Improving Thermal Cycle and Mechanical Drop Impact Resistance of a Lead-free Tin-Silver-Bismuth-Indium Solder Alloy with Minor Doping of Copper Additive

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Abstract
For a demanding automotive electronics assembly, a highly thermal fatigue resistant solder alloy is required, which makes the lead-free Sn-Ag-Cu type solder alloy unusable. Sn-Ag-Bi-In solder alloy is considered as a high reliability solder alloy due to significant improvement in thermal fatigue resistance as compared to a standard Sn-Ag-Cu alloy. The alloy has not only good thermal fatigue properties but it also has superior ductility and tensile strength by appropriate addition of In; however, initial results indicated a sub-par performance in joint reliability when it is soldered on a printed circuit board (PCB) with Electroless Nickel Immersion Gold (ENIG) surface finish. Numerous experiments were performed to find out appropriate alloying element which would help improve the performance on ENIG PCBs. Sn-Ag-Bi-In solder alloys with and without Cu additions were prepared and then tests were carried out to see the performance in a thermal fatigue test and a drop resistance test to investigate the impact of Cu addition towards the improvement of joint reliability on ENIG finish PCB. Also, the mechanism of such improvement is documented.

Introduction
Sn-Ag-Cu type solder alloy has become the standard lead-free solder alloy. There have been a large number of experiments in developing a new generation high reliability alloy for demanding applications. However, a solder alloy which could be used in an extremely demanding application is yet to be determined. Among the new generation alloys Sn-Ag-Bi-In type solder alloys[1,2] have been used as an alloy which shows significant improvement in thermal fatigue resistance, due to appropriate amount of In addition. The improvement in thermal fatigue strength is important as the ductility of the alloy was not sacrificed in the process, which is often the case. When SABI alloy was developed, the initial data suggested significant improvement in the PCBs with Cu-OSP surface finish but there was significant reduction in the performance on PCBs with ENIG surface finish. Numerous experiments were carried out to see if any minor alloying element would help this phenomenon. The results with Cu-OSP board finish suggested that ‘Cu’ helps on strengthening the joint. Taking the same into consideration, different alloys with varying percentage of copper were formulated. Material characterization was performed by preparing dumbbell samples to get the right amount of Cu for the application. Board level reliability tests were carried out to see the thermal fatigue and drop shock resistance of the alloy.

Experimental
Solder Alloy Composition and Melting Point
Three different solder alloy compositions were prepared for this experiment (Table 1).

<table>
<thead>
<tr>
<th>Alloy No.</th>
<th>Composition/wt%</th>
<th>Melting Temperature/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sn</td>
<td>Ag</td>
</tr>
<tr>
<td>SA1 (SnAgCu)</td>
<td>Bal.</td>
<td>3.0</td>
</tr>
<tr>
<td>SA2 (SABI)</td>
<td>Bal.</td>
<td>3.5</td>
</tr>
<tr>
<td>SA3 (SABI + Cu)</td>
<td>Bal.</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Since more In which is an element which lowers the melting point, is added to SA2 and SA3, their melting points are lower than SA1. In addition, the melting point of SA3 is lower than SA2, as SA3 contains less than 1wt. % Cu which lowers the melting point.

Tensile Test
Tensile testing was conducted on the micro-dumbbells as shown in Figure 1. The micro-dumbbells were manufactured by casting molten solder at around 300°C into a die which is preheated to the same temperature. Then the die was immersed in a coolant which was formulated to set the cooling rate around 5K/second at the time of reaching the solidus temperature, so
that the micro-dumbbell would have roughly the same micro-structure as the soldered joints from the SMT process.

![Image of Micro-Dumbbell](image)

**Figure 1 - Appearance of Micro-Dumbbell**

Micro-dumbbells were divided into 2 groups, namely, as cast and aged. No post-casting treatment was given to the as-cast group, whereas the aged group was stored at 150°C for 500 hours to compare the thermal resistance. Tensile testing was conducted by pulling the dumbbell with a constant strain speed of 1.0 x10³ s⁻¹, in an air atmosphere at room temperature. The elongation is measured by the crosshead displacement of the tensile testing machine.

**Assembly**
The PCBs for this experiment were assembled using solder paste containing Type 4 solder powder of each alloy and no-clean flux. Solder pastes were printed using a 120µm thick metal stencil and reflowed using the specific reflow profile indicated in Figure 2 in air atmosphere. The time over liquidous temperature for the SA1 profile was 52 seconds and peak temperature of 245°C. The time over liquidus temperature for the SA2, SA3 profile was 53 seconds and peak temperature of 240°C. Different PCBs and components were used for thermal fatigue and drop tests.

![Reflow Profile](image)

**Figure 2 - Reflow Profile (Air Atmosphere)**

**Thermal Cycling Test**
The test vehicle for the thermal fatigue test is shown in Figure 3. This test vehicle was intended to measure the electrical resistance of the soldered circuit as well as to measure the shear strength of the 1206 (3216 metric) and 0805 (2012 metric) chip resistors. Two different PCBs with surface finishes Cu-OSP and ENIG with the same 1.6mm thickness and FR-4 grade material were used.
Test vehicles were then placed in two separate test chambers. One was set to cycle from -40°C to +125°C and the other is set to cycle from -40°C to +150°C. Dwell time at each temperature was 30 minutes; which makes each thermal fatigue cycle about an hour.

Shear Strength Test
Shear strength tests were performed on the soldered test vehicles after taking some of the boards out every 500 cycles for each of the two profiles. The bond tester for the shear strength test is shown in the left of Figure 4 and the schematic image of the shear strength test is illustrated in the right of Figure 4, respectively. The clearance between the shearing jig and PCB is 0.2mm and the shear strength was calculated at a tool speed of 0.5mm/sec. Shear strength was recorded based on the maximum load that caused solder joint failure.

Measuring the Resistance of the Soldered Electrical Circuit
During the thermal cycling test, combined resistance of the chip resistors mounted on the test PCBs was measured to determine out how many chip resistors became open due to the solder joint failure after each cycle. For this experiment, chip resistors were connected in parallel; therefore, the relationship between the resistance of individual chip resistors and the combined resistance of the entire circuit can be described as

\[
R_{cb} = \frac{R_0}{n}
\]

where \( R_{cb} \) is the combined resistance [Ω], \( R_0 \) is the resistance of an individual chip resistor [Ω], and \( n \) is the number of chip resistors which are conducting. \( R_0 \) is \( 10^6 \)Ω and initial \( n \) is 30. As the thermal cycling increases, cracks occur and propagate within the solder joint. When the crack penetrates the entire solde joint, a chip resister is no longer electrically conducting and becomes an open circuit. As a consequence, \( n \) in the Eq. (1) decreases, while \( R_{cb} \) increases.
The test PCB for the thermal cycling test is shown in Figure 3. The condition of the thermal cycle is -40°C to +150°C. The combined resistance was measured 10 to 20 minutes after the chamber was switched to the dwell time at high temperature, to let the sample temperature stabilize. Measurements were taken at a high temperature because the circuit is likely to be open, as the thermal expansion enlarges the crack. On the contrary, measurement during the dwell time at the low temperature was omitted as at a low temperature, cracks close up. In such a case, even if the solder joint has already been open owing to a penetrating crack, it may appear to be conducting on the measurement data.

**Board Level Drop Test**
To evaluate the shock resistance property of each solder alloy, board level drop tests were performed. Figure 5(a) shows the drop test machine and Figure 5(b) shows the shockwave. The drop test machine drops the test PCB from a pre-determined height to generate a 1500G, 0.5msec half sine impulse, the image of which is shown in Figure 5(b), until the voltage monitor detects electrical discontinuity.

The test PCB for the board level drop test is indicated in Figure 6. This PCB has 8 layers and is 1 mm thick. The material is FR-5 grade and the board surface finish is Cu-OSP or ENIG. To detect the circuit failure by electrical discontinuity, the circuit is patterned so that all BGA balls are in one series circuit. One 15mm x 15mm BGA with 196 pins was mounted at the center of the test PCB. Solder balls on the BGA were Sn-3Ag-0.5Cu. The test PCB was then aged in an air atmosphere oven set at 150°C for 500 hours to promote the growth of the intermetallic compound phase at the solder joint interface. Bias voltage was constantly monitored to detect any change derived from the drop shock and to determine whether the circuit had failed [3]. Any change which exceeded bias voltage by more than 20% was regarded as a failure.

**Results and Discussion**
**Mechanical Property**
Figure 7 shows stress-strain curves from the tensile test. SA2 (SABI - SnAgBiIn) and SA3 (SABI + Cu - SnAgBiIn + Cu) display almost 3 times higher pull strength than SA1 (SnAgCu), a normal Sn-Ag-Cu type solder alloy. Since the difference between SA2 and SA3 is 0.8% Cu in their compositions, they were not significantly different. SA2 and SA3 had lower
elongation than SA1, which suggests that ductility is reduced by Bi in the solder structure.

All aged samples of tested alloy compositions showed reduced pull strength and increased elongation compared to as-cast samples. However, although SA1’s pull strength reduced almost by half, SA2 and SA3, which contained In and Bi, showed rather insignificant loss of pull strength after aging. It can be noted that In and Bi are forming solid solution in the Sn matrix which strengthen the alloys.

![Stress Strain Curves (SA1, SA2, SA3 alloys: as-cast and aged)](image)

**Figure 7** - Stress Strain Curves (SA1, SA2, SA3 alloys: as-cast and aged)

**Thermal Cycle Resistance Property**

Shear strength test results for 1206 (3216 metric) chip resisters after reflow (As Reflow) and after every 500 thermal cycles up to 3000 thermal cycles from -40°C to + 125°C, are provided in Figure 8 (a) and Figure 8 (b) for Cu-OSP finish and ENIG board surface finishes, respectively. According to the transition of the shear strength, loss of strength was about the same between SA2 and SA3 on ENIG. In addition, SA2 and SA3 exhibited a smaller degree of strength loss as cycles increased. On the contrary, SA2 on ENIG board finish showed a more significant loss of the strength than on the Cu-OSP board finish, and the difference between SA2 and SA3 was larger on the ENIG board surface finish.

![Shear Strength Transition by Thermal Cycle for SA1, SA2, SA3 Alloys, (a) Cu-OSP Board Finish and (b) ENIG Board Finish](image)

**Figure 8** - Shear Strength Transition by Thermal Cycle for SA1, SA2, SA3 Alloys, (a) Cu-OSP Board Finish and (b) ENIG Board Finish

The combined resistance of the chip resisters during the thermal cycling test at -40°C to +125°C is shown in Figure 9. In this data, increase in measured resistance indicates decrease in $n$ from Eq.(1), which means more solder joints in the circuit became open. At the beginning of the thermal cycling test, 30 chip resisters were electrically conducting; therefore, the combined resistance was 3.3x10^6 Ω. Similar to the behavior seen in the shear strength test, increase in resistance is suppressed for SA2 and SA3 compared with SA1. In addition, SA2 and SA3 perform similarly in terms of an increasing trend in combined resistance on Cu-OSP board finish, whereas on ENIG board finish SA2 shows a more significant increasing resistance trend than SA3. According to these observations, it can be stated that SA2 and SA3 solder joints on ENIG board finish show different crack propagation behavior, unlike the solder joints of SA2 or SA3 on Cu-OSP board finish.
Mechanical Drop Test Impact Property

Board level drop testing was conducted on test samples prepared by soldering SA2 and SA3 solder alloys on ENIG board finish and ageing at high temperature. Five samples were prepared and dropped repeatedly until circuit failure was detected. The number of drops until circuit failure was plotted as Weibull plots as shown in Figure 10. Although the sample size was small for the Weibull plot, SA3 shows significantly better mechanical drop shock resistance as the solder alloy than SA2.

Cross-Sectional/ Microstructural Analysis

Two of the tested solder alloys, SA2 and SA3, were reflowed on test PCBs with ENIG board finish and cross-sectioned for the analysis by SEM-EDX. For each solder alloy, as reflowed and thermal cycled (from -40°C to +125°C for 1500 cycles) samples were prepared. SEM and elemental mapping images for different elements are shown in Figures 11 and 12.

As the lands on the PCB have ENIG surface finish, Phosphorus (P) exists in the Ni layer and Au exists on top of the Ni layer. Comparison between SA2 and SA3 for as reflowed samples revealed that the intermetallic compound layer at the joint interface was thicker for SA2. The compound layer for SA2 mainly consisted of Sn-In-Cu, while SA3’s compound layer consisted of Sn-Cu-Ni. By adding a small amount of Cu in the solder alloy, the intermetallic compound layer at the joint interface on ENIG board finish incorporates Cu, and inhibits the growth of the compound layer. This has contributed to improved joint reliability performance during the thermal cycling for SA3 versus SA2 soldered on the ENIG finished PCBs.
P is slightly concentrated at the interface between the intermetallic compound layer and the Ni layer. This suggests that originally, Ni and P were uniformly distributed in the Ni layer, but while Ni moved to the compound layer, the P did not move but rather concentrated around the interface. Thus, when compared to SA3, SA2 exhibits a higher P concentration at the intermetallic/solder interface as its Ni layer at the joint interface has been eroded further.

As for the Ag, it forms an intermetallic compound with Sn and In in the solder phase; however, it is scarcely detected within the compound layer with Ni content at the joint interface. Au, the plated and outermost layer of the ENIG finish, and Bi, an additive element in the solder alloy, are not detected in the vicinity of the joint interface and are difficult to identify, as they are forming solid solution uniformly in the solder phase.
Figure 12- Solder Joint Interface of ENIG Board Finish: As Reflow and Thermal Cycled (In, Ag, Au, Bi Analyzed)

Figure 13 shows the cross-sectioned solder joints after they failed in the board drop tests. Each sample suggests that the joint fracture initiated from one of four corners as it is assumed that these four corners are exposed to the most stress, as the joint fracture occurs when the board is warped by the drop impact and the solder joints beneath the BGA are stressed.

Evaluation of the fractured solder joint at the BGA revealed that the location of the fracture is different between SA2 and SA3. For SA2 fracture occurred between the solder ball and PCB, and for SA3, fracture occurred between the solder ball and the component. Since the lands on the PCB are larger than those on the component, it is anticipated to fracture at the component side. However, on all SA2 samples, all fractures occurred between solder ball and PCB.
In the board drop testing, abrupt loads were applied to the test PCB, and it was expected that the most vulnerable location prone to fracture would be the interface where materials with different hardness values meet. This is due to high speed strains causing cracking at the interface of materials of different hardness, an example being the tin-bismuth ball bump not being cracked in the bulk ball but at the interface with the substrate.

The most vulnerable location in the solder joint is the joint interface. In this test, test PCBs were prepared by printing SA2 and SA3 solder paste, mounting the BGA with Sn-Ag-Cu type solder balls and reflowing. During the reflow, SA2 and SA3 pastes melted first, as their melting points are lower than SAC305, forming joints between the solder ball and land on the PCB. Thus, the solder joint composition between the solder ball and land mainly consisted of SA2 and SA3, while the solder joint composition between solder ball and component side mainly consisted of SAC305.

As for the distinctively short life in the board level drop test and the fracture at solder ball and land interface on the PCB side, phosphorus may have contributed to these phenomena. Phosphorus concentration causes embrittlement of the metal; therefore, once the P concentrates at the interface as seen in the SA2 element mapping in Figure 11, the embrittlement effect can be accelerated which can deteriorate impact resistance. The phosphorus concentration layer of SA2 is thicker than that of SA3.

![Figure 13: Solder Joints Fractured in Board Level Drop Testing (Top: Whole Cracked Ball, Bottom: Magnified Crack) (a) SA2 (b) SA3](image)

**Conclusions**

Three different kinds of lead-free solder alloys, SA1 as Sn-Ag-Cu type, SA2 as Sn-Ag-Bi-In type and SA3 as Sn-Ag-Bi-In-Cu type, were tested to assess the mechanical and thermal cycle properties by implementing board level drop test and thermal cycle tests. The test results combined with the cross-section observation revealed following the characteristics.

- According to the solder joint strength and monitoring of the electrical resistance, thermal cycle properties of the solder joints on Cu-OSP board finish were evaluated as SA1<SA2≈SA3, whereas on ENIG board finish, it was evaluated as SA1≈SA2<SA3.
- For the drop shock resistance test of SA2 and SA3 soldered on ENIG board finish, SA3 had higher mechanical drop test resistance than SA2.
- Owing to the Cu addition in SA3, even if it is soldered on ENIG board finish, the growth of the intermetallic compound layer at the joint interface can be inhibited. The copper addition in the alloy also helps to inhibit the phosphorus...
concentration in the nickel layer at the PCB side.

References