applied at the two interfaces, i.e. between the chip and spreader and between the spreader and sink.] The thermal interface material (TIM) must be able to conform to the topography of the mating surfaces thereby filling in localized interstitial spaces between their asperity contacts to reduce the thermal contact resistance. Consequently, fluidity is an important characteristic of any TIM. TIMs must also easily deform to accommodate mechanical stresses that arise from thermal expansion mismatches between various materials in the package. Thermal greases are designed with these characteristics in mind and are used in many high-performance microelectronics packages.

Thermal greases are highly-filled composite systems consisting of solid fillers of high thermal conductivity (typically metal, metal-oxide, or carbon) dispersed in an organic matrix. This matrix is typically of silicone, olefin, or glycol chemistry. The matrix viscosity must be carefully chosen to achieve filler lubrication such that the fillers can slip past each other during flow while yielding a reasonable paste viscosity to ease processing at high filler loadings. Filler geometry is commonly spherical, but mixing of spherical fillers with flakes has been found to increase both the thermal conductivity and viscosity of greases, the latter being less desirable [1].

Within a package lifetime, an extensive amount of thermal and mechanical stresses are imparted to the grease. These stresses arise from repeated heating and cooling of the package during chip operation and downtime. It is important that the grease remains structurally intact throughout the lifetime of the package, though it is well known that most greases exhibit some form of structural degradation during this period. Reliability assessment tests are therefore conducted to probe grease performance over long cyclic stressing periods and to correlate poor performance results with grease structural degradation. Universally, air inclusions are the main cause of grease performance failure due to the substantial increase in the thermal resistance of the interface when air is present [2, 3]. Some mechanisms of air inclusion in the thermal grease are well understood [3, 4] and processing and assembly methods are adjusted to eliminate these mechanisms, e.g. vacuum processing to eliminate entrapped air from mixing and preform manufacture to eliminate the possibility of entrapped air from inadequate grease application [5].

Other mechanisms by which air becomes present in the grease are less understood such as air dendrites that are observed in thermal greases stressed over extended time periods. This grease failure mode occasionally referred to as “erosion” [2] or “river patterned” [4] due to its resemblance to river networks is a common failure mode that

impacts both the mechanical and thermal integrity of the grease, but its mechanism is yet to be elucidated. In this study, we investigate the mechanism by which dendritic air inclusions evolve in thermal greases by monitoring the grease microscopically during cyclic thermal stressing. The evolution of the dendritic air inclusions is further evaluated using theories describing fluid flow through porous media.

II. Experimental Methodology

Several thermal greases were subjected to cyclic thermal stress with the chip junction temperature cycling between ambient (1 hour) and 55-75 deg C (1 or 2 hours) for 30 cycles. The set-up for the experiment is shown in Figure 1. The grease is compressed to a 2-3 mil (50 – 75 microns) bondline between a copper heat spreader and a circular sapphire window. The copper heat spreader is attached to a 3M flexible heater circuit using a high conductivity silver epoxy and the circuit is adhered to a Macor® glass ceramic substrate. The use of sapphire for the optical window enables both visible and IR transmission for combined optical microscopy and IR thermography studies.

The module is designed to closely simulate thermal expansions seen in a real package, but there are some notable differences. The thermal expansion coefficient of sapphire is about 2-3 times that of silicon (8.4 ppm/K vs. 3.6 ppm/K [6]). However, since the thermal expansion coefficient of the copper spreader is much larger (16 - 17 ppm/K) [7], this difference is approximated as negligible. Additionally, the sapphire window is circular which is contrary to the rectangular geometries of the TIM interfacing materials in the package. However, the results obtained with this module have been found to be comparable to those obtained using an apparatus that more closely mimics an actual flip chip package [2].

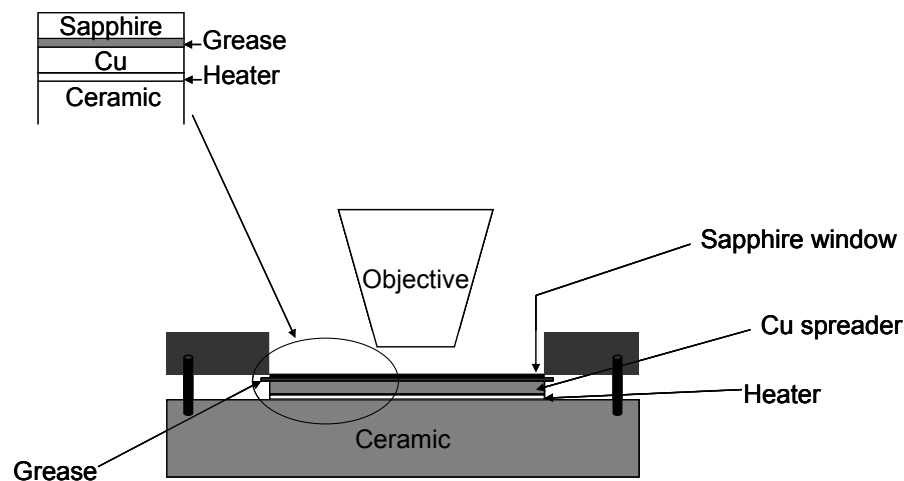


Figure 1. Schematic of optical microscopy module used for grease structural evolution studies.

Microscopic changes in the grease with thermal cycling were monitored in-situ using an optical microscope. 50x optical images and movies were captured using a Moticom 1000 Camera and Moticom Image Software. On occasion, the finer structures were correlated with larger macroscopic images of overall grease evolution (9 cm² area) captured via IR thermography with a FLIR infrared camera.

The thermal greases investigated will be referred to using generic names, but their relative properties are listed in Table 1. The distribution of the pore size, i.e. the interstitial space between filler particles, of the greases was not quantitatively determined as it is complex to determine for pre-formulated samples. However, a qualitative average pore size comparison (in order of smallest to large) is given based on information on the grease such as viscosity and particle size distribution. All greases studied contained approximately spherical solid fillers. A measure of the matrix-filler interaction, $\gamma_{sv} - \gamma_{sl}$, where γ_{sv} is the solid-vapor surface tension and γ_{sl} is the solid-liquid surface tension is given in column 4 as determined from matrix-filler contact angle measurements and matrix surface tension data (conducted by Augustine Scientific, OH).

Generic Name	Matrix Chemistry	Relative Pore Size	$(\gamma_{sv} - \gamma_{sl})^1$
TG1	Olefin	Medium	25.39
TG2	Silicone	Medium/Large	18.42*
TG3	Alkyene glycol	Medium/Large	27.25
TG4	Olefin	Small	25.39

¹ Values were determined from liquid-vapor interfacial tension data and contact angle data measured on fillers used in the thermal greases

* Value is a crude estimate based on interfacial tension data of a common silicone oil and wetting data with metal oxide filler and does not account for the effect of dispersant/surfactants in the sample.

III. Results and Discussion

A. Mechanism of Air Channel Formation

Rapid development of air dendrites was observed to occur in an aged batch of TG1. To improve the image contrast and to directly track the movement of the fluid phase, an olefin-soluble dye (Oil Red O) was incorporated into several batches of TG1 via an imprinting method. This imprinting of the grease with the dye was found to not affect the microstructural evolution with thermal stress, as similar structures were observed in batches with and without the dye.

At time 0, i.e. after initial compression of the aged batch of TG1, dark channels are observed in the grease. These channels are for the most part dendritic in structure, with some spanning the width of the grease (up to 2 cm). In the batches of TG1 containing Oil Red O, the dye is present within these dark channels, as shown in Figure 2. This indicates that the matrix, i.e. the olefin oil in this grease, is forming these structures. In future discussion, these structures will be referred to as *drainage networks*.

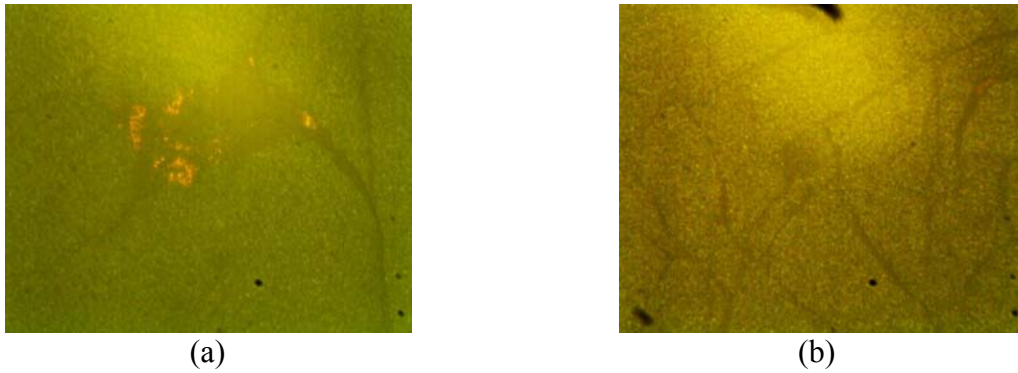


Figure 2. 50x optical images of drainage network formation (dark structures) in an aged batch of TG1 with Oil Red O used to tag the matrix (liquid) phase.

The drainage networks are observed to rapidly proliferate and intersect across the grease with repetitive thermal stressing (see Figure 2b) and, once a channel is in contact with the edge, gradual displacement of the oil by air occurs. Figure 3 shows this process by which air from the edge displaces the oil in the drainage channels during the cooling segment of the thermal cycle. Additionally, residual entrapped air in the grease readily diffuses into these channels during thermal cycling. Figure 3b shows the displacement of oil by both air from the edge (lhs) and air in the bulk of the grease (rhs). Successive displacement of the matrix olefin oil by air occurs during repeated cycling and eventually leads to a dried-out grease that readily cracks under further stress, as observed in many reliability assessment studies.

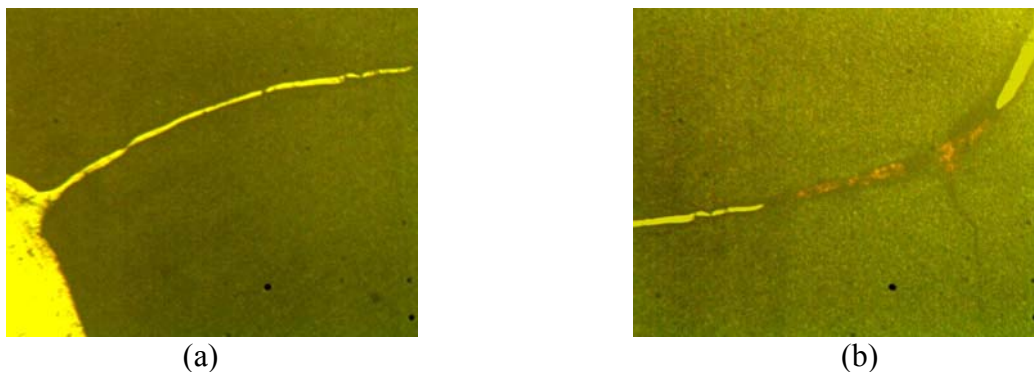


Figure 3. Optical images of air (yellow) displacement of the oil (tagged red) in TG1 during power cycling from the edge (a), but also from the bulk of the grease (b-rhs).

B. Correlation Between Sample Inhomogeneity and Air Channel Formation

Remixing aged batches of TG1 mitigates the formation of the matrix drainage networks and subsequent air dendrite development. The structural degradation of an aged and remixed batch of TG1 are markedly different as can be seen in the IR thermographs shown in Figure 4. While the aged sample contains drainage networks and air dendrites originating from the periphery of the grease, the remixed sample contains few drainage networks and mainly globular air pockets. These globular air inclusions are

expected for a sample that has not been degassed completely, though some of this air may have been introduced into the grease during the hand-mixing process.

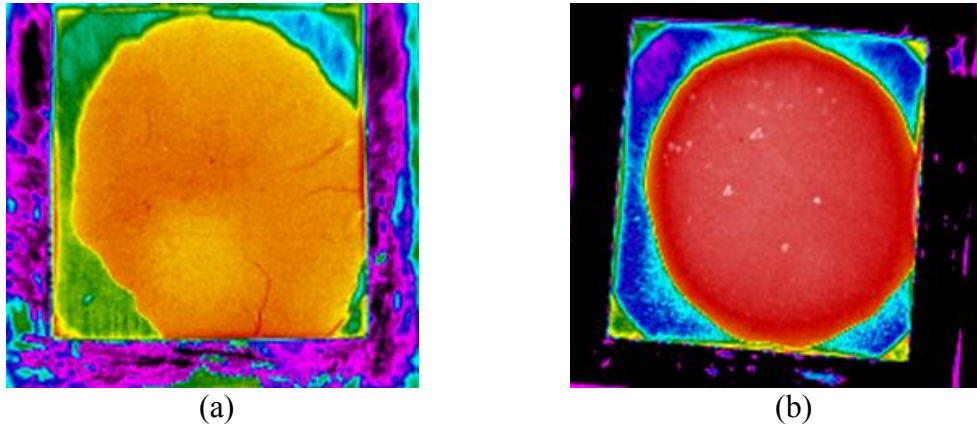


Figure 4. IR thermographs of aged TG1 (a) and hand-remixed TG1 (b) subjected to ~ 20 power cycles.

The existence of air dendrites in the aged batch but not the remixed batch of TG1 can be understood by considering grease evolution and flow as multiphase and not single phase. At any instance in time, the grease can be modeled as a static porous medium with a characteristic pore size distribution that is dependent on the spatial distribution of the inorganic filler particles at that instance.

For the aged batch of TG1, the pore size distribution is likely broader with a larger mean pore diameter due to inhomogeneity in the sample that develops over time. This inhomogeneity can be due to agglomerates present in the sample or segregation of the components in the grease. Figure 5 illustrates in a cartoon format the effect of agglomerates on the pore size distribution for a porous medium composed of nested spherical particles (representative of many thermal greases). The local pore space close to agglomerates is found to be larger as particles cannot pack as efficiently next to the agglomerate. This effect is known as the “*wall effect*” in the cement paste literature [8].

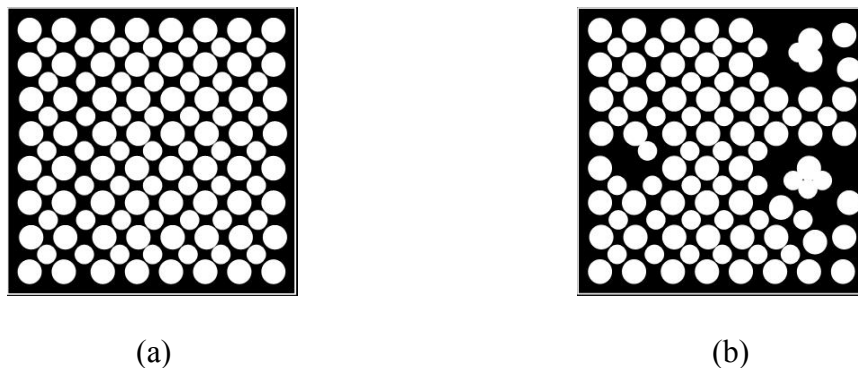


Figure 5. Cartoon of the effect of agglomerates on the pore size distribution (black region) in a porous medium created from the close packing of nested spherical particles (white) for a case of (a) zero agglomerates and (b) a few agglomerates.

When a porous sample is compressed, the local solid volume fraction increases with a concomitant increase in the pressure within the porous spaces [9]. The broad pore size distribution in the aged sample of TG1 leads to gradients in pore pressures within the sample during thermal stressing. When the heater is powered on and the system temperature rises, all the materials in the package expand with an expansion characterized by their thermal coefficient of expansion and dimensions. Considering the grease as a porous medium, compression due to the thermal expansion of the interfacing materials combined with the rising grease temperature results in an increase in the average pore pressure within the grease. The applied pressure drives matrix drainage from high pressure regions to low pressure regions with eventual drainage to the area of lowest pressure which is the periphery of the grease.

When the heater is powered off and the package cools, the system materials contract, increasing the grease confinement gap and creating a negative pore pressure that prompts overall flow of the grease back into the gap with imbibition of the lowest viscosity fluid phase, air, by the pores. Occasionally, some matrix fluid is observed to be imbibed into the porous spaces, but overall successive depletion of the matrix occurs with repetitive cycling. This, we reason, is due to the disparate matrix viscosity in the heating and cooling cycle. During the heating cycle, the matrix viscosity is lowered which eases the drainage process, while during the cooling cycle the matrix viscosity increases which retards re-imbibition. Eventually, air displaces all of the matrix phase in its dendritic drainage channels which leads to the observed air dendrites and subsequent cracking of the dried up grease.

When the sample is re-homogenized through hand-mixing, the gradient in pore pressures is negligible and drainage and air dendrite formation is not observed. This result is also observed in TG4, which is a grease that is similar to TG1 but with decreased agglomerate content as judged by its lower viscosity. It is important to note also that TG4 has a higher solids volume loading and therefore the pore spaces are smaller than in TG1 which would also mitigate drainage.

We have shown the formation of air dendrites in an aged sample that becomes inhomogeneous after long shelf storage due to segregation or aggregation of filler components. However, it is important to note that inhomogeneities may exist in fresh batches of thermal greases depending on their manufacturing process. Sample inhomogeneity may arise from insufficient distributive mixing (mixing with a focus on even spatial distribution of components) and/or dispersive mixing (mixing with a focus on breaking up agglomerates) during grease formulation. Further, inhomogeneities that arise in aged samples may be aggravated by the former condition of imperfect mixing.

An additional variable that is important to understand drainage and displacement processes in porous media is the matrix-filler interaction, and this will be discussed in the next section.

C. Correlation between Matrix-Filler Interaction and Drainage

The mobilization of fluid in a pore is determined by competition between viscous force (force that acts to move the fluid according to pressure gradients in the medium) and capillary force (force that acts to hold the fluid within the pores). When the viscous

force exceeds the capillary force, mobilization of the pore fluid occurs. The capillary force (F_c) is expressed as [10];

$$F_c = \frac{4\gamma_{lv} \cos \theta}{D_a} \quad (1)$$

where γ_{lv} is the interfacial tension between the matrix liquid and the vapor phase (in this case air), θ is the contact angle, and D_a is some average pore diameter. Equation 1 can be rearranged using Young's equation into terms that characterize the solid interfacial tensions with both the matrix (γ_{sl}) and vapor (γ_{sv}) phases:

$$F_c = \frac{4(\gamma_{sv} - \gamma_{sl})}{D_a} \quad (2)$$

It can be deduced from equation (2) that the capillary force increases when $\gamma_{sl} \ll \gamma_{sv}$ or when $(\gamma_{sv} - \gamma_{sl}) \gg 1$, i.e. when the solid-vapor surface tension is larger than the solid-liquid surface tension. Thus, it would be expected that air displacement of the matrix is less significant in greases with larger $(\gamma_{sv} - \gamma_{sl})$, since the larger capillary force acts against mobilization of the matrix fluid. Further, drainage networks should be less likely to form in greases in which the solid-liquid surface tension is low, i.e. favorable interaction exists between the solid and liquid.

To investigate this, greases with different matrix chemistries were studied. Although the pore size distribution is variable among the greases studied and the relative sample homogeneity was not quantified, the study lent some useful insights into the effect of matrix-filler interactions on drainage network formation and propagation.

The most favorable matrix for the metal and metal oxide fillers used in the grease set studied is the alkylene glycol matrix (see Table 1). When the grease containing this fluid (TG3) was subjected to cyclic thermal and mechanical stressing in the optical microscopy module, no drainage networks nor air displacement of the matrix were observed to develop in any of the samples studied. Rather, interfacial air was the significant problem with this grease (Figure 6a) which may be attributed to the high liquid-vapor interfacial tension of the matrix fluid that results in poorer wetting of the fluid at the solid interfaces confining the grease. The expansion of interfacial air was found to be lower in samples containing a lower viscosity alkylene glycol fluid.

Another matrix chemistry studied was silicone. Silicone is used in most commercial thermal greases and adhesives due to its exceptional high temperature stability. The silicone-based grease (TG2) is found to also develop drainage networks with cyclic stresses. However the drainage network structures observed in this grease (see Figure 6b and 6c) are dramatically different than those observed in the olefin-based grease, TG1. The structure of these drainage networks are more akin to dense fractals and despite rapid air displacement of the matrix, the imbibition of the matrix fluid back into the pores is equally rapid. As such, sustained air dendrites were not observed in this sample over the time period studied. The rapid imbibition of the silicone fluid back into the drainage spaces may be due to the very low contact angle of silicone with the filler (most silicone fluids exhibit low contact angles with even unmodified metals and metal oxides) which would ease its imbibition into the porous spaces.

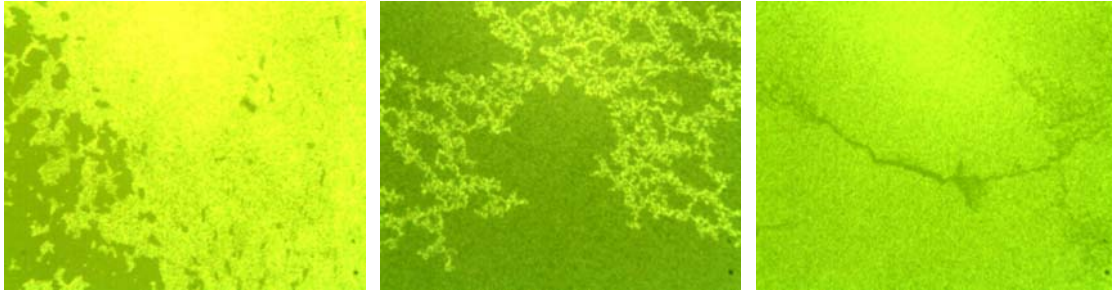


Figure 6. Grease degradation structures observed for greases of different matrix chemistry: (a) interfacial air proliferation (yellow structure) in glycol based grease (green background); (b) air displacement (yellow structure) of silicone drainage networks and (c) imbibition of silicone matrix fluid (dark structure) back into drainage networks in silicone based grease (green background).

III. Conclusions

The mechanism behind a major failure mechanism of thermal greases, air dendrite formation, has been elucidated and shown to originate from drainage networks formed by the matrix phase during cyclic compressive stresses induced by power cycling. The formation of these drainage networks has been correlated with sample inhomogeneity. It has been shown that weak matrix-filler interactions may also drive formation of these networks. Theories pertaining to flow through porous media were used to understand this complex grease degradation mechanism and its correlation with the parameters identified. The use of these theories combined with models on the confined flow of highly concentrated suspensions may aid in thermal grease reliability prediction with overall impact on cost and evaluation time in reliability assessment.

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