A STUDY ON PROCESS, STRENGTH AND MICROSTRUCTURE ANALYSIS OF LOW TEMPERATURE SnBi CONTAINING SOLDER PASTES MIXED WITH LEAD-FREE SOLDER BALLS

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ABSTRACT

As the traditional eutectic SnPb solder alloy has been outlawed, the electronic industry has almost completely transitioned to the lead-free solder alloys [1] [2]. The conventional SAC305 solder alloy used in lead-free electronic assembly has a high melting and processing temperature with a typical peak reflow temperature of 245ºC which is almost 30ºC higher than traditional eutectic SnPb reflow profile. Some of the drawbacks of this high melting and processing temperatures are yield loss due to component warpage which has an impact on solder joint formation like bridging, open defects, head on pillow [3], and other drawbacks which include circuit board degradation, economic and environmental factors [4], and brittle failure defects in the circuit board like pad cratering. To overcome this, a detailed study has been carried out on low temperature lead-free solder paste that utilizes Bi bearing alloys.

Three low temperature lead-free solder pastes Sn-58Bi, Sn-57Bi-1Ag and Sn-40Bi-Cu-Ni with the melting temperatures around 138ºC (which is 45ºC below eutectic SnPb and 79ºC below SAC) were printed on Cu-OSP finish test boards. These pastes were assembled with SAC305, Sn99CN and Sn100C solder spheres. The range of Bi concentrations for various resulting mixtures used in this study was calculated to be in the range of 2 to 4 wt%. The mixtures were reflowed under two different low temperatures reflow profiles; (a) a traditional SnPb profile with a peak temperature 217ºC and (b) a low temperature SnBi profile with a peak temperature 177ºC (recommended by the paste manufacturer). After the assembly process, the mixed solder joints were shear tested to study the failure modes and shear strength at rate of 27.50mils/sec. Cross sectioning was performed to evaluate the possible microstructural changes at room temperature and after aging conditions that may have led to the changes in failure mode observed in shear testing. The isothermal aging condition used in the study is 125ºC for 200 hours which mimics 21 years of field storage at 25ºC degrees using Arrhenius extrapolation for Cu_6Sn_5 intermetallic formation. Our study suggests that high temperature reflow profile (217ºC peak profile) had better mechanical strength than the low temperature reflow profile (177°C peak profile). A metallurgical explanation for the improvement is presented in this paper. Thus, this paper describes that by generating a robust reflow assembly process for SnBi solder paste, the shear strength can be increased, cost of manufacturing can be reduced and high temperature assembly process (SAC) issues can be minimized which may improve product yield in production.

Key words: Low temperature assembly process, SnBi containing solder alloys, Reflow profile, Shear testing, alloy mixing

INTRODUCTION

SnPb was proven to provide desirable soldering performance and reliability. However, the use of lead in the consumer products has been outlawed by Restriction of Hazardous Substances directive (RoHS) [5]. At present, PCB's that are used in consumer electronic products are assembled with components by reflow soldering with lead-free solder SnAgCu (SAC) which was recommended by NEMI [6]. SAC solder alloys has peak assembly processing temperatures ranging from 240ºC to 260ºC. Some of the issues with this high temperature SAC solder alloys are:

a) High melting and processing temperatures which necessitated the use of high Tg boards which is expensive [7].
b) Due to high processing temperature CTE mismatch issue arises which may lead to warpage. This warpage has an impact on solder joint formation like bridging, head on pillow, open defects etc. [8] [9]
c) SAC solder exhibits coarsening of microstructure during thermo mechanical fatigue resulting in degradation of mechanical and thermo-mechanical properties. [10]
d) The economic impact of a high melting point solder alloy due to the need for high Tg boards and the energy costs in running the reflow oven at higher temperatures result in an increase in the cost of manufacturing. Moreover, higher CO_2 emissions from these high temperature reflow is an environmental issue [4].

To address these issues various research has been carried out to study low temperature lead-free solder alloys. NASA, DOD and other previous researchers carried out studies with SAC solder containing small amount of Bi. These alloys were found to reduce the melting temperature as low as 206ºC and shown to improve thermal cycling reliability [11] [12]. This showed that when Bi is added to SAC solder in low concentrations the melting temperature is reduced and the reliability can be improved. But these researches were focused mainly on reducing the melting temperature of the solder alloy and they lacked in detailed investigation of mechanical strength, material behavior, failure mechanisms and microstructural analysis. It was also shown that a risk was associated with mixing SnBi paste with SnPb terminated component. It was found that the melting temperature of the resulting mixture could produce a low temperature alloy (96ºC melting point) which is very low when compared to the operating and processing temperatures of most electronic devices. This posed a risk in the early years of lead-free adoption when many factories did not have adequate quality control protocols in place to separate SnPb and lead-free product lines. Finally, one of the studies suggests that by adding bismuth in concentrations of 2 to 4 wt% to tin, tin whisker growth can be reduced to some extent [13].

Currently research is being carried out on low melting point, high concentration bismuth tin based solder alloys like Sn-58wt%Bi, Sn-57wt%Bi-1wt%Ag wt% and Sn-40wt%Bi-Cu-Ni. SnBi solder paste is in the market already but one drawback of not using in consumer products has been its brittleness of Bi under mechanical shock conditions [14]. A few studies proved that by adding 0.25wt% to 1.0wt% of silver to SnBi solder alloy, can improve the ductility and reduce the brittle deformation behavior of SnBi alloys [15] [16]. Moreover, recent research has revealed that by mixing BGA solder balls with Bi-Sn-Ag solder paste has shown significant reduction in mechanical drop reliability when compared with solder joints formed with SAC solder paste with SAC ball [17] [18]. However, no paper has discussed the mechanical behavior, or the microstructure of the solder joint and its effect on failure mechanism in mixing SnBi solder paste with the lead-free solder balls.

The objective is to provide the industry with processing recommendations for the products that are assembled using high temperature SAC solder balls with low temperature SnBi solder paste.

METHODOLOGY

In this study we have focused on the analysis of mixing lead-free solder spheres composed of SAC305(Sn-3.0Ag-0.5Cu), Sn100C(Sn-0.7Cu-0.05Ni+Ge) and Sn99CN(Sn-1.1Ag-0.7Cu-0.05Ni+α) with the following low temperature SnBi solder pastes; L20(Sn-58wt%Bi), L23(Sn-57wt%Bi-1wt%Ag) and L27(Sn-40 wt%Bi-Cu-Ni - the wt% of Cu-Ni is less than 1% cumulatively) manufactured by Senju Metal Industry Co. Limited.

A) Solder Alloys

Three different SnBi bearing low temperature solder paste and three lead-free solder balls were used in this study. The list of solder spheres, their diameters and the solder pastes used in this study are listed in table 1.

Table 1. List of Solder Alloys

Solder Alloys	Composition Wt %	Melting Point (°C)	Sphere Diameter/ Particle Size of Powder
SAC 305	Sn/3.0Ag/0.5Cu	217ºC	30mils
Sn100C	Sn/0.7Cu/0.05Ni+Ge	227ºC	20mils
Sn99CN	Sn/1.1Ag/0.7Cu/0.05Ni+α	227ºC	18mils
L20	Sn/58Bi	139ºC ~ 141ºC	Type 4 Solder Paste
L23	Sn/57Bi/1Ag	138ºC ~ 204ºC	Type 4 Solder Paste
L27	Sn/40Bi-Cu-Ni	138ºC ~ 174ºC	Type 4 Solder Paste

Sample test boards with Cu-OSP surface finish used in this study is shown in figure 1. The board dimensions and thickness are 66mm x 66mm and 2mm respectively. The board has 7 different pad dimensions with 75 pads for each dimension which are all solder mask defined. The nominal and measured pad dimensions are in table 2.

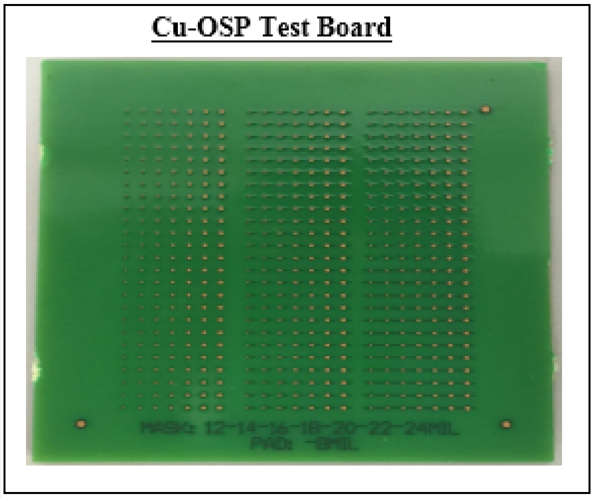


Figure 1. Cu-OSP Test board

Table 2. Board Dimensions

Nominal Pad Diameter (mils)	Measured Pad Diameter (mils)
12	10.8
14	12.8
16	14.7
18	16.8
20	18.9
22	21.0
24	23.0

B) Reflow Profiling

Two different reflow profiles were used, a) High temperature profile and b) Low temperature profile (figure 2). The peak temperature of high temperature profile and low temperature profile are 215ºC and 177ºC respectively.

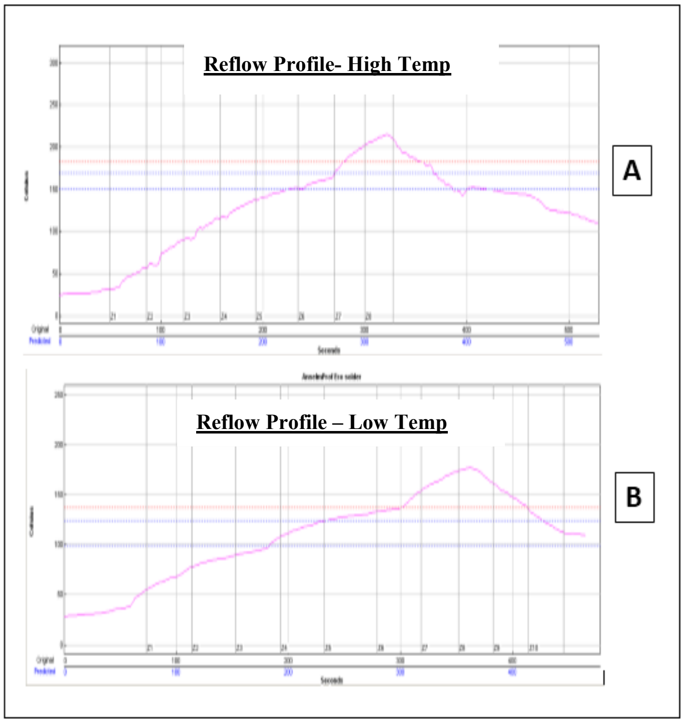


Figure 2.Reflow Profile a)High Temperature SnPb and b) Low Temperature SnBi.

The solder manufacturers recommended reflow specification for low temperature SnBi profile and high temperature SnPb profile is as follows in table 3.

The actual generated reflow profile specification for high temperature process and low temperature process are shown in table 4 below. All the reflow parameters are within the specification given by the solder manufacturers.

Table 3. Solder Manufacturers Recommended Specifications

Reflow Profile	Max Rising Slope (°C/seconds)	Soak Time (seconds)	Peak Temp (°C)	Time Above Liquidus (seconds)
High Temp	0 - 1.5	0 - 60	205 - 225	30 - 90
Low Temp	0 - 2	0 - 60	165 - 200	60 - 120

Table 4. Generated Reflow Specifications

Reflow Profile	Max Rising Slope (°C/seconds)	Soak Time (seconds)	Peak Temp (°C)	Time Above Liquidus (seconds)
High Temp	1.45	48	215	76
Low Temp	0.98	50	177	101

C) Solder Paste – Ball Resulting Mixture after Reflow

The resulting mixture of solder paste-ball after reflow are shown in table 5 below. The range of Bi concentrations for various resulting mixtures used in this study was calculated to be in the range of 2 to 4 wt% [19].

Table 5. Resulting Solder paste-ball Mixture after Reflow

Mixed Solder Alloy	Composition in Wt % of Solder Mixture After Reflow
L20 + SAC305	Sn - 93.14% Bi - 3.56% Ag - 2.81% Cu - 0.47%
L23 + SAC305	Sn - 93.15% Bi - 3.50% Ag - 2.87% Cu - 0.47%
L27 + SAC305	Sn - 94.31% Bi - 2.33% Ag - 2.82% Cu - 0.5% Ni - 0.029%
L20 + Sn100C	Sn - 95.21% Bi - 4% Cu - 0.651% Ni - 0.023% Ge - 0.023%
L23 + Sn100C	Sn - 95.14% Bi - 4% Ag -0.07% Cu - 0.65% Ni - 0.023% Ge - 0.023%
L27 + Sn100C	Sn - 96.55% Bi - 3% Cu - 0.687% Ni - 0.057% Ge - 0.023%
L20 + Sn99CN	Sn - 94.47% Bi - 4% Ag - 1.02% Cu - 0.65% Ni+α – 0.047%
L23 + Sn99CN	Sn - 94.51% Bi - 3.71% Ag - 1.08% Cu - 0.65% Ni+α - 0.046%
L27 + Sn99CN	Sn - 95.71% Bi - 2% Ag - 1.03% Cu - 0.68% Ni+α - 0.078%

D) Shear Testing

Ball shear testing is a destructive test method that is used to study the solder joint strength. This tests are not intended as a field reliability study, rather as a representation of the manufacturability of these alloys through the final box build and final product packaging and handling. The reflowed solder balls were sheared individually using the shear tool (figure 3) and shear force is measured (in grams) throughout the test. Fifteen solder balls were sheared for each solder mixture and the readings were noted. A 100kg load cartridge was used with test speed of 27.50mils/sec and the height of the tool from the PCB is 1 mil. The shear force in grams is converted to Newton's which is then normalized to MPa for the various pad sizes studied in this research. The parameters used for shear testing are as follows in table 6.

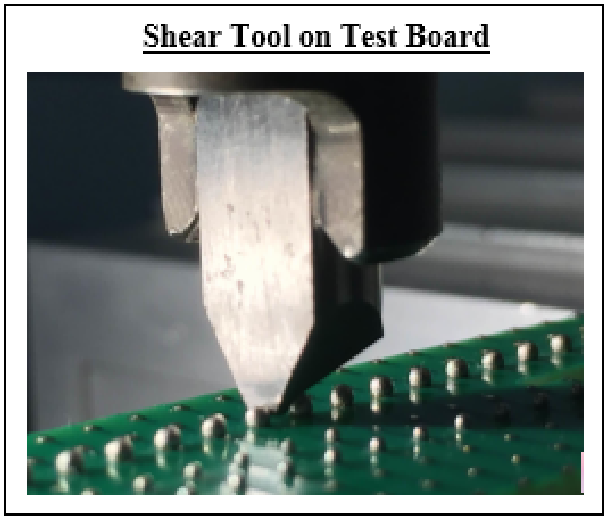


Figure 3. Shear tool on Test Board

Table 6. Ball Shear Test Parameters

Parameters	Description
Load Cartridge	100kg
Range	0 to 5 kg (+/- 1.25)
Test Speed	27.5 mils/sec
Test Load	2000g
Land Speed	19.6 mils/sec
Shear Height	1 mil

E) Aging Treatment

Isothermal aging is done to study the consequence and effect of constant prolonged elevated temperature on solder alloys and to study the effect of intermetallic growth on solder joint strength. The Arrhenius Equation is used to correlate time in the field at normal use temperature to a constant temperature accelerated life test.

The Acceleration Factor (AF) calculation by using Arrhenius extrapolation is as follows,[20]

$AF = e^{[(-Ea/K)(1/T1-1/T2)]}$

T_1 = Field Temperature (K)

T_2 = Test Temperature (K)

$E_a = 0.7eV$

$K = 8.62x10^{-5}$ eV/K (Boltzman constant)

To mimic end of life conditions, isothermal aging of our sample solder joints were aged at 125ºC for 200 hours.

RESULTS AND DISCUSSION

Fifteen solder bumps were sheared for each combination and the shear forces were noted. Box plot graph was also plotted for all the paste ball combinations in after reflow and aging conditions (figure 4).

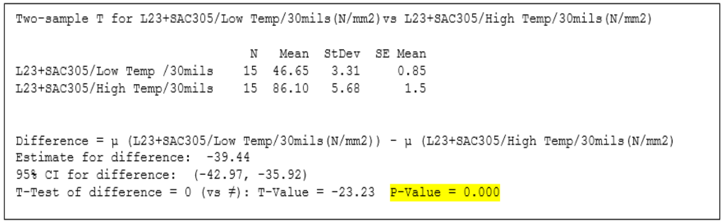
The mean shear strength of various mixed lead-free solder alloy combinations in two different reflow profiles are shown in table 7.

From the shear strength analysis, it can be seen that in all the three solder ball alloys (SAC305, Sn100C and Sn99CN) the shear strength of the high temperature reflow profile is higher than the low temperature reflow profile. A 2 sample t-test statistical analysis was carried out which clearly shows that there is a significant change in the shear strength of high temperature reflow profile and low temperature reflow profile which can be seen below in table 8. This result is consistent with all the solder paste-ball combinations.

Table 7. Mean Shear Strength of Various Solder Mixtures under After Reflow and After Aging Conditions.

Solder Sphere	Solder Paste	Reflow Profile	Mean Shear Strength in MPa (After Reflow)	Mean Shear Strength in MPa (Aging)
Sn99CN	L20	Low Temp	65.54	73.43
		High Temp	79.36	99.17
	L23	Low Temp	76.39	70.48
		High Temp	91.72	101.45
	L27	Low Temp	68.13	66.11
		High Temp	74.53	96.51
Sn100C	L20	Low Temp	73.05	67.97
		High Temp	81.63	82.95
	L23	Low Temp	64.48	67.31
		High Temp	83.07	85.19
	L27	Low Temp	68.70	63.29
		High Temp	71.57	76.78
SAC305	L20	Low Temp	40.05	45.83
		High Temp	68.19	65.22
	L23	Low Temp	46.65	40.30
		High Temp	86.09	75.82
	L27	Low Temp	48.86	35.01
		High Temp	81.87	79.87

Table 8. Two sample t-Test Results Showing Significance of Low Temperature and High Temperature Reflow Process



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Two-sample T for L23+SAC305/Low Temp/30mils(N/mm2)vs L23+SAC305/High Temp/30mils(N/mm2)

                             N   Mean  StDev  SE Mean
L23+SAC305/Low Temp /30mils   15  46.65   3.31     0.85
L23+SAC305/High Temp/30mils   15  86.10   5.68      1.5


Difference = μ (L23+SAC305/Low Temp/30mils(N/mm2)) - μ (L23+SAC305/High Temp/30mils(N/mm2)
Estimate for difference:  -39.44
95% CI for difference:  (-42.97, -35.92)
T-Test of difference = 0 (vs ≠): T-Value = -23.23  P-Value = 0.000
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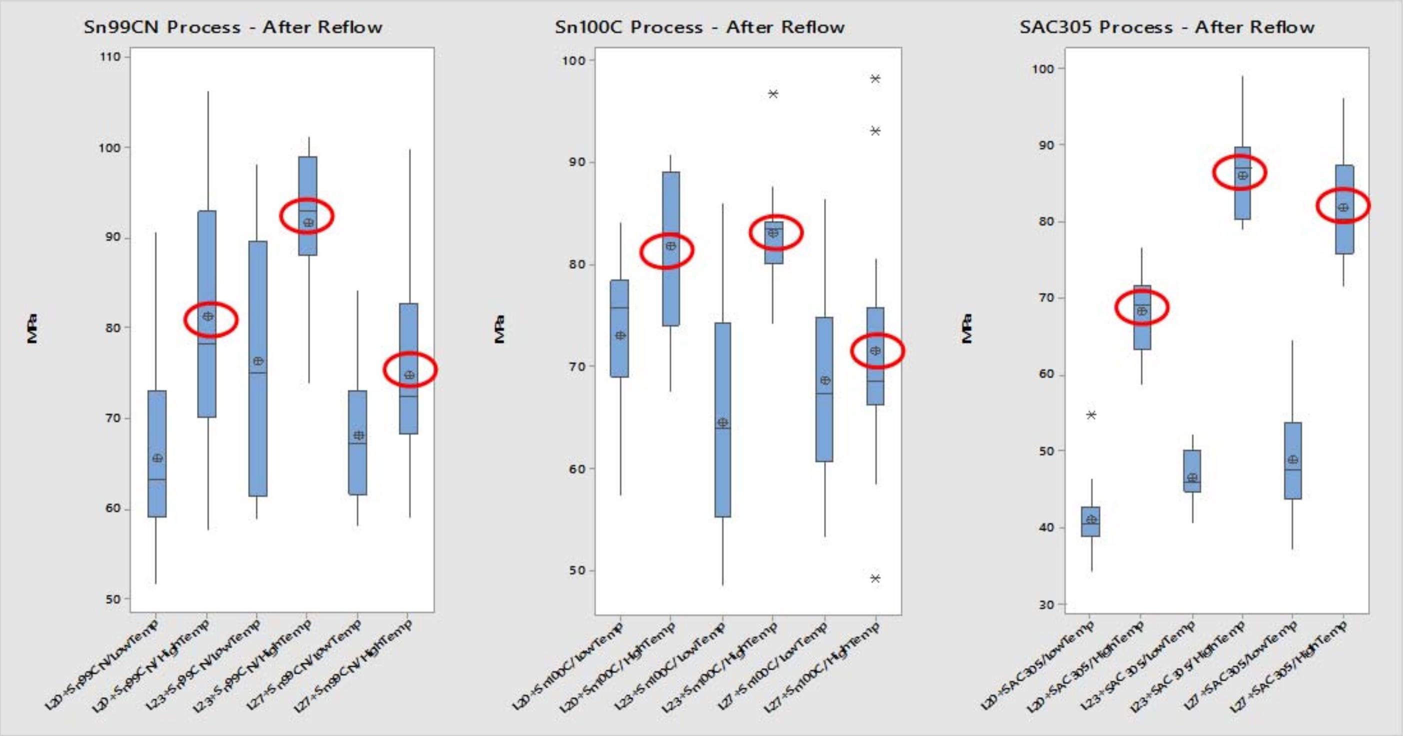
The cross section samples were evaluated using the optical microscopes to study the solubility of SnBi paste on lead-free solder balls. The figure 5 shows that not all alloys completely mixed in the high temperature reflow process.

Most notably the L23 paste mixed with Sn100C resulted incomplete mixing in the high temperature process. This is likely due to thigh high melting point and large pasty range of the Sn100C alloy.

When analyzing the combination of L20+SAC305 processed with the low temperature reflow profile (a) there was not much dissolution in the mixed solder alloy combinations which can be seen in figure 5 where the paste on the bottom and the ball on the top can be seen clearly. Whereas with the high temperature reflow profile (b), the tin has completely dissolved into the bismuth where the ball and paste are completely dissolved. This change in the dissolution is likely due to the difference in the peak temperature of the two reflow profiles. With the low temperature reflow profile the SAC ball is not able to melt completely as its melting temperature is 217ºC and peak temperature of the reflow profile is 177ºC. But in the high temperature reflow profile, with the peak reflow temperature of 215ºC, the SnBi paste and SAC305 balls are able to dissolve better than the low temperature reflow profile process.

In L23+Sn100C sample, for the low temperature reflow profile (a) there is no dissolution between SnBi paste and the Sn100C ball which is same as the SAC305 process, whereas for the high temperature reflow profile (b) the SnBi paste is partially dissolved with Sn100C solder ball which can be seen in figure 5.

Box Plot – After Reflow Condition



Box Plot – After Aging Condition

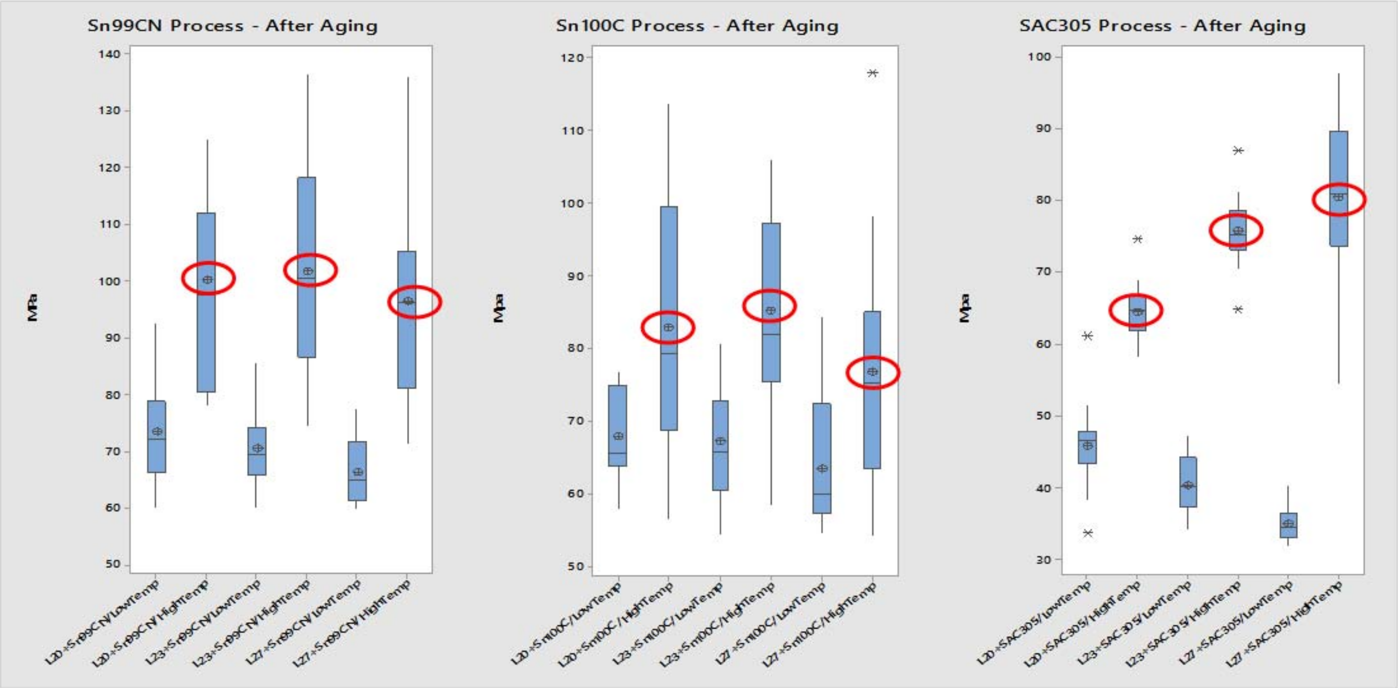


Figure 4. Boxplot Comparison of High Temperature and Low Temperature Reflow Process in After Reflow and After Aging Conditions. From the highlighted circles it is evident that the shear strength of the high temperature (SnPb) process is higher that the shear strength of the low temperature (SnBi) process in all the paste ball calculation.

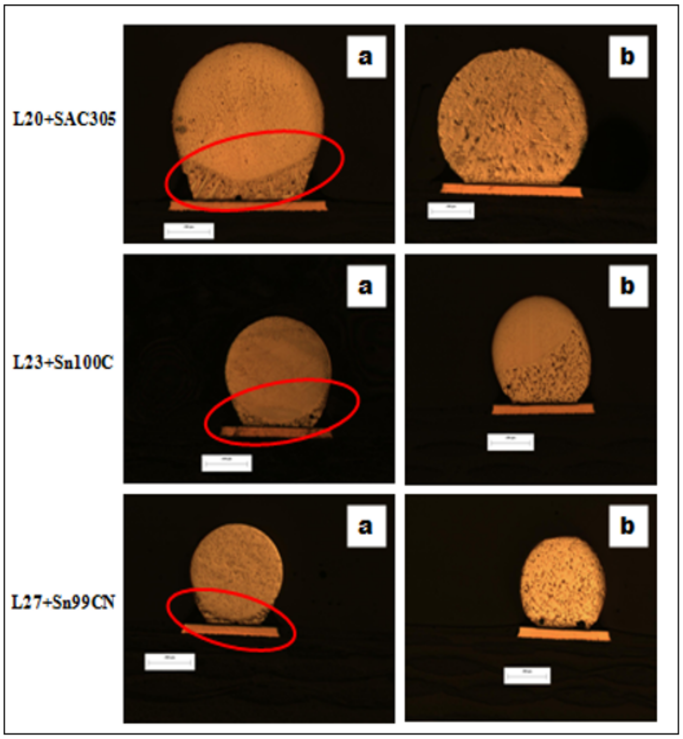


Figure 5. Dark field image of L20+SAC305, L23+Sn100C, L27+Sn99CN a) Low Temperature Reflow Profile (SnBi) b) High Temperature Reflow profile (SnPb). The red circles highlight regions of low temperature solder below the unreflowed lead-free solder ball.

The partial dissolution in Sn100C process is because of very high melting temperature of Sn100C ball (227ºC) and its high pasty range. Therefore, at a peak reflow temperature of 215ºC the Sn100C ball is not able to dissolve completely as it did for SAC305 ball.

In L27+Sn99CN sample, for the low temperature reflow profile (a), there is no dissolution between SnBi paste and the Sn99CN ball. This is consistent with all the three processes for low temperature profile. With the high temperature reflow profile (b) the SnBi paste and the ball has completely dissolved.

From this analysis, Sn100C process looks to be different from the other two process (SAC305 and Sn99CN) in terms of high temperature profile. The reason for the partial dissolution in the Sn100C process is due to the absence of silver content in the solder ball. With SAC305 and Sn99CN there are 3% and 1.1% of silver in the solder ball respectively. So, with the silver content in the solder ball, the tin is able to dissolve well in SnBi paste. Moreover the pasty range of L23 paste is 75ºC whereas L20 is eutectic and L27 it is 30ºC. With the higher pasty range the tin is not able to completely dissolve into the paste and hence we have the partial dissolution. So, the higher pasty range tend to affect the dissolution of the L23+Sn100C process. From this evaluation, it is evident that the Ag content in the solder ball and SnBi pasty range tends to affect the dissolution of the paste and ball.

After shear testing, the pad surfaces were investigated to study the failure mode. For low temperature process, all the failure modes were brittle and for the high temperature process, we observed few dual failures (brittle + ductile). The failure mode of the low temperature profile L27+SAC305 in aged condition shows that the crack is propagating transgranularly along the weak Bi rich phase near the Cu pad intermetallic which can be seen in figure 6b. There is little tin-rich phase in the crack region due to the high concentration of bismuth near the tin copper interface. A continuous Bi-rich region can propagate brittle failures though the solder joint for low temperature processes. The high concentration of bismuth in the pad surface was observed for the low temperature reflow process which resulted in 100% brittle defects which can be seen in figure 6a as bismuth is said to have brittle mechanical property.

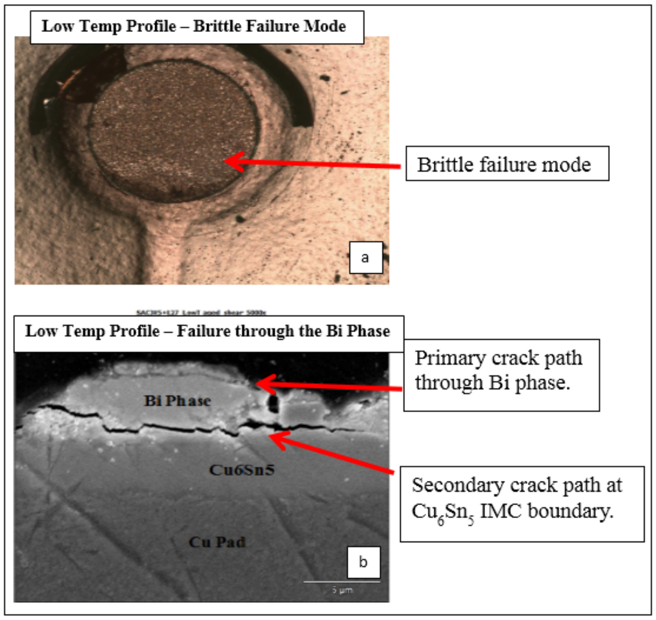


Figure 6. Failure mode of Low Temp Profile L27+SAC305 (aged condition) a) Top-down image of pad surface after Shear Testing b) Cross-section image after Shear Testing.

Thus, from this investigation it is clear that with the higher peak temperature in the high temperature reflow profile process there is an improved mixing of the paste and ball than the low temperature reflow process. With this improved mixing the shear strength of the higher temperature process is higher than the shear temperature of the low temperature process.

In figure 4 we observe that SAC305 performs better in shear test strength as compared to the other two alloys. We also observed that despite Sn100C not mixed as well (as seen in figure 4) shear test strength is similar to Sn99CN. Micro-alloying of the SN100C and Sn99CN may have exceeded its effectiveness when mixed with L27 (small concentration of Cu and Ni) alloy. It appears that the addition of a small concentration of Ag in the L23 provides the best improvement in strength for the Sn99Cn and Sn100C alloys.

Figure 4 also shows a consistent improvement in strength regardless of aging condition for the high temperature profile. In most cases aging of the low temperature profile reduces the strength of the solder joint with the exception of SAC305 mixed with L20 paste in the low temperature profile. This is likely due to the coarsening of the Bi-phase and the fracture through that phase in shear testing. [19].

CONCLUSION

From the ball shear test, the high temperature reflow profile process resulted in a greater strength than low temperature reflow profile process. With the low temperature reflow process, the peak temperature (177ºC) is insufficient to melting and dissolve the lead free ball. The solder ball alloys used in the study have a melting point range from 217ºC to 227ºC. Incomplete mixing creates a high concentration of Bi precipitates in the high stress region of the shear test resulting in weak solder joint. Whereas with the high temperature reflow profile process, (peak reflow temperature 217ºC), the lead-free balls are able to more completely melt and coalesce with the SnBi paste (excluding Sn100C).

From the cross sectional analysis, for the low temperature reflow profile process there is no proper dissolution between the paste and ball, whereas with the high temperature reflow profile process, the paste and the ball are completely dissolved. The reason for this is the higher peak temperature in the high temperature reflow process. With L23+Sn100C process there is partial dissolution between the paste and the ball as the pasty range of L23 is very high and the Ag content in the ball tend to affect the dissolution.

From this study a consistent improvement in high temperature assembly process is observed with the SAC305 solder paste. In addition the results show a tighter distribution of the data for this alloy. Although an improvement in the SN99Cn and SN100C was observed it standard deviation of the results indicate a non-repeatable result and overlap in strength between the two processes.

Micro-alloying improvements in strength for the Sn99Cn and SN100C alloys seems to be limited. Addition of Cu and Ni in the L27 solder paste does not appear to have a comparable increases in strength as compared to SAC305. In fact, L23 (addition of 1wt%Ag) appears to provide the highest strength for the SN99Cn and Sn100C alloys in the high temperature process prior to and following aging.

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