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# Thermal Stability of Thermal Interface Pastes, Evaluated by Thermal Contact Conductance Measurement

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*Thermal interface pastes based on silicone, lithium doped polyethylene glycol (PEG), and sodium silicate were evaluated in their performance before and after heating up to 120°C. The thermal contact conductance of any of the pastes between copper disks decreased after heating, such that the fractional decrease was less for the silicone-based paste than the PEG-based and sodium-silicate-based pastes. Nevertheless, the conductance was lower for the silicone-based paste than the other pastes both before and after heating up to 100 cycles.* [DOI: 10.1115/1.1371925]

*Keywords: Thermal Interface, Thermal Contact, Thermal Conductance, Composite, Silicone, Polyethylene Glycol, Sodium Silicate, Boron Nitride*

## Introduction

Thermal contacts are commonly encountered. An example is the thermal contact between a printed circuit board and a heat sink [1,2]. The quality of a thermal contact significantly affects the heat conduction. To improve a thermal contact, a thermal interface paste may be applied at the contact interface. Thermal interface pastes are predominantly based on polymers, particularly silicone [3–6]. They should have a high thermal conductivity (as provided by the use of fillers), in addition to being conformable and thin (i.e., small in thickness after application). As polymers tend to degrade at elevated temperatures, the performance of thermal interface pastes after heating or thermal cycling is of concern.

This paper provides an experimental evaluation of this performance by measuring the thermal contact conductance before and after heating or thermal cycling. The thermal interface pastes included in the comparative study are zinc-oxide-particle-filled silicone, boron-nitride-particle-filled lithium-doped polyethylene glycol (PEG) [7], and boron-nitride-particle-filled sodium silicate [8]. The first two are polymer based. The last one is ceramic based, but the moisture content in the silicate decreases with increasing temperature, thus leading to thermal degradation.

## Experimental Methods

The zinc oxide particle filled silicone used in the comparative study is 340 silicone heat sink compound from Dow Corning Corp., Midland, MI.

The boron-nitride-particle-filled lithium-doped PEG involved PEG, or $HO(CH_2CH_2O)_nH$, a liquid with molecular weight 400 amu, as obtained from EM Science, Gibbstown, NJ (PEG 400). Lithium ($Li^+$) ions were provided by trifluoroacetic acid lithium salt ($CF_3CO_2Li$) from Aldrich Chemical Company, Inc. (Milwaukee, WI). The salt was a solid, which we dissolved in ethanol. N, N-dimethylforamide ($HCON(CH_3)_2$, or DMF) from Aldrich Chemical Company, Inc., and water, were used to help the dissociation of the lithium salt for the purpose of releasing $Li^+$ ions. Hexagonal boron nitride (BN) particles (Polartherm 180 from Advanced Ceramics Corp., Cleveland, OH) were used as a thermally conductive filler. The particle size was 5–11 $\mu$m. The thermal conductivity was 280 W/m.K. The sample preparation method is as described in reference [7]. Four types of BN-particle-filled lithium-doped PEG, labeled $F_2$, $F_1$, $G_3$ and $G_1$ (as defined as reference [7]) were used. $F_2$ and $F_1$ used lithium salt in the amount of 1.5 wt. percent, whereas $G_3$ and $G_1$ used lithium salt in the amount of 3.0 wt. percent. $F_2$ contained 18.0 vol. percent BN, whereas $F_1$ contained 16.0 vol. percent BN. $G_3$ contained 19.5 vol. percent BN, whereas $G_1$ contained 16.0 vol. percent BN.

The BN-filled sodium silicate involved sodium silicate liquid (Siliceous-40) from Occidental Chemical Corp., Dallas, Texas. It consists of water and 38.3 wt. percent $Na_2O \cdot x\ SiO_2$, where x corresponds to a weight ratio of $SiO_2$:$Na_2O$ of 3.22. The specific gravity is 1.40. It is a colorless liquid. The paste containing 16.0 vol. percent BN was prepared by mixing water, sodium silicate liquid, and boron nitride particles in the weight ratio 3.24:1.00:1.63. Mixing was conducted using a ball mill for 4–5 h. A surfactant was added to decrease the surface tension and increase the wettability of the particles with the fluid.

Various thermal pastes were sandwiched between the flat surfaces of two copper disks, which had diameter 12.6 mm and thickness 1.16 mm for one disk and 1.10 mm for the other disk. The thermal contact conductance between two copper disks with and without a thermal interface material was measured using the transient laser flash method [8]. The pressure on the sandwich was controlled at 0.46 MPa. The thickness of the thermal interface material was 0.001 in (25 $\mu$m). The finite element program ABAQUS was used to calculate the thermal contact conductance through temperature versus time curves, which were experimentally obtained. The calculation [8] assumed no thickness and no heat capacity for the interface between the two copper disks. In addition, it assumed no heat transfer between sample and environment except for the absorption of laser energy by the sample. Moreover, it assumed that the laser energy was uniformly absorbed on the surface of the sample, that the heat flow was one-dimensional, and that the thermal contact conductance between the two copper disks was uniform.

A Coherent General Everpulse Model 11 Nd glass laser with a pulse duration of 0.4 ms, a wavelength of 1.06 $\mu$m, and a pulse energy up to 15 J was used for impulse heating. The laser power

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**Table 1 Thermal contact conductance ($10^4 W/m^2 \cdot °C$) for various thermal interface pastes between copper disks at 0.46 MPa contact pressure.**

| | Before heating | After 6 cycles | After 15 cycles | After 100 cycles | After isothermal heating |
|---|---|---|---|---|---|
| Silicone/ZnO | 13.4±0.7 | 13.4±0.7 | 13.1±0.6 | 13.1±0.6 | 13.0±0.5 |
| PEG/BN ($F_2$) | 18.9±0.8 | 18.9±0.8 | 18.0±0.8 | 17.7±0.7 | 12.3±0.6 |
| PEG/BN ($F_1$) | 18.8±0.8 | 18.7±0.8 | 18.2±0.7 | 18.0±0.6 | 13.0±0.7 |
| PEG/BN ($G_3$) | 14.9±0.6 | 14.0±0.6 | 14.0±0.7 | 13.8±0.6 | 11.2±0.5 |
| PEG/BN ($G_1$) | 17.1±0.5 | 16.0±0.5 | 15.5±0.5 | 15.0±0.5 | 9.2±0.4 |
| Sodium silicate/BN | 18.2±0.7 | 18.1±0.7 | 17.7±0.7 | 17.2±0.6 | 10.9±0.8 |

was adjusted to allow the temperature rise of the sample to be between 0.5 and 1.0°C. Both surfaces of each copper disk (diameter 12.6 mm) had been mechanically polished by using 0.05 $\mu$m alumina particles. The upper surface of the disk on which the laser beam directly hit had been electroplated by black nickel in order to increase the extent of laser energy absorption relative to the extent of reflection. An E-type thermocouple (#1) was attached to the back surface of the other disk for monitoring the temperature rise. Another thermocouple of the same type was put ~30 cm above the sample holder to detect the initial time when the laser beam came out. A National Instruments DAQPad-MIO-16XE-50 data acquisition board with a data acquisition rate up to 20,000 data points per second at 16 bites resolution, along with NI-DAQ interface software coded in Visual Basic, was used to monitor the responses of both thermocouples simultaneously. A plexiglass holder was used to facilitate pressure application. Due to the holder, only the central disk area of diameter 8.0 mm was hit by the laser beam. An Omega LCKD-100 load cell was used for pressure measurement. Calibration using a standard graphite sample was performed before testing each sample in order to ensure measurement accuracy. The data acquisition rate used for each test was adjusted so that there were at least 100 temperature data points during the temperature rise.

The experimental error in transient thermal contact conductance measurement consists of random error due to experimental data scatter, and systematic error mainly due to the lag of the thermocouple response and partly due to the method used to calculate the conductance from the temperature data. The higher the thermal contact conductance, the greater is the error. The thermal diffusivity of a standard NBS 8426 graphite disk (thickness = 2.62 mm), which had a similar transient temperature rise time as the copper sandwich with the highest thermal contact conductance, was measured prior to testing each sample in order to determine the systematic error. The measured thermal diffusivity of the graphite was about 7 percent less than the reference value, which corresponds to a time lag of about 0.0006 s. Moreover, a single copper disk (thickness = 2.66 mm) was also tested and a time lag of about 0.0008 s was found upon comparison of the measured thermal diffusivity with the reference value. From multiple measurements of both copper and graphite, the time lag of the thermocouple was found to be about 0.0007 s, which was used to correct for the measured rise time for each sample. The conductance reported in Table 1 for each sample was based on the corrected rise time. The random error shown by the ± value in Table 1 was determined by six or more measurements of each sample.

The thermal interface pastes, while sandwiched between copper disks in the absence of pressure, were subjected to two styles of heating in air, i.e. (i) isothermal heating at 100°C for 24 h and (ii) thermal cycling for 6, 15 or 100 cycles, such that each cycle involved heating from 30 to 120°C at a rate of 10°C/min and immediate cooling back to 30°C at a rate of 10°C/min.

Thermogravimetric analysis (TGA) was conducted in air upon heating from 30 to 130°C at a rate of 10°C/min. The cumulative weight loss at 120°C is reported in this work for various thermal interface pastes.

## Results and Discussion

Table 1 shows the thermal contact conductance before and after heating. Before heating, sodium-silicate-based and PEG-based pastes (except $G_3$) gave significantly higher conductance than the silicone-based paste. All pastes degraded slightly after thermal cycling; the conductance decreased by up to 6 percent after 6 cycles, up to 9 percent after 15 cycles and up to 12 percent after 100 cycles. After isothermal heating, the degradation was much more significant; the conductance decreased by up to 46 percent. For any of the heating conditions, the silicone-based paste degraded the least; the conductance decreased by up to 3 percent. For any of the heating conditions, the PEG-based paste $G_1$ degraded the most; the conductance decreased by up to 46 percent. In spite of the small fractional decrease in conductance for the silicone-based paste, the conductance was lower for the silicone-based paste than the PEG-based and sodium-silicate-based pastes after 100 thermal cycles, and the conductance was similar for the silicone-based paste and the PEG-based pastes $F_1$ and $F_2$ after isothermal heating.

The relatively low conductance given by the silicone-based paste before heating is due to the relatively poor conformability resulting from the relatively high viscosity [7]. The superior thermal stability of the silicone-based paste is due to the superior thermal stability of silicone resulting from the molecular structure.

Among all the pastes studied, the PEG-based pastes $F_1$ and $F_2$ are the most attractive both before and after heating.

The weight loss upon heating to 120°C was 0.02 percent, 1.65 percent, 1.78 percent and 33.4 percent for silicone/ZnO, $F_2$, $F_1$ and sodium silicate/BN, respectively. The low weight loss of silicone/ZnO is consistent with its small fractional decrease in conductance (2.2 percent after 100 cycles of heating). The higher weight losses of $F_2$ and $F_1$ are consistent with their higher fractional decreases in conductance (6.3 percent and 4.3 percent, respectively, after 100 cycles of heating). The high weight loss of sodium silicate/BN is consistent with the high fractional decrease in conductance (7.7 percent after 100 cycles of heating), though the weight loss is much more dramatic than the conductance loss. This means that the dramatic weight loss of sodium silicate (due to water loss) is not as damaging to the conductance as what the dramatic weight loss might suggest. Hence, weight loss measurement is not a very good indication of the performance of thermal interface pastes at elevated temperatures.

## Conclusion

The silicone-based thermal interface paste was more thermally stable than the PEG-based and sodium-silicate-based pastes, but it was inferior in the thermal contact conductance than the others both before heating and after up to 100 cycles of heating from 30 to 120°C. The fractional decrease in conductance after up to 100 cycles of heating was 2 percent for the silicone-based paste and was up to 12 percent for the other pastes.

After isothermal heating at 100°C for 24 h, the fractional decrease in conductance was 2 percent for the silicone-based paste and up to 46 percent for the other pastes. Nevertheless, the conductance was similar between the silicone-based paste and the PEG-based pastes $F_1$ and $F_2$.

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# Effect of Stress Ratio on Fatigue Crack Growth in 95Pb-5Sn Solder

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*The stress ratio effect on the fatigue crack growth behavior of 95Pb-5Sn solder has been investigated. It is found that both* $\Delta J$ *and* $\Delta K$ *can correlate fatigue crack growth data well, which means that the crack growth behavior of the 95Pb-5Sn solder under the frequency of 10 Hz was dominantly cyclic dependent. The* $da/dN$*-*$\Delta J$ *relationship can be expressed as:* $da/dN = 1.1 \times 10^{-11} \cdot \Delta J^{1.45}$. *Low level of crack closure was found only in the near-threshold region. Except in this region, no crack closure was observed in the present test conditions. Both transgranular and intergranular fractures were observed on fracture surfaces: the former was dominant in most test conditions and the latter was dominant at the high stress ratio of 0.7. Striations and striation-like features were also found. Many slip bands and cavities along the grain boundary were observed on the crack wake and ahead of the crack tip in the high crack growth rate region.*
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*Keywords: Solder, Fatigue Crack Growth, Stress Ratio, Cyclic Dependence, Crack Closure*

## 1 Introduction

Alloys based on the Pb-Sn system are widely used as interconnections in the electronic industry. For the sake of reliability and full understanding of solder behavior, considerable efforts have been expended (Plumbridge [1], Lau [2]), many of them focused on isothermal fatigue, especially those of eutectic solder material. Only a limited knowledge of the fatigue crack growth behavior for 63Sn-37Pb has been reported (Logsdon et al. [3], Solomon [4]). Solder alloys of lead-rich compositions, i.e., 95Pb-5Sn, have found common use as joining materials at relatively high temperature and act as an electrical and mechanical contact in the first level of the electronic package (Frear et al. [5], Vaynman [6]).

95Pb-5Sn solder is a two-phase alloy comprised of a lead-rich $\alpha$ phase and a tin-rich $\beta$ phase with low strength (tensile strength of 23 MPa, yield strength of 10 MPa), low hardness (8 HB), low solidus (270°C), and liquidus (312°C) (Cubberly et al. [7]). Frear et al. [5] and Frost et al. [8] studied the precipitation of lead-rich solder. The precipitation was found to be dependent on aging temperature, composition (Frost et al. [8]), and cooling rate from the supersaturated $\alpha'$-Pb phase (Frear et al. [5]). Upon prolonged aging at room temperature, the precipitates coarsen, which results in a decrease in microhardness with aging time. Strength of aged samples was also found to be independent of precipitate distribution (Frear et al. [5]).

For the cyclic deformation and fracture behavior of lead and lead-rich alloy, Snowden [9,10], Langdon et al. [11,12], and Betrabet and Raman [13] have demonstrated that grain boundary migration and sliding occurred during cyclic deformation at room temperature. Vaynman et al. [6] indicated that at high plastic strain range, the predominant failure mode was mixed-trans/intergranular, while at low strain range the failure occurred in pure intergranular manner for lead-based solders. Berriche et al. [14,15] observed predominant transgranular cracks at high plastic strains and mixed failure at lower strains in vacuum, mainly intergranular fracture in air or $CO_2$ for lead-based solders. Raman and Reiley [16] concluded that the fracture mode is intergranular for Pb-Sn solution alloy. However, basic characteristics and mechanics of fatigue crack growth of lead-based solders are not yet fully understood.

The purpose of the current work is to investigate basic characteristics and mechanics of fatigue crack growth (FCG) of 95Pb-5Sn solder. The effects of stress ratio and creep deformation on fatigue crack growth have also been discussed in detail.

## 2 Experimental Procedures

The material used was a 95Pb-5Sn solder (in wt. %), which was as-cast and natural aged at room temperature for at least one month to reach an equilibrium microstructure. Microstructure of the material is shown in Fig. 1. It is found from the figure that blocky $\beta$-Sn is distributed in $\alpha$-Pb matrix. The grain size of Pb matrix was 50-100 $\mu$m and the particle size of Sn phase was about 10 $\mu$m.

Fatigue crack growth (FCG) tests were conducted using compact-tension specimens with dimensions of 6 mm thick (B), 39 mm wide (W), and 50 mm high (H), in air at a constant temperature of 20°C which is equivalent to about $0.54T_m$ for the 95Pb-5Sn solder, where $T_m$ is the absolute melting point. All tests were performed according to the ASTM standard test method for measuring fatigue crack growth rates (ASTM E647-95a) using a servo-hydraulic test machine. The load sensor capacity of the machine was 2 kN. The FCG tests were conducted at various stress ratios of $R = 0.1$, 0.3, 0.5, 0.7, where $R = K_{\min}/K_{\max}$, with fixed frequency of 10 Hz. The side surfaces of all the specimens were hand-polished before testing to measure the crack length and to observe the crack path.

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