Thermal Performance of Liquid Metal Pastes Containing low Content of Metal Particles for Thermal Interface Materials in IC Module Electronics

Guangyu Fan*[1], Jeff Kurish, Sofia Tagliaferri [2], Kyle Green [3], Christine LaBarbera [1]

[1]Indium Corporation of America, 34 Robinson Rd, Clinton, NY 13323, USA

[2]System Engineering and Engineering Management, The North Carolina State University, 9201 University City Blvd, Charlotte, NC 28223, USA

[3]Chemical Engineering, Stevens Institute of Technology, 1 Castle Point Terrance, Hoboken, NJ 07030, USA

Abstract

In recent years, considerable attention has been paid to gallium-based liquid metal alloys in their use as thermal interface materials for GPU, APU, and HPC in PC and super computers due to its considerably high thermal conductivity and low contact thermal resistance. Gallium-based Liquid metal paste containing low content of metal particles (LMP-MPs) to enhance thermal performance and controllable BLT of the prepared liquid metal composites for thermal interface materials (TIMs) prepared by in-situ introducing gallium oxide into the liquid metal alloys will be reported in our recent research. In this paper, we will report effect of the composition, particle size/types, and bond line thickness on thermal properties of the LMP-MPs. Thermal properties of the LMP-MPs were measured at 50ºC using a thermal tester, TIMA5, based on ASTM-D5470 test methodology. It was found in the present study that the composition and types of metal particles, and BLT have significant influence on thermal conductivity, and the conductivity values increase with an increase of the content of metal particles and BLT. However, thermal resistance varies with the change of composition and BLT of LMP-MPs. Scanning electron microscope (SEM) was used to characterize microstructure of LMP-MPs with different metal particles and sizes. Micrographic morphology of the LMPs-MPs shows continuous frame structure observed with SEM, which could keep liquid metals from spreading out and stabilize the phase. We eventually found the LMP-MPs have the better wetting and adhesion properties on bare Cu, glass and bare Si surface than liquid metal alloys that endows good printability to the LMP-MPs. Continuous monitoring of thermal resistance of LMP-MPs at 45ºC and 89ºC using a house-made thermal tester shows stable thermal resistance after a few months, which indicates LMP-MPs have excellent thermal reliability in ambient atmosphere.

Key words: Thermal interface materials, liquid metal alloys, metal particles, thermal conductivity, microstructure.

I. Introduction

Thermal interface materials (TIMs) are used to minimize thermal boundary resistance between heating source i.e. microprocessors, heat spreader and/or heat sink due to microscopic surface roughness and non-planarity of these component surfaces [[1, 2, 3].
Most of the TIMs, thermal grease or paste, pad, phase change materials, adhesive, widely used in electronics devices are polymer-based composites with metal or ceramic conductive particle fillers [4, 5, 6]. For instance, thermal grease is the most widely used TIM with thermal contact resistances in the range of 0.2–1.0 cm^2 K/W [3, 7] . This could be reduced to 0.053 cm^2K/W using polyethylene glycol mixed with boron nitride [8]. However, there are a few of drawbacks with these traditional TIMs that consist of polymer and metal and/or ceramic fillers. For examples, greases are messy and challenging to apply and rework, and have a long-term reliability issues with pump out, phase separations, and dry-out, which eventually deteriorate thermal conductivity of TIMs and limit the use of grease as an efficient TIM over a nominal lifespan of operation[3, 9]. Another kind of the classic TIMs that have been widely used are solder pastes because of higher thermal conductivity of metals and low contact thermal resistance as low as 0.05 cm^2 K/W [8]. For example, the thermal resistance of Sn–Bi solder paste is less than 0.05cm^2 K/W and it also shows very good reliability, which would be a promising TIM candidate for power electronics applications [10], but it has poor re-workability and needs high process temperature which would cause void formation and thermal stress transferred to the components [11,12]. Recently, liquid metal and liquid metal alloys such as Ga, GaIn, GaInSn and GaInSnZn have drawn considerable attention for usage as TIMs because of high heat transfer capacity, good thermal conductivity, and very low contact thermal resistance[13, 14, 15, 16, 17, 18]. Research group from Auburn University recently reported low melt alloys containing gallium (Ga), indium (In), bismuth(Bi) and tin (Sn) had a lowest thermal contact resistance of 0.005 cm^2 K/W, which was much lower than that of polymer-based thermal greases[14, 15]. Despite LMAs having low thermal interface resistances, Ga-based TIMs have several issues and challenges such as oxidation, corrosion, intermetallic growth, dry-out, de-wetting after oxidation of Ga in the alloys. Several research groups have demonstrated various methods to mitigate these problems [19, 20, 21, 22]. For examples, the oxidation of LMAs can be minimized by a hermetic seal, and the formation of intermetallic compounds can be prevented by applying a diffusion barrier layer [22]. Hill and Strader reported that the use of a gasket sealant could reduce the oxidation of LMAs significantly. Liquid metal alloys can be used in TIM1 and TIM0 applications for digital electronics like PC, high performance computing and gaming. Schematic configuration of flip chip is shown in Figure 1. However, Ga-based TIMs have poor wettability and adhesion to Si, Cu and other surface finish substrates based on traditional deposition processes such as printing and dispensing using surface mount equipment. Thus, it is interesting and worth to explore the possibility of developing innovative LMAs with good wettability and adhesion on bare Si and Cu and Ni-plated or Au-plated substrates, and excellent automation process performance, and new methodologies for deposition of LMAs onto electronic components. In our recent research, we have developed a series of Ga-based LMAs containing metal additives to enhance thermal properties, deposit performance, controllable BLT, wettability/adhesion. We will report viscosity, adhesion and wetting on Cu, Si and glass in this paper.

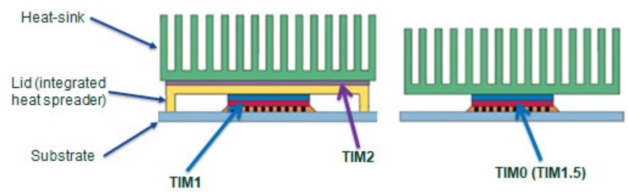


Fig.1 Schematic Diagram of Flip Chip Electronics Configuration with TIM1 and TIM0 or TIM1.5.

II. Experiment

A. Preparation of liquid metal pastes

Liquid metal pastes (LMPs) are directly made from pure liquid metal alloys (LMAs) such as EGaIn and GaInSn via an in-situ process to introduce the oxide into the LMAs to form the liquid metal pastes with and/or without metal additives. The dispersed metal additives and solids mainly consists of Ga_2O_3, forms microstructure or nanostructure frame network soaked with LM and LMAs, which yields viscous paste-like format of LMPs. We have prepared two series of LMPs based on primary liquid metal alloys (51E and 300E) with/and w/o metal additives. DOE of the liquid metal pastes containing low content of metal particles less than 5wt% has been made as listed in Table I, including different composition, types of metal particles and size.

Table I Basic Composition of LMPs Containing Metal Particles

Code No.	LMAs	Metal particles	MPs, Wt%
897-46-1	300E	M1	1.000
897-46-2	51E	M2	1.000
897-71-1	51E	M1	1.000
897-71-2	51E	M1	1.000
897-71-3	51E	M1	5.000
897-71-4	51E	M1	5.000
897-71-5	51E	M2	1.000
897-71-6	51E	M2	5.000
897-71-7	51E	M1	2.500
897-57-1	300E	M1	1.000
897-57-2	300E	M1	0.500
897-57-3	300E	M1A	1.000
897-57-4	300E	M1B	1.000

B. Measurement of Viscosity

Brookfield DV2T Viscometer was used to measure viscosity of LMPs with and/or w/o metal particles at different shear rate at 25°C.

C. Measurement of thermal conductivity and resistance

Thermal tester, TIMA5, made by Nano test, was utilized to measure thermal conductivity and resistance of LMPs based on ASTM D-5470-18 at 50°C and different pressure. House-made thermal tester was also used to measure and monitor thermal resistance of LMPs over time at 45°C and 89°C.

D. SEM morphology of LMPs

Scanning electron microscopy (SEM) and energy dispersive spectrum (EDS) were used to identity microstructure of LMPs and distribution of metal particles in the LMPs matrix.

III. Results and Discussion

A. Viscosity of Liquid Metal Alloy and LMPs

Fig.1 presents viscosity values of the primary liquid metal alloys (300E) measured at the different shear rate of 38.4 and 76.8 (1/s) at 25°C, which shows that viscosity could fully recover as shear rate changes from high to low and back to high shear. It indicates that there is no significant change of microstructure and/or chemical composition of 300E as it undergoes shear. Viscosity values of LMPs with and/or without metal additives show the different properties than primary liquid metal alloys, as shown in **Fig.2**.

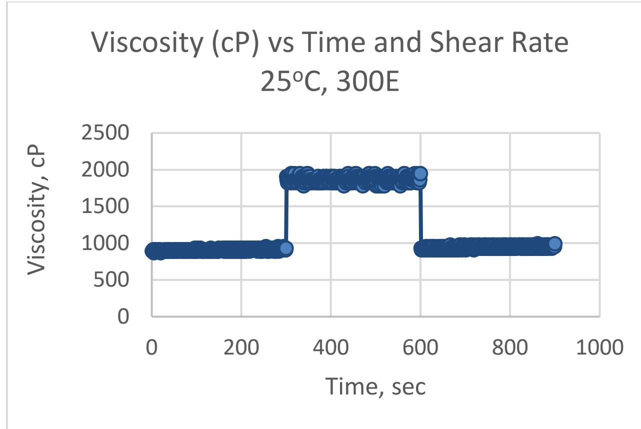


Fig.1 Viscosity of liquid metal alloy (300E) measured with different shear rate of 38.4 and 76.8 (1/s) at 25°C.

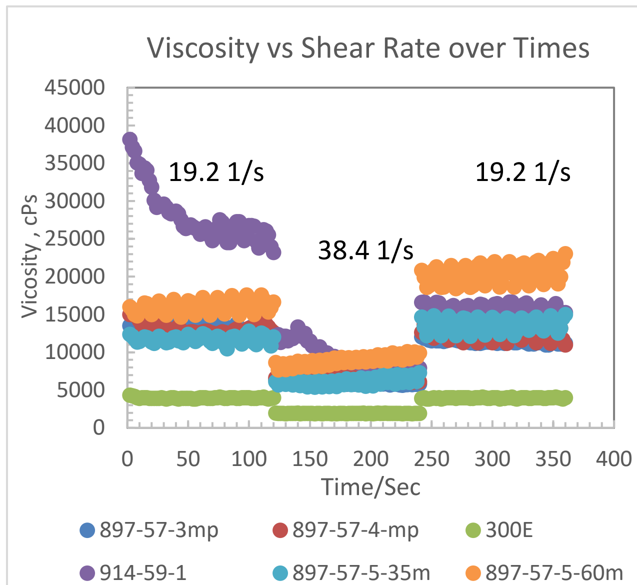


Fig.2 Viscosity of liquid metal alloy (300E) and LMPs with and/or w/o metal additives measured with different shear rate of 19.21 and 38.41 (1/s) at 25°C.

It can be seen from **Fig. 2** that the sample of 914-59-1 has much higher viscosity values at the beginning and dramatically decrease at the shear rate of 19.1 (1/s) over time from 0 to 125sec, and then the viscosity drops from 25000cPs to 15000cPs at the shear rate of 38.41(1/s), but continuously decreases. The viscosity values jump up 15000cPs when shear rate change to 19.21 (1/s) from 38.4 (1/s) and is consistent, but could not recover fully to the original value. It implies that there was phase separation occurring during measurement of viscosity of LMPs. The samples with metal additives (897-57-3 and 897-57-4) much more stable than the samples without metal additives (897-57-5-35m and 60m), but still viscosity could not recover completely to the same as the beginning. Thus, phase separation more or less might be an intrinsic characteristic of LMPs.

B. Wettability and Adhesion of LMPs

Duo to high surface tension of liquid metal alloys [16], EGaIn and Galinstan have very high contact angles on glass and Cu and so on, which would cause poor adhesion and wettability on the surface of most substances. Therefore, they are very difficult to handle during deposit process such as printing and dispensing.

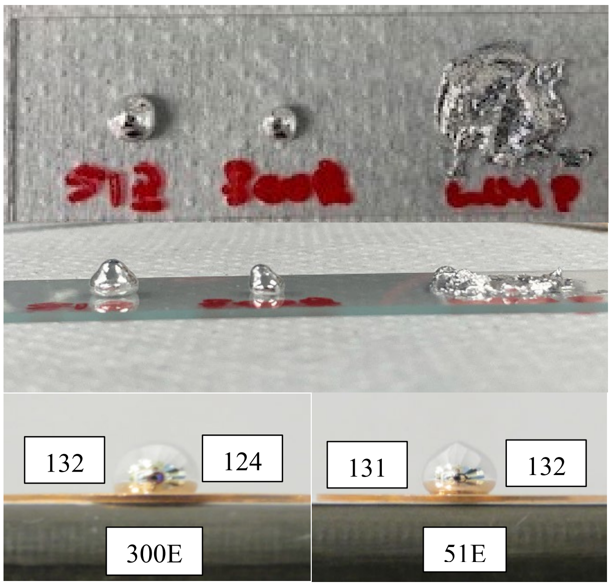
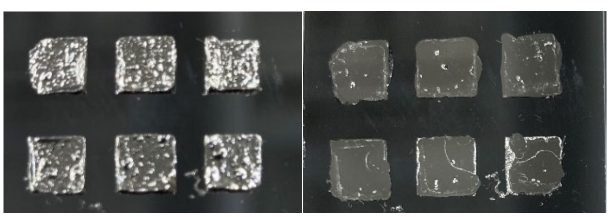
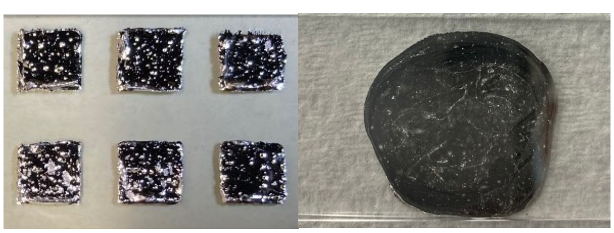


Fig. 3 Optical images of liquid metal droplets and LMPs on glass slide and bare Cu substrates.



a. Printing on Si chip b. Glass on top

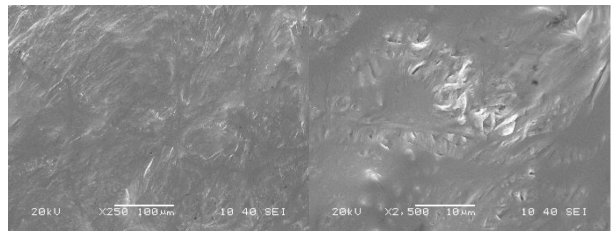


c. Printing on glass d. Paste between glass slides

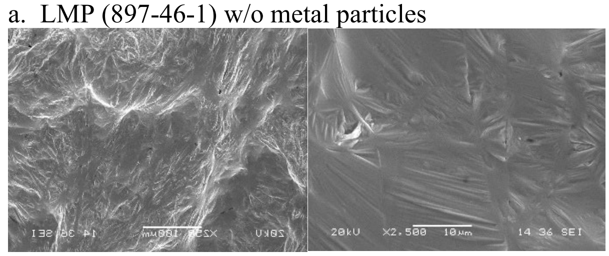
Fig. 4 (a, b, LMPs printed on bare Si and glass.

To improve automation process of liquid metal alloys, we have developed a series of liquid metal pastes that could be deposited using conventional printing or dispensing process. As a result, LMPs with and w/o metal additives could be printed on bare Si, glass and copper substrate, but not on ceramic substrate. As shown in Fig. **4 (a, b)**, LMP was printed manually using MINI stencil and show very good adhesion and wettability on bare Si, and there is no squeeze out after putting glass slide on the top of LMP. It also shows good wettability on glass and spreading performance as well, as shown in Fig. **4 (c, d).**

C. SEM microstructure of LMPs



a. LMP (897-46-1) w/o metal particles



b. LMP (897-57-1) with metal particles

Fig 5 (a, b). SEM morphology of LMPs with and w/o metal **particles**

Scanning electronic microscopy (SEM) was used to characterize microstructure of LMPs with and/or without metal additives. We can see from **Fig. 5a** that the existence of microstructure frame of the oxide in LMPs and some rough domain structure, which shows phase separation of the solid structure from liquid metals, which might affect thermal performance of LMPs. The sample with metal particles shows more continuous phase microstructure and less chucky domain structure in the LMPs, as shown in **Fig. 5b**. In the meantime, the sample containing metal particles do show better wettability than that of the samples without metal particle somehow.

D. Thermal properties of LMPs

Thermal conductivity and resistance of LMPs were measured using thermal tester, TIMA5, based on ASTM D-5470 at 50ºC and 5psi. Bond line thickness, thermal resistance (Rth), thermal conductivity (k) values are summarized in table II.

Overall, LMPs have much higher thermal conductivity and lower resistance than that of silicone thermal grease as control sample in the same measurement conditions. During thermal test, however, BLT and pressure have significant influence on thermal properties of LMPs with and/or without metal additives. When BLT is thinner, thermal resistance is much lower and decrease over time whereas thermal conductivity increases. For an instance, **Fig. 6** presents thermal conductivity and resistance as a function of time at the consistent pressure of 5psi and temperature of 50ºC. It is very interesting that thermal conductivity values of 897-57-1 increases from around 8.5 W/m K at day 0 to 10.5W/m K at day 3 whereas thermal resistance values reduce from 0.018 K/W to 0.013K/W.

Table II. Thermal Resistance and Conductivity of LMPs

Code No.	BLT, µm	Metal, wt%	Rth, K/W	k, W/m K
Grease	76		0.14	1.18
897-46-1	207	1.0	0.09	5.35
897-46-2	183	1.0	0.08	5.14
897-57-1	196	1.0	0.06	6.72
897-57-2	112	0.5	0.05	5.38
897-57-3	155	1.0	0.06	5.52
897-57-4	102	1.0	0.04	6.27
897-71-1	118	1.0	0.07	3.92
897-71-2	131	0.5	0.04	6.79
897-71-3	270	5.0	0.10	6.04
897-71-4	116	5.0	0.03	8.98
897-71-5	149	1.0	0.09	3.79
897-71-6	101	5.0	0.07	2.97
897-71-7	377	2.5	0.09	9.05

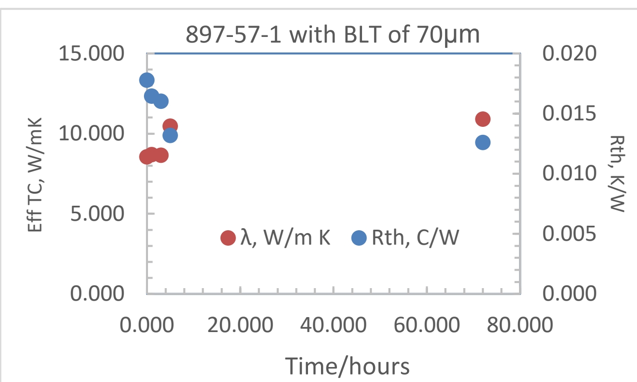


Fig. 6 Thermal resistance and conductivity of LMPs (897-57-1) at 5psi and 50ºC over time.

However, thermal conductivity of 897-46-1 without metal additive deceases from day 0 to day 7, as shown in **Fig. 7,** whereas thermal resistance increases over time. When test pressure changes, thermal resistance value drops from 0.09K/W at 5psi to 0.06K/W at 15psi whereas thermal conductivity remains quite similar to each other, as shown in **Fig. 8**.

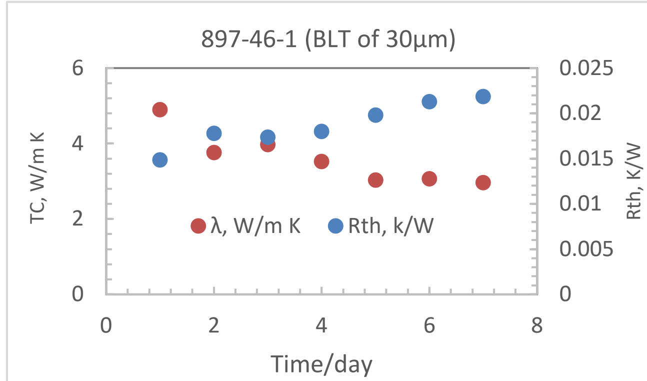


Fig. 7 Thermal conductivity and resistance of LMPs (897-46-1) measured at 50ºC and 5psi over time.

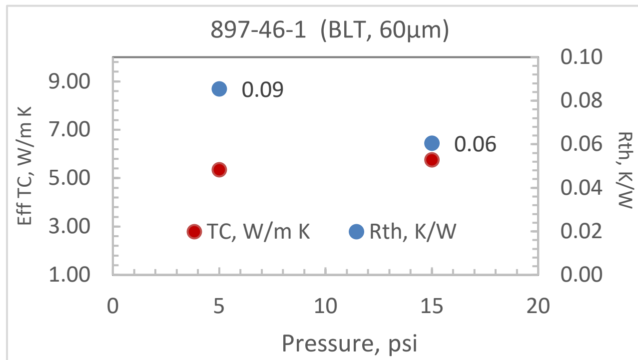


Fig. 8 Thermal conductivity and resistance of LMPs (897-46-1) measured at 50ºC and 5psi.

To determine intrinsic thermal conductivity and contact resistance, we have measured thermal resistance of LMPs with different thickness of LMPs and then determine intrinsic or bulk thermal conductivity from the reciprocal value of the slope of linear plot, as shown in **Fig 9**.

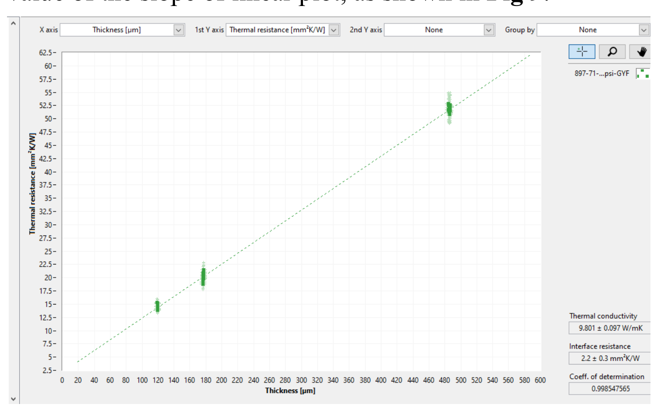


Fig. 9 Thermal impedance vs thickness (897-60-7) measured at 5psi and 50ºC.

For example, we have measured three samples of 897-60-7 with different thickness and then plot a graph of thermal impedance versus thickness. The determined intrinsic conductivity from the reciprocal of the slope value of linear plot is 9.163W/m K with contact thermal resistance of 0.0358K/W. The same method was used to determine thermal conductivity of 897-57-1 and intrinsic thermal conductivity is 16.019W/m K with contact resistance of 0.0354K/W.

In the present research, we also designed and fabricated a house-made thermal tester with a single thermal sensor on cold and hot Cu block based on ASTM D-5470 to measure thermal resistance values.

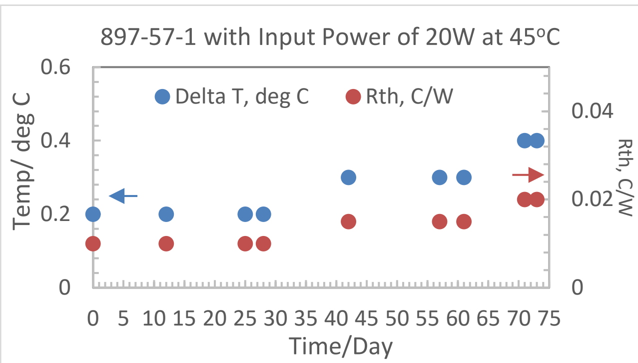


Fig. 10 Thermal resistance of LMPs (897-57-1) with input power of 20watts at 45°C over time

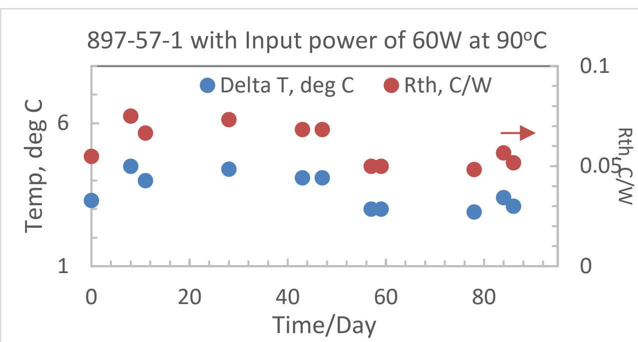


Fig. 11 Thermal resistance of LMPs (897-57-1) with input power of 60watts at 90°C over time.

Power inputs with 20 and 60watts were used to run test on the samples of LMPs (**897-57-1**), as shown in **Fig. 10** and **11**, respectively. **Fig. 10** presents thermal resistance of LMPs (**897-57-1**) at 45°C as a function of time. It can be seen that the resistance at time 0 is around 0.02K/W, and gradually increases to 0.03K/W after 40days and then jumps to 0.04K/W, but the resistance is still less than 0.04K/W. The test on **897-57-1** performed at 90°C shows thermal resistance is 0.055K/W at time zero, and then rise to 0.07K/W, followed by dropping back to 0.055K/W and remaining the same values until the end of the test, which indicate that LMPs show good reliability.

Conclusion

We have successfully developed a series of liquid metal pastes with and without metal additives, and measured viscosity of the prepared samples. Due to the existence of gallium oxide, viscosity of LMPs are much higher than that of liquid metals. Change of viscosity values of the LMPs as shear rate changes indicates that phase separation occurs during test and metal additive could suppress phase separation, which shows the metal particles could influence the shear force of LMPs. Compared to liquid metal alloys, LMPs have good wettability and adhesion on the surface of Cu, Si and glass and printability on Si and glass although liquid metal could not be printed well due to high surface tension. SEM micrograph reveals that microstructural frame network that consists of the oxide contains liquid metal in the pastes. Thermal conductivity and resistance of LMPs measured by ASTM D-5470 method indicate that LMPs have much better thermal properties than that of thermal grease. LMPs have high thermal conductivity and lower thermal resistance, but BLT and pressure have significant influence on thermal conductivity and resistance. Thicker BLT of LMP's seems to result in higher thermal conductivity. However, thermal resistance is higher when BLT is thicker. Preliminary data obtained from the test on thermal resistance of LMPs over time reveal that LMPs have excellent reliability. Power cycling test on LMPs and PMP with metal additives will be performed in near future.

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