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Sample Preparation for Mitigating Tin Whiskers in alternative Lead-Free Alloys

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Abstract
With the impending deadline for RoHS II and the elimination of exemptions for lead bearing solders in electronics for mission critical electronics, the issue of tin whiskers remains unresolved. Building on earlier data developed using unique test methods; the company is collaborating with universities in developing other methods of promoting whisker growth. In previous testing with specially prepared pure tin, these methods grow whiskers exponentially more quickly than the company bent wire method. The availability of new test methods would allow for dozens of alloy combinations to be tested more rapidly and in combination, thus accelerating the development of an alloy with a demonstrable benefit in reducing tin whisker formation and the attendant risks. In addition, this work has expanded the understanding of the growth mechanism for tin whiskers and what other mitigation strategies can be employed to reduce their propagation.

Concurrent to test method development, the company has continued alloy development and has finalized several alloys that have demonstrated minimizing whisker formation when compared to widely used tin-silver-copper and tin-copper alloys. These novel alloys have also been developed within the context of manufacturability, regulatory restrictions and end user processes. These alloys meet the requirements of demonstrable reduction of tin whisker formation and would be 'drop-in' replacements for existing alloys.

Test Methods
The company's Alloy Development Task Force has collaborated with Dr. E. Chason of Brown University building off of the success in promoting tin whisker formation in a matter of hours. Chason has developed a technique using specially prepared tin plating under unique conditions that not only grow tin whiskers, but allow for observation of their formation and growth. This work has deepened our understanding of the mechanisms behind whisker formation and what may be done to prevent or reduce them.

Summarizing Chason's findings [1], there are certain conditions that must be met in order for a tin whisker to form:

The mechanism of whisker growth involves:
1) Copper (Cu) diffusion into Sn to form intermetallic compounds (IMC)
2) As the IMC grows stress spreads through Sn-dislocation motion/point defects
3) An oxide prevents defect annihilation at surface – stress builds up in the layer
4) Stress causes yield of "weak" grain – allows whisker to grow
5) Stress gradient drives diffusion to SnCu whisker base

Chason's suggestions for mitigation include:
1) Enhance stress relaxation in Sn - Modify microstructure of Sn or IMC to reduce stress
2) Promote horizontal grain boundaries
3) Weaken oxide layer - enhance stress relaxation at top surface

Chason's work confirms that tin whiskers are the result of stresses that accumulate as intermetallic compounds form and these stresses subsequently need to be relieved. Both the columnar nature of tin grain structure and the presence of an oxide 'cap' prevent the stresses from migrating upwards causing the stress to seek a weak point in the alloy matrix. Once this point is found, the stress gradient drives whisker formation and growth. (Figure 1)

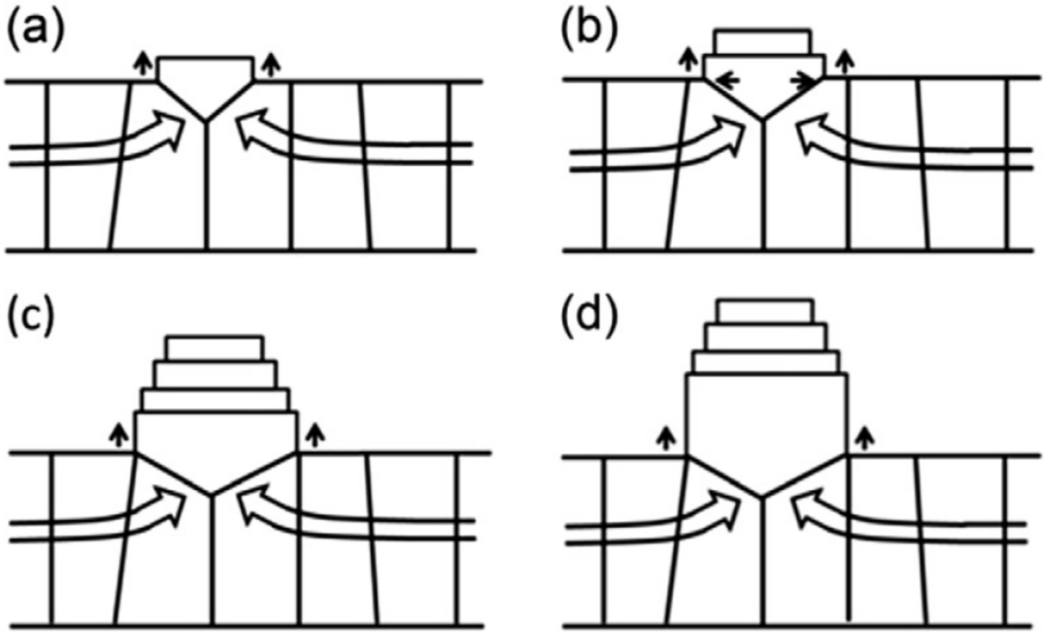

Figure 1. Whisker formation (image courtesy of E. Chason)

The company's 'Bent Wire' (Figure 3 and Figure 4) test method has proven to provide reliable and repeatable evidence as to an alloy's likelihood to form tin whiskers. The limitation of this test is the 3000 hour exposure time required. Chason's test is capable of generating tin whiskers in as little as 12-14 hours. If this technique could be adapted to alloyed metal opposed to tin plating, the impact on data generation and alloy development would be profound.

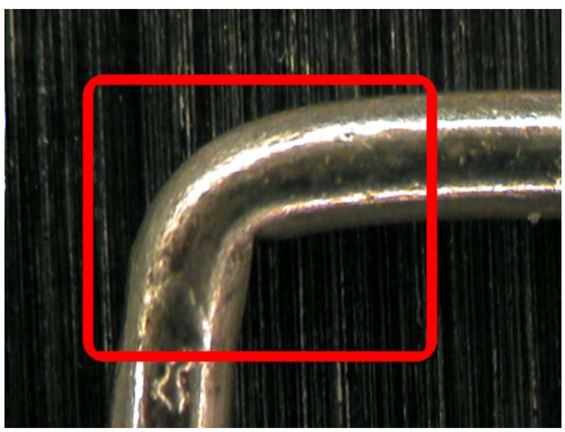

Figure 2.

Figure 3.

The first phase of the testing was to determine if tin whiskers could be reproduced in alloys prone to whisker formation by using the accelerated test procedure. Dr. Chason's work relies on the application of external stresses to accelerate IMC formation. One technique induces stress by thermal expansion (CTE) mismatches on specially prepared tin plated copper samples. With a test vehicle uniquely tailored to the tests capabilities, the formation of tin whiskers was rapid and repeatable. The company produced special foils from these whisker prone alloys and subjected to the same strain as tin plated samples and compared results. Unfortunately, the tests failed to produce any tin whiskers indicating the foils were not adaptable to the test procedure. The hypothesis for this failed outcome is based on the following:

There are fundamental differences between the testing of the copper/tin plating of Chason's tests and the rolled alloy foils that were tested. The SAC/SnCu alloys used in the tests cannot be plated onto the test substrate and an alternate method needed to be developed. In an attempt to replicate the plating process, very thin alloy foils were applied to the test vehicles and fixed. Once it was established that the fixative process was not adversely impacting the test procedure; there was consensus that the tests may yield positive data. As tin plating is an additive process, the tin grain structure is markedly different than the grain structure of a cast and milled alloy foil. Plated tin has a columnar honeycomb type grain structure unlike the cast, milled foil. The milling/rolling process compresses the grain into a finer more consistent matrix believed to reduce the stress in the alloy thus preventing the formation of tin whiskers.

Cast alloy samples more closely resemble the grain structure of a solder joint, however, cast samples are too thick for the CTE stress input technique and a compressive test was developed to introduce stress into the alloy samples. The images below depict the equipment developed to introduce the compressive stresses needed to force the development of tin whiskers. Figure 4 shows the samples as they are placed into the equipment for testing and Figure 5 is the testing underway. Several different stress profiles were used and the samples analyzed for tin whiskers. The test that promoted the formation of whiskers was after twelve (12) days as shown in Figure 6. This was considered a significant development in the evolution of the testing as the cycle time was reduced ten-fold from 125 days to 12.

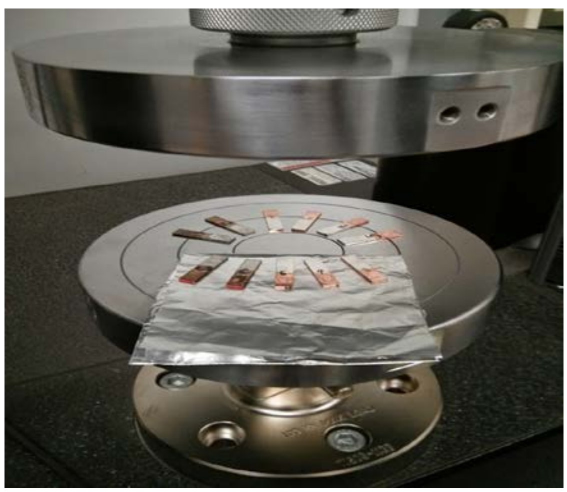

Figure 4. Samples placed into equipment for testing

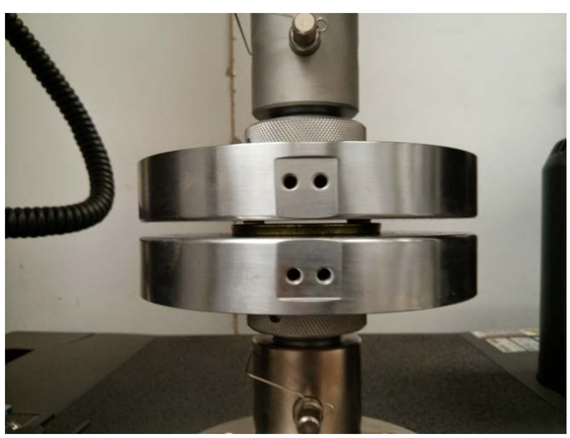

Figure 5. Testing

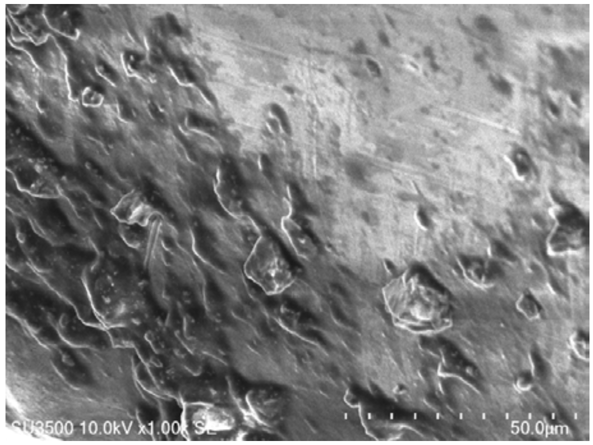

Figure 6. Early formation of tin whiskers after 12 days under stress

Armed with this deeper understanding, company metallurgists surmised that the key to whisker formation was to provide an outlet for these stresses. It is believed tin-lead solders reduce formation of whiskers due to the formation of horizontal grain boundaries which relieve the accumulated IMC stresses. With this knowledge, different alloy combinations grain structures could be analyzed for this desirable property. The combinations can then be reduced to focus on the options that had the most preferential complimentary characteristics. With a manageable sample size the testing could commence to determine if the alloys with the most favorable grain structure would yield the desired outcome in whisker growth tests.

The evolution of the PCB assembly processes and marketplace has created new opportunities in the alloy development field. Firstly, as experience has been gained, the limitations of the SAC family of alloys that have become the established replacement for tin-lead alloys are now more evident. Consequently, niche alloys have been/are being introduced to address application specific requirements. An example would be the use of SAC105 alloys to improve drop shock performance in handheld devices. As the industries experience with alternate alloys grows, confidence in their implementation will grow accordingly. This reality, coupled with the evolution of materials that comprise the PCB assembly, has permitted the incorporation of materials that may have not been feasible in the earlier phases of RoHS process and material development.

The use of bismuth (Bi) in lead-free alloys was discounted early in the transition to RoHS compliance because, when combined with tin and lead, a ternary alloy formed with a melting point of 96°C. Even a small amount of this alloy forming in a solder joint would have a dramatic negative impact on reliability. The concern was that lead (Pb) bearing components were still present in the material stream making this potential reliability risk intolerable. With RoHS compliance in its seventh year, the component supply chain has largely been cleansed of lead (Pb) bearing finishes, and an opportunity to revisit Bi has been revealed.

Incorporating bismuth would offer several significant benefits over standard SAC alloys. The first is a lower melting point. Bismuth alloys can drop the liquidus of SAC alloys by over 10°C. The second is increased thermal cycling performance as demonstrated by the development of the alloys such as Sn3.8Ag2.9Bi1.4Sb0.15Ni for its thermal cycling characteristics. The questions that the company posed to their metallurgists were, 'can we simplify the alloy for manufacturability purposes, can we enhance the performance both in production and in the field and can we demonstrate a positive impact on the formation of tin whiskers through the incorporation of bismuth'?

Results

Homing in on the best combination of elements, company metallurgists settled on Sn/Bi3/Ag0.6/Cu0.7 (SBAC) alloy. Development revealed the alloy physical properties as depicted in the following table:

Table 1. Sn/Bi/Ag/Cu (SBAC) (2nd column) compared to Sn/3.8Ag/2.9Bi/1.4Sb/0.15Ni (3rd column)

Alloy/ parameters	Sn-0.7Cu-0.6Ag-3Bi	
Tonset(°C) (Heating)	204	212
Tonset(°C) (cooling)	197	199
Undercooling (°C)	7	13
Wetting time, t2/3 (s) (300°C)	0.74	0.8
Wetting force F1 (mN) (300°C)	4.77	4.2
Wetting time, t2/3 (s) (265°C)	1.5	1.58
Wetting force F1 (mN) (265°C)	4.35	3.7
Hardness (HV10) (aged 96hr 125C)	25	29
Tensile strength (Mpa) (2mm/min, aged 96hr 125C)	81	97
Elongation (%)	25	13

Sn/3.8Ag/2.9Bi/1.4Sb/0.15Ni was chosen as the comparator as this alloy was developed in 2005 and has demonstrated better test results than SAC305 in thermal shock testing. The above alloy comparison shows that they are similar in many ways. The advantages of the SBAC alloy is better wetting at lower temperature and the lack of antimony (Sb) promote soldering on silver finishes.

The subsequent batteries of tests were performed to determine how the SBAC alloy compared to SAC305. There are several interesting and positive test outcomes.

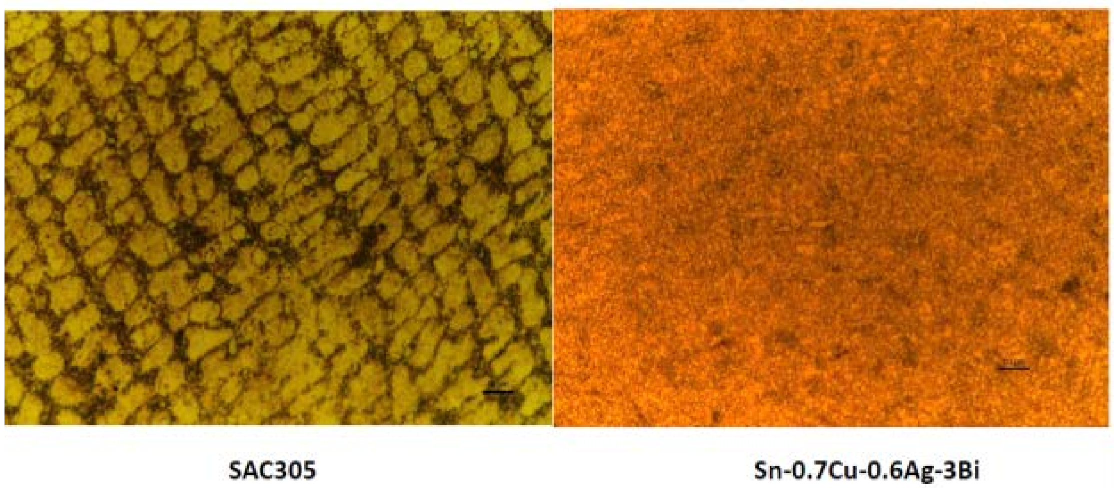

Figure 7. The difference in the grain structure between SAC305 and SBAC

The SAC305 and SBAC samples were aged to compare intermetallic (IM) growth rates. The results below indicate a smaller IM layer was formed in the SBAC alloy both ‘as soldered’ and after aging.

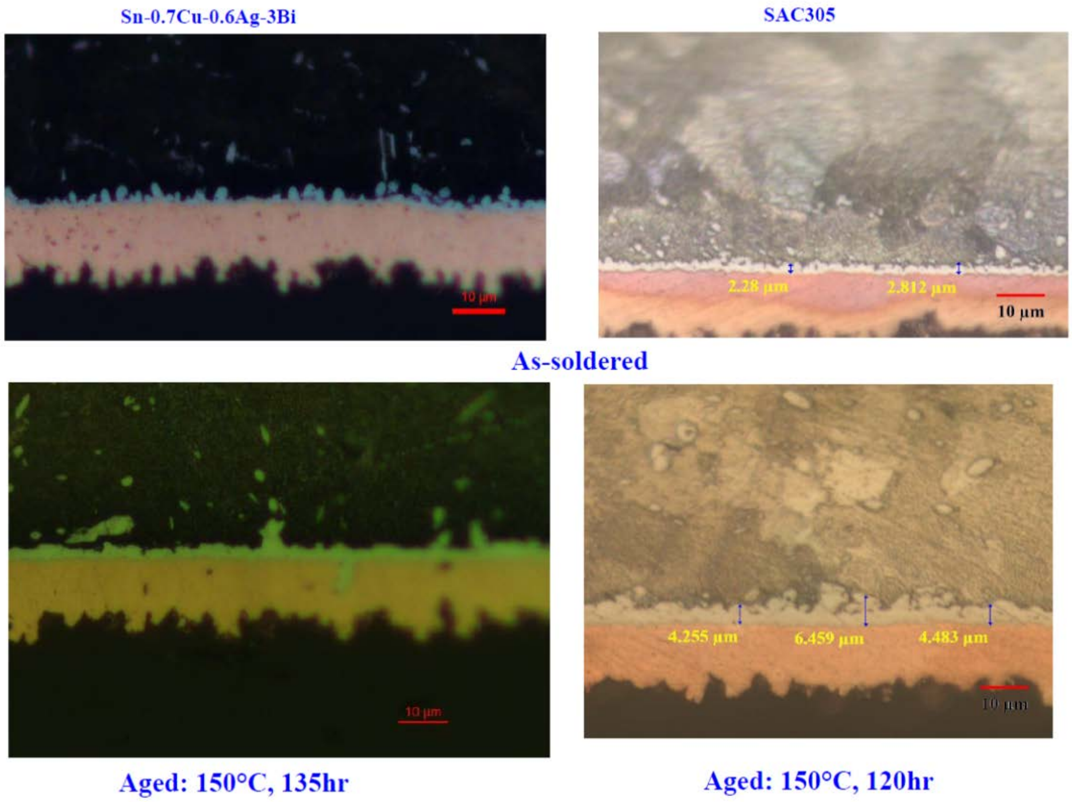

Figure 8. Comparison between SAC305 and SBAC alloys – comparable or smaller IMC formed in SBAC alloy.

A tensile test was performed on round specimens (Dimensions are in inches in Figure 9) at room temperature and a strain rate of $10^{-3}s^{-1}$. The specimens were tested as cast and aged (96 hrs at 125C) conditions. The cast SBAC alloy shows brittle behavior with low elongation; however, as with all cast alloys and bismuth in particular, aging increases both the elongation and strength. Compared with aged SAC305, the SBAC alloy shows higher strength and lower elongation to failure. The increase in elongation of SBAC upon aging is attributed to the fine equiaxed grain structure observed in optical micrograph.

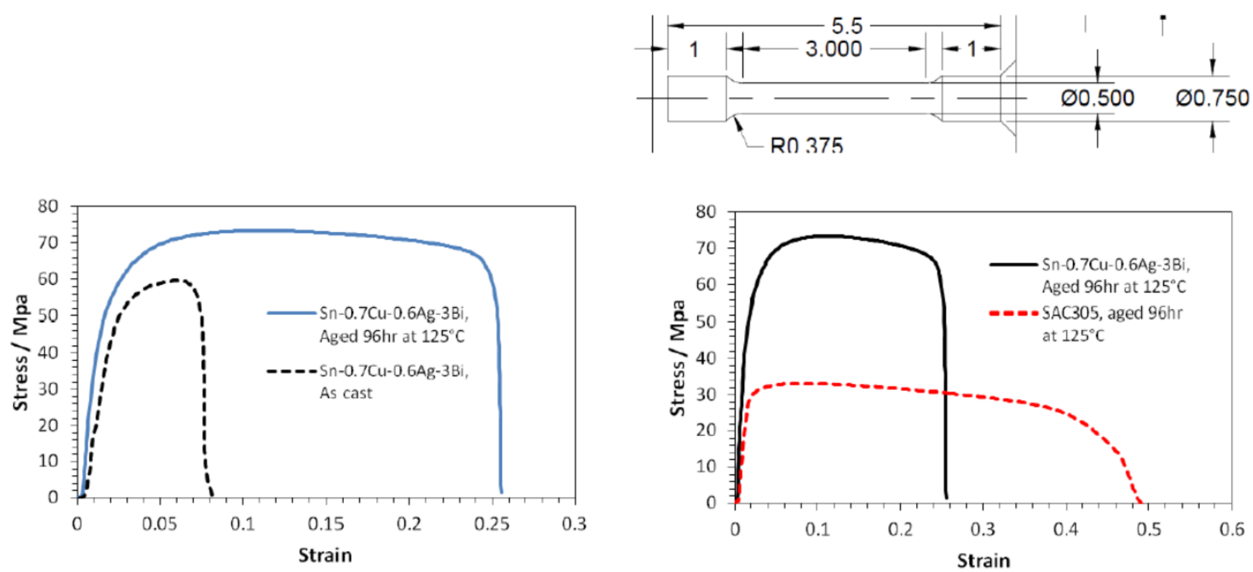

Figure 9.

Below are 'Company Bent Wire' test results for SAC305 (Figure 10 and Figure 11) and SBAC (Figure 12 and Figure 13). After 3100 hours of temperature and humidity exposure. As expected, SAC305 grew whiskers whereas the SBAC alloy was whisker-free.

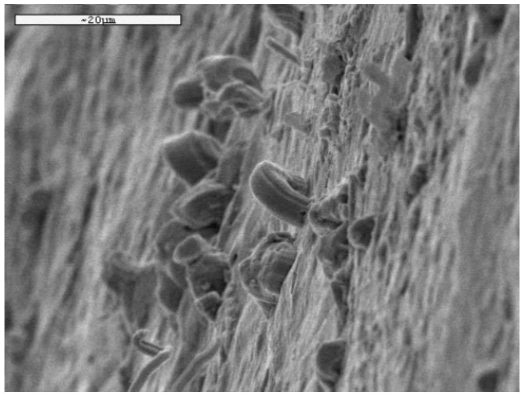

Figure 10.

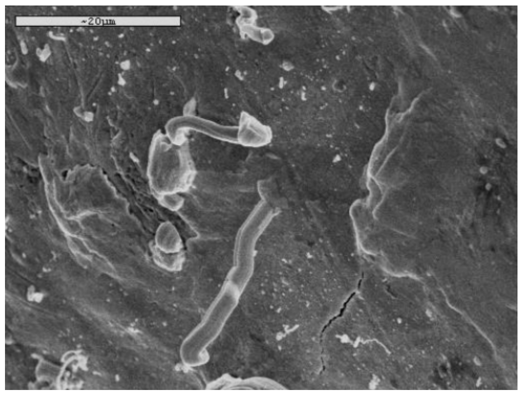

Figure 11.

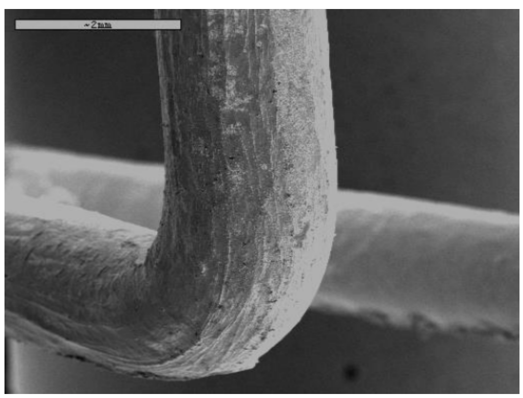

Figure 12.

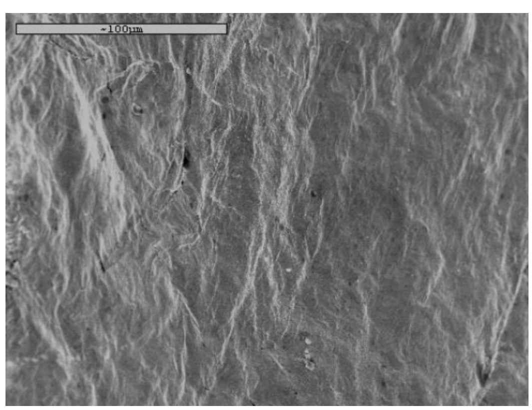

Figure 13.

As previously mentioned, the alloy not only had to equal or surpass SAC305 in the context of reliability, it has to meet/exceed SAC's performance for manufacturability and process compatibility.

Wetting performance of SBAC when compared to SAC305 is very similar to SAC305. Wetting balance test was performed on copper coupon using No Clean flux. As pictured in Figure 14, comparable wetting behavior is observed between SAC305 and SBAC alloy.

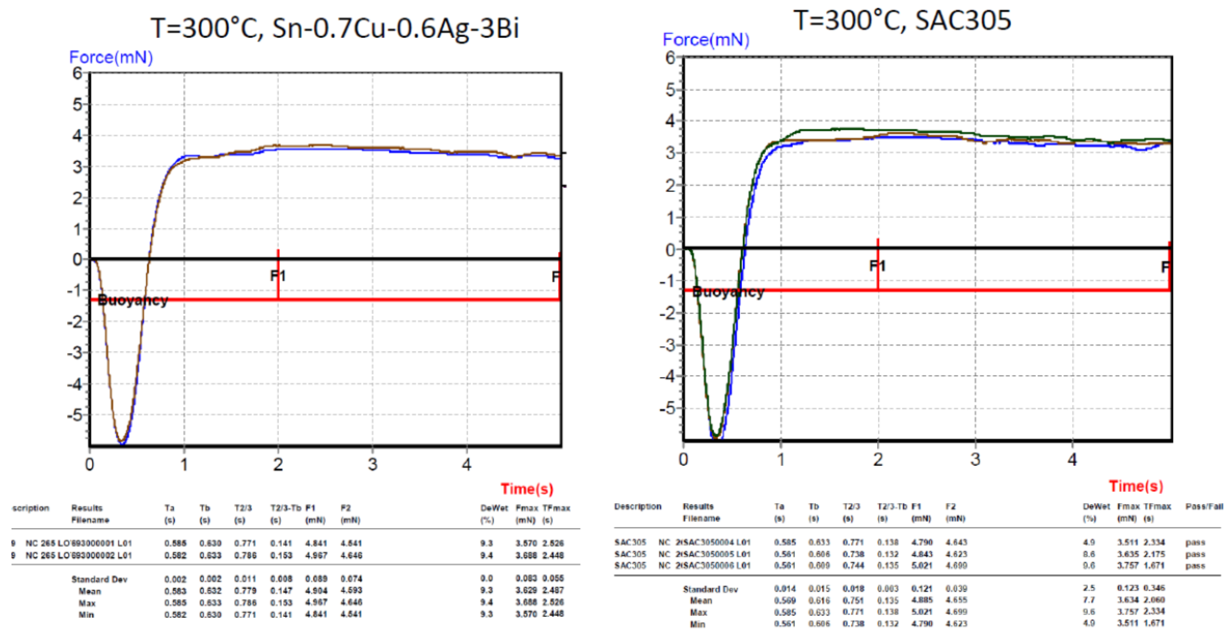

Figure 14. Wetting Behavior

The manufacture of alloy powder is comparable to SAC305 with similar yields and powder quality.

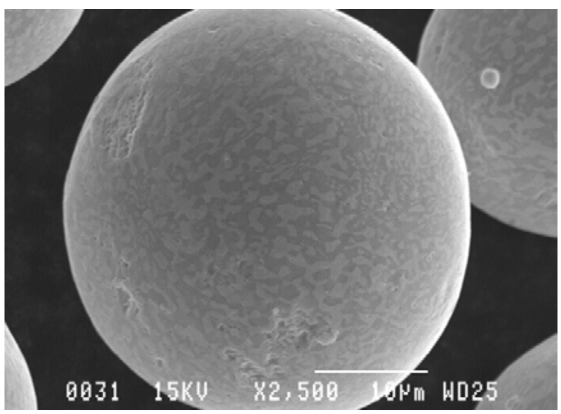

Figure 15. Powder quality

Solder paste was produced with SBAC using existing No Clean and Water Soluble solder paste chemistries. The resulting pastes were tested for print and reflow characteristics. Print quality was similar to the SAC305 paste with transfer efficiency and stencil life all falling within the prescribed tolerances for SAC305 solder pastes. Utilizing SAC305 profiles, reflow results were similar, producing solder joints that all meet IPC Class III criteria. Results could be further optimized given more experience with the alloy and the development flux chemistries that are better suited to the alloys unique properties.

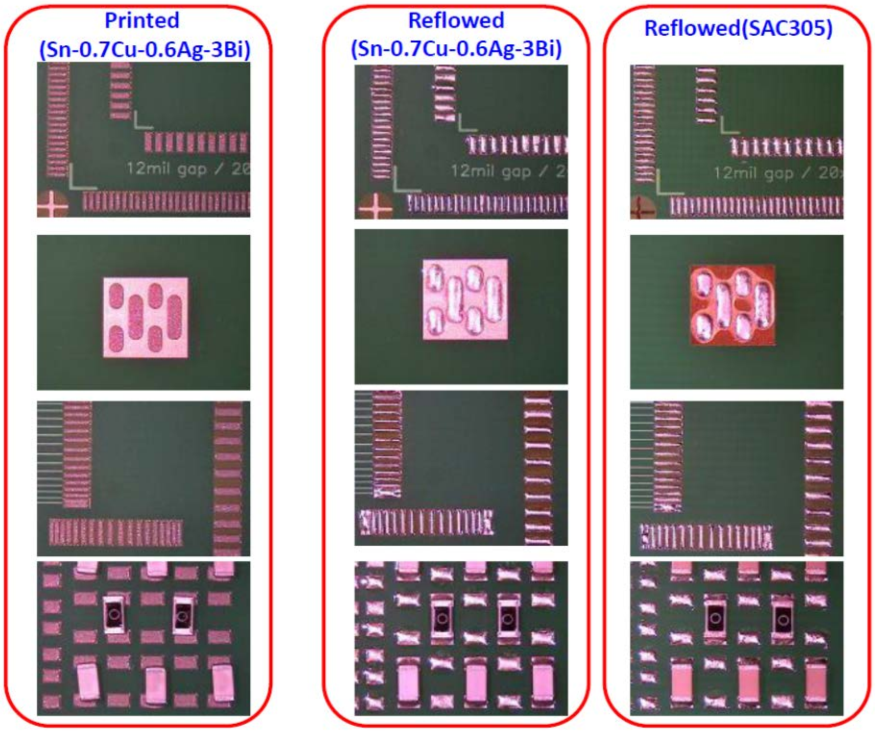

Figure 16. Comparable printing results for both SAC305 and SBAC alloys for the same reflow and flux condition.

BGA voids were measured with the SBAC alloy on SAC305 sphered BGA packages on OSP, Immersion Tin and ENIG surface finishes using standard SAC305 reflow profiles with results well below the IPC acceptable 30% and similar to SAC305.

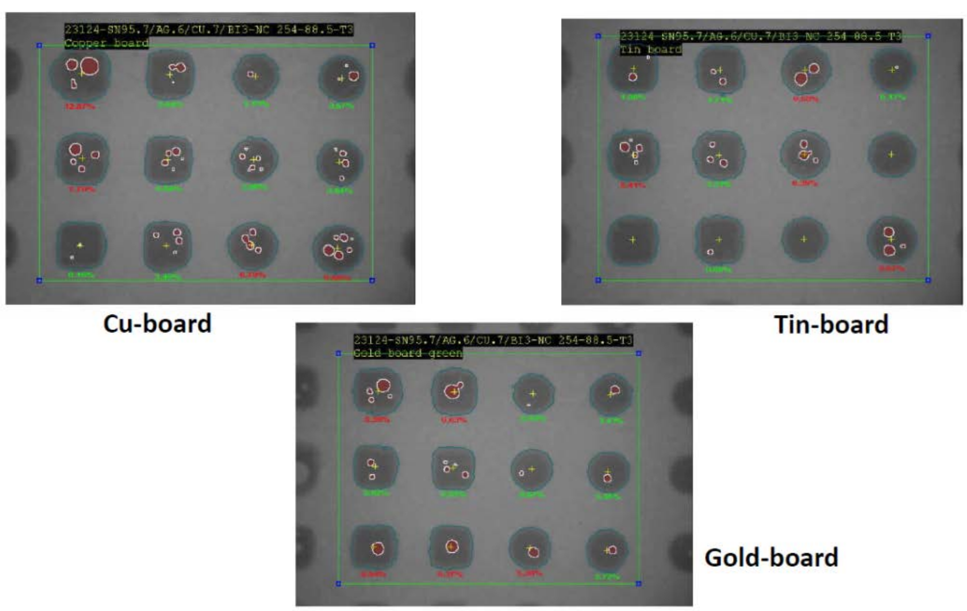

Figure 17. Voids under components were detected using production x-ray technique technology and quantified with production image analyzer software .

Summary

Properties of solder alloy SBAC were studied thoroughly compared with reference SAC305.

Advantages of SBAC over SAC305:

1) Lower melting temperature
2) Smaller solidification range (lower undercooling)

3) Lower cost
4) Higher tensile strength
5) Finer grain structure after aging

Comparable properties:

1) Wetting force and wetting time
2) Spreading
3) Intermetallic compound layer thickness
4) Except for copper boards, voiding is in the same range. For copper plate voiding percentage is lower with SBAC.

Future Work

Company metallurgists will attempt lowering Bi content and doping with micro-alloying elements to improve mechanical properties.

References

[1] E. Chason, N. Jadhav, F. Pei, E. Buchovecky, A. Bower, Growth of whiskers from Sn surfaces: Driving forces and growth mechanisms (2013)