

# An Investigation into Lead-Free Low Silver Cored Solder Wire for Electronics Manufacturing Applications

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## Abstract

The electronics industry has widely adopted Sn-3.0Ag-0.5Cu solder alloys for lead-free reflow soldering applications and tin-copper based alloys for wave soldering applications. In automated soldering or rework operations, users may work with Sn-Ag-Cu or Sn-Cu based alloys. One of the challenges with these types of lead-free alloys for automated / hand soldering operations, is that the life of the soldering iron tips will shorten drastically using lead-free solders with an increased cost of soldering iron tool maintenance/ tip replacement.

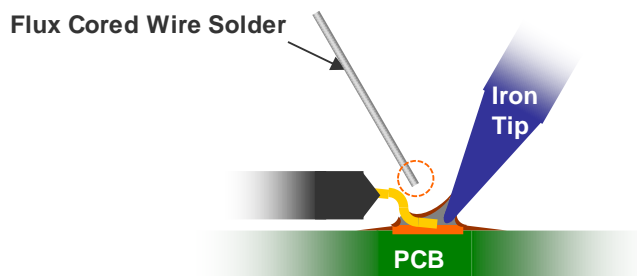
Development was done on a new lead-free low silver solder rework alloy (Sn-0.3Ag-0.7Cu-0.04Co) in comparison with a number of alternative lead-free alloys including Sn-0.3Ag-0.7Cu, Sn-0.7Cu and Sn-3.0Ag-0.5Cu and tin-lead Sn40Pb solder in soldering evaluations. Tests included solder alloy spread tests on copper, brass and nickel substrates. Soldering iron tip tests done with low silver cobalt containing alloy showed reduced erosion as compared to Sn-3.0Ag-0.5Cu solder alloy. The cobalt in the lead-free solder wire was found to create barrier layers between the iron in the soldering tip and the solder, reducing solder tip erosion by as much as 50%. In addition, Sn-3.0Ag-0.5Cu surface mount soldered component test boards were reworked at the soldered chip component locations with Sn-0.3Ag-0.7Cu-0.04Co and Sn3Ag0.5Cu wire to simulate rework in manufacturing operations. Assessment also included pull tests of the soldered lead-frame component joints. The results of the tests are reported.

## Introduction

Surface Mount Technology (SMT) is the major technology applied to today's electronic device manufacturing and solder paste is the mainstream soldering material. However, insertion mount components, such as connector modules or large electrolytic capacitors, use flow/wave soldering or manual soldering by soldering iron. Therefore, flux and wire solders are as important materials for the soldering as solder pastes.

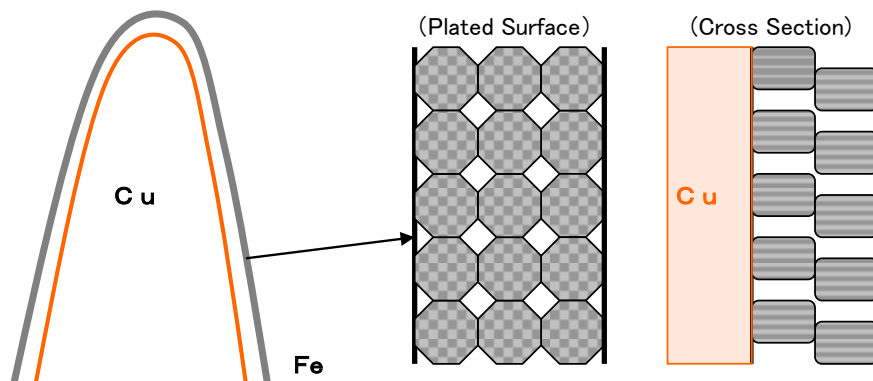
Slide soldering is one of the soldering techniques useful to solder connectors to obtain high joint strength at a narrow location by selecting the appropriate rework wire diameter and solder iron tip size. Slide soldering by automation enables a large number of connector pins to be soldered in a single stretch; therefore, it is widely used at many manufacturing factories. To achieve both speed and quality using slide soldering, pins or leads must wet quickly and the solder must wrap around them very quickly.

For a quality solder joint with flux cored solder wire, the flux should remove all the oxidized layers on the component as well as printed circuit board pads. Also, care should be taken to apply the appropriate quantity of wire solder at an appropriate temperature at specific durations (Figure 1). These principals are common for both manual and automated soldering. Among these principals, maintaining appropriate temperature is difficult and is the main cause of the majority of the defects. When the tip temperature is low, solder fluidity starts to worsen and causes improper wetting of the pads. This may cause either bad solder fillet formation, insufficient through hole filling and/ or solder bridging.



**Figure 1: A Typical Solder Wire Application**

The conventional alloy composition of lead free rosin flux cored wires is typically by Sn3Ag0.5Cu (SAC305), which results in much higher tin content as compared to eutectic tin/lead solder alloy. Usually, the soldering tips are made up of copper and plated with iron to about 250 ~ 300  $\mu\text{m}$  thickness. The micro-structure of the plated iron shows, crystal grains aligned in a direction perpendicular to the Cu material, and since they are porous crystals, there is a gap between the crystals as shown in Figure 2.



**Figure 2: Soldering tip cross section**

During soldering, iron-tin (Fe-Sn) intermetallic compounds are formed on the plated surface. Although this intermetallic compound has a melting temperature as high as  $\sim 500^{\circ}\text{C}$ , it does not melt and spread completely on the Fe plated surface due to high surface tension. As a result of which there is a partial barrier to protect the copper core of the tip. As soon as the soldering begins in full flow, tin in solder can penetrate through this gap dissolving the copper tip core in the process. The dissolved copper then flows outside of the core making the core thinner and disrupting the iron plating. This is a typical phenomenon by which the tip gets eroded causing to the replacement of the soldering iron tip which increases cost.

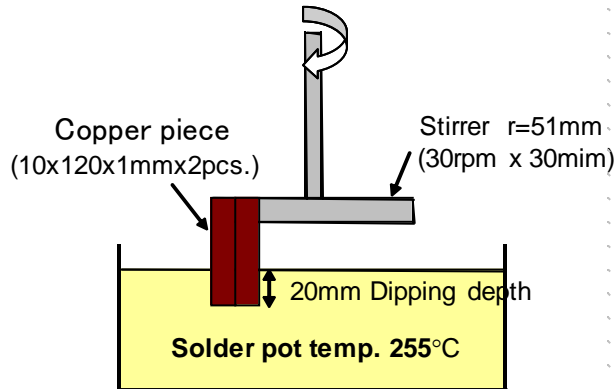
A method of preventing such a phenomenon can be to simply increase the plating thickness of the iron to about 500  $\mu\text{m}$ , but it is not a complete solution due to the crystal lattice structure and physical properties of the material. Furthermore, it has been found that the plated iron surface gets substantially eroded due to the higher tin content in many lead-free alloys. This leads to further risk of exposing the copper core. Development work focused on evaluation of different lead-free solder alloys to reduce solder iron tip erosion.

## Experimental

### A. Plate Erosion Tests in Molten Solder

#### a. Copper Erosion

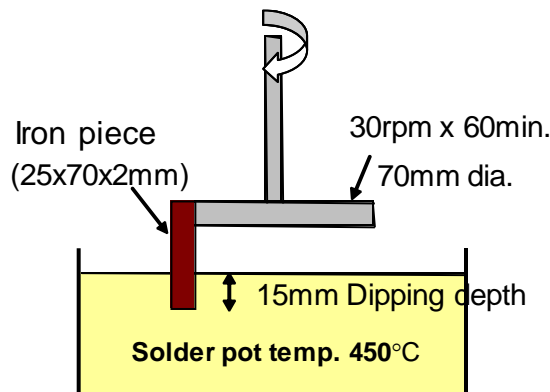
The amount of eroded copper during soldering with different alloys (Sn3Ag0.5Cu, Sn0.7Cu, Sn0.3Ag0.7Cu, Sn0.3Ag0.7Cu0.04Co) was tested by attaching two copper piece test samples to a stirrer and applying a relatively aggressive no-clean soldering flux in a molten solder pot. After drying of the applied flux, the tips of the copper test pieces were dipped into the molten solder bath to a depth of 20mm. The test pieces were stirred for 30 minutes and the amount of Cu eroded into the solder was measured. The test equipment used is shown in Figure 3. The test piece was copper plate of 10×120 mm dimensions and 1mm thickness. The solder pot temperature was 255°C with an agitation speed of 30 rpm.



**Figure 3:** Copper Plate Erosion Test Schematic

**b. Iron Plate Erosion**

The amount of eroded iron during solder with different alloys (Sn3Ag0.5Cu, Sn0.7Cu, Sn40Pb, Sn0.3Ag0.7Cu0.04Co) was tested by attaching an iron plate piece test samples to a stirrer and applying a relatively aggressive no-clean soldering flux in a molten solder pot. After drying of the applied flux, the tip of the iron test piece was dipped into the molten solder bath to a depth of 15mm. The test pieces were stirred for 60 minutes and the amount of Fe eroded into the solder was measured. The test equipment used is shown in Figure 4. The test piece was iron plate of 25×70mm dimensions and 2mm thickness. The solder pot temperature was 450°C with an agitation speed of 30 rpm.



**Figure 4:** Iron Plate Erosion Test Schematic

## B. Solder Spreading Test

Two lead-free alloys were tested in the solder spreading test, Sn3Ag0.5Cu and Sn0.3Ag0.7Cu0.04Co. To test the spreading of the solder on different surfaces, three different metal plates were used for the study. Copper, nickel and brass plates were used after cleaning / degreasing with organic solvent. One of the sides of the plate was polished with abrasive paper, then cleaned with alcohol and dried. Each resin flux cored solder wire of 0.8 mm  $\phi$  was placed in a wound circular position condition (Ring inner diameter: 1.6 mm  $\phi$ ) at the center of the respective plate as shown in Figure 5. The same ROL0 no-clean flux in the rework wire was used for both lead-free alloys tested. The test vehicle was heated by keeping it floating in a solder bath kept at 300°C for 5 sec. The test vehicle was removed from the solder bath and allowed to cool down to room temperature. Flux residue was removed with a suitable solvent.



**Figure 5:** Solder ring for spreading test

The height of the spread solder was measured by a micrometer. Using the measured value, the spreading ratio was calculated from Equation (1). This procedure was carried out on 5 test pieces for each solder alloy/ substrate combination and the mean value obtained as the spreading ratio of the specimen.

$$S_R = \frac{D - H}{H} \times 100 \quad \dots (1)$$

$S_R$ : Spreading ratio (%),  $H$ : height of the spread solder (mm),  $D$ : diameter of the solder, when it is assumed to be a sphere (mm)  $D = 1.24 \cdot V^{1/3}$ ,  $V$ : mass /density of tested solder (Note: The mass of solder used for the test was the mass of the specimen subtracting the contained flux)

## C. Solder Iron Tip Erosion Test

This test was performed to calculate the life of the solder iron tip when soldered using different solder alloys. Three different solder alloys, standard Sn3Ag0.5Cu, an anti-erosion solder alloy(Sn0.3Ag0.7Cu0.04Co) and Sn40Pb tin-lead alloy were used for the study. The flux type was ROL0 no-clean for the three alloys tested. An automatic soldering iron robot was used to standardize the process and remove any human interaction use with the solder wire. Iron coating thickness was measured on each of the tips before the start of the test. The thickness of the coating was measured as 500  $\mu\text{m}$ . Tip temperature was set at 400°C. A 1.2 mm wide solder iron tip with a 3 mm thick end was used for the study. Wire was fed at an amount of 5 mm per shot with a speed of 1 mm/s by the automatic soldering robot. An amount of wire equivalent to total of 10,000 shots(uses) was used for the study.

## D. Intermetallic Thickness Measurements during Rework

The study was conducted using a test vehicle board which had a 1.6mm thickness and an Aluminum core. The non-solder mask defined pads on the boards were designed for surface mount resistors and LED components with an immersion silver board surface finish. The surface mount resistors were (standard) 1206 (3.20 mm x 1.60 mm). The LED components had body size (3.45mm x 3.45mm x 2.68mm).

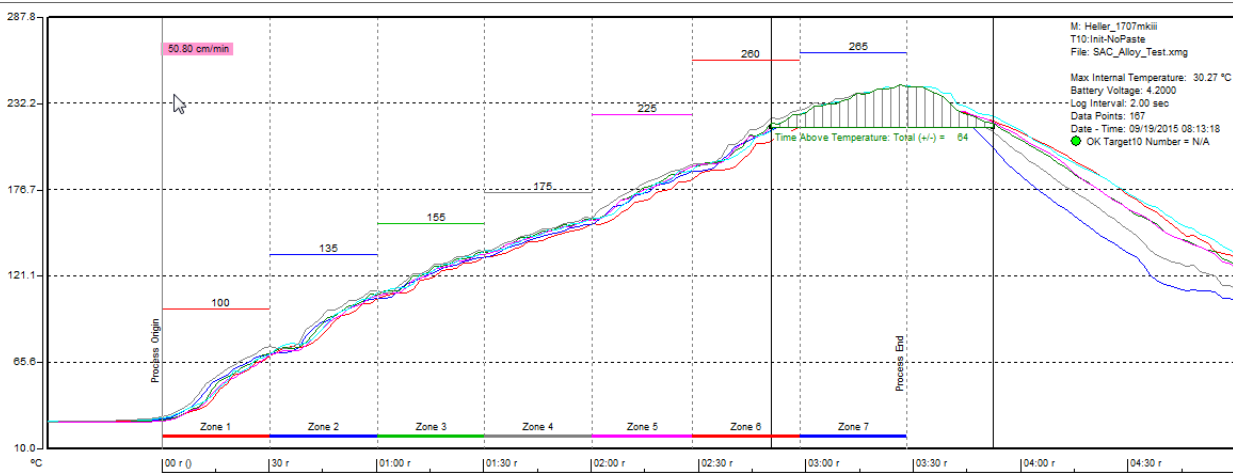
Printed circuit boards were assembled in 3 different combinations as shown in Table 1. One of the combinations was assembled with SAC305 solder paste and no rework was performed on that board (Control). In combination A, parts soldered with Sn3Ag0.5Cu paste were removed and new parts were soldered using SAC305 cored flux wire. In combination

B, the only difference was the Sn0.3Ag0.7Cu0.04Co anti-erosion cored solder alloy wire was used instead of SAC305. Conventional thermal cycling experiments on each of the combination boards were carried out with thermal cycling profile -40C to 125°C with 1 hour dwell time at each extreme (2 hour total cycle) for 500 cycles to see the growth of intermetallic thickness for the soldered components (what was the total cycle time).

**Table 1:** Different combinations of solder paste and rework wire (Control, A, B)

Type	Solder Paste	Wire Solder	Description
Control	SAC305	-	First Pass OK. No Rework
A	SAC305	SAC305	Solder reflow using SAC305. Parts removed/ Solder Wicked and new parts soldered with using SAC305
B	SAC305	Anti Erosion Alloy	Solder reflow using SAC305. Parts removed/ Solder Wicked and new parts soldered again using Anti Erosion Alloy

Test vehicles were 1<sup>st</sup> pass reflow soldered in a forced convection oven under air atmosphere using Sn3Ag0.5Cu paste. The reflow profile was pre-heat for 50sec from 150°C to 200°C with a peak temperature of 244°C with Time over 217°C of 68 sec. as shown in Figure 6.



**Figure 6:** Reflow profile used to build lead-free boards.

The rework soldering iron temperature for Combinations A and B was 800 F (426 C). A high soldering iron temperature was used because of the thermally challenging test board.

A total of 6 boards were assembled (2 control boards, 2 Combination A, 2 Combination B). 3 of the boards were analyzed in time zero (no-thermal fatigue cycling) and other 3 were analyzed after 500 cycles of -40C to +125°C thermal fatigue cycling. Intermetallic compound thickness (IMC) was measured at the board side (3 locations measured on board side).

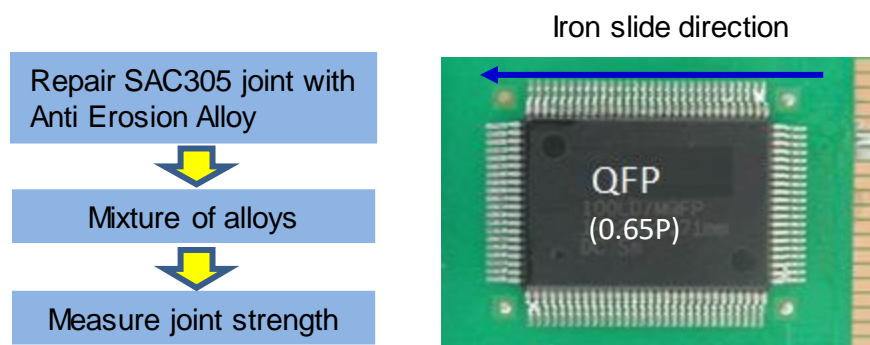
**E. Rework Experiment for Reliability Testing**

A rework experiment was performed on a 0.65mm pitch quad flat pack (QFP) device of the company test vehicle. Five different combinations of the alloys were prepared for this study as shown in Table 2. Board Serial Number 1 was soldered with Sn3Ag0.5Cu. Boards 2 to 5 were soldered with increasing amounts of the rework alloy (Sn0.3Ag0.7Cu0.04Co) added to the solder joint composition until Board 5 was a soldered joint of Sn0.3Ag0.7Cu0.04Co.

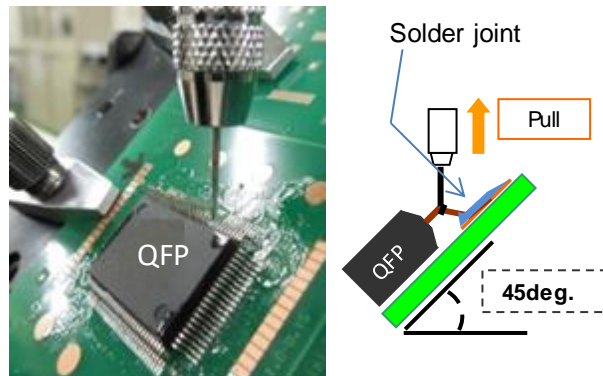
**Table 2:** Different combinations of the alloys

Sr. No.	SAC 305	Anti Erosion Alloy
1	100 %	-
2	75%	25%
3	50%	50%
4	25%	75%
5	-	100%

Soldered QFP component boards were then pull tested at the QFP leads at time zero and after up to 2,000 ATC cycles from -30C to +80C as indicated in Figure 7 and 8. 15 QFP leads were pull tested for each combination with the pull test results averaged for each combination.



**Figure 7:** Test method



**Figure 8:** Pull Test Schematic

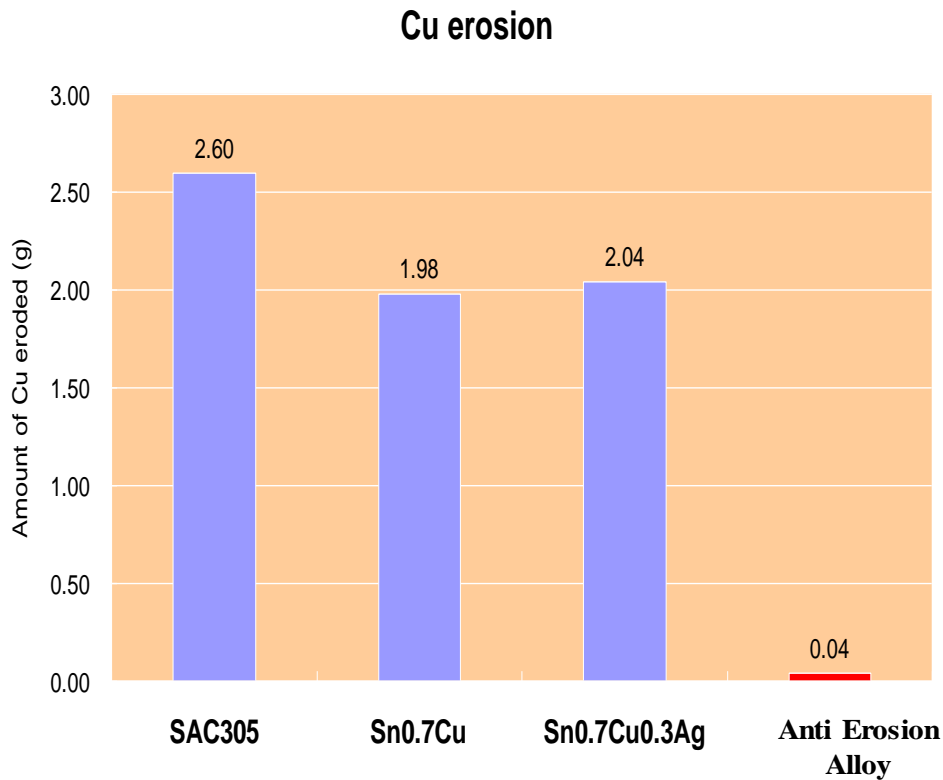
The results of the experiments are shown in the next section.

## Results and Discussion

### A. Plate Erosion Tests in Molten Solder

#### a. Copper Plate Erosion Test

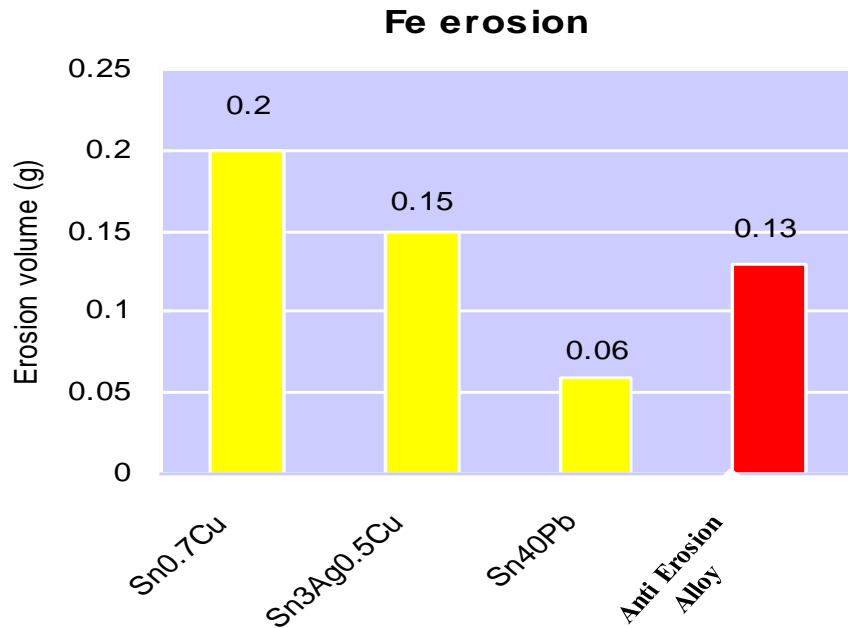
The copper plate erosion test results are shown in Figure 9. Based on the results, the anti-erosion alloy (Sn0.3Ag0.7Cu0.04Co) has less erosion than Sn0.7Cu which has less than Sn0.3Ag0.7Cu which is less than Sn3Ag0.5Cu. This shows the benefit of the cobalt addition to the lead-free solder to reduce copper erosion.



**Figure 9:** Erosion Results of Copper Plate on different alloys (Anti-erosion alloy is Sn0.3Ag0.7Cu0.04Co)

#### b. Iron Plate Erosion Tests

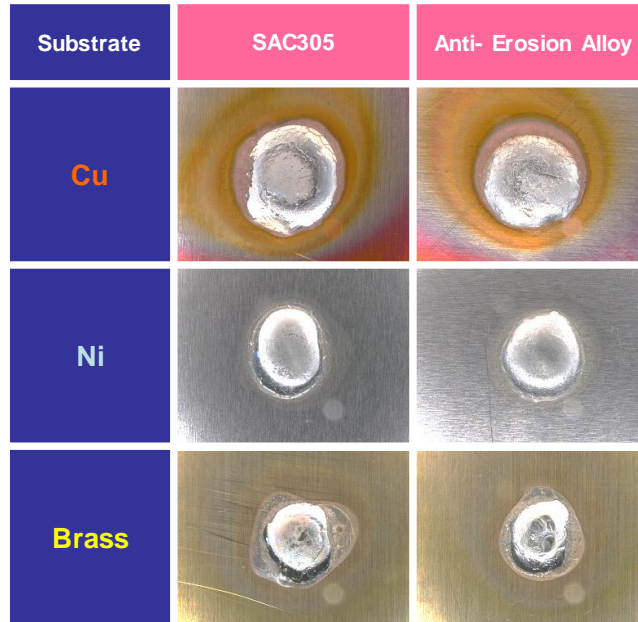
The iron plate erosion test results are shown in Figure 10. Based on the results, the 60Sn40Pb tin-lead solder has less erosion than the anti-erosion lead-free alloy (Sn0.3Ag0.7Cu0.04Co) which has less erosion than Sn3Ag0.5Cu which has less than 99.3Sn0.7Cu. This shows the benefit of the cobalt addition to the lead-free solder to reduce iron erosion and indicates the iron erosion is more dependent on the tin content of the solder alloy with higher tin content giving higher iron erosion.



**Figure 10:** Erosion Results of Iron Plate on different alloys

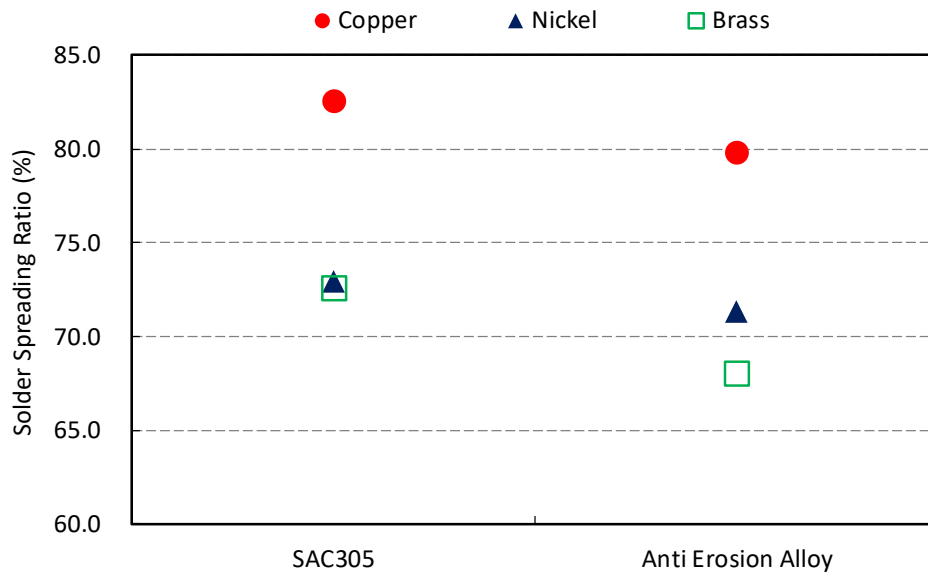
## B. Solder Spreading Test

Both the Sn3Ag0.5Cu and Sn0.3Ag0.7Cu0.04Co alloys showed good wetting performance on different difficult to solder substrate including nickel as shown in Figure 11.



**Figure 11:** Wetting results of SAC305 and Sn0.3Ag0.7Cu0.04Co on different substrates (Copper, Nickel and Brass).

The spreading ratio of Sn0.3Ag0.7Cu0.04Co anti-erosion solder wire on different substrates was found to be similar to Sn3Ag0.5Cu as shown in Figure 12.

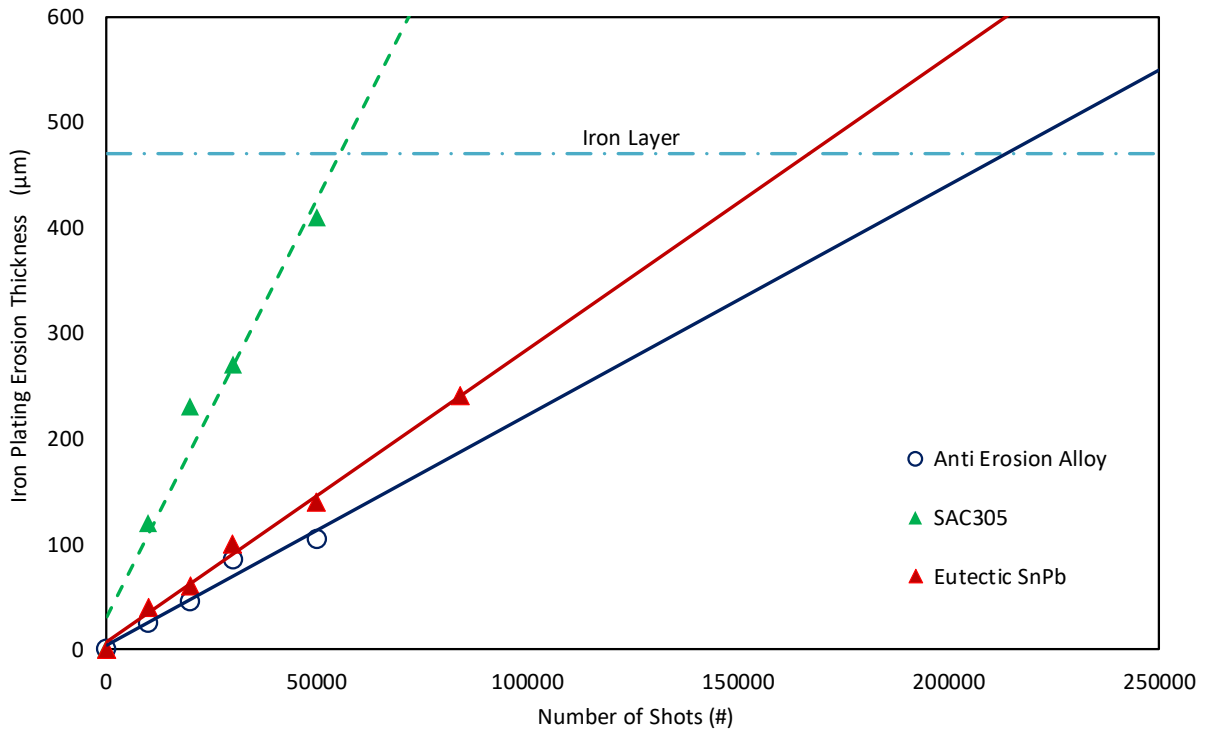


**Figure 12:** Solder Spreading Ratio on different substrates with the two lead-free solder alloys

## C. Solder Iron Tip Erosion Test

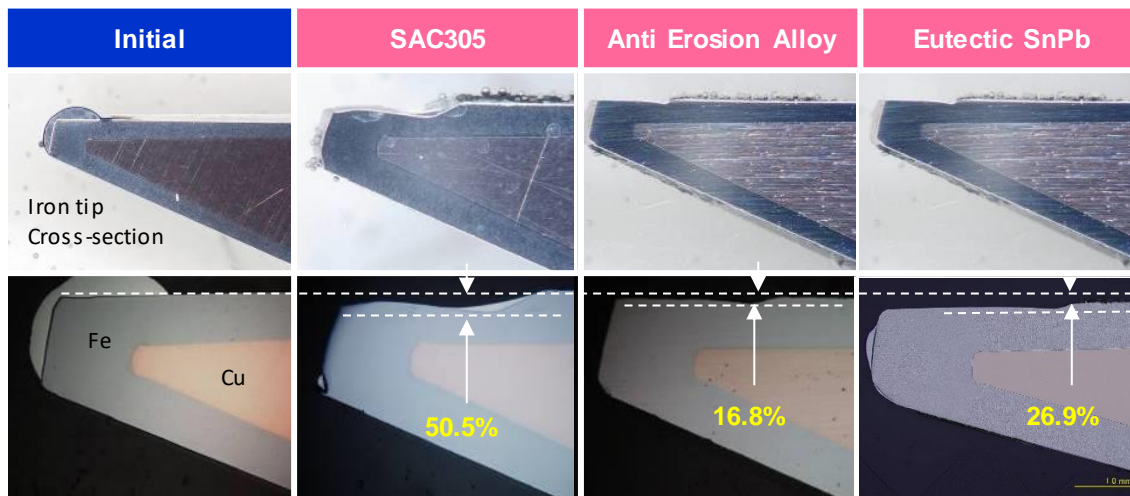
The results of the soldering iron tip erosion test are shown in Figure 13 which indicates the Sn0.3Ag0.7Cu0.04Co solder alloy has much lower solder iron tip erosion than lead-free Sn3Ag0.5Cu alloy and is similar to Sn40Pb tin-lead solder.





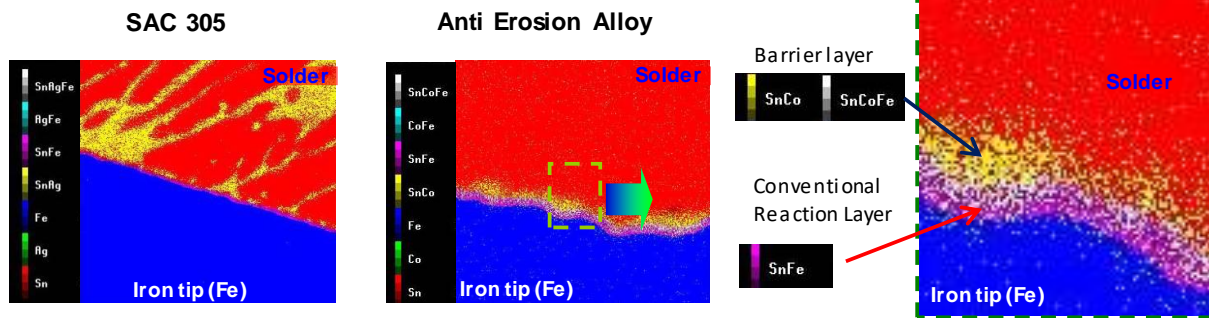
**Figure 13:** Iron Plating Erosion Thickness for different alloys.

After 10,000 shots (uses), the soldering iron tips used with the three solder alloys were cross-sectioned as shown in Figure 14. Based on the results in Figure 14, solder iron tip erosion is large with Sn3Ag0.5Cu alloy but is reduced with the Sn0.3Ag0.7Cu0.04Co alloy which is similar or better than Sn40Pb tin-lead solder.

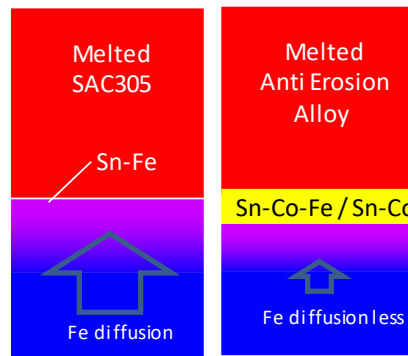


**Figure 14:** Cross Section of Iron Tips for different alloys (Sn3Ag0.5Cu, Sn0.3Ag0.7Cu0.04Co, Sn40Pb) after 10,000 shots (uses).

Figure 15 shows elemental analysis of the soldering iron tips with a schematic view of the reaction between the solder iron tip and the melted solder shown in Figure 16. Based on these results, there is a barrier layer being formed of Sn-Co-Fe/ Sn-Co with the Sn0.3Ag0.7Cu0.04Co lead-free alloy which is helping to reduce the solder iron erosion.



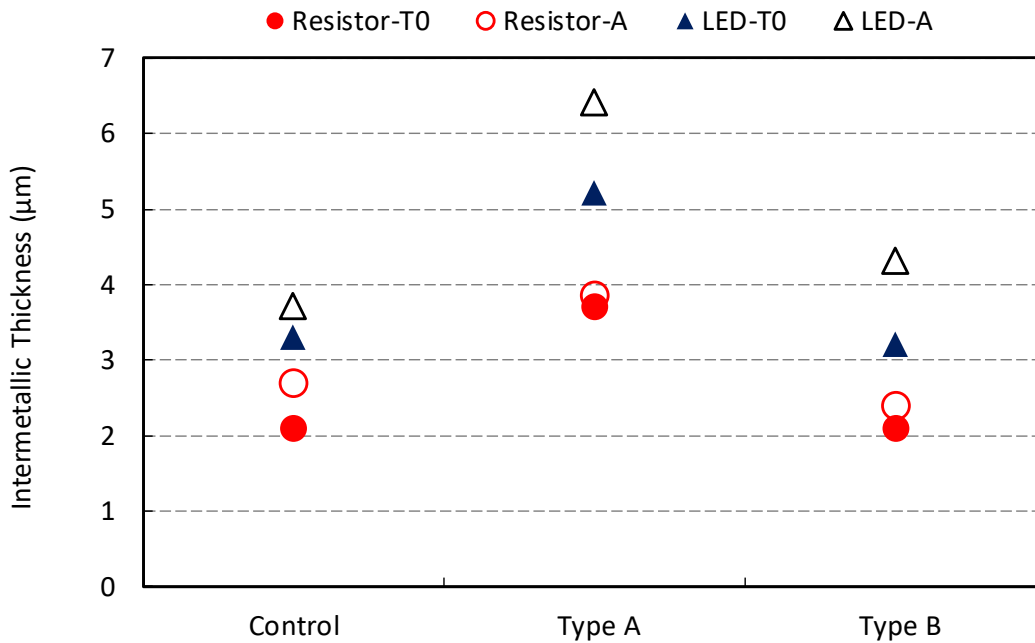
**Figure 15:** EPMA (Electron probe micro-analysis) of boundaries between solder and iron tip. (Sn3Ag0.5Cu compared with Sn0.3Ag0.7Cu0.04Co alloy)



**Figure 16:** Schematic view of reaction between iron tip and melted solder (Sn3Ag0.5Cu compared with Sn0.3Ag0.7Cu0.04Co alloy)

#### D. Intermetallic Thickness Measurements During Rework

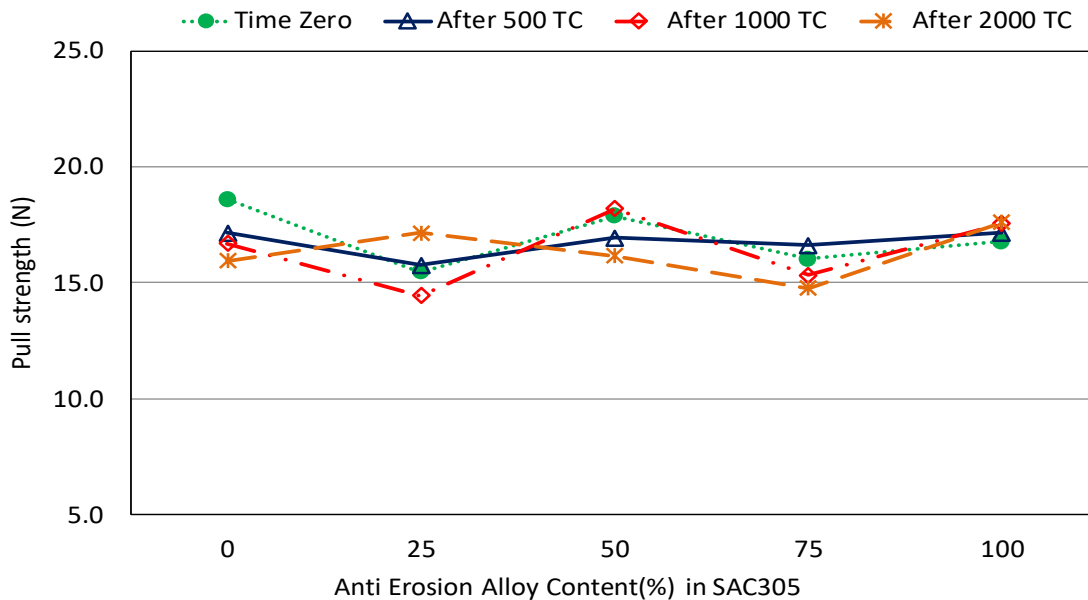
Figure 17 shows the intermetallic thickness measurements for soldered chip resistor and LED components for the 3 combinations tested (Control- SnAgCu 1<sup>st</sup> pass, A- SnAgCu 1<sup>st</sup> pass + SnAgCu rework, B- SnAgCu 1<sup>st</sup> pass + Sn0.3Ag0.7Cu0.04Co rework) at time zero and after thermal cycling. The amount of IMC formed at the board side with the resistor component is less than the LED component at Time zero and after thermal cycling. IMC grows after thermal cycling for all combinations with the less amount for the SnAgCu 1<sup>st</sup> pass Control and Combination B test cells (SnAgCu 1<sup>st</sup> pass and Sn0.3Ag0.7Cu0.04Co rework). As combination B is reworked with the Sn0.3Ag0.7Cu0.04Co rework alloy this is a good indication of reduced IMC growth with this alloy. Previous work with a similar alloy (Sn0.1Ag0.7Cu0.04Co) showed reduced IMC growth on copper at 250C compared with Sn3Ag0.5Cu, Sn0.3Ag0.7Cu and Sn0.7Cu0.05Ni lead-free alloys [1].



**Figure 17:** Board Side Intermetallic Thicknesses for different components (Resistor and LED) under different conditions (Control- SnAgCu 1<sup>st</sup> pass, A- SnAgCu 1<sup>st</sup> pass + SnAgCu rework, B- SnAgCu 1<sup>st</sup> pass + Sn0.3Ag0.7Cu0.04Co rework) before and after thermal cycling

**E. Rework Experiment for Reliability Testing**

Figure 18 shows the QFP lead pull test results for the soldered QFP components at time zero and after up to 2,000 ATC cycles from -30C to +80C. Comparing Test Cell 1 (Sn3Ag0.5Cu) with the other test cells (Cell 2: 25% Sn0.3Ag0.7Cu0.04Co- 75% Sn3Ag0.5Cu, Cell 3: 50% Sn0.3Ag0.7Cu0.04Co - 50% Sn3Ag0.5Cu, Cell 4: 75% Sn0.3Ag0.7Cu0.04Co - 25% Sn3Ag0.5Cu, Cell 5: Sn0.3Ag0.7Cu0.04Co) at time zero and up to 2,000 ATC cycles there is little difference between the pull test force results. This indicates mixed Sn3Ag0.5Cu/ Sn0.3Ag0.7Cu0.04Co solder joints have good reliability.



**Figure 18:** QFP Pull Strengths Results for different solder joint alloy combinations (Cell 1 (Sn3Ag0.5Cu) , Cell 2: 25% Sn0.3Ag0.7Cu0.04Co- 75% Sn3Ag0.5Cu , Cell 3: 50% Sn0.3Ag0.7Cu0.04Co - 50% Sn3Ag0.5Cu, Cell 4: 75% Sn0.3Ag0.7Cu0.04Co - 25% Sn3Ag0.5Cu, Cell 5: Sn0.3Ag0.7Cu0.04Co)

### Conclusions

The evaluations indicated that the spreading of the developed Sn0.3Ag0.7Cu0.04Co solder wire on different substrates was equivalent to Sn3Ag0.5Cu solder wire. The Sn0.3Ag0.7Cu0.04Co showed low erosion on copper and iron compared with other lead-free solder alloys tested (Sn3Ag0.5Cu, Sn0.7Cu).

The results of the soldering iron tip erosion test showed the Sn0.3Ag0.7Cu0.04Co solder alloy had much lower solder iron tip erosion than lead-free Sn3Ag0.5Cu alloy and was similar or less than Sn40Pb tin-lead solder.

The intermetallic thickness growth for a 1<sup>st</sup> pass SnAgCu soldered chip component reworked with Sn0.3Ag0.7Cu0.04Co rework wire was lower than the chip components reworked with Sn3Ag0.5Cu rework wire at time zero and after thermal cycling and similar to 1<sup>st</sup> pass soldered SnAgCu soldered chip components.

Based on pull testing results of SnAgCu 1<sup>st</sup> pass soldered components and SnAgCu 1<sup>st</sup> pass soldered components reworked with Sn0.3Ag0.7Cu0.04Co rework wire at time zero and up to 2,000 ATC cycles there are similar pull test force results which indicate good reliability.

The results show promise for the use of the Sn0.3Ag0.7Cu0.04Co lead-free solder rework wire alloy in terms of good wetting, reduced solder iron tip erosion, reduced IMC growth and good reliability.

### References

1. J.Bath, M.Itoh, G.Clark, K.Mori, H.Takahashi, K. Yokota, R.Garcia, An investigation into low silver lead-free solder alloy paste for electronics manufacturing applications, SMTAI 2011 conference.