

Effect of Silver in common lead-free alloys

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Abstract

Silver bearing alloys have been used in electronics soldering for many years. Silver has been used in tin-lead solders (Sn62Pb36Ag2) to combat silver scavenging from silver plated electronic components as well as to improve thermal fatigue resistance. Many of the common lead-free alloys contain some amount of silver. Silver bearing alloys have good electrical and thermal conductivity as well as the ability to wet to the common surface finishes used in printed wiring assemblies, thus giving it all the attributes needed for an electronic solder alloy. Presence of silver in Sn based solders increases the bulk solder modulus and is generally believed to improve resistance to fatigue from thermal cycles. Increased solder modulus can be advantageous or disadvantageous depending on the desired performance attribute. For example in high strain rate situations, higher modulus of the bulk solders results in lower life time.

A wide variety of leaded and lead-free solders containing different levels of silver has been studied and is in use in electronics industry for a wide range of applications right now. Studies specific to application process, or performance attributes have been conducted and reported in technical and commercial publications. At Cookson Electronics we have investigated a whole range of solder alloys containing various levels of silver for various reasons and for a variety of applications. There is need in the

industry to understand the effects of silver presence in solders from various applications perspective. This article will attempt to present a review of the key published results on the silver containing alloys along with results of our internal studies on wave soldering, surface mount and BGA/CSP applications. Advantages and disadvantages of silver at different levels will be discussed. Specifically this report will focus on the effect of silver on process conditions, drop shock resistance, solder joint survivability in high strain rate situations, thermal fatigue resistance, Cu dissolution and effects of silver in combination with other alloy additives. Specific application problems demanding high silver level and other requiring silver level to the minimum will be discussed.

Introduction

In the recent past, the electronics industry has seen an increase in the number of Pb-free solder alloy choices beyond the near-eutectic Sn-Ag-Cu (SAC) alloys most companies chose in order to comply with the RoHS regulatory requirement restricting use of lead in electronic assembly. The most popular of these alloys is SAC305. This alloy contains 3% silver, 0.5% copper and the balance tin. The price of silver has increased dramatically over the last several years driving a need for lower silver alternatives. SAC305 has also exhibited higher than desired rates of copper dissolution and solder dross formation providing technical drivers for

change. Around the same time an explosive increase in popularity of portable electronics brought in an increased focus on the poor mechanical shock performance of the most popular near-eutectic SAC alloys (SAC305, SAC405). This provided even further motivations for the development of low Ag ball alloys to improve the mechanical properties of BGA and CSP solder joints, especially under dynamic loading conditions. Most recently, investigations into new solder paste alloys for mass reflow have begun. The full impact of these materials on the final product reliability has yet to be determined.

The increasing number of alternative Pb-free alloys available provides opportunities to address the issues described above. At the same time, these alloy choices present challenges in managing the supply chain and introduce a variety of risks. For example, high melting point, low Ag alloys represent a risk in the reflow process if not managed properly. They may also present risks for thermal fatigue failure of solder joints in some circumstances, though much appears to be unknown about the impacts of Ag, Cu, and the various additives on the thermal fatigue resistance of these alloys. Further, many "high reliability" OEMs have not switched to Pb-free technology and have rigorous requirements for evaluation and qualification of Pb-free materials and processes. The introduction of new alloys creates a "moving target" for these companies in making their transition (or partial transition) to Pb-free technology. Also, experience with near-eutectic SAC alloys is small relative to Sn-Pb, but even less information exists for the new low-silver alloys. Overall, there is a general lack of knowledge throughout the industry regarding new Pb-free alloys, their properties, advantages, and risks [1]. Thus, the wide variety of Pb-free alloy choices is both an opportunity and a risk for the electronics

industry. In order to take advantage of the former while minimizing the impact of the latter, much still needs to be learned and the visibility to existing knowledge needs to be improved.

For the lead free soldering of electronic assemblies, the inclusion of silver in the alloy results in better wetting compared to non-silver containing alloys and also allows for a broader process window. Silver also improves joint reliability compared to non-silver lead-free and tin-lead alloys.

This paper will discuss the differences in the more popular low or no silver Pb-free alloys and highlight the advantages and disadvantages of the inclusion of some amount of silver in the alloy used in making the soldered connection.

Silver bearing alloys have been used in electronics soldering for years. Silver has been used in tin-lead solders (Sn62Pb36Ag2) to combat silver scavenging from silver plated electronic components. Silver bearing alloys have good electrical and thermal conductivity as well as the ability to wet to the common surface finishes used in the printed wiring assemblies, thus giving them all the attributes needed for an electronic solder alloy. Silver provides mechanical strength and it improves resistance to fatigue from thermal cycles. Other solder alloys have been used in applications requiring a high melting point alloy. Silver solders (lead-silver) melt in a range of 260 to 315C. The eutectic alloy (97.5%Pb/2.5Ag) melt at 305C.

The relatively low liquidus of the silver containing SAC alloys means that a peak reflow temperature of >230°C for SMT / Reflow and a pot temperature of 260°C for wave soldering are well within the capabilities of standard equipment used at present as well as within the temperature capabilities of

the vast majority of components used in assembly. Therefore, even though these alloys are not a true drop-in replacement they can easily drop into the current assembly processes only requiring some slight changes to the thermal profile. These alloys also give a manageable process window in terms of the maximum soldering temperature needed not being so high as to damage the laminates, components and other assembly materials that may have been used.

In general SnAgCu based lead-free alloys show better thermal fatigue resistance as compared to eutectic SnPb alloy but the presence of Ag in these alloys increases their bulk modulus making them more likely to fail early in high strain rate mechanical shocks.

In short the addition of silver to solder alloys can be an advantage or a disadvantage depending on the application, package and reliability requirements. Following is a short list of the effects of silver addition that will be discussed in this article.

Advantages

- Lower melting point
- Improved wetting
 - A result of lower liquidus temperature
 - Metallurgical effect resulting in lower surface tension
- Better thermal fatigue resistance
- Improved ductility of eutectic SnBi alloy
 - Grain refining effect
- Reduced electro-migration in eutectic SnBi alloy

Disadvantages:

- Poor performance in high strain rate situations (Drop Shock)

- Ag₃Sn separation at high Ag levels
- Higher cost
- High Cu dissolution rate – in the absence of Cu dissolution decreasing dopants

Others:

- Effect of silver and copper combined.
- Effect of other alloy additives.

Melting and freezing characteristics of SnAgCu alloys

Lots of work has been reported on the melting and freezing behavior of SnAgCu alloys. A detailed experimental study and thermodynamic calculations were reported by the NIST metallurgy group[2]. Figure 1 shows the calculated liquidus surface in the SnAgCu phase diagram as reported in that article. SAC305 and SAC405 are close to the eutectic. There are some differences in the ternary eutectic composition reported by different groups. In this article the reported eutectic alloy composition is approximately Sn_{3.7}Ag_{0.9}Cu with 217°C eutectic temperature. Low silver alloys typically show two distinct melting phases. A low temperature melting phase corresponding to SnAg eutectic and high temperature phase corresponding to SnCu eutectic melting around 228°C. Please see DSC plots of SAC305, SAC105 and SAC0307 shown in Figure 2. As the silver level goes down so does the first, low temperature peak. Calculated isothermal sections of SnAgCu phase diagram at 223°C, a temperature in between the two major peaks seen in low silver SAC alloys DSC, are shown in Figure 3. Lower left section, corresponding to low silver and low copper alloys consists of liquid alloys and solid Sn phase. Upper left side sections

corresponds to high silver and medium copper level SAC alloys and consists of liquid phase along with Ag_3Sn intermetallic solid phase. Shaded section to the right corresponds to medium range Ag and high Cu level and consists of liquid and Cu_6Sn_5 intermetallic. Triangular area in the center is all liquid for all practical purposes. In reality true liquidus is usually higher. As reported by Moon et al [2], a tiny peak is seen in the DSC/DTA plots corresponding to the melting of the primary intermetallic phase high temperature. That temperature will be the true liquidus temperature. But since the fraction of this intermetallic phase very small, for all practical purposes the liquidus temperature is where rest of the phases have completely melted.

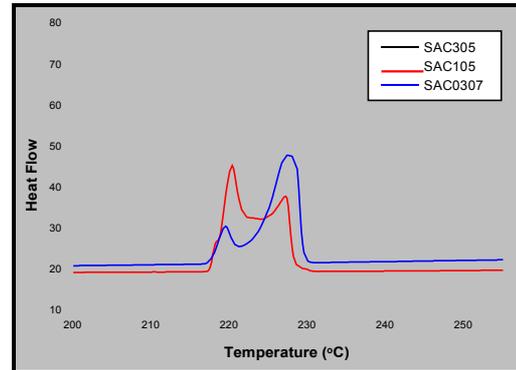


Figure 2: Melting behavior of SAC305, SAC105 and SAC0307. SAC305 is close to eutectic but the low silver alloys show two distinct peaks corresponding to SnAg eutectic phase and SnCu eutectic.

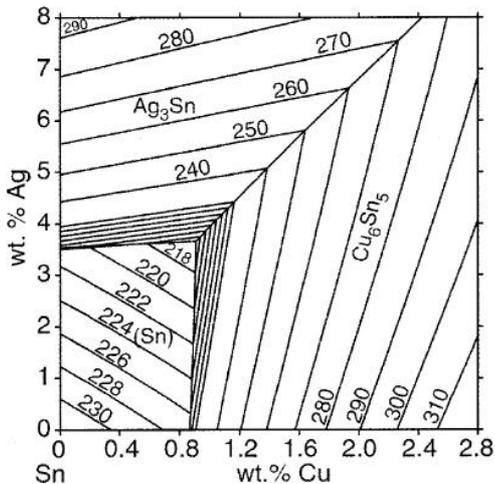


Figure 1: Calculated liquidus surfaces for SnAgCu alloys [2]

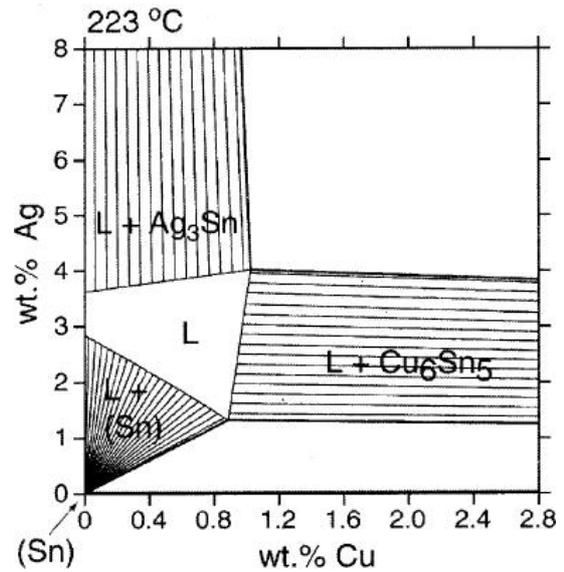


Figure 3: Calculated isothermal sections for SnAgCu at 223°C. [2]

Knowing melting and freezing points is only part of the information. For in-depth understanding of the solder joint formation and its reliability one has to understand the solidification behavior in more detail. Anderson [3] reported a detailed study of the solidification behavior of several near eutectic SAC alloys and showed significant differences in microstructure of as soldered joints even though alloy compositions are not

that different. Figure 4 show shows microstructures of a) Sn3.0Ag0.5Cu, b) Sn3.9Ag0.6Cu, c) Sn3.7Ag0.9Cu, and d) Sn3.6Ag1.0Cu. Coarse Sn dendrites for SAC305 are quite different from extremely fine Sn dendrites for Sn3.9Ag0.6Cu. Sn3.7Ag0.9Cu shows Sn dendrite pattern similar to SnAg eutectic while Sn3.6Ag1.0Cu microstructure doesn't appear dendritic at all. Also, noticeable is the large Ag₃Sn needle present in Figure 4(b), Sn3.9Ag0.6Cu. Considering most manufacturers tolerances, this composition may be considered SAC405 .A slight change in composition may results in a significant difference in solder performance. That is not a good news for electronics manufacturers. Good news though is that this kind of large variations can be expected only near the eutectic point.

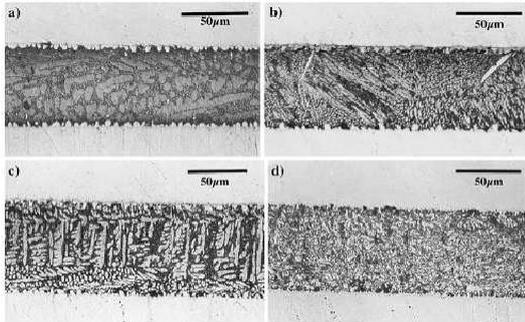


Figure 4: Microstructure of as soldered joints of (a) Sn3.0Ag0.5Cu, (b) Sn3.9Ag0.6Cu, (c) Sn3.7Ag0.9Cu, and (d) Sn3.6Ag1.0Cu.

The long thin Ag₃Sn plate seen is seen in figure 4(b) only. This alloy, Sn3.9Ag0.6Cu, is the only alloy shown in this picture that is on the Ag-rich side of the eutectic. Probability of Ag₃Sn precipitation increases dramatically on that side of the eutectic as one would expect. Henderson et al [4] studied this Ag₃Sn platelet formation phenomenon in detail. Figure 5 shows micrographs of cross-sectioned solder joints formed with two SAC alloys, Sn3.8Ag0.7Cu

and Sn2.5Ag0.9Cu. All the solder joints were reflowed up to 240°C peak temperature. Three different cooling rates were studies, 0.2°C/min, 1.2°C/min and 3.0°C/min. It can be clearly seen that a combination of high silver content and slow cooling rate results growth of large size Ag₃Sn platelets. Ag₃Sn in itself has a higher melting temperature, thus these platelets start precipitating and growing while solder is still in the liquid state. Higher Ag level enhances precipitation while longer cooling time means longer growth time.

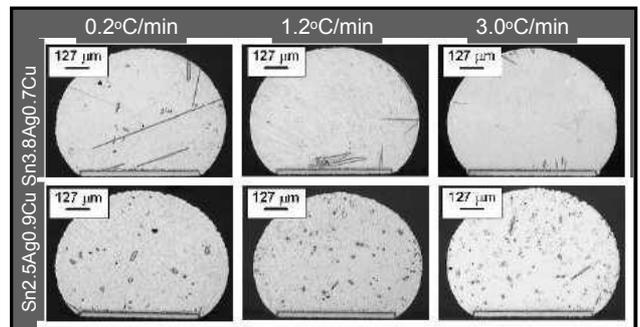


Figure 5: As soldered solder joints x-section. High Ag level and slow cooling rate increases probability of Ag₃Sn platelet formation. From [4]

Ag₃Sn in itself has a higher melting temperature, thus these platelets start precipitating and growing while solder is still in the liquid state. Higher Ag level enhances Ag₃Sn precipitation rate while longer cooling time means longer growth time. Sometimes the Ag₃Sn platelets can grow so large in the liquid stage that when solder shrinks during freezing, the Ag₃Sn platelet protrudes outwards severely deforming the solder interconnection. Figure 6 shows a SAC405 solder sphere reflowed under a reflow profile with very slow cooling rate. A large Ag₃Sn platelet appears at the surface of the sphere. Therefore, even though most of the OEM's would treat SAC305 and SAC405 alloys near eutectic and tend to use same reflow profile, these results show that more care must be taken with SAC405. Apart from deforming

the solder spheres (or interconnections in general), such large size Ag_3Sn platelets lead stress build up around them and results in crack initiation in thermally or mechanically stressed solder joints.

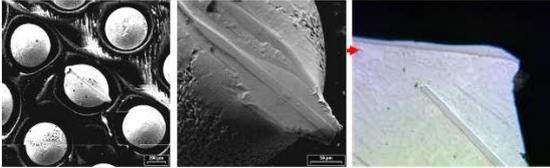


Figure 6: SEM and optical images of a severely deformed SAC405 solder sphere.

Effect of silver on wetting behavior of SnAgCu alloys

Intrinsic wetting ability of solder alloys is an important performance property, which directly affects the integrity of solder interconnections. This intrinsic wetting ability also controls the production yield and throughput when using a dynamic soldering process, such as wave or reflow soldering.

The wetting balance test is a method used by some industry segments to test wettability of components. This test measures the forces imposed by the molten solder upon the test specimen as the specimen is dipped into and held in the solder bath. This wetting force is measured as a function of time and automatically recorded. A typical wetting balance curve is shown in Figure 7. The commonly used performance measure is the time to cross the zero axis of wetting force. Maximum wetting force F_{max} is the measured force between specimen surface and the molten solder.

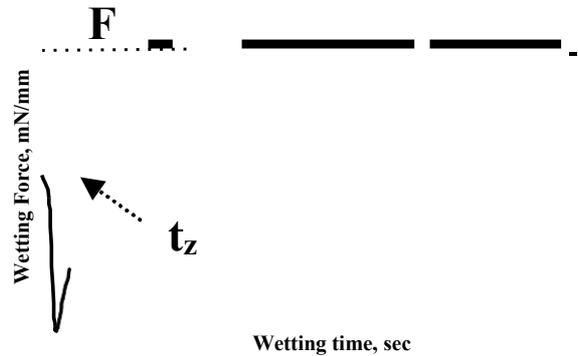


Figure 7: A typical wetting balance curve.

Solderability tests of lead free alloys of interest had been carried out by the wetting balance method. A Minisco ST50 solderability tester was used for wetting balance testing. Copper test coupons that were 25.5mm X 12.78mm X 0.28mm were cleaned in isopropyl alcohol and then dipped in 10% fluoroboric acid solution, rinsed with tap water, flushed with DI water, and then dried. The solder pot was heated to 260°C. The copper coupons were dipped for approximately 5 seconds to a depth of 10mm in a flux. Excess flux was removed by touching the end of the coupon to clean filter paper. The coupon was then positioned in the machine. The coupon was immersed in the solder to a depth of 5mm for 10 seconds at a dip rate of approximately 21mm/s. The machine automatically corrects for buoyancy and calculates wetting force at every 1/8th second.

In this study, wetting time (t_z) and maximum wetting force (F_{max}), were measured for SAC305, Sn0.7Cu and SAC307 alloys. Five No Clean fluxes were used to study wetting characteristics of these alloys.

This is one of the major differences between Ag bearing and Ag free alloys. Ag free alloys have higher surface tension at

standard operating temperatures and don't wet as well. An optimized balance of Ag and other additives helps to lower the surface tension of solder alloys at standard Pb-free operating temperatures. This lower surface tension results in faster wetting contributing to better hole fill and SMD soldering at lower contact times.

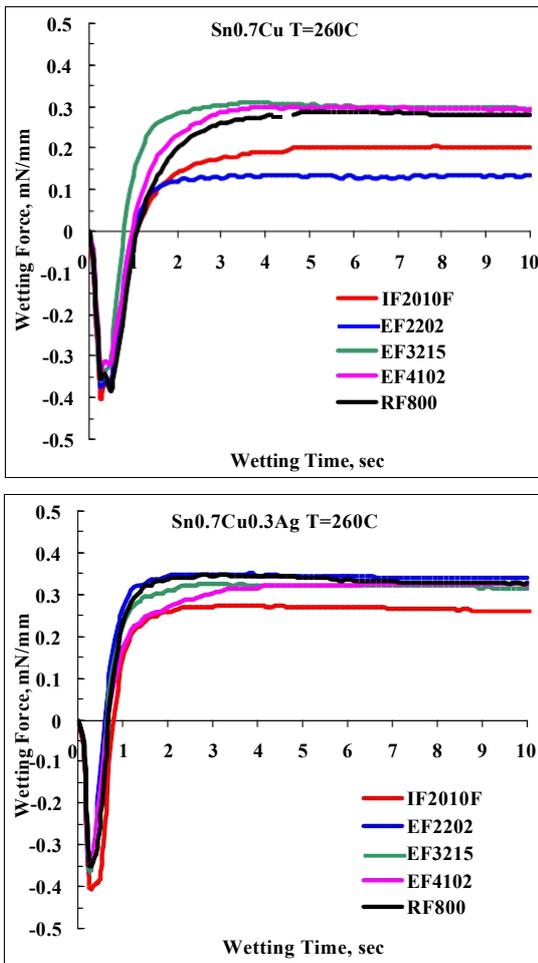


Figure 8: Wetting comparison of Sn0.7Cu and Sn0.3Ag0.7Cu

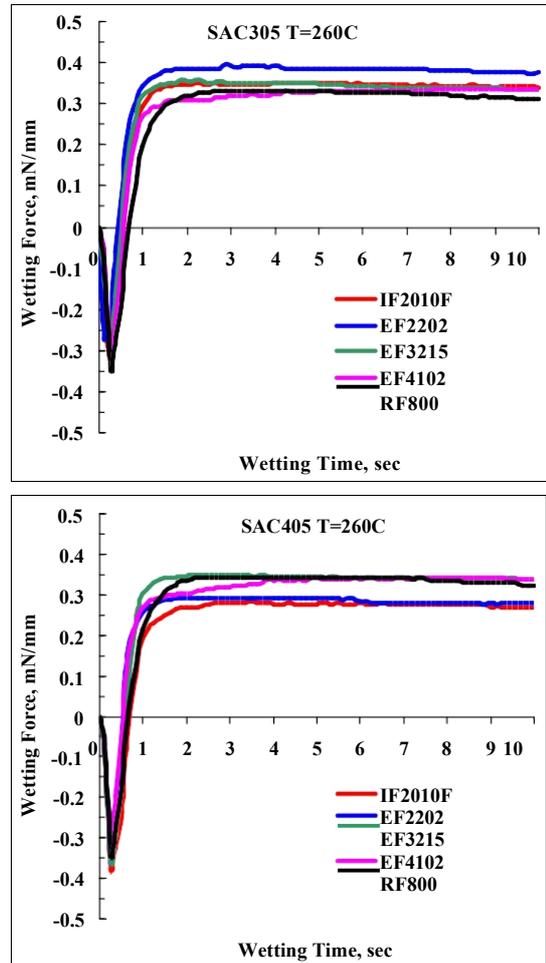


Figure 9: Wetting comparison of SAC305 and SAC405

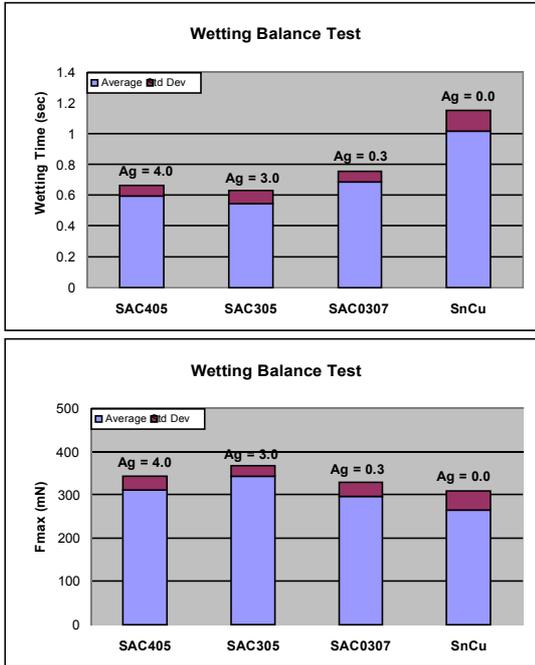


Figure 10: Wetting balance Test. Comparison of wetting time and wetting force.

As seen in figures 8, 9 and 10, SAC305 and SAC405 show comparable wetting time and wetting force irrespective of the flux used. Both of these alloys show slightly faster wetting and marginally higher force than SAC0307 and Sn0.7Cu. SAC0307 with only 0.3% silver clearly shows faster wetting than Sn0.7Cu eutectic alloy. Difference in the maximum wetting force is not that dramatic though. Addition of 0.3% silver introduces a low temperature melting phase as seen in the DSC plot shown in figure 2. Even though the weight fraction of that phase appears to be small, it has a noticeable difference on the wetting behavior of the solder. Faster wetting is indicative of the lower surface tension of the molten solder which is equivalent to raising the operating temperature in wave soldering.

Another wetting balance test was run on Sn-xAg-0.7Cu family of SAC alloys with Ag level varying from 0% to 1%. Test was run at two pot temperatures, 250°C and

260°C. A summary of these results is shown in figure 11. There is a significant difference in the wetting times of alloys with different level of Ag content when the test is carried out at 250°C pot temperature. Wetting time drops from ~2.3 sec to ~1.1 as Ag level goes up from 0% to 0.6%. A further increase in Ag level to 1.0% results in only a very small reduction in wetting time; from 1.1 sec to 0.96 Sec. In fact the difference is within the experimental error margin. Wetting balance test run on SAC305 under identical conditions shows a wetting time ~ 0.9 sec (Not shown in the graph). These results show that most of the benefit of adding silver can be achieved by adding <1% Ag. This is especially true for the wave soldering process where the wetting time and alloy fluidity determine its performance in tests such as hole-fill. Beyond 1%, effect of Ag on wetting is small.

Figure 11 also shows the wetting times for these Ag bearing alloys at 260°C. Difference in wetting times of these alloys at 260°C is small in absolute values but trend is the same. This would indicate that alloy fluidity is a significant factor determining the wetting times. For low Ag alloys, a large fraction of the alloy melts at 228°C as compared to 217-221°C for near eutectic alloys. Therefore a higher temperature means that homologous temperatures of these alloys are closer to each other as compared to that at lower temperatures.

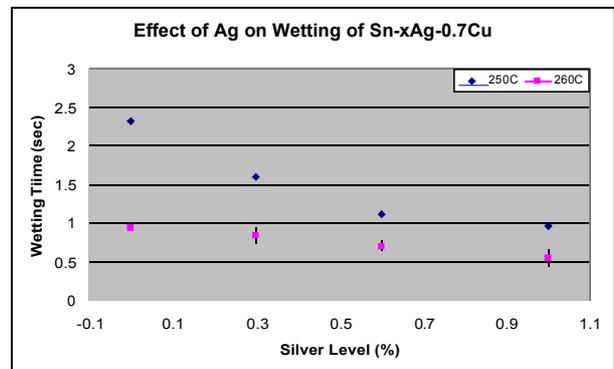


Figure 11. Wetting balance test of Sn-xAg-0.7Cu family of alloys.

Effect of Ag in wave soldering alloys

Wetting behavior of alloys plays an important role in the wave soldering process. The surface tension of the molten alloy at the required operating temperature is important for hole fill and other soldering related performance. Addition of Ag to Pb-free alloys results in lowering the melting temperature, this helps lower the alloys surface tension allowing for faster wetting at lower operating temperatures. A faster wetting is preferred to achieve good hole-fill in a short contact time between the component and the wave.

Figure 12 shows the hole fill performance of SAC305 and SACX0307 at different contact times. Tests were run on SAKT 5.1, 6 layer test board with Entek OSP finish. Pot temperature was set at 260°C and three different conveyer speeds were used. Contact time high (6.5 sec) corresponds to a conveyer speed of 0.7 m/min, medium (4.8 sec) to 1.05 m/min and low (3.9 sec) corresponds to 1.4 m/min. Three different no-clean fluxes with similar flux loading were used in the test.

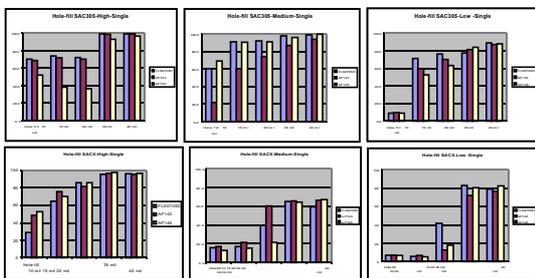


Figure 12: Wave Soldering Data. Hole fill comparison of SAC305 and SACX

At the longer contact times (left side graphs) both alloys appear to perform

similarly, however at the shorter times (middle and right side graphs) the SAC305 exhibits better overall hole fill performance. Higher silver content lowers the molten alloys surface tension enabling improved wetting at lower operating temperatures and wave contact times

Effect of Ag on mechanical properties of the SAC alloys

Even though the near eutectic ternary alloys like SAC305 or SAC405 clearly met many of the initial requirements for a suitable Pb-free solder, there were early suspicions that they may have some performance gaps. We discussed one major gap earlier, high copper dissolution rates and will now discuss another.

Concurrent with the world wide Pb-free alloy initiative we have seen the proliferation of portable “hand-held” electronics. These devices have highlighted the need for good drop shock reliability and it is in this arena that SAC305 and other relatively high Ag SAC alloys have exhibited significant shortfalls.

The root cause of the poor high strain rate response of SAC305 like alloys relative to eutectic SnPb lies in the bulk alloy properties. Most Pb-free solders are high Sn alloys with up to 5%Ag and 1% Cu. These alloys have a relatively higher strength and modulus and lower acoustic impedance and therefore under conditions of drop shock more readily transfer stress to the solder-substrate interface. The intermetallic compounds (IMC) formed during soldering are of low ductility and it is this interface that exhibits brittle failure in test. As the Ag level increases, so does the probability of Ag₃Sn intermetallic compound in the bulk of the solder which strengthens the matrix. Figure 13 is an optical micrograph of a SAC405

solder ball cross section clearly showing Ag_3Sn platelets.

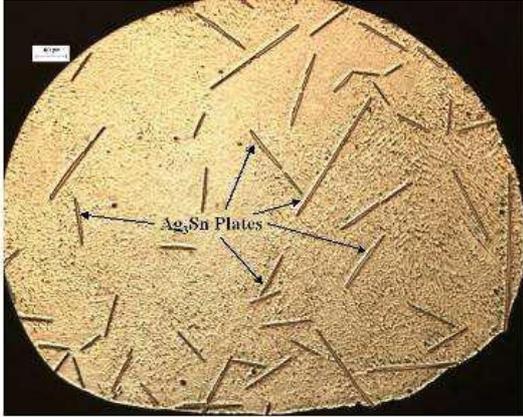


Figure 13: Ag_3Sn platelets can be clearly seen in the SAC405 cross section.

A large number of alloys have been evaluated and discussed in literature as alternatives to high-silver SAC alloys for BGA and CSP dependent devices. The first factor addressed is bulk alloy properties. The effect of the higher bulk alloy strength of high Ag alloys can be minimized through the selection of a lower Ag alternative. At lower Ag there is less Ag_3Sn IMC in the bulk alloy with concomitant reduction in mechanical strength [5,6]. This is demonstrated in the shear test results for the SAC family of alloys shown in Figure 14 [5]. This lower strength delivers the advantage of absorbing the effect of high strain rate deformation (i.e. drop shock) and transferring less of the strain to the solder – substrate interface.

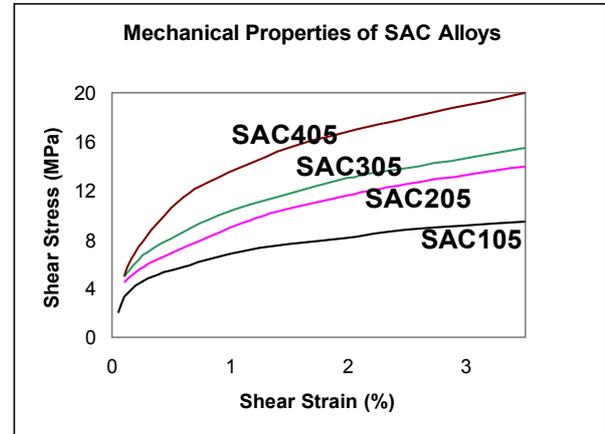


Figure 14: Mechanical (shear) properties of SAC alloys as a function of Ag content. Data is from Ref. [5].

It is important to note that with high Ag alloys, there is more Ag_3Sn intermetallic compound (IMC) in the bulk solder matrix and greater mechanical strength, resulting in best temperature cycling reliability. At low Ag there is less Ag_3Sn IMC in the bulk solder matrix and better ductility, resulting in better performance in high strain rate situations. High speed ball pull/shear test and drop shock tests are the two common lab tests to understand the solder joint performance in such situations. In addition to the bulk alloy characteristics, interfacial IMCs also have an impact on drop shock reliability.

Drop Shock Test

Figure 15 shows drop shock test results for a BGA soldered with SAC405, SAC305, SAC105 and SACX0307. As one would expect from the mechanical properties discussed above, SAC405 and SAC305 fail earlier than SAC105 and SACX.

High-speed ball pull test results on SAC305, SAC105 and SACX0307 are summarized in Figure 16. Plot shows fraction of mode 4 failures for each of these alloys at various test speeds. Mode 4 failures are the

interfacial fractures that indicate an early failure in drop shock [7].

Alloys with Ag levels down to 0.3% have been evaluated for different applications. Many of the alloys show improved drop-shock performance but this can come with degradation in temperature cycling reliability [8]. Therefore the alloy used will depend on the package requirements, performance needed and the end use application.

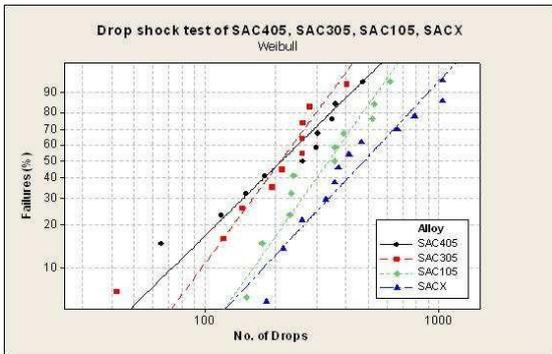


Figure 15: Drop shock test; Comparison of SAC405, SAC305, SAC105 and SACX0307 BGA solder joints.

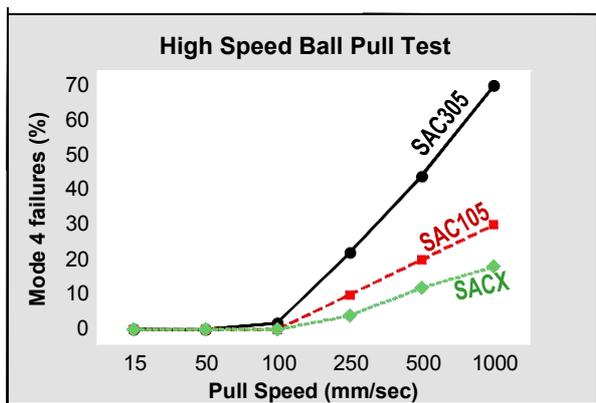


Figure 16: High-speed ball pull test results. Mode 4 failures are interfacial fractures indicative of brittle failure.

Thermal Fatigue Test

It is generally accepted that high Ag SAC alloys (SAC305/405) in general have good thermal fatigue resistance and, in general, perform better than the popular SnPb solders. The element responsible for this is silver. As we have seen, the presence of Ag results in Ag_3Sn IMC precipitates in the bulk solder. It is these precipitates that are responsible for hardening of the matrix. Depending on what impact they have on the growth of the microstructure during thermal aging or temperature cycling will determine the solder joint performance in such situations.

Figure 17 is a summary of results of a study by S. Terashima et al [9] on the thermal fatigue life of SnAgCu flip chip joints with different levels of Ag. SAC105 fails first followed by SAC205, SAC305 and SAC405. It appears there is direct relationship between the silver level and fatigue life. Irrespective of the silver level, all the failures occur near the solder pad interface. To understand the mechanism, authors recorded solder microstructure before and after the failure. SAC105 shows showed large Sn grains with coarse Ag_3Sn particles interspersed. On the other hand SAC405 showed very small size Sn grains and very fine particles of Ag_3Sn uniformly distributed. After temperature cycling there a little coarsening of the microstructure is seen in SAC405. It appears that small size Ag_3Sn particles distributed uniformly don't move enough to coalesce. SAC305 shows relatively larger Sn grains for Ag_3Sn particles are still small. In SAC205 Sn grains are about the same size as that in SAC405 but Ag_3Sn particles appear slightly larger. SnAgCu solder is reported to have Precipitation strengthening. That means dispersion morphology of Ag_3Sn strongly affects the mechanical properties of the alloy.

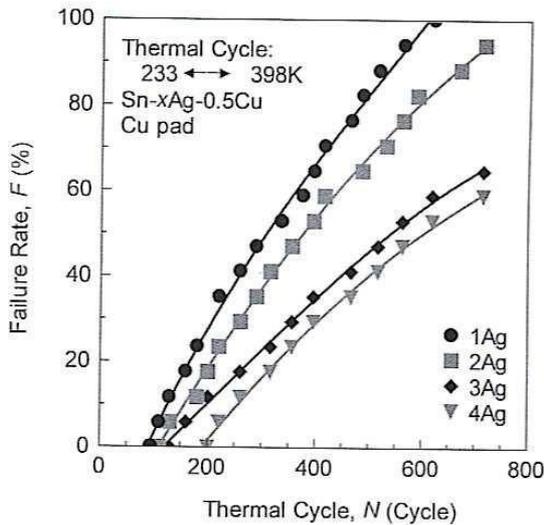


Figure 17: Temperature cycling test data from Terashima et al [9] showing the direct relationship between Ag content and thermal fatigue life.

In our internal testing we started temperature cycling test on selected low Ag alloys. Test was run a six layer boards, each with 15 daisy chained dummy BGA84 components. Components have NiAu surface finish and each was assembled with 12mil spheres with a water soluble BGA flux WSX. Surface finish on board side was Cu-OSP. Since the intent was to understand the alloy behavior, we used the same water soluble BGA flux to assemble the boards as well instead of using a solder paste. Alloys included in this test were SAC305 (control), SAC105, SAC0307, SAC105+Ni and SACX0307 (SAC0307+0.1Bi). The test results to date are shown in figure 18. Most of the low-Ag alloys such as SAC0307 and SAC105 fail around 4,000 cycles. However, high silver alloys (SAC305) used as control has shown no failure until 6,500 cycles. Also, the SACX alloy (Cookson Electronics' Bi-containing SAC0307 alloy) has not shown any failure so far. SAC0307 without Bi has failed around 4,000 cycles just like all other low-Ag SAC alloys.

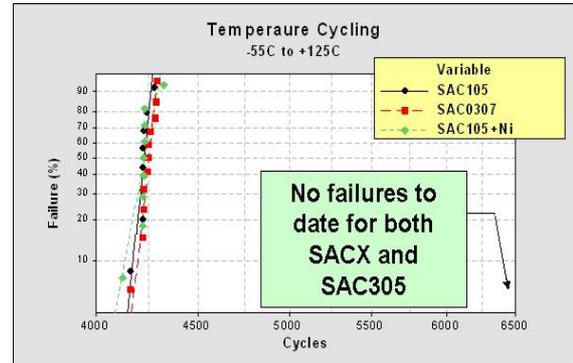


Figure 18: Temperature cycling test of SAC alloys. All common low-Ag SAC alloys fail around 4,000 cycles. However, SACX and SAC305 show no failure up to 6,500 cycles.

In addition to exhibiting exceptional temperature cycling performance, drop-shock results of the SACX alloy have also been confirmed.

To understand how alloy additives affect drop shock and temperature cycling performance, it is important understand their effect on bulk alloy properties. Comparing the alloy microstructure [5-7] is one tool to understand how these alloys will behave in actual performance tests. Representative alloy samples were micro-sectioned and SEM images recorded. In some cases, EDAX was used to map the element distribution. “

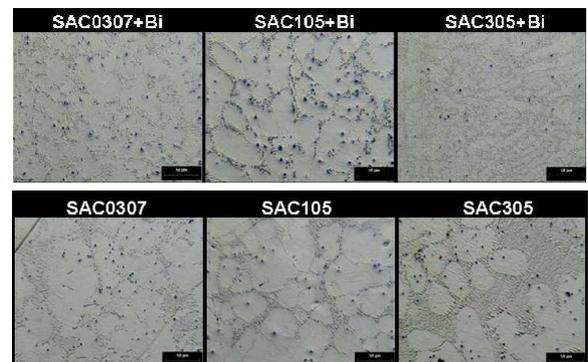


Figure 19: Microstructure of SAC alloys, with and without Bi addition.

Figure 19 shows cross section of the bulk solder [8]. Alloy samples were prepared under identical conditions. Samples of SAC0307, SAC105 and SAC305 alloys and same three alloys with Bi addition were prepared in air and cooled down at ambient temperature. Special care was taken to make sure that all samples were subjected to identical cooling rate, because cooling rate can impact the microstructure. It is clear from these images that Bi contributes to a refinement of grain structure in SnAgCu alloys. This means that during temperature cycling there will be less chance of stress buildup at the grain boundaries. Also, since the starting grain sizes are smaller, overall impact of grain coarsening will be small. Both of these would result in improved temperature cycling performance.

Summary

Presence of silver in soldering alloys impact the soldering process and solder joint reliability in several ways. A wide range of Ag containing alloys have been studied by electronic manufacturers, materials suppliers, and universities and other research groups. Published reports relevant to understanding the effect of silver in solder alloys as well as Cookson electronics' internal data has been summarized in this report. All the data summarized here reaches the following conclusions:

- In general high-silver SnAgCu alloys perform poorly in high-strain rate situations (ie, drop shock) but exhibit better thermal fatigue resistance than lower or no Ag alternatives.
- Presence of Ag results in lowering the liquidus temperature thus effectively decreases the surface tension at normal operating temperature or increasing molten solder fluidity. Even small amount of silver shows

noticeable improvement in wetting characteristics of the solder.

- SnAgCu alloys near the ternary eutectic point follow different solidification routes depending on the Ag and Cu levels. Reflow profile of such alloys, especially those on the Ag-rich side of the eutectic, should be carefully controlled to avoid the unnecessary precipitation and growth of large size Ag₃Sn platelets.
- Addition of a small amount of Ag to SnBi eutectic alloy, improves its ductility by altering the bulk solder microstructure.
- Addition of Ag to SnBi alloy also is reported to improve the electromigration of Bi atoms in the solder.
- Common low-Ag SAC alloys show good drop shock performance but generally exhibit lower thermal fatigue resistance compared to higher Ag alloys.
- Low and no silver alloys in general show coarse microstructure with large Sn grains which grow during temperature cycling or isothermal aging resulting in a poor thermal fatigue resistance of these alloys.
- Addition of grain refining elements such as Bi changes the microstructure and improves the thermal fatigue resistance of low silver alloys.

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