Novel TIM Solution with Chain Network Solder Composite

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ABSTRACT

A novel epoxy SAC solder paste TIM system has been developed with the use of non-volatile epoxy flux. Cu filler was added to the solder paste, with Cu volume % of metal ranged from 17 to 60 volume % of metal. Formation of semi-continuous high melting Cu chain network was achieved, with the use of CuSn IMC bridges between Cu particles. This chain network, at sufficient concentration, serves as skeleton and maintains the shape of the sandwiched solder paste layer, thus prevented further spread out and outgassing upon subsequent SMT reflow process, and also allowed formation of TIM joint even in the absence of solderable metallization on flip chip and packaging housing. Presence of significant amount of ductile solder within TIM joint promises high resistance against brittle cracking under stress. The Cu content could be further optimized between 17 and 33 volume % of metal to avoid flux bleeding and maintain good epoxy adhesion between TIM phase and parts. The 20°C thermal conductivity achieved was 6.1 W/mK and could be up to about 13 W/mK with further epoxy flux optimization.

KEY WORDS

Thermal interface material, TIM, solder, SAC, solder paste, epoxy flux, reflow, Cu filler, thermal conductivity

INTRODUCTION

Thermal management is always a challenge in the electronic industry. The need for faster, more powerful devices makes this challenge even harsher and more difficult to overcome, thus the need for improved high performance materials continues to grow. The solutions for thermal interface material (TIM) include thermal grease, thermal gel, phase-change material, solder preform, and liquid solder [1-3]. All of those suffer from either performance limitation such as pump-out, or building of liquid solder dam, or poor thermal conductivity. Solder paste and solder preform are thermally effective as TIM. However, the constraint is that both sides have to be solderable metallization. Consequently, the flip chip backside and the package housing or heat sink need to be plated with solderable surface finishes, such as NiAu. This inevitably increases the cost. Solder paste suffers further from flux fume and voids generated, therefore is obviously unacceptable. The voids are results of outgassing within liquid solder joints.

With solder preform being a good thermal conductor, a solder preform-like material which maintains the shape of preform but forms intimate contact in-between flip chip and housing without metallization will be desired. Furthermore, the shape of preform should be maintained even at subsequent SMT assembly reflow process, similar to our earlier work [4]. If a type of filler particle with thermal conductivity better than that of solder can be incorporated in the solder paste, this TIM material will have an enhanced thermal conductivity.

DESIGN

Ideally, a specialty solder paste with the use of non-volatile flux can be formulated. The solder paste contains solderable metal filler particles with thermal conductivity better than solder. The paste can be dispensed or printed. After being deposited on top of flip chip followed by housing placement, if the paste maintains the sandwiched shape without coalescence into a liquid solder droplet, then it would serve as a good TIM material.

EXPERIMENT

1. Materials

A specialty solder paste system was designed, with the use of non-volatile epoxy flux and with incorporation of solder copper filler particles, as shown in Table 1. Three epoxy pastes samples EP1, EP2, and EP3 were prepared. The solder powder was Sn3.5AG0.5Cu (SAC305), type 4 (20-38 microns), and Cu powder is 10-25 micron in size. The metal load was 88% w/w, and the volume ratios of SAC305 to Cu were 5/1, 2/1, and 1/1.5. For comparison purpose, a series of regular solder paste samples, SP1, SP2, and SP3, were also prepared, with metal load being 87% w/w. The volume ratio of SAC305 and Cu were also 5/1, 2/1, and 1/1.5. Here the flux used is a no-clean halogen-free flux.

Table 1 Specialty solder paste samples prepared

Sample	EP1	EP2	EP3	SP1	SP2	SP3
SAC305/Cu Volume ratio	5/1	2/1	1/1.5	5/1	2/1	1/1.5
Cu volume % of metal	17%	33%	60%	17%	33%	60%
Epoxy flux (gm)	7.2	7.2	7.2			
Regular flux (gm)				9.1	9.1	9.1
SAC305T4 (gm)	42.5	32.9	18.7	49.1	38.0	21.6
Cu (10-25u) (gm)	10.3	19.9	34.1	11.8	22.9	39.3
Total (gm)	60	60	60	70	70	70

2. Reflow Process and Results

1) First reflow

Pastes were dispensed into a 28 mm diameter aluminum dishes. The dishes with full amount of pastes were reflowed though BTU VIP-70 convection oven running a time-temperature profile with a peak temperature at 250°C (Figure 1) and in a nitrogen atmosphere.

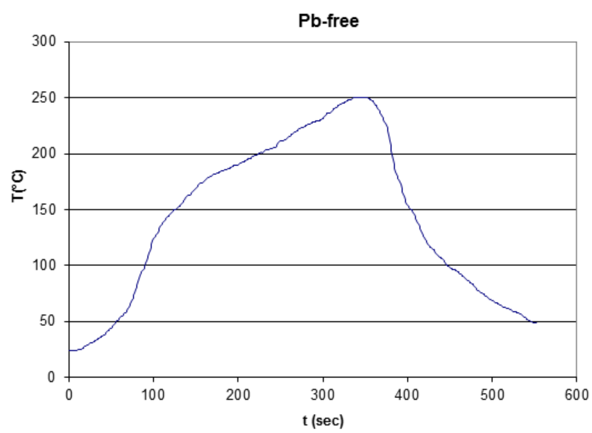

Figure 1 Time-temperature profile with peak temperature at 250°C

After cooled down to room temperature, EP1 exhibited a little bit volume reduction when compared to the volume of solder paste, but EP2 and EP3 did not have volume reduction at all (Figure 2).

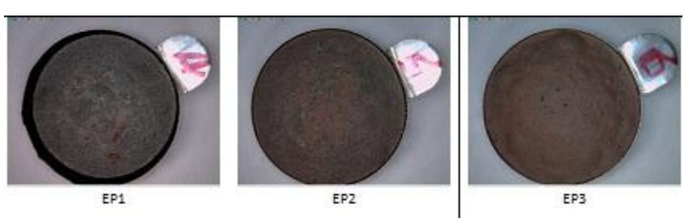

Figure 2 Epoxy pastes after first reflow

Similarly after the first reflow, the volume of SP1 was reduced slightly, and SP2 and SP3 did not have volume reduction (Figure 3)

Figure 3 Solder pastes after first reflow

2) Second reflow

The disk shape solder composites were transferred to bigger aluminum trays, and sent to the BTU oven for the second reflow under the same conditions. All solder composites made from EPs did not re-melt therefore their sizes and shapes did not change. But EP1 has a small amount of epoxy flux bled out (Figure 4).

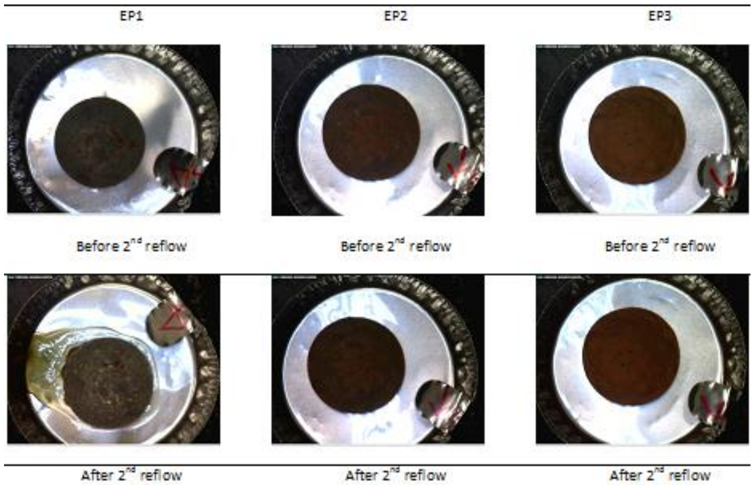

Figure 4 Epoxy pastes before and after second reflow

Similarly, solder composites made from SPs did not re-melt therefore their sizes and shapes did not change, but SP1 has a small amount of solder flux bled out (Figure 5).

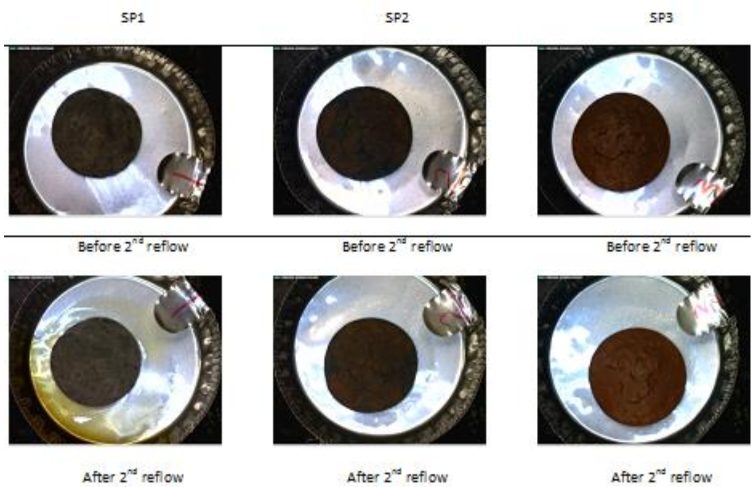

Figure 5 Solder pastes before and after second reflow

3. Differential Scanning Calorimetry (DSC)

DSC was employed to check if there is any solder material remains meltable at reflow after few prior reflow processes. The DSC procedure is, first heating the paste sample to 250°C and hold for 2 min before cooling down to 25°C to simulate a reflow cycle. Repeat above process to simulate a 2^{nd} reflow. The reason to study the thermal property of double reflowed pastes is to mimic the TIM heat history, with the first reflow representing TIM solder joint formation, and the second reflow mimic the SMT assembly of packages. Finally the sample was heated at 20°C/min to 450°C and the heat flow was recoded vs. temperature.

Figure 6 is the DSC curves of epoxy pastes after double reflow. From the curves it can be seen that the low melting phase of SAC with melting peak at ~217°C exist for all double reflowed epoxy pastes. This is the key difference between our composites and the composite invented by Gallagher et al [5].

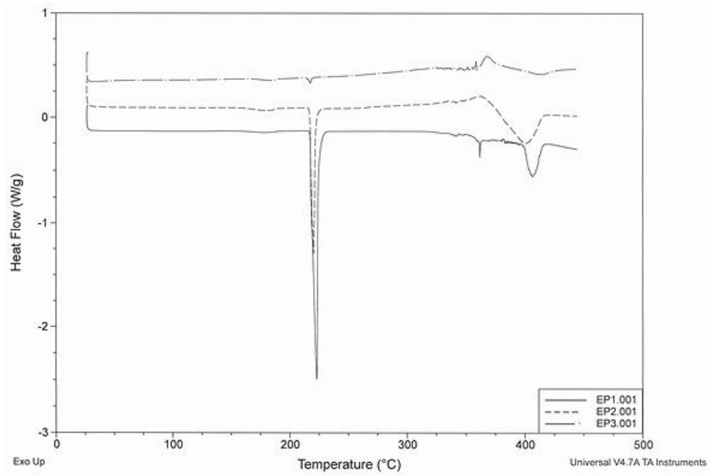

Figure 6 DCS curves of double reflowed epoxy pastes EPs

Figure 7 is the DSC curves of solder pastes after double reflow. For SP1 and SP2 the low melting phase of SAC with melting peak at ~217°C is very clear. But for EP3, the DSC curve needs to be re-scaled to see that peak, as shown in Figure 8.

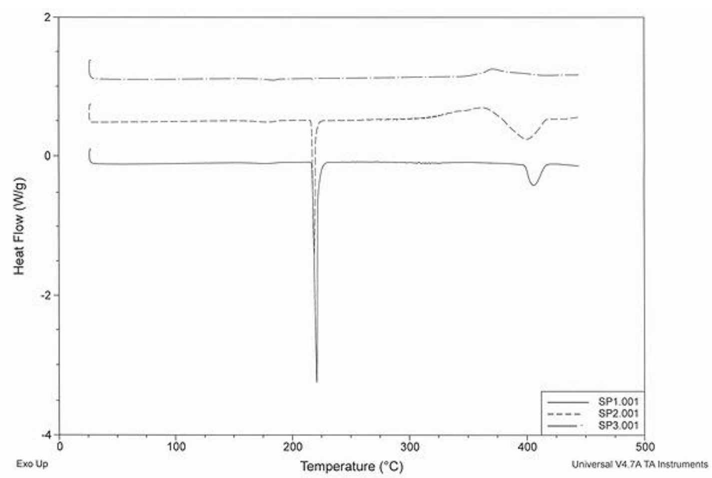

Figure 7 DCS curves of double reflowed solder pastes SPs

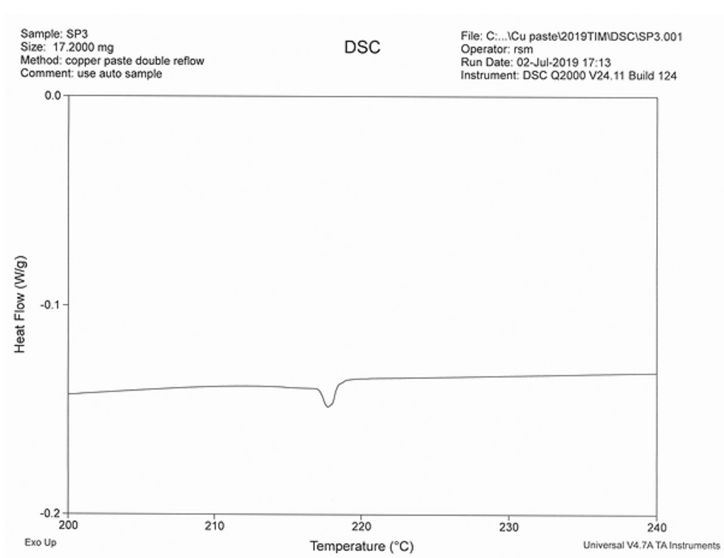

Figure 8 Re-scaled DCS curve of double reflowed solder paste SP3

4. Thermal Conductivity

The thermal conductivity k measured by ASTM D5470 for reflowed pastes at 20 and 36°C are shown in Table 2.

Table 2 Thermal conductivity of paste samples.

Sample	EP1	EP2	EP3	SP1	SP2	SP3
Cu volume % of metal	17%	33%	60%	17%	33%	60%
k at 20°C (W/mK)	2.9	5.2	6.1	12.9	6.5	5.9
k at 36°C (W/mk)	2.9	6.1	6.4	14.6	7.8	6.2

For epoxy pastes EPs the thermal conductivity k increases with increasing Cu content. Since thermal conductivity of Cu and SAC305 is 385 [6] and 58.7 W/mK [7], respectively, the high k value for high Cu content can be rationalized easily.

However, the same cannot be said about regular solder pastes SPs. Here the k value decreased with increasing Cu content. In Figure 9, the dark Cu particles and grey CuSn intermetallic compounds, together with some small very light colored AgSn particles, dispersed in Sn matrix. Some crevices can be noticed, mostly around Cu and CuSn particles. By comparing the cross-sectional SEM pictures of SP samples shown in Figure 9, 10, and 11, the crevices within the solder body were observed to increase with increasing Cu content. Presence of crevices is direct evidence that the liquid solder failed to fill the gaps. This can be attributed to (1) more Cu oxides caused by a higher Cu loads, and (2) more CuSn IMC formation which, together with Cu particles, further constraint the flow of liquid solder. Apparently, the higher content of crevices resulted in a poorer continuity of solder, and consequently a lower thermal conductivity.

It is interesting to note that for EP samples, the amount of crevices are more than that of SP samples, as shown in Figure 12, 13, and 14. In the sample EP1, as shown in Figure 12, besides the presence of crevices, the light colored AgSn interface lines are everywhere. This suggests that the solder powder may not be well coalesced, and AgSn IMC very likely were segregated at grain boundary. By comparing Figure 9 to 11 with Figure 12 to 14, the density of crevices is seen to be considerably higher for EP samples than that of SP samples. In other words, the continuity of EP samples is much poorer than that of SP samples. This poor continuity can be seen in sample EP3 in Figure 15, where the presence of solder powder and Cu particles can be very easily recognized. The poor coalescence of EP samples inevitably resulted in metal powder segregated by either oxides or cured epoxy flux, and consequently a very poor thermal conductivity. With the system composed of segregated individual metal powders, the thermal conductivity of the system accordingly was dictated by the thermal conductivity of metal powder, and a higher Cu content would result in a higher thermal conductivity, as shown in Table 2 and Figure 16. In summary, Figure 16 showed two opposite trends for two different paste systems. For EP system, where powders were segregated, thermal conductivity dictated by thermal conductivity of filler particles. On the other hand, for SP system, where continuity decreased with increasing Cu content, the thermal conductivity is dictated by continuity of metals.

For both EP and SP systems, the thermal conductivity at 36°C was seen to be higher than that at 20°C.

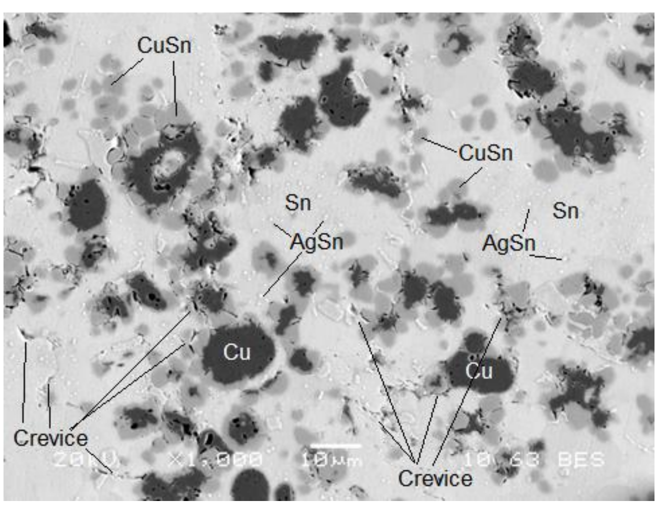

Figure 9 1000X SEM picture of cross section of reflowed SP1

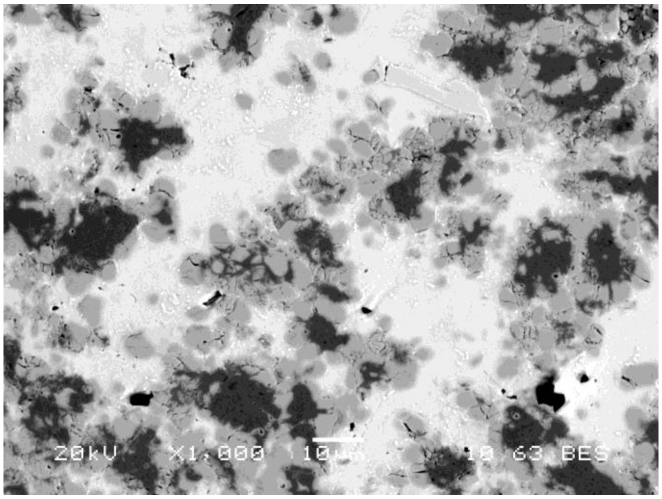

Figure 10 1000X SEM picture of cross section of reflowed SP2

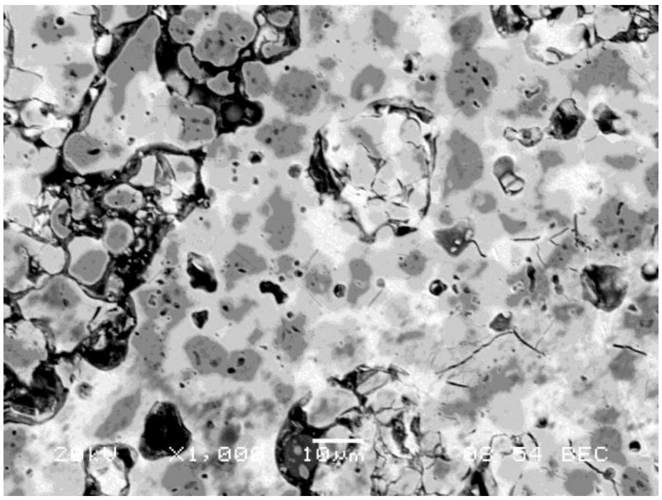

Figure 11 1000X SEM picture of cross section of reflowed SP3

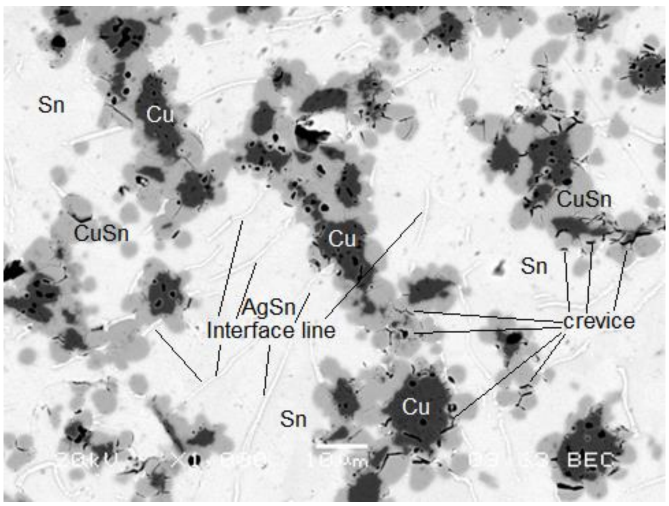

Figure 12 1000X SEM picture of cross section of reflowed EP1

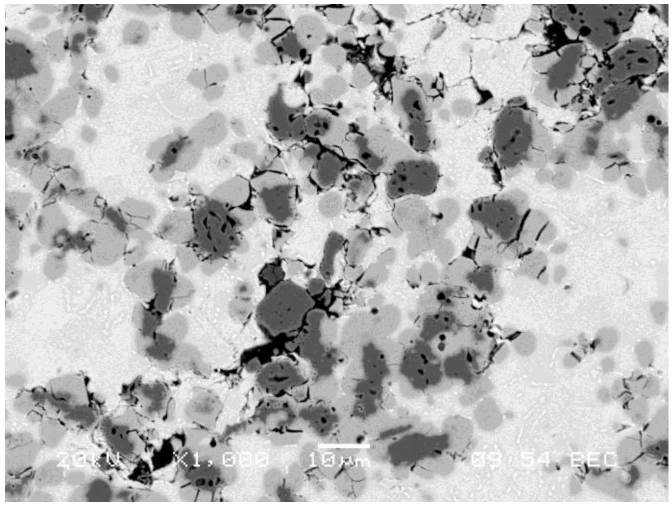

Figure 13 1000X SEM picture of cross section of reflowed EP2

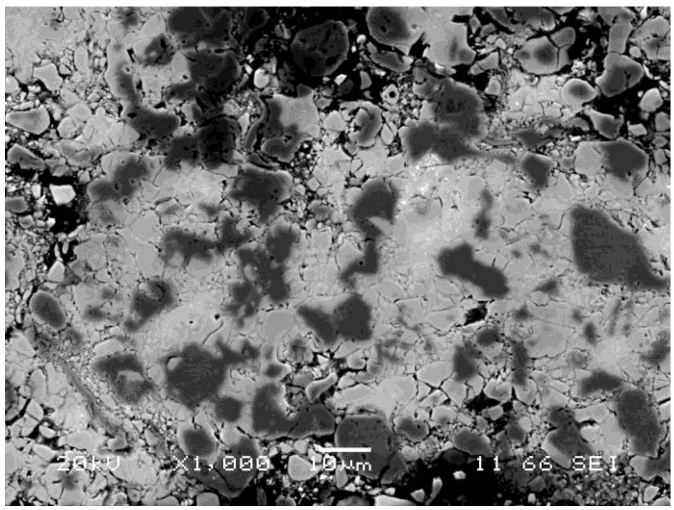

Figure 14 1000X SEM picture of cross section of reflowed EP3

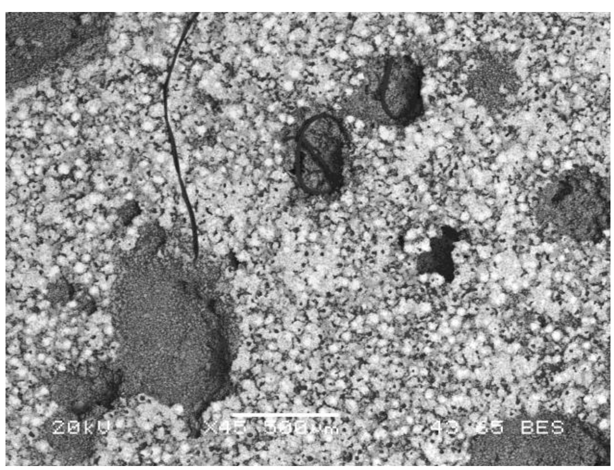

Figure 15 45X SEM picture of cross section of reflowed EP3 shows not fully coalesced area

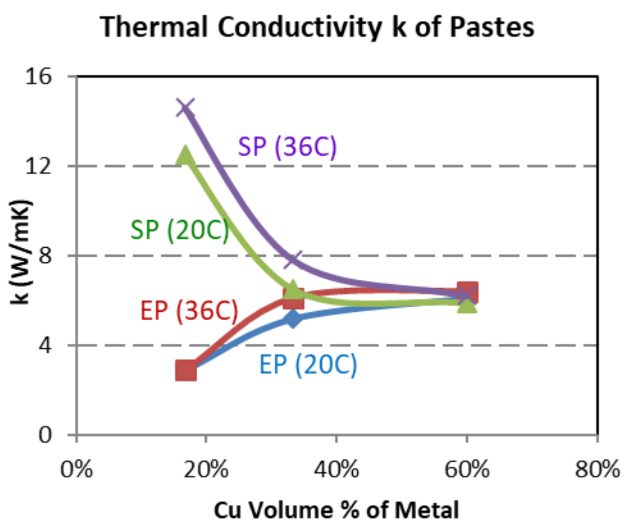

Figure 16 Thermal conductivity of reflowed pastes EPs and SPs

5. Shear Strength

The shear strength of solder joints sandwiched between FR4 or between Cu coupons are shown in Table 3 and Figure 17. For Cu/Cu system, a lower Cu content rendered higher shear strength, regardless of EP or SP systems, indicating a better solder continuity would result in a higher metallic joint strength. For FR4/FR4 system, the difference between EP and SP system is fairly minute, although at high Cu content, EP system does show a lower joint strength. For SP system, the only shear strength is attributed to the adhesion of flux residue between solder entity and FR4, and it is comparable among SP samples. For EP system, it is interesting to note that the difference in shear strength versus that of SP system is insignificant. This can be attributable to that the regular flux residue mainly composed of rosin which is also a commonly used glue. Presumably the flux residue of EP system would show a higher shear strength at elevated temperature, where the thermoset epoxy flux residue is expected to be stronger than rosin which will melt when heated.

Table 3 Shear strength of solder joints sandwiched between FR4 coupons or between Cu coupons

Sample	EP1	EP2	EP3	SP1	SP2	SP3
Cu volume % of metal	17%	33%	60%	17%	33%	60%
Substrate	**FR4/FR4**	**FR4/FR4**	**FR4/FR4**	**FR4/FR4**	**FR4/FR4**	**FR4/FR4**
Ave (psi)	123	154	83	148	161	145
Std Dev (psi)	44	56	55	36	39	38
Substrate	**Cu/Cu**	**Cu/Cu**	**Cu/Cu**	**Cu/Cu**	**Cu/Cu**	**Cu/Cu**
Ave (psi)	1315	578	341	1150	885	332
Std Dev (psi)	256	25	31	523	107	44

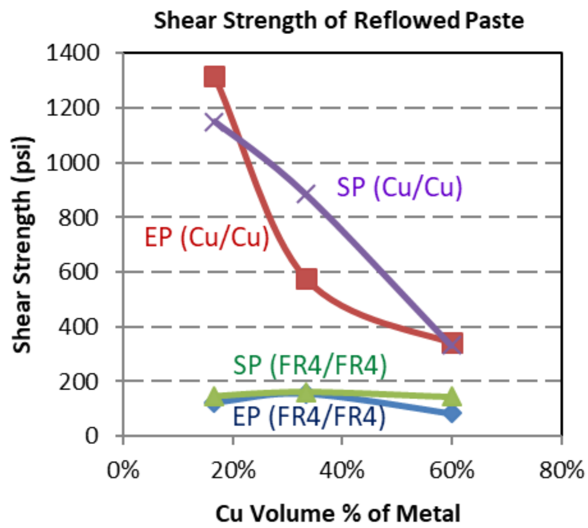

Figure 17 Shear strength of solder joints sandwiched between FR4 or between Cu coupons at RT

TIM APPLICATION

1. Semi-continuous High Melting Chain Network

Both EP and SP system can be dispensed or printed onto the backside of flip chip. After placement of housing and reflowed, both maintained the shape of paste, as shown in Figure 2 and Figure 3, even in the absence of solderable metallization on chip. The shape stability is attributed to the high melting semi-continuous Cu particle chain network, as shown in Figure 18. The IMC bridges between Cu particles were verified in Figure 9, 10, 12, and 13, where the high melting network froze the shape of the paste. For Figure 11 and 14, virtually the whole Cu particle clusters were embedded in IMC matrix. The frozen shape of paste assured the TIM joint stability at subsequent SMT assembly reflow process, where the contact with flip chip or housing was achieved by the flux residue at interface.

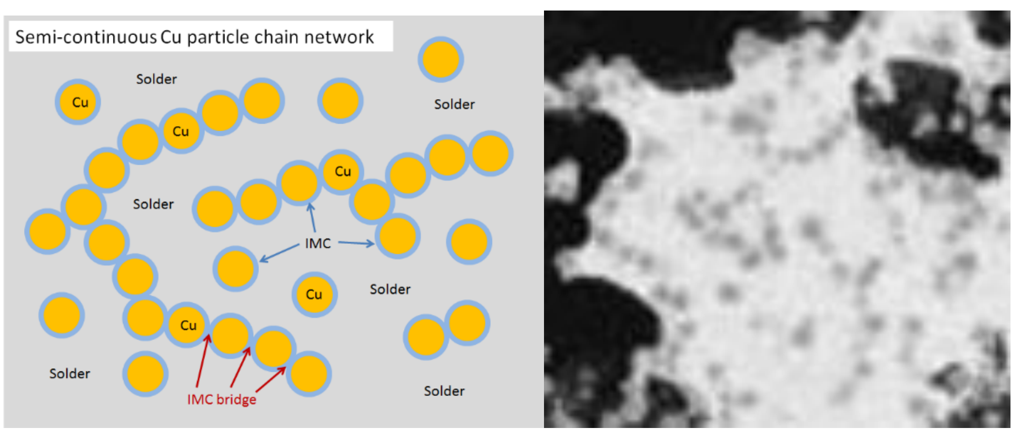

Figure 18 Semi-continuous Cu particle chain network model (left) and cross-sectional view of reflowed Cu filled solder paste (right)

2. Epoxy Flux versus Regular Flux

Both epoxy flux and regular flux could achieve formation of frozen paste shape. However, the volatile ingredients of regular flux would pose concern when reflowed within the housing of chip package. On the other hand, use of non-volatile thermally curable epoxy flux could avoid this issue, although the epoxy flux can be further optimized to assure adequate fluxing, and consequently better solder continuity and thermal conductivity. The 20°C thermal conductivity achieved was 6.1 W/mK, and could be up to about 13 W/mK.

3. Optimization of Cu Content

Apparently the Cu particle content would affect the frozen extent of the semi-continuous network. Figure 4 and 5 showed that at 17% volume % of metal load, bleeding of flux still occurred at second reflow, while at 33% volume %, no flux bleeding observed. Obviously flux bleeding is not desired. Considering that a thin layer of flux between frozen paste and housing/flip chip is preferred for intimate adhesion, the Cu content should be further optimized between 17 and 33 volume % of metal.

BRITTLE OR DUCTILE?

A frozen TIM paste shape is desired to maintain good contact with both flip chip and housing. However, a fully frozen glassy TIM material implied a brittle joint which tends to crack readily under stress.

1. TLPS Approach

Work reported by Gallagher et al [5] employed solder paste with Cu filler to form Transient Liquid Phase Solder (TLPS) at reflow. After reflow, the low melting phase fully vanished, and TLPS provided strength and avoided softening or melting at elevated temperature. The system design is show in Figure 19, and 100% conversion into high melting glassy TLLP phase at reflow is shown in Figure 20.

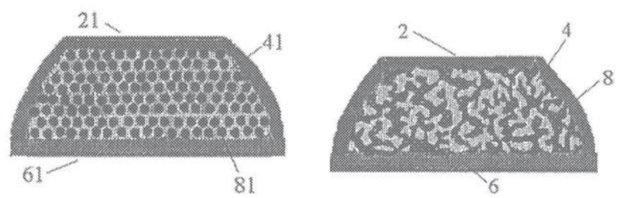

Figure 19 TLPS Design before and after reflow [5]

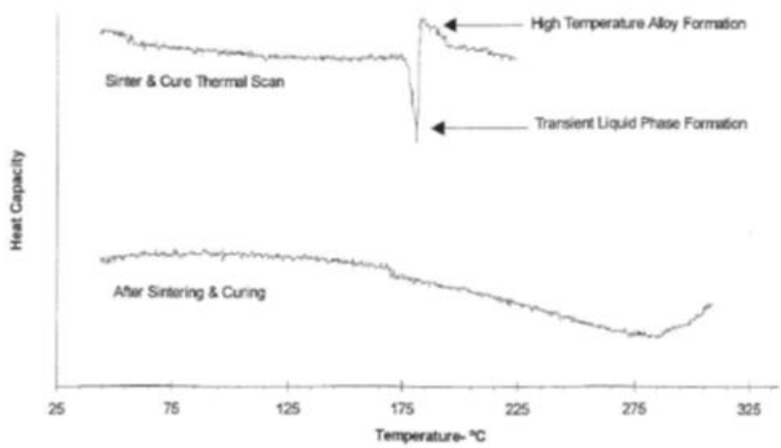

Figure 20 DSC of material design shown in Figure 19, and all materials was converted into high melting glassy phase after reflow [5]

2. Semi-continuous High Melting Chain Network

Figure 6, 7, and 8 showed ductile low melting solder pastes still exist after two reflow processes, even for EP and SP systems with Cu volume % of metal up to 60%. This shape stability at reflow despite the presence of some liquid solder at peak temperature was attributed to the high melting chain network formation. This shape stability was observed for system with Cu volume % of metal at least down to 33%. Obviously, the more ductile solder remain in the solder material, the higher the resistance of joint against occurrence of brittle cracking under stress.

CONCLUSION

A novel epoxy SAC solder paste TIM system has been developed with the use of non-volatile epoxy flux. Cu filler was added to the solder paste, with Cu volume % of metal ranged from 17 to 60 volume % of metal. Formation of semi-continuous high melting Cu chain network was achieved, with the use of CuSn IMC bridges between Cu particles. This chain network, at sufficient concentration, serves as skeleton and maintains the shape of the sandwiched solder paste layer, thus prevented further spread out and outgassing upon subsequent SMT reflow process, and also allowed formation of TIM joint even in the absence of solderable metallization on flip chip and packaging housing. Presence of significant amount of ductile solder within TIM joint promises high resistance against brittle cracking under stress. The Cu content could be further optimized between 17 and 33 volume % of metal to avoid flux bleeding and maintain good epoxy adhesion between TIM phase and parts. The 20°C thermal conductivity achieved was 6.1 W/mK, and could be up to about 13 W/mK with further epoxy flux optimization.

REFERENCE

[1] D. Blazej, "Thermal Interface Materials", Electronics Cooling, Vol 9, No 4, 2003. pp 14-20.
[2] R. Prasher, "Thermal Interface Materials: Historical Perspective, Status, and Future Directions" Proceedings of the IEEE, Vol. 94, No. 8, 2006. pp 1571-1586.
[3] D. DeVoto, J. Major, P. Paret, G.S. Blackman, A. Wong, and J.S. Meth, "Degradation Characterization of Thermal Interface Greases", in: 2017 16th IEEE Intersoc. Conf. Therm. Thermomechanical Phenom. Electron. Syst., IEEE, 2017, pp. 394–399, https://doi.org/10.1109/ITHERM.2017.7992501.
[4] N.C. Lee and R. Mao, "Lead-Free Solder Paste for Thermal Via Filling", US Patent Application No 16/251,481, filed on January 18, 2019.
[5] C. Gallagher, G. Matijasevic, and A. Capote, "Transient Liquid Phase Sintering Conductive Adhesives" US Patent No. 5853622, December 29, 1998.
[6] THERMAL CONDUCTIVITY OF ALUMINUM, COPPER, IRON, AND TUNGSTEN FOR TEMPERATURES FROM 1 K TO THE MELTING POINT, National Bureau of Standards U.S. Department of Commerce Boulder, Colorado 80303 June 1984
[7] Lead Free Solder Sn96 (SAC305) 4900 Technical Data Sheet, MG Chemicals, QMI File # 004008, Burlington, Ontario, Canada

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