

# MICROSTRUCTURE AND RELIABILITY OF LOW AG, BI-CONTAINING SOLDER ALLOYS

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## ABSTRACT:

Accelerated thermal cycling (ATC) was performed on a test vehicle which included various components, built with three low (or no) Ag, Bi-containing solders and compared to a baseline of SAC305 (Sn/Ag3%Cu 0.5%). Lead free SAC305 has become the default lead-free alloy for consumer electronic application use since the implementation of the RoHS legislation banning the use of Pb in solder. SAC305 however does not perform as well as SnPb in some key areas which are of importance to consumer electronic applications; specifically drop/shock performance and survival under accelerate thermal cycling conditions. Efforts have been made in the consumer sector to improve upon these properties of SAC305 by, for example reducing the amount of Ag in order to improve drop/shock performance, however an alternate alloy is still required to meet all of the existing concerns. It has been shown in the previous paper presented at last year's ICSR conference "Assembly Feasibility and Property Evaluation of Low Ag, Bi-Containing Solder Alloys" that these alloys show promise in drop/shock performance. This work shows that these same Bi-containing ternary and quaternary alloys also show promise in ATC. ATC of 3000 cycles was performed from 0 C to 100°C. The results of the three Bi containing alloys were compared to SAC305. Additionally microstructural evaluation was performed at time zero and after ATC. Bi containing solders may prove to be adequate replacement for SAC305 in consumer electronic applications.

Keywords: Lower Melt Pb-free solder, Bi-containing alloys, Accelerated Thermal Cycling

## INTRODUCTION:

As the consumer electronic market transitioned to Pb-free electronics due to the introduction of RoHS in Europe, SAC305 has emerged as the prominent alloy for such products as hand held devices and consumer electronic systems. SAC305 however has been found to perform poorly in comparison to Sn-Pb in a number of key areas. While SAC alloys have been found to perform well in thermal cycling, they do not show good properties in drop/shock testing.<sup>1</sup> As consumer applications require a solder to perform well under

both drop/shock and thermal cycling conditions, an alloy which shows sufficient reliability characteristics in both situations is required. Additionally, SAC305 has been found to have a propensity to grow tin whiskers when even small amounts of ionic contamination are present.<sup>2</sup> Another major concern when using SAC305 is that the higher process temperature may damage the board material and components on an assembly. Higher  $T_g$  board materials are now required to withstand these process temperatures, however, they are prone to an additional failure mode – pad cratering.<sup>3</sup> Finally, the high cost of Ag makes SAC305 undesirable for the cost sensitive consumer market.

This paper investigates a number of low (or no) Silver (Ag), Bi-containing Pb-free alloys for performance in accelerated thermal cycling (ATC). In previous work, these alloys were shown to have improved drop/shock performance using a low  $T_g$  board material as compared to SAC305 on a higher  $T_g$  board.<sup>4</sup> While this improvement in drop/shock performance can be attributed more to the low  $T_g$  board material, it indicates that a solder with a lower processing temperature than SAC305 is required in order to utilize board materials which had previously been suitable for SnPb. The higher  $T_g$  board materials necessitated by SAC305 introduced a new failure mode, pad cratering, in which the laminate material failed in many cases leading to electrical failure as the traces within the board are compromised.

Bi, when used as an alloying element, will reduce the melting temperature of most alloys. The three Bi-containing alloys in this study were chosen as they had a melting range approximately 10-18°C below that of SAC305. It is important to note that Bi had not been considered an appropriate alloying element during the initial transition to Pb-free solder as there was a time when a mix of Pb-free and Sn-Pb components was possible. A Sn-Bi-Pb phase with a dangerously low melting temperature (98°C) exists<sup>5</sup>. However, now that the Pb-free transition is well entrenched in the supply chain, this risk is considered minimal.

The effect of Ag is also examined through the alloy selection. The 3%Ag present in SAC305 is contrasted with the three other alloys containing 2%, 1% and no Ag. The addition of

Bi is also thought to inhibit the growth of  $Ag_3Sn$  intermetallic compound (IMC), large platelets of which are thought to contribute to poor drop/shock performance as they are large, faceted compounds providing ideal stress concentrators within the microstructure.<sup>6</sup> The presence of  $Ag_3Sn$  in smaller disersoids within the bulk solder on the other hand, is thought to contribute to an improved ATC performance as they may act to suppress recrystallization during a thermal fatigue cycle similar to that experienced in ATC.

Therefore, the ideal low melt solder for consumer electronic applications would have a lower processing temperature than SAC305, enabling the use of lower  $T_g$  board material, exhibit improved properties in drop/shock testing, at least equivalent properties in thermal cycling and a reduced risk of forming Sn whiskers. It should also be less expensive.

The primary goal of this study is to provide a screening experiment for three alloys Bi-containing, Low (or no) Ag alternatives to SAC305. The results will be used to downselect to one or two alloys for full qualification testing.

## EXPERIMENTAL:

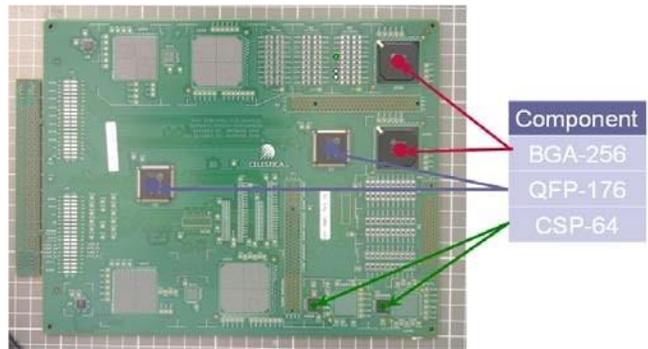
### Test Vehicle

The test vehicle use in this study is Celestica's RIA3 vehicle which was designed primarily for researching medium complexity assemblies and has been used on a number of other Pb-free alloy studies. While this test vehicle was not designed to evaluate alloys intended for consumer electronic applications specifically, it was adequate for this screening experiment.

It is a 12 layer 0.093" thick board with an organic solderability preservative (OSP) finish. It measures 8"x10". Two different board materials were used in this study: a high  $T_g$  board material 170°C and a low  $T_g$  board material 140°C. The following components were included on this test vehicle and monitored throughout the ATC: PBGA256, LQFP176 and CSP64. The PBGA256 was made up of SAC305 solder balls and the LQFP176 had a matte Sn finish on the leads. Figure 1 shows a RIA3 board populated with the above mentioned components.

### Alloy Selection

The alloys were selected in a prior stage of this overall investigation by P. Snugovsky, et al. In this previous work, Celestica, in partnership with the University of Toronto has proposed a number of alloys for Aerospace harsh environment<sup>7</sup>, Telecommunications complex boards and consumer electronics. It is believed that there is currently no optimal solution which will meet the requirements of all three market segments.



**Figure 1:** Test Vehicle used for ATC

This paper focuses on three alloys specifically selected for use in consumer electronics. The main driver in this alloys were developed was the reduction (as in Kester and Sunrise) or elimination (as in Sunflower) of Ag and the introduction of Bi to reduce the melting temperature. Table 1 gives the alloy and assembly temperatures.

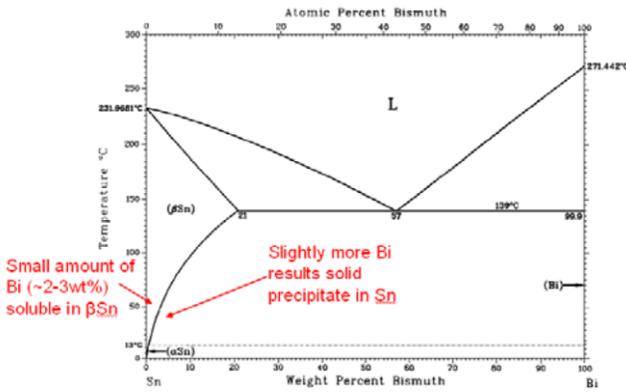
**Table 1:** Alloys under Test

| Paste Alloy | Composition          | Assembly Temperature |
|-------------|----------------------|----------------------|
| SAC305      | Sn 3%Ag 0.50%Cu      | 240°C                |
| Kester      | Sn 2%Ag 0.75%Cu 3%Bi | 224°C                |
| Sunrise     | Sn 1%Ag ?.%Cu ?%Bi   | 222°C                |
| Sunflower   | Sn 0%Ag ?.%Cu ?%Bi   | 226°C                |

The reduction or elimination of Ag is driven by a couple of factors. Ag is thought to contribute to poor drop/shock properties therefore, if this does not negatively impact the thermal cycling properties, should at least be reduced. Also, as the consumer electronic industry is very price sensitive, it would also be optimal to reduce or eliminate the most expensive item from the alloy. Ag does however improve the wetting properties of the alloy which should also be taken into consideration.

The Bi content selected for the alloys falls within two categories; a small amount which remains dissolved in  $\beta$ -Sn and a slightly higher amount of Bi which is likely to precipitate out of the  $\beta$ -Sn as shown in Figure 2. While the primary motivation for including Bi in an alloy is to reduce the melting temperature, it is also believed that the presence of Bi in a minimal quantity will mitigate the formation of Sn whiskers.

Note that, assuming proper mixing is achieved on all solder joints, the QFP solder joints are comprised of 100% of the selected assembly alloy while the BGA components, which have SAC305 solder balls, will be composed of ~75% SAC305 and ~25% of the selected alloy.



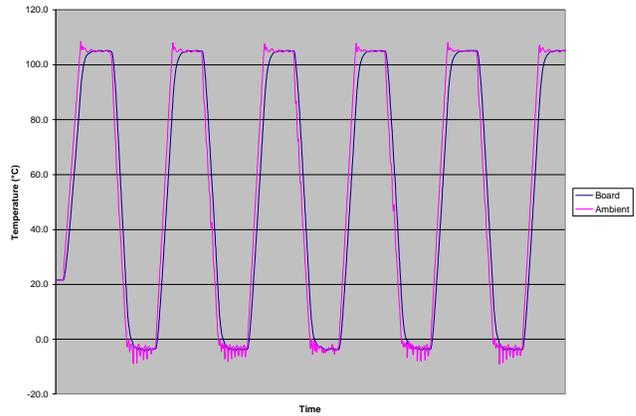
**Figure 2:** Sn-Bi Phase Diagram

**Accelerated Thermal Cycling**

ATC testing was performed in accordance with JESD22A104D test condition J and soak mode condition 3, which is in accordance with requirements of many consumer electronics.

A total of 35 test vehicles, including various alloy and board material combinations, were exposed to ATC as per Table 2. The ATC was performed to a target of 0°C to 100°C with a ramp rate of approximately 10°C /minute with a minimum soak time of 10 minutes. Figure 3 shows a sample of the ATC profile used in this test; the pink line represents the ambient temperature of the oven and the navy line represents the temperature as measured at the center of a board.

Figure 4 shows the cards inserted into fixtures and monitored from within the ATC chamber.

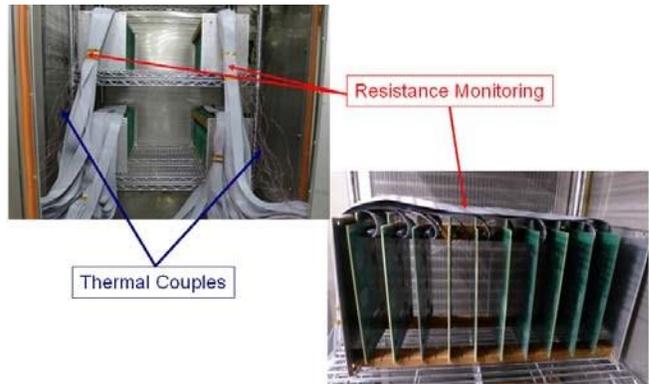


**Figure 3:** ATC Profile

**Table 2:** ATC Test Matrix

| Alloy     | Laminate Material                    | # of Test Vehicles |
|-----------|--------------------------------------|--------------------|
| SAC305    | High Tg (required for SAC)           | 3                  |
| Kester    |                                      | 5                  |
| Sunrise   |                                      | 4                  |
| Sunflower |                                      | 4                  |
| SAC305    | Normal Tg (previously used for SnPb) | 3                  |
| Kester    |                                      | 5                  |
| Sunrise   |                                      | 6                  |
| Sunflower |                                      | 5                  |

Each of the 35 boards was monitored in two ways. A thermal profile was maintained by monitoring, via thermal couple, each board at the center. The ambient temperature within the chamber was also monitored throughout the test. Resistance on each component is monitored via data logging (Agilent 3852). A failure was recorded if the resistance value increased by 20% or more as compared to the maximum resistance reading from the first cycle.



**Figure 4:** ATC Chamber Set Up

As failures occurred during ATC testing, the chamber was periodically stopped and the failure diagnosed. If a cabling issue was identified, or if a trace from within the board failed, the board was repaired and returned to the chamber and the testing resumed. If a component was determined to have failed, the component was cut out from the board, care taken not to cut through any live traces, and the remainder of the test vehicle was returned to the chamber and the testing resumed.

**Metallurgical Assessment**

Optical microscopy, scanning electron microscopy (SEM, Hitachi S-4500 and SEM Hitachi S3000N) and X-Ray Spectroscopy were used to evaluate quality of the solder joints. Where possible, polarized light microscopy and electron backscatter diffraction detection was also used on a subset of the solder joints. A Dye and Pry technique was also used to evaluate the failure mode of a subset of samples.

Analysis of all alloys at time zero samples was performed by cross sectioning. IMC layers and characteristic microstructures were evaluated. Additionally, one sample from each alloy was removed from the ATC chamber at 3000 hours and cross sectioned for analysis. Finally, as

components failed, the failed solder joint was isolated and cross sectioned in order to determine the failure mode.

### Preliminary Whisker Testing

A small set of samples from each alloy was also tested for propensity to grow whiskers. These tests were based on the environments required in JESD201A and previous testing performed by Celstica, however the sample size, as this is still preliminary work, was significantly smaller.

Two QFP assembled with each of the four alloys (3 new alloys plus SAC305) were placed in a temperature humidity chamber set to 85°C and 85%RH. After 1000 hours the samples were removed and inspected, using a VP SEM, for the presence of whiskers. When not being inspected, the samples were stored in a nitrogen dry box. Where whiskers were found, the length and an estimate of quantity were recorded. Figure 5 shows the samples within the test chamber. The QFPs were selected for testing as they are known to produce whiskers. These are fine pitch components (0.4mm) with a copper lead frame and matte Sn finish.



Figure 5: 85°C/85% RH Whisker Testing

Two QFP assemblies with each of the four alloys was also tested using thermal shock as specified in JESD201A from 55°C to 85°C air-to-air with a 10 minute soak. The samples were exposed to approximately 1600 cycles with a profile shown in Figure 6.

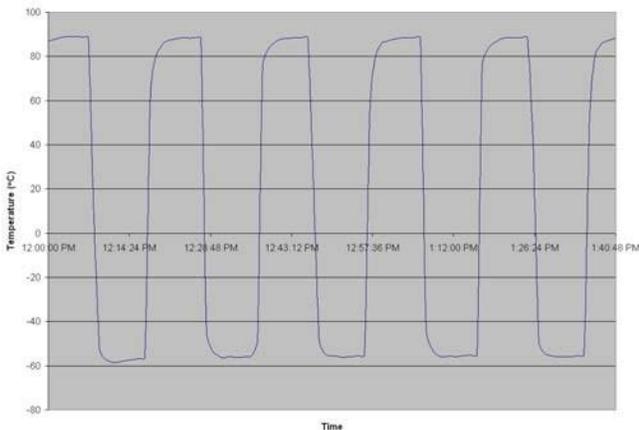


Figure 6: Thermal Shock Profile for Whisker Testing

At the end of the ~1600 cycles, these samples were also removed from the chamber and inspected using a VP SEM, for the presence of whiskers. When not being inspected, the samples were stored in a nitrogen dry box.

### RESULTS AND DISCUSSION:

#### Metallurgy

At time zero, all assemblies had acceptable solder joints with good mixing of the BGA alloy with the paste alloy and proper formation of fillets on the QFP.

Figure 7 illustrates the wetting properties of the four tested alloys. Picture d shows Sunflower – the no-Ag alloy has significantly poorer wettability as compared to the other, Ag containing alloys. All alloys did however pass a preliminary study of printability and wettability within a manufacturing setting.

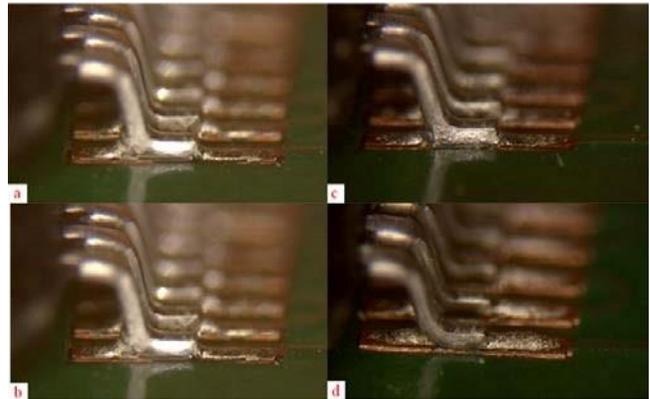
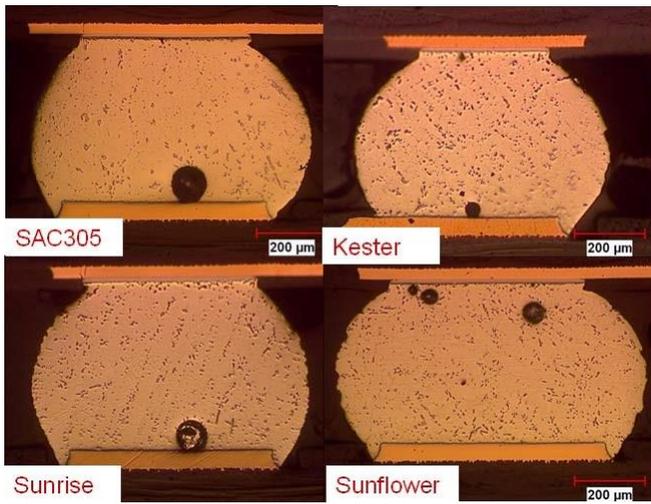


Figure 7: Solder Wetting to OSP Finish a)SAC305 b)Kester c)Sunrise d)Sunflower

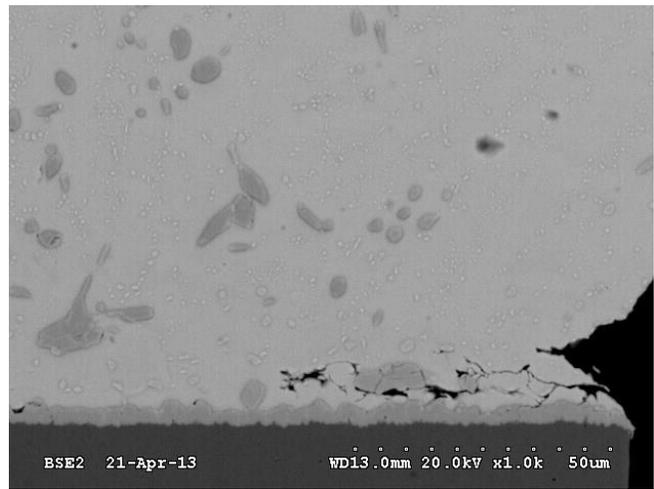
After 3000 cycles, there were no component failures identified as a result of ATC environmental testing. One sample of each alloy on high T<sub>g</sub> board material was removed for cross sectional analysis. The time to failure data, which will be used to produce Weibul plots in the future, has been censored to account for these removed samples and the test was then allowed to resume.

After 3000 cycles of ATC exposure, the majority of the BGA solder joints remained completely intact as seen in Figure 8. There were however a number of BGA solder joints which showed signs of crack formation, as in Figure 9. This figure shows the crack initiating near the top of the solder joint in the region where stresses are concentrating. The stresses are generated from a number of sources including the difference in coefficient of thermal expansion between the interface materials, the growth of the brittle IMC layer caused by continuous thermal cycling and possibly by microstructural coarsening and recrystallisation in the thermally stressed region.<sup>8</sup> The IMC layer is both more brittle than the bulk solder material, and exhibits different thermal conductivity properties.

Figure 10 shows a thermal fatigue crack which has propagated almost entirely across a solder joint.



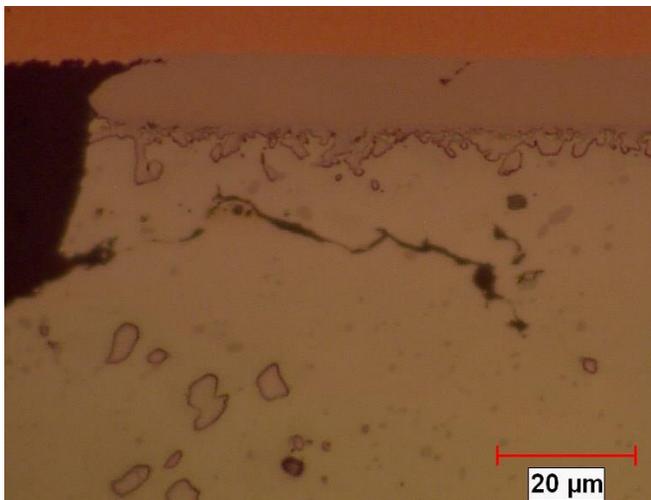
**Figure 8:** BGA Solder Joints after 3000 cycles ATC



**Figure 11:** SEM Image (BSE) of Thermal Fatigue Crack Propagating Near Board Side IMC (Kester Alloy)

As illustrated in Figure 11, thermal fatigue cracks also formed near the board side IMC in the BGA components.

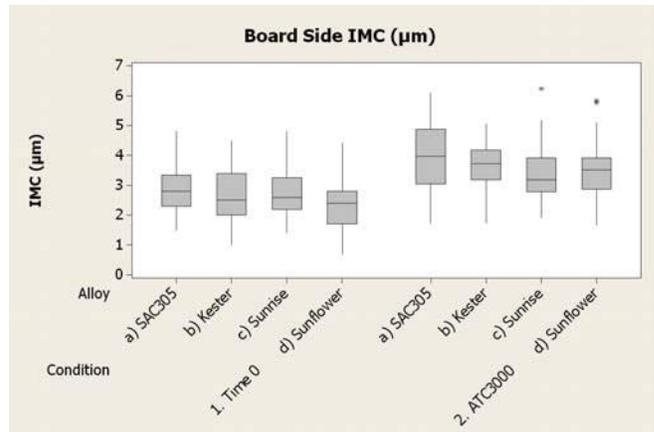
The IMC which forms between the component and the copper pad on the board, referred to is the board side IMC contains the  $Cu_3Sn$  and  $Cu_6Sn_5$ . At Time 0, there was very little variation in the size of the Board Side IMC amongst the various alloys as shown in Figure 12. After 3000 cycles of ATC exposure however, it appears that the IMC attach layer grew in all samples.



**Figure 9:** Optical Image of Incomplete Crack Propagating Through Solder Joints after 3000 hours ATC (Sunflower Alloy)



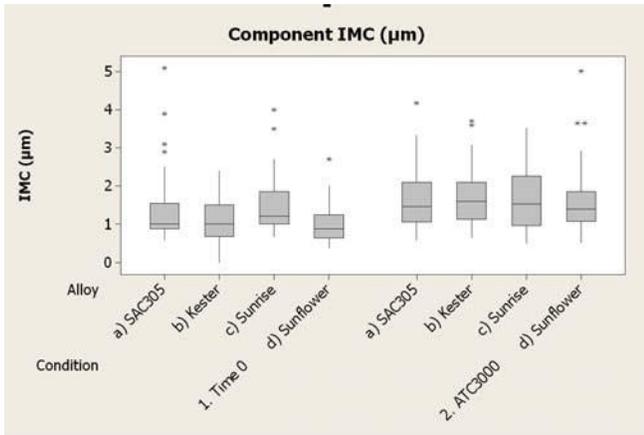
**Figure 10:** SEM Image of Incomplete Crack Propagating Through Solder Joint after 3000 hours ATC, near board side IMC (Sunrise Alloy)



**Figure 12:** Plot of BGA Board Side IMC for Time Zero and after 3000 cycles ATC

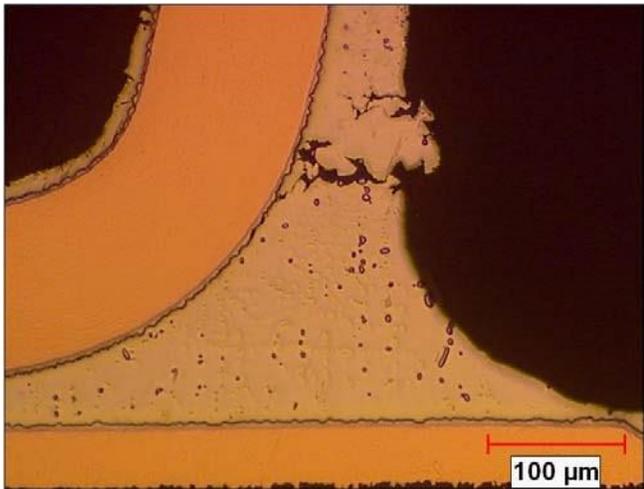
The IMC which forms between the component body and the solder ball did showed the same tendency. In this case, IMC was formed between the solder alloy (mix of SAC305 solder ball and paste alloy) and the Ni interface. While there was an increase in the average size of the IMC after 3000 cycles of ATC exposure, it did not show any variation between the different alloys. This is illustrated in Figure 13.

One BGA of each alloy after 3000 cycles ATC will also be evaluated using dye and pry to gain a better understanding of the amount of crack formation present.



**Figure 13:** Plot of BGA Component Side IMC for Time Zero and after 3000 cycles ATC

The QFPs showed similar crack formation as the BGAs. These thermal fatigue cracks did not lead to any component failures after 3000 cycles, but were present and were propagating along the IMC layer formed with the component lead. Figure 14 and Figure 15 show typical examples of crack propagation through the QFP solder joints.

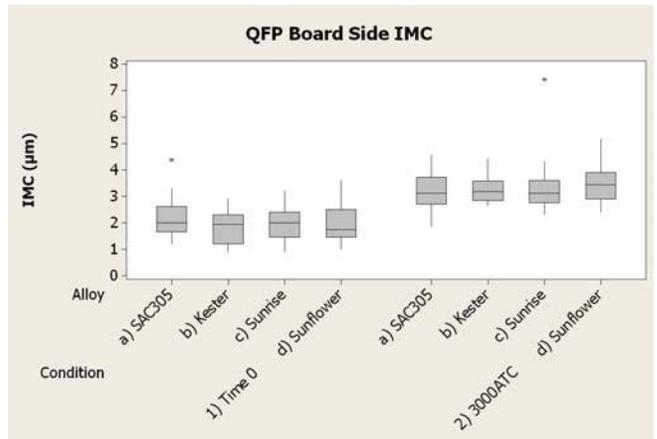


**Figure 14:** QFP after 3000 cycles ATC showing Thermal Fatigue Crack formation (Kester Alloy)

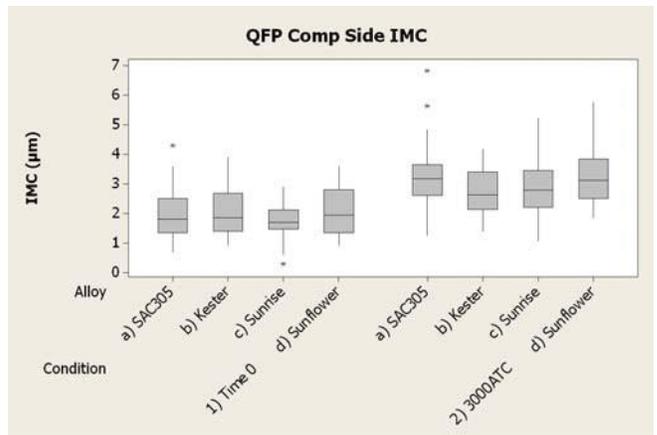
A comparison of the IMC layers formed on the QFP components was also performed. This data is of interest because it looks at solder joints which are composed of approximately 100% solder paste alloy. Despite this fact, the IMC layer formed follows the same pattern as for the BGA components, there was an overall increase in the size of the IMC layer from the time 0 samples to the end of the 3000 cycles of ATC, however there was no significant difference between SAC305 and the other alloys. This can be seen in Figure 16 and Figure 17.



**Figure 15:** SEM Image of Thermal Fatigue Crack in QFP Solder Joint (SAC305 Alloy)



**Figure 16:** Plot of QFP Board Side IMC for Time 0 and after 3000 cycles ATC



**Figure 17:** Plot of QFP Component Side IMC for Time 0 and after 3000 cycles ATC

**ATC Reliability Data**

Currently the testing has reached 4559 cycles. Table 3 summarizes the failures that have occurred up to this point.

**Table 3:** List of Component Failures at 4559 cycles

| High T <sub>j</sub> |        |        |         |           |
|---------------------|--------|--------|---------|-----------|
| Component Type      | SAC305 | Kester | Sunrise | Sunflower |
| PBGA256             | 00/06  | 00/10  | 00/08   | 00/08     |
| CSP64               | 00/06  | 00/10  | 00/08   | 00/08     |
| QFP176              | 00/06  | 00/10  | 00/07   | 00/08     |
| Low T <sub>g</sub>  |        |        |         |           |
| Component Type      | SAC305 | Kester | Sunrise | Sunflower |
| PBGA256             | 01/06  | 02/10  | 01/12   | 02/10     |
| CSP64               | 00/06  | 00/10  | 01/12   | 01/10     |
| QFP176              | 02/06  | 00/10  | 00/12   | 00/10     |

The failures listed in Table 3 were isolated to the specific solder joint and cross sectioned in order to determine the failure mode. This data will be provided at a future date.

### Whisker Testing Results

Whisker testing is ongoing and will be discussed in future publications.

### CONCLUSION AND OBSERVATIONS:

This screening experiment for selecting a Pb-free solder with a lower melting temperature than conventional SAC305 for consumer electronics is on going.

Observations and conclusions that can be made at this time are as follows:

- All for Pb-free solders survived 0°C-to-100°C ATC in excess of 3000 cycles.
- Even though there were no electrical failures at 3000 cycles ATC (i.e. all solder joints were electrically sound), cracks had initiated and were propagating through the solder joint.
- These fatigue cracks form along the high strain region where recrystallization is occurring rapidly, induced by the stress that thermal cycling induces in materials with mismatched CTE

### FUTURE WORK:

As this test is still in progress, further publication will focus on ATC test beyond 3000 cycles – until all monitored components experience failure. At this point, further reliability analysis can be performed on the ATC data. Weibull plots will be generated for each alloy-board material combination in order to identify any statistically relevant trends.

The Preliminary whisker testing is also ongoing. Thermal shock testing is completed and inspection for whiskers using SEM is currently in process. High Temperature and High Humidity exposure will be complete and ready for inspection for next publication.

Further analysis of strain will be performed using the EBSD in the region of crack propagation on the

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