A Comparison Study on Sn3.5Ag and Sn3.8Ag0.7Cu C5 Lead Free Solder System

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Abstract
A comparison study was carried out with Sn3.5Ag and Sn3.8Ag0.7Cu solder balls on Ball Grid Array (BGA) components with Cu/Ni/Au pad finishing. This study shows that Sn3.5Ag C5 solder system performs better than Sn3.8Ag0.7Cu in terms of joint strength and brittle mode failure. Experimental works were carried out to observe the melting properties of the solder alloys by Differential Scanning Calorimetry (DSC). Solder ball shear and cold pull strength after ball attach, high temperature storage (HTS) and multiple reflow were measured by *Dage* to gauge the solder joint strength and intermettalic compound (IMC) thicknesses were measured after cross-sectioning,. Drop Tests were done per ASE & Freescale methods to study the solder joint performance against vibration and impact shock. Liquid-liquid thermal shock was done to assess Board Level Reliability. A comprehensive study was done using SEM and EDX to study the effect of microstructure and interface intermetallics of both solder system at ambient, HTS at 150ºC for 168 hours and 6x multiple reflow towards the joint integrity. Microstructure studies on SnAg solder reveals that formation of rod shape Ag_3Sn IMC distributed across the solder surface helps to act as dispersion hardening that increases the mechanical strength for the Sn3.5Ag solder. EDX analysis confirmed that in SnAgCu solder/Ni interface, Cu-rich IMC formed on top of the Ni-rich IMC. For SnAg system, only Ni-rich IMC is found. Therefore, it is highly suspected that the presence of Cu-rich IMC posed a detrimental effect on the joint strength and tends to cause brittle joint failure. Both of the effect is then showed in ball pull result that after HTS, SnAgCu solder has 99.5% brittle mode failure, where SnAg solder has 0%. This result correlates with missing ball responses after packing drop tests as well as liquid-liquid thermal shock result. Thus, despite having 4ºC higher melting temperature than SnAgCu, improvement on SnAg was obtained using the SnAgCu reflow profile. Thus, SnAg eutectic solder is a potential candidate for lead-free solder joint improvement for overall lead-free package robustness.
Keywords: Intermetallics; Sn3.5Ag, Sn3.8Ag0.7Cu, Shear and pull strength

INTRODUCTION
Environmental and health concerns have resulted in significant activities to find substitutes for lead-contained solders for microelectronics. The potential candidates such as Sn-Ag[1] and Sn-Ag-Cu[1] eutectic solders with melting temperatures of 221ºC and 217ºC, respectively are the most prominent solders because of their excellent mechanical properties as compared with that of eutectic Sn-Pb solder[2]. Other candidates as drop in replacements for eutectic Pb-Sn solder, such as Sn-In-Zn alloys, may have melting point close to 185ºC, though not eutectic, and an acceptable solidification range but have received only limited attention due to various reasons & concerns[1].

During soldering, various interfacial reactions can occur between liquid solders and metallic substrates forming intermetallic compounds. Such interface formation can bring wetting as well as joint strength to secure joint ability, however excessive growth of intermetallic layers cause brittleness which adversely affects joint strength[2]. This happens after lengthy aging and multiple reflows, resulting in the excessive growth of compounds, such as Cu_6Sn_5 or the formation of another compound in the edge of the solder such as Cu_3Sn.

In lead free soldering, the interfacial reactions become complex due to multicomponent systems to improve their chemical and mechanical properties. Thus, to understand the microstructure and mechanical effect of alloying elements in solder on the interface formation becomes the key objective in this paper. Many reports claimed that SAC alloy is the most suitable candidate, however this study shows that Sn3.5Ag solder system performs better than Sn3.8Ag0.7Cu in terms of joint strength and brittle mode failure.

A detailed experimental work was carried out to study both the alloy systems in terms of melting behavior, microstructure, and mechanical strength. This was done with the effect of high temperature storage aging and multiple reflow conditions. Besides that, the study also included drop test evaluation and liquid-liquid thermal shock board level reliability result.

EXPERIMENTAL APPROACH
Two solder systems were studied, namely Sn3.5Ag and Sn3.8Ag0.7Cu on BGA components with Cu/Ni/Au pad finishing. Table 1 shows the solder composition and test vehicle of the experiment.

Table 1 - Solder Composition and Test Vehicle

Solder Composition	96.5wt%Sn3.5wt%Ag and 95.5%Sn3.8wt%Ag0.7wt%Cu
Test vehicle	480 TBGA
Package size	37.5 x 37.5mm
Ball Pitch	1.27mm
Ball diameter	30 mils (0.76 mm)
Solder Pad Solder Mask Opening	25 mils (0.64 mm)
Pad-to-ball Ratio	0.84
Solder Pad finishing	Electrolytic Ni-Au Plating

Similar lead free flux (water soluble) & ball attach reflow profile were used in this study. The ball attach profile is ramp-to-peak with 240^{0}C peak temperature & 35 second time above 230^{0}C as shown in Figure 1.

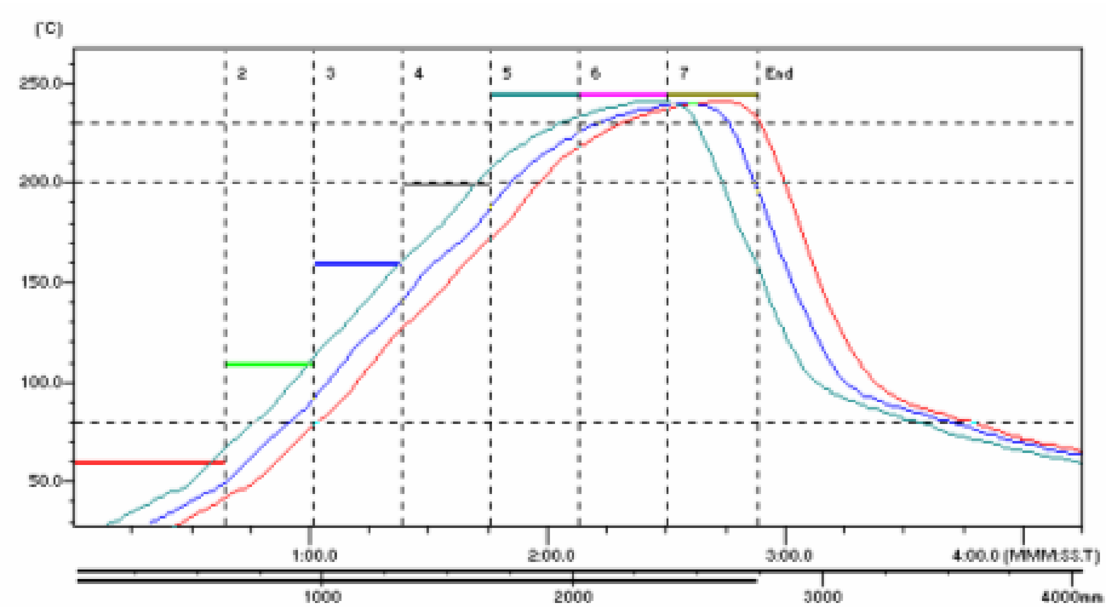


Figure 1 - Ramp-to-peak ball attach profile

Melting properties of each solder type was tested with differential scanning calorimeter (DSC). DSC model *Metler Toledo* 822e was used and the method is heating at rate of 5ºC/min from 180-260ºC. It is believe that melting properties affects the IMC growth as larger melting range is subjecting the unit to a longer heating period that will encourage IMC growth. Therefore, it is important to understand the melting properties of each solder composition.

IMC thicknesses were measured after cross-sectioning and solder joint strength between the solder ball and substrate was measured by shear and cold pull test using *Dage* 4000. Sample size for cross-sectioning is 3 units per read point, 2 balls per unit, and 3 maximum IMC peaks per ball. For ball shear, test height is 30µm and test speed is 300µm/s. For cold ball pull, pull speed is 5mm/s. Each run for shear & pull test will be 5 units and each unit will be sheared 8 balls (4 outer corner balls & 4 inner conner balls).

Samples for ball shear test, cold ball pull test and cross-sectioning for IMC thickness were prepared in two different tests conditions, which are high temperature storage (HTS) and multiple reflow. Samples of HTS were dry baked in oven at 150ºC. In this study, storage time tested were 0, 48, 96 and 168 hours. Besides observing the aging time, samples were multiple reflowed for 1x, 2x, 3x and 6x at peak temperature 240ºC using the 7-zone BTU production reflow furnace. In this study, T0 will be referred as fresh samples after assembly and T168 are samples after 168 hours of 150ºC thermal aging.

Microstructure and elemental analysis were done to evaluate the intermetallic structure and phases that were present at the joint. The cross sectioned units were etched for 1 minute in 10wt%HCL and 90wt%Ethanol solution before observing under SEM and EDX. The units were also gold coated to improve electron conductivity for a better imaging.

Drop test was done per ASE & Freescale methods to obtain drop till fail data. This is important to judge the solder joint's ability to absorb vibration & impact shock.

In terms of Board Level Reliability, liquid-to-liquid thermal shock data was gathered to study the solder joint's performance against thermal fatigue.

RESULT AND DISCUSSION

3.1 Melting properties

Table 2 shows the summary results of DSC for both solder alloy and each were tested three runs. Result on Figure 1 shows that composition Sn3.5Ag has melting peak ~ 4ºC higher than SAC 387. Average melting range is 2.3 ºC for Sn3.5Ag and 1.8 ºC for SAC 387, which is insignificantly different in terms of statistical t-test of the melting range, assuming normal distribution of the melting range data. The melting profile is shown in Figure 2 and 3.

Table 2 - Summary results of the melting behaviour

Solder	Onset (ºC)	Peak (ºC)	Endset (ºC)	Melting Range (ºC)	Average Melting Range (ºC)
Sn3.5Ag (# 1)	221.02	222.05	222.82	1.8	2.3
(# 2)	221.38	222.24	223.50	2.1	
(# 3)	220.58	223.03	223.68	3.1	
SAC 387 (# 1)	217.29	217.91	218.94	1.7	1.8
(# 2)	217.51	218.42	219.42	1.9	
(# 3)	217.39	218.04	219.09	1.7	

From the DSC result, both Sn3.5Ag & SAC 387 solder alloys have considerably small melting range. This is because Sn3.5Ag is the eutectic composition with melting point of 221 ºC, whereas SAC 387 solder is located near the ternary eutectic composition[4] with melting temperature of 217ºC. It is believe that the melting range influences intermetallic growth as the onset melting indicates the start of the molten solder reaction and endset indicates the end. Hence, the larger melting range indicates a longer temperature range of intermetallic formation, and hence a thicker intermetallic formation. General perception is that larger melting range will cause a higher IMC growth. However, in this study, this is not observed. Section 3.2 elaborates on the IMC cross-sectioning result.

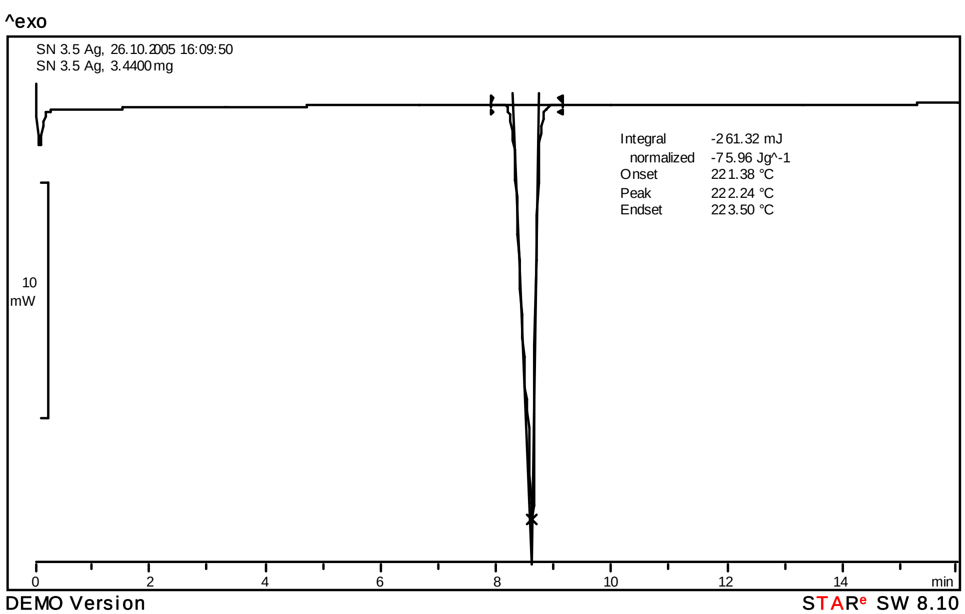


Figure 2 - DSC graph for Sn3.5Ag

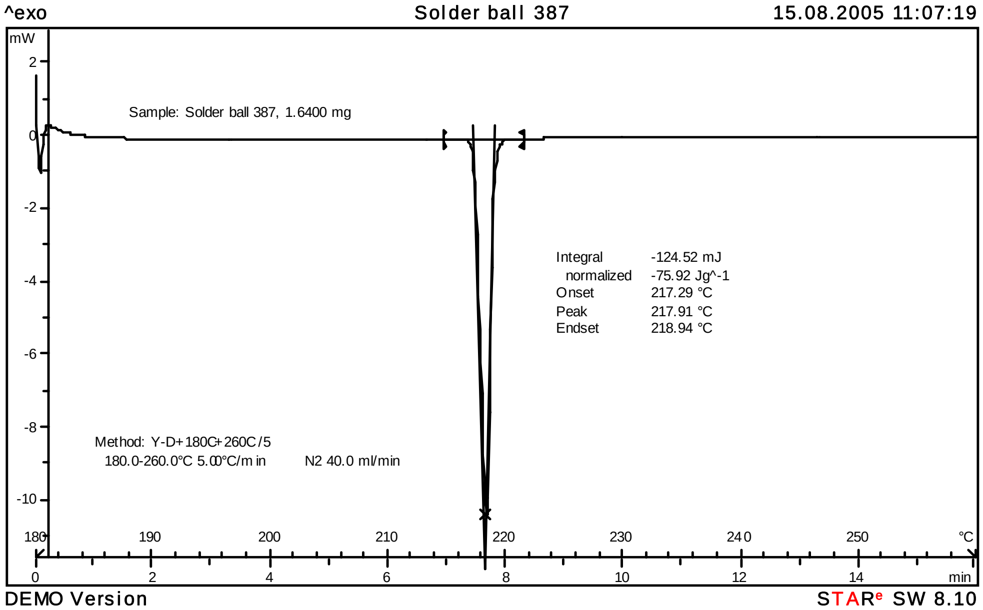


Figure 3 - DSC graph for SAC 387

3.2 IMC cross-sectioning result

IMC thickness is one of the major concerns to predict the solder joint reliability. It is reported that higher IMC thickness will cause the joint to be more susceptible to brittle failure. The thicker the IMC layer at the interface, the lower the shear strength of the joint[4]. Part of this study was focused on IMC cross-sectioning measurement using high power scope of 100x and Image Analyzer to measure the IMC thickness.

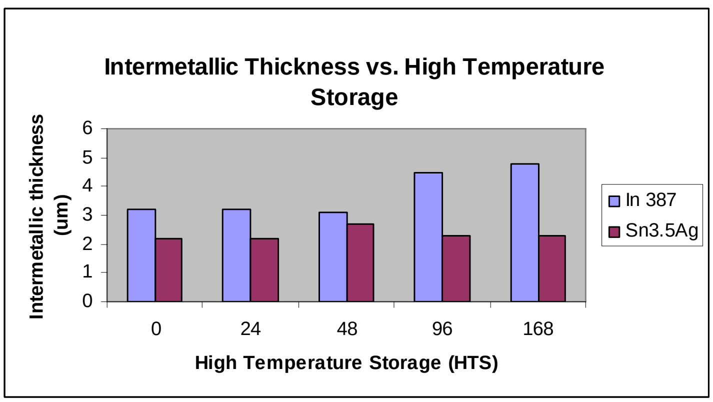


Figure 4 - Intermetallic thickness for HTS samples

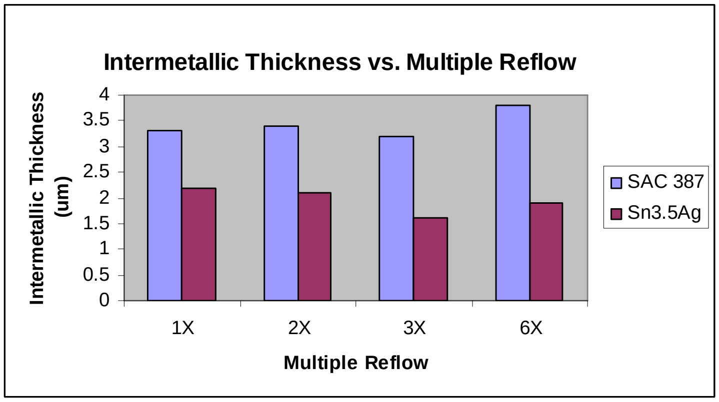


Figure 5 - Intermetallic thickness for multiple reflow samples

Figure 4 and 5 shows that Sn3.5Ag has lower intermetallic thickness for all the conditions of HTS and multiple reflow, compared to SAC 387. IMC thickness for Sn3.5Ag does not show significant growth after thermal aging & multiple reflow, but SAC 387 demonstrated significant growth. This proves that correlation between melting range and intermetallic thickness is not established in this study. Study has shown that SAC alloy with Cu-rich IMC has bigger grain size resulted in thicker IMC than Ni-Sn IMC[15] which in found in Sn3.5Ag alloy. Lower intermetallic thickness for Sn3.5Ag implies less brittle joint effect. Therefore, from this part of study, better joint reliability is expected for the Sn3.5Ag solder system.

3.3 Ball shear result

Ball shear test is used to estimate the joint strength of each solder composition with the pad metallurgy. Result of Figure 7 shows the average of shear result for both the solder system at different multiple reflow conditions. Both the alloys show ductile failure mode in all the stress conditions (see figure 6). Sn3.5Ag solder has relatively lower shear strength but still much higher above the lower spec limit of the shear strength (1000g). It is believe that the lower shear value is due to the nature of the solder that is softer (with Vickers hardness at 17.4 Hv) and less rigid compared to SAC 387 (with Vickers hardness at 18.2 Hv). Thus the alloy is malleable and able to absorb shearing impact.

Figure 6 - Ductile failure mode was observed after ball shear test in all the test conditions.

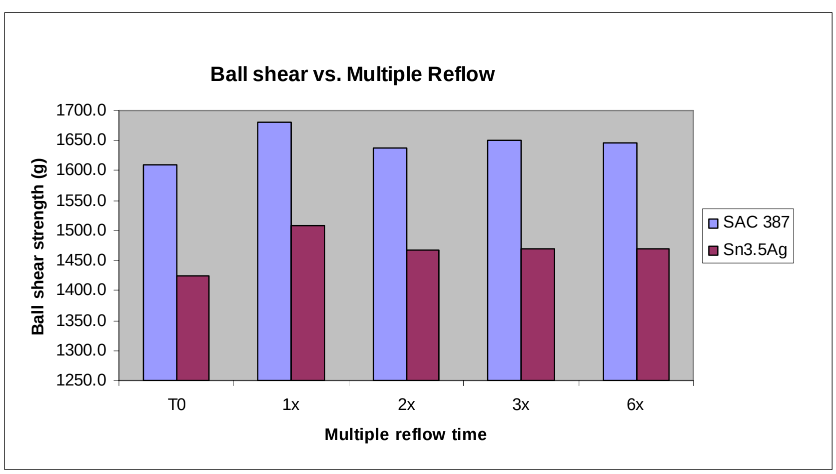


Figure 7 - Ball shear strength with multiple reflow time of 1x, 2x, 3x and 6x.

However, shear result for the high temperature storage units shown in Figure 8 shows a slightly different behavior compared to multiple reflow. Sn3.5Ag is found to have higher shear strength at T48, T96 & T168. This could be explained by the growth of Ag-Sn microstructure at the Sn3.5Ag solder after HTS condition that creates a dispersion hardening effect that further strenghens the alloy after thermal aging. Further explaination can be found in section 3.5.

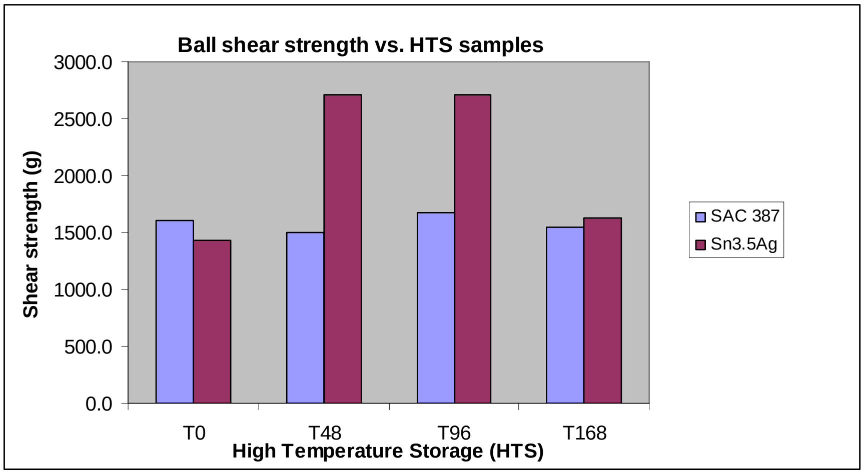


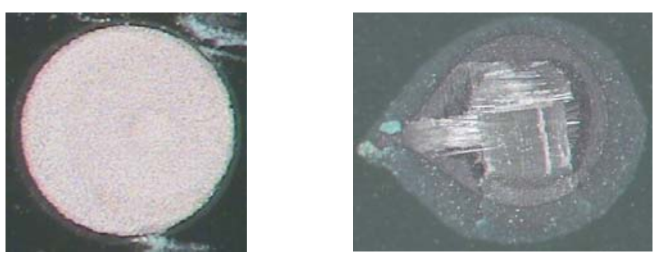
Figure 8 - Ball shear strength with HTS time of T0, T48, T96 and T168 hours.

3.4 Cold ball pull result

Cold ball pull method is widely acknowledged by the industry in the recent years to fully determined the weak interface and the joint strength. Ball pull is found to be more stringent than ball shear because of the pulling mechanicism that minimizes ball deformation above the bond site, as well as causes the bond not to be supported by the solder pad cavity wall, thus exposes the true bond strength. In the case of ball shear, higher ball deformation above the bond site is found at the peak of shear force which will result in smaller test area, and support from solder pad cavity wall could substantially shield a bad bond from failing[16].

Figure 10 and Figure 11 shows the pull strength of both the alloy system after multiple reflow and high temperature storage, respectively. Generally two break modes were observed: 1. IMC brittle failure and 2. lifted pad (see figure 9). Sn3.5Ag alloy system shows a significantly better solder joint performance where even at prolonged aging of reflow and HTS conditions, it has 0% of brittle failure and capable to maintain & even increase its joint strength throughout the aging conditions.

SAC 387 however shows a very high percentage of brittle failure (~100%) for both multiple reflow and HTS conditions. Both the conditions shows that joint strength decrease from T0 condition to 6x reflow and T168@150ºC storage.



(a) (b)

Figure 9 - Ball Pull failure mode: (a) IMC brittle failure, (b) lifted pad.

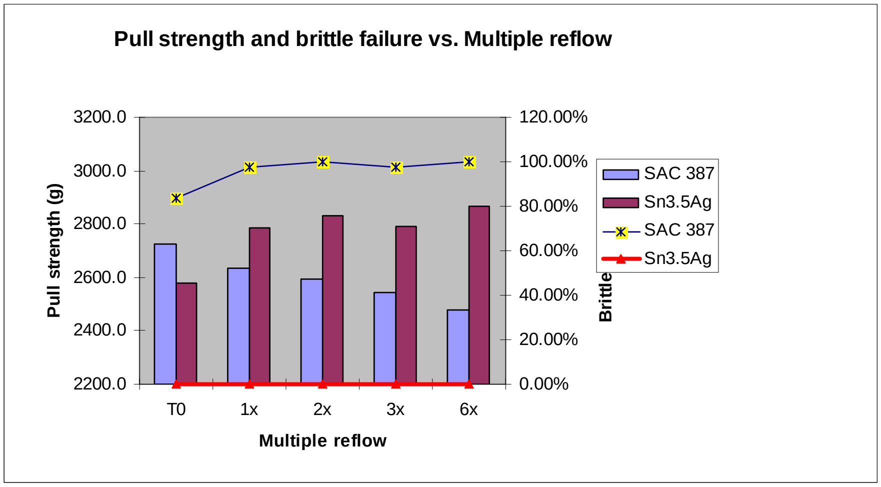


Figure 10 - Pull strength at 5000 um/s and percentage of brittle failure at multiple reflow of 1x, 2x, 3x and 6x.

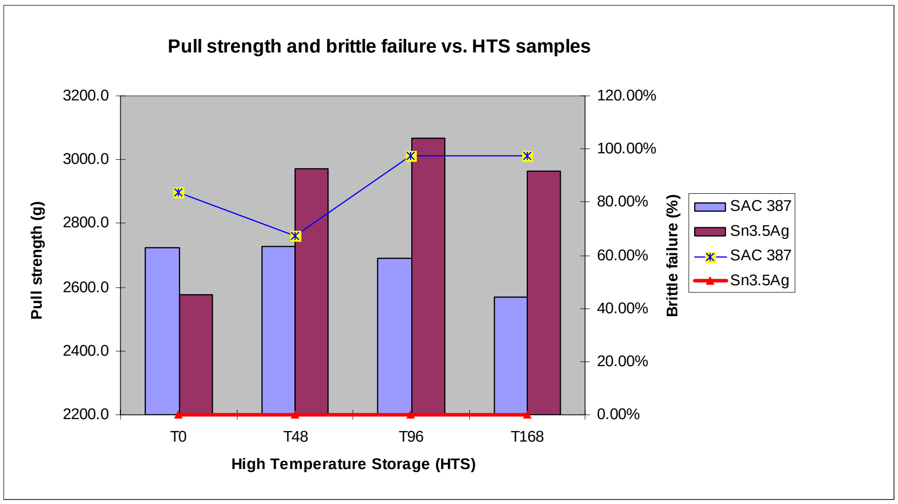


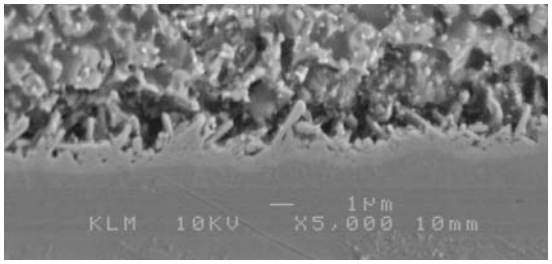
Figure 11 - Pull strength at 5000 um/s and percentage of brittle failure at HTS of T0, T48, T96 and T168.

From the ball pull result, it is obvious that Sn3.5Ag provides a far more superior solder joint than SAC 387.

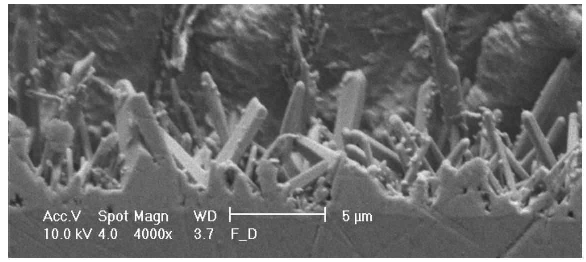
3.5 IMC microstructure and elemental analysis

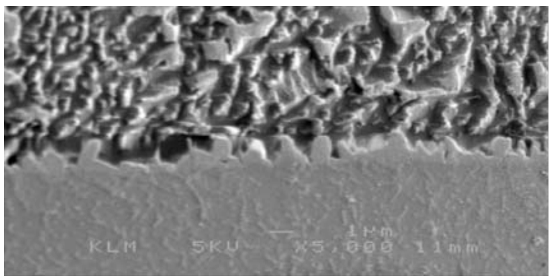
This part of study concentrates on microstructure and elemental analysis of SAC 387 and Sn3.5Ag at T0, T168 and 6x multiple reflow. It is utmost important to study the microstucture and elemental of the IMC to understand the joint physical structure and phases that present. This will help in understanding the effect of elemental and microstructure of IMC towards it's mechanical properties.

Figure12 shows the micrograph of a SAC 387 and Sn3.5Ag IMC at T0 (time zero). Microstructure of SAC 387 IMC has thin dendritic or needle like structure. As for Sn3.5Ag, the IMC has polygonal shaped Ni_3Sn_4 formed between the solder and Ni layer[5] and the IMC has better uniformity. This difference in physical IMC structure could explain why Sn3.5Ag has zero brittle failure at T0 condition. Compared to polygonal structure, dendritic structure has higher IMC peaks which create stress concentration points for crack initiation and resulted in IMC brittle failure.

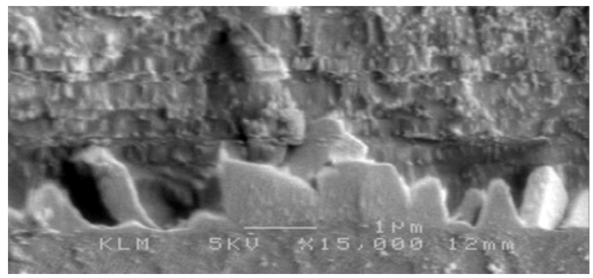


(a)



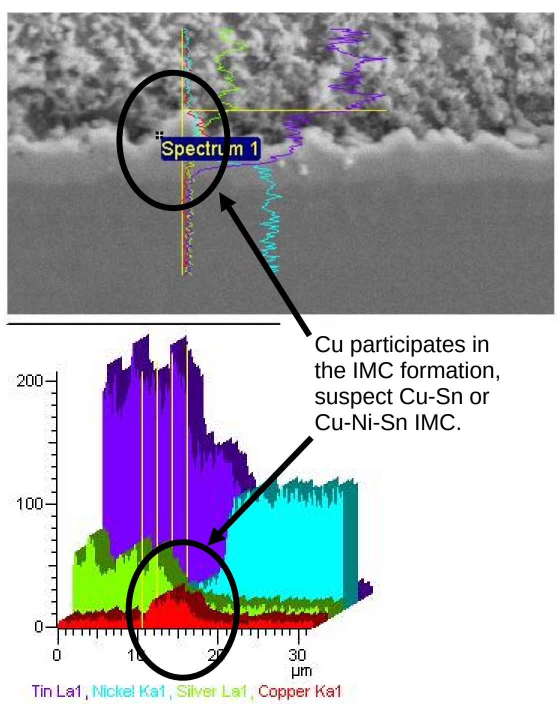


(c)

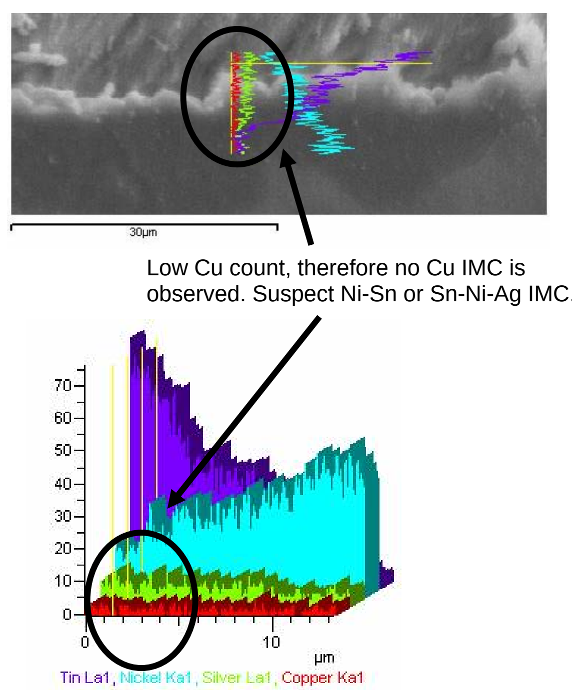


(d)

Figure 12 - Microstructure analysis at T0 (a) & (b) SAC 387 shows needle like/ dendritic structure (c) & (d) Sn3.5Ag shows polygonal structure with better uniformity



(a)



(b)

Figure 13 - Elemental analysis at T0 (a) SAC 387 shows Cu-Ni-Sn IMC formation (b) Sn3.5Ag shows Ni-Sn IMC and no copper IMC form.

Further EDX analysis in Figure 13(a) shows formation of Cu-Sn or Cu-Ni-Sn IMC phases present in SAC 387 solder with the pad metallization. In the Sn3.5Ag IMC however, no copper is detected to take part in the IMC formation, as shown in Figure 13(b). This is due to the solder has no copper in the composition and nickel act as barrier layer for the copper diffusion.

The first IMC phase to form during soldering in the Sn3.5Ag/Ni-Au systems was Ni_3Sn_4[6]. However, a very small addition of Cu to the Sn-rich solder alloys changed the behavior of the interconnection system completely. This could be seen in SAC 387 interphase has Cu-Ni-Sn IMC phases present, which are mainly $(Cu,Ni)_6Sn_5$ and $(Ni,Cu)_3Sn_4$[7]. Since the reaction rate of Ni and Sn is very slow compared to that of Cu and Sn[8], the initially formed IMC in SAC 387 is $(Cu,Ni)_6Sn_5$ phase and secondary formed IMC is $(Ni,Cu)_3Sn_4$ phase [9 & 10]. According to Paik, even though there are plenty of Ni and Sn souces at the interface, Cu-Sn IMC firstly formed, probably due to $(Cu,Ni)_6Sn_5$ phase is thermodynamically more stable than $(Ni,Cu)_3Sn_4$. A report from [11] mentioned that because there is lower interface energy between Cu_6Sn_5 and Ni, and Cu concentration is high enough (0.2-0.6wt%), the precipitation of Ni_3Sn_4 will be restrained.

At T168 hours of 150ºC storage, as shown in Figure 14(a) and (c), IMC microstructure of both solder system shows coarsening effect. The structure is not refined and thicker IMC layer is observed compared to T0 condition. A more distinctive observation is on the overall solder structure of Figure 14 (b) and (d), where IMC plate was found growing from the solder of SAC 387. On the Sn3.5Ag alloy, rod shape particles grow throughout the whole solder area. After storage in high temperature for a long time, these fine Ag_3Sn compounds grow and coarsen as rods. The existence and distribution of fine and hard Ag_3Sn result in dispersion hardening, which increases the mechanical strength for the Sn3.5Ag solder[12].

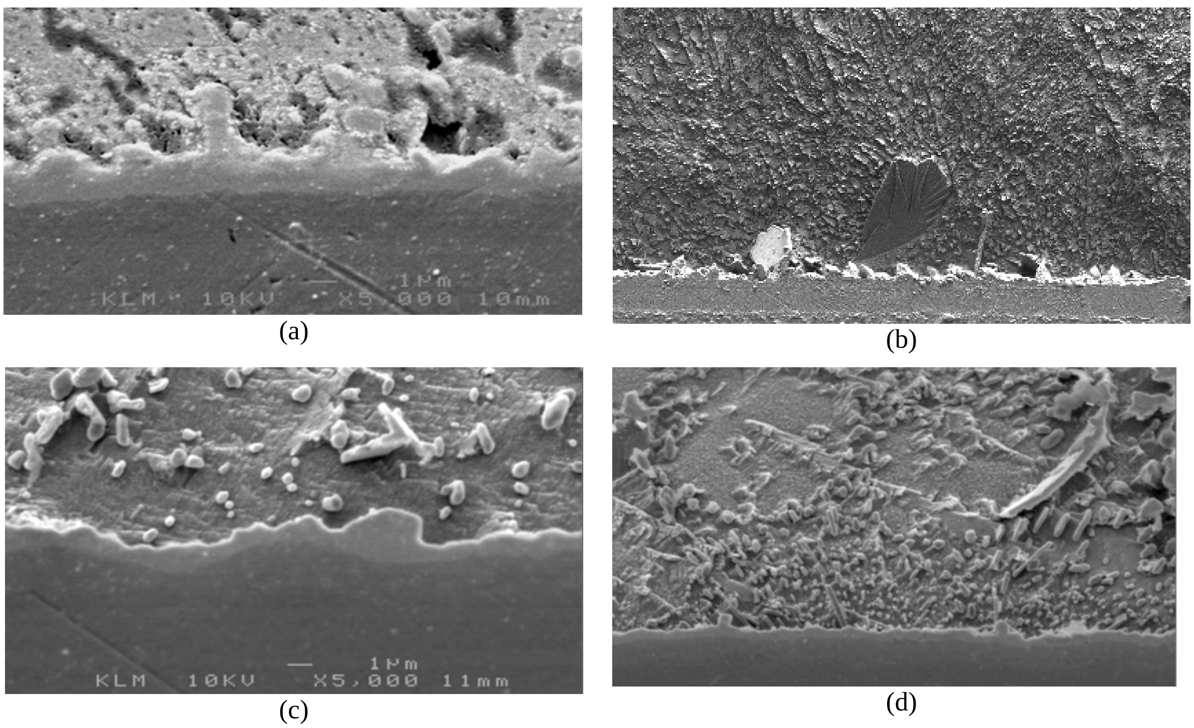
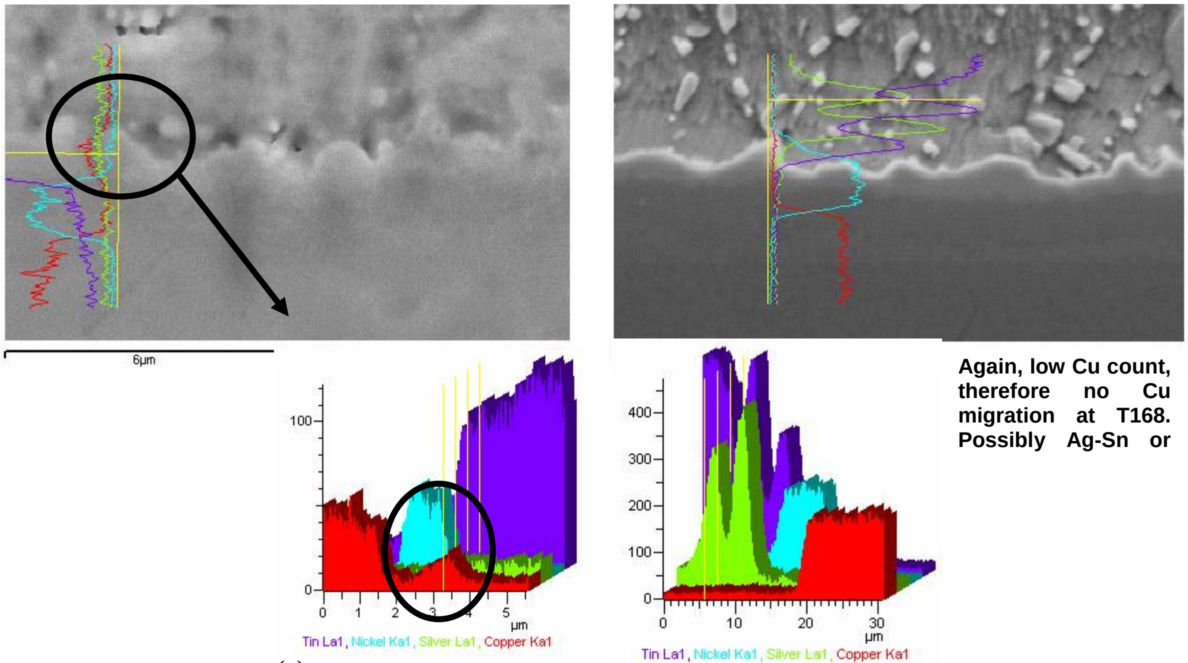


Figure 14 - Microstructure analysis at T168@150ºC (a) & (b) SAC 387 shows coarse dendrite structure with large IMC plate, (b) & (c) Sn3.5Ag shows coarse polygonal structure with rod shape particles disperse on the whole solder



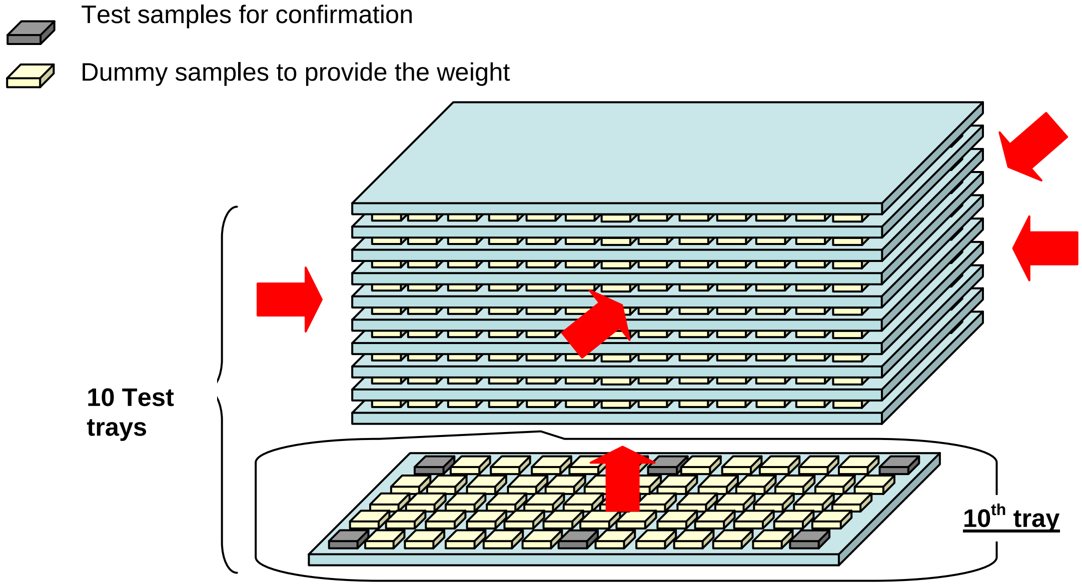
(a) (b)

Figure 15 - Elemental analysis at T168@150ºC (a) SAC 387 shows Cu-Ni-Sn IMC formation (b) Sn3.5Ag shows Ni-Sn or Ag-Sn IMC and no copper IMC form.

Figure15 is the EDX result of the intermetallic of both solder system after T168@150ºC. Again, the SAC 387 shows Cu-Ni-Sn IMC at the interphase and Sn3.5Ag still has no sign of Cu in the intermetallic. Many reports have pointed that brittle cracking involves Cu-Sn IMC, mainly on the present of Cu_6Sn_5 IMC. For SAC alloy where two IMC layers normally present (Ni-rich on top of Ni layer, Cu-rich on top of Ni-rich layer), failure mainly occurs due to brittle cracking in the Cu-rich IMC or within the interfacial area between the two IMC layers[13 & 14]. This does not happen in Sn3.5Ag solder system as Cu_6Sn_5 IMC does not exist and there is only one IMC layer which is Ni_3Sn_4.

3.6 Drop Tests

Two drop tests were carried out to assess the solder joints robustness againt vibration & impact shock. They were ASE drop test (6 units sample size) & Freescale packing drop test (60 units sample size) as illustrated in Figure 16 & Figure 17, respectively. The most stringent package chosen for this test was 740TBGA (37.5x37.5mm) with 1mm ball pitch and 0.68 pad-to-ball ratio. The samples were dropped through many cycles until dropped ball was found, with maximum 20 cycles tested. After every cycle, the samples were inspected for dropped balls and any broken trays were replaced to prevent dropped balls caused by chips from the trays. The number of cycles was recorded and shown in Table 2 for ASE drop test & Table 3 for Freescale Packing Drop Test.



1. Lay out 6 test samples in the 10th (Bottom) tray.
2. Lay out dummy samples in the rest of the trays.
3. Fix all the 10 trays with straps.
4. Drop 10 trays from 10cm height from the table/hard surface in 5 angles as shown by the arrows.

Figure 16 - ASE Drop Test

Freescale Packing Drop Test:-
Sample Size : 60 good units/lot
(6 units/tray with one unit at 4 corners and 2 units at the center and rest are dummy units,
5 full trays/bundle plus one empty tray on top, 2 bundles/box per packing spec)

Packed 2 bundles into one box

Packing Completed

Performed drop test in 10 angles per FSL requirement

Figure 17 - Freescale Packing Drop Test

Table 2 - ASE Drop Test Result

Solder Composition	No of Cycle tested	No of Cycle when ball drop happened	No of units with ball drop	No of balls drop
Sn3.5Ag	17	17	2	2
SAC 387	2	2	1	4

Table 3 - Freescale Packing Drop Test Result

Solder Composition	No of Cycle tested	No of Cycle when ball drop happened	No of units with ball drop	No of balls drop
Sn3.5Ag	20	No ball drop seen	0	0
SAC 387	3	3	3	5

From the drop test result, it can be concluded that Sn3.5Ag solder system is more robust than SAC 387 against vibration and impact shock.

3.7 Board Level Reliability

Liquid-to-liquid thermal shock (LLTS) data at -55^{0}C to 125^{0}C was gathered to study the solder joint's performance against thermal fatigue. Table 4 shows the test vehicle details. LLTS result is displayed in Figure 18.

Table 4 - Test vehicle for liquid-to-liquid thermal shock

Test vehicle	388 PBGA
Package size	27 x 27 mm
Ball Pitch	1mm
Die Size	387.70 x 401.50 mils
Wafer Thickness	14 mils
Mold Cap Size/Thickness	24 x 24 mm/1.15mm
Pkg Thickness (exclusive of Solder Balls)	1.71 mm
Ball diameter	23.6 mils (0.60 mm)
Solder Pad Solder Mask Opening	20 mils (0.50 mm)
Pad-to-ball Ratio	0.84
Solder Pad finishing	Electrolytic Ni-Au Plating
PCB Solder Pad finishing	Cu OSP
Solder Paste for Component Attachment on Board	SAC

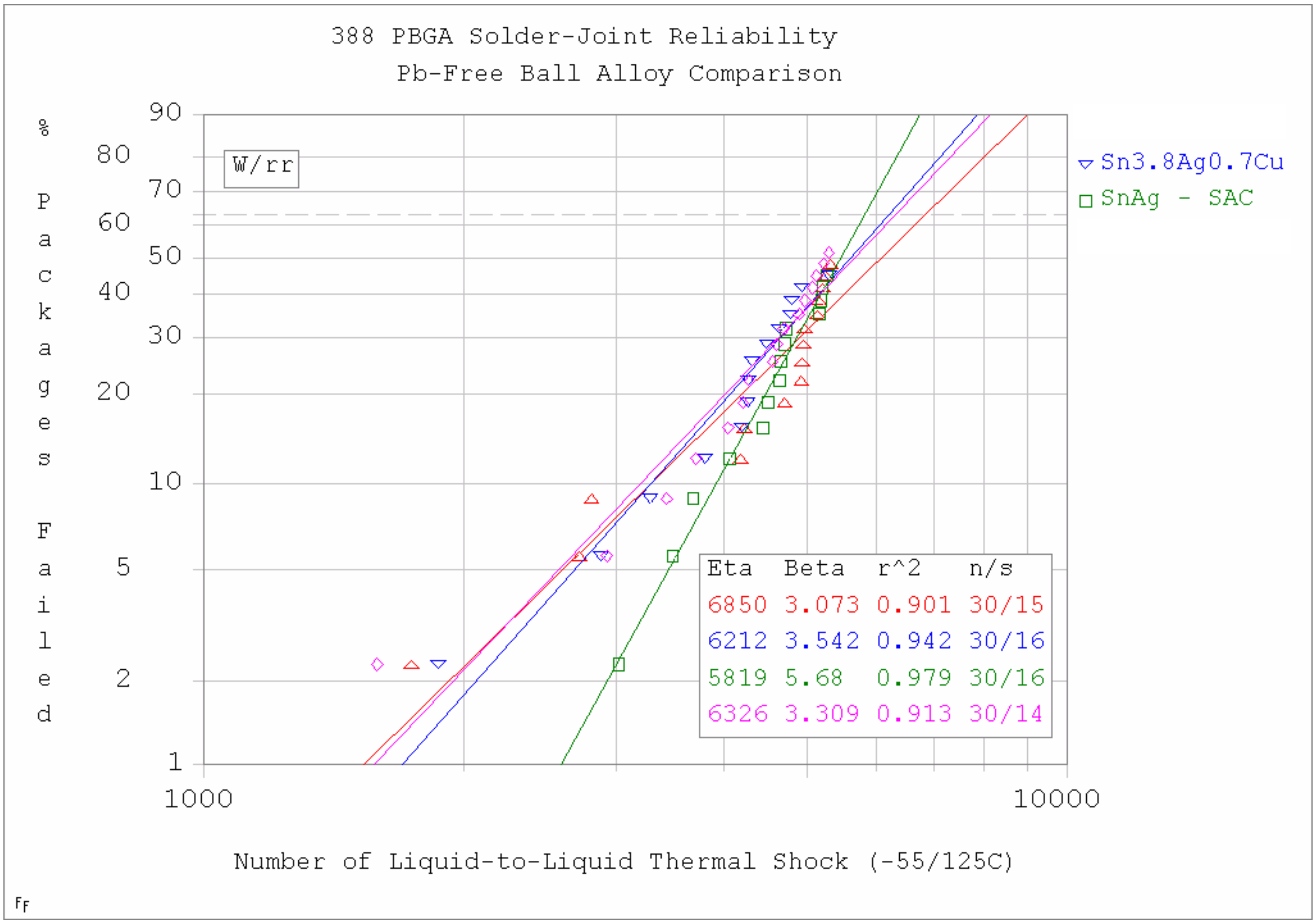


Figure 18 - LLTS result on 388 PBGA

From the LLTS result in Figure 18, Sn3.5Ag has shown better performance than SAC 387 in terms of robustness against thermal fatigue.

CONCLUSION

i. Sn3.5Ag has 4^{0}C higher melting temperature but similar melting range as compared to SAC 387. This will not affect ball attach reflow as well as component mounting on PCB at PCB assembly because this study has proven that the same ball attach reflow profile with 240^{0}C peak temperature & 35 second time above 230^{0}C is able to provide outstanding solder joint improvement on Sn3.5Ag over SAC 387.

ii. Microstructure and IMC formation for

a. SAC 387 : Cu-Ni-Sn, with dendrite/needle like IMC

b. Sn3.5Ag : Ni-Sn, with polygonal like IMC

c. No Cu IMC detected for Sn3.5Ag after 168 hrs of baking at 150^{0}C and after 6x reflow.

iii. After thermal aging of Sn3.5Ag, fine Ag_3Sn compounds grow and coarsen as rods distribute to the whole solder and thus further strengthens the solder system.

iv. Sn3.5Ag performs better compared to SAC 387 in terms of ball pull and ball shear. No brittle failure reported for ball pull upto 168 hrs of baking at 150^{0}C and 6x reflow, but SAC 387 has ~100% of brittle failures.

v. Sn3.5Ag encountered ball drop after 17 cycles of ASE drop test but SAC 387 failed for ball drop after just 2 cycles. No failure for Sn3.5Ag after 20 cycles of Freescale Packing Drop Test but SAC 387 failed at the 3rd cycle of drop test. This shows that Sn3.5Ag solder system is more robust than SAC 387 against vibration and impact shock.

vi. LLTS board level reliability data shows better result for Sn3.5Ag in terms of robustness against thermal fatigue.

Therefore, two possibility of the higher joint strength in Sn3.5Ag:

- No Copper involved in IMC formation, thus eliminates Cu-Ni-Sn IMC formation and resulted in only one IMC layer, which eliminates risk of IMC interfacial cracking.
- The rod IMC of Ag3Sn acts as strengthening factor to the solder.

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