Effects of Alloying in Near-Eutectic Tin–Silver–Copper Solder Joints

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This study included a comparison of the baseline Sn–3.5Ag eutectic to one near-eutectic ternary alloy, Sn–3.6Ag–1.0Cu and two quaternary alloys, Sn–3.6Ag–1.0Cu–0.15Co and Sn–3.6Ag–1.0Cu–0.45Co, to increase understanding of the effects of Co on Sn–Ag–Cu solder joints cooled at 1–3°C/s, typical of reflow assembly practice. The results revealed joint microstructure refinement due to Co-enhanced nucleation of the Cu₆Sn₅ phase in the solder matrix, as suggested by Auger elemental mapping and calorimetric measurements. The Co also reduced intermetallic interface facetting and improved the ability of the solder joint samples to maintain their shear strength after aging for 72 h at 150°C. Some recent additional results with Co and Fe additions are consistent with this catalysis effect, where a reduced total solute level was tested. The baseline Sn–3.5Ag joints exhibited significantly reduced strength retention and coarser microstructures.

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1. Introduction

Environmental concerns and worldwide market forces have accelerated the development of Pb-free solders for electronic assembly with considerable effort focussed on near-eutectic Sn–Ag–Cu alloys, based on the discovery of a ternary eutectic at 217°C with Sn–4.7Ag–1.7Cu (mass%) as the proposed composition.1,2 While many studies have demonstrated that Sn–Ag–Cu may substitute for Sn–Pb for high temperature applications, recent results have shown that these solders also provide a marked improvement over Sn–Pb in high temperature, high stress applications, even exceeding Sn–3.5Ag (mass%) eutectic solder.3 Although Sn–Ag (Tₑ = 221°C) is a well-known alternative to Sn–Pb for high temperature applications, alloys in the Sn–Ag–Cu solder family have baseline advantages of a reduced melting temperature and an additional strengthening phase, Cu₆Sn₅.2 When studied in comparison to many other binary, ternary, and quaternary Pb-free alloys, the broad potential of Sn–Ag–Cu solders has been recognized by several industrial consortia throughout the world.2 The European IDEALS consortium currently recommends one specific alloy, Sn–3.8Ag–0.7Cu (mass%), for Pb-free reflow applications.4 The Pb-free roadmap of the Japan Electronic Industry Development Association (JEIDA) recommends in its “short list” the Sn–(2 to 4)Ag–(0.5 to 1)Cu (mass%) alloys both for wave applications and for reflow at “medium and high temperatures.”5 In North America, the Lead-free Assembly Project of the National Electronics Manufacturing Initiative (NEMI) has established a very specific list of Pb-free solder alloys for accelerated development, focussing on Sn–3.9Ag–0.6Cu (mass%) for reflow applications.6

As an ongoing fundamental research activity, our group has concentrated most recently on understanding of the compositional relationship of the Sn–Ag–Cu solder samples made from one near-eutectic (NE) ternary alloy, Sn–3.6Ag–1.0Cu–Co, to facilitate single mode shear testing, both as-solidified and after aging for 72 h at 150°C. Shear tests were performed with the fixture shown in Fig. 1(b) on a screw-driven testing machine in a compressive mode at a rate of 0.1 mm/min at ambient temperature. Joint sample microstructures were examined in the as-solidified condition. Solder alloy melting and solidification behavior was measured by differential scanning calorimetry (DSC) in droplet emulsion samples7 to assess the undercooling differences between the ternary NE alloy, Sn–3.6Ag–1.0Cu, and one Co-modified quaternary, Sn–3.6Ag–1.0Cu–0.45Co. The DSC...
Fig. 1 Schematic showing a) the specimen geometry with dimensions in mm and b) a side view of the test fixture used in the asymmetric four-point bend tests, where $x = 30\,\text{mm}$ and $y = 4\,\text{mm}$. Adapted from ref. 7.

Fig. 2 SEM micrographs, using backscattered electron imaging, showing Cu substrate (bottom), intermetallic Cu/solder interface, and solder matrix microstructures at moderate magnification of slowly cooled joints. a) Sn–3.5Ag, b) Sn–3.6Ag–1.0Cu, c) Sn–3.6Ag–1.0Cu–0.15Co, and d) Sn–3.6Ag–1.0Cu–0.45Co. Arrows indicate examples of the blocky intermetallic phase in the solder matrix regions.

Fig. 3 SEM micrographs, showing Cu substrate (bottom), intermetallic Cu/solder interface, and solder matrix microstructures at moderate magnification of slowly cooled joints. a) Sn–3.5Ag, b) Sn–3.6Ag–1.0Cu, c) Sn–3.6Ag–1.0Cu–0.15Co, and d) Sn–3.6Ag–1.0Cu–0.45Co. Arrows indicate examples of the blocky intermetallic phase in the solder matrix regions.

heating (250°C, reversal point) and cooling thermograms were measured at 40°C/min., after instrument calibration with pure Sn at the same rate. Scanning Auger electron microscopy also permitted analysis of the distribution of Co in the microstructure of a solder joint made from the Sn–3.6Ag–1.0Cu–0.45Co alloy.

3. Results

The SEM results in Fig. 2(a) through Fig. 2(d) revealed a progression in microstructural refinement of the joint matrix and the solder/substrate interface; first, from Cu modification of the Sn–Ag eutectic, which suppressed Sn den-
Effects of Alloing in Near-Eutectic Tin-Silver-Copper Solder Joints

The Co additions to the near-eutectic Sn–Ag–Cu also appeared to refine the as-solidified microstructure scale by adding additional Cu₆Sn₅ primary phase particles to the ternary eutectic mixture. In general from Figs. 2(c) and (d), the Co addition appeared to reduce intermetallic interface faceting, as evidenced by the fine scale “bumps” seen along the interface with the solder joint matrix phase. Also, the Co addition seems to enhance formation of the Cu₆Sn₅ phase in the solder matrix as a well-distributed, blocky intermetallic phase (arrows point to examples in Figs. 2(c) and (d)), compared to that in the near-eutectic phase mixture of Fig. 2(b).

One explanation for the transition in as-solidified microstructure from the addition of as little as 0.15Co could be related to the initial alloy design hypothesis that considered Co as a substitutional solute addition to the Cu₆Sn₅ phase. To investigate whether Co was not only distributed within the Cu₆Sn₅ phase as a solute, but perhaps was also concentrated in some regions as an effective nucleation catalyst for Cu₆Sn₅, a polished and lightly etched cross-section of a joint made from Sn–3.6Ag–1.0Cu–0.45Co was examined by scanning Auger electron microscopy. The elemental mapping results, reproduced in Fig. 3, showed that Co was concentrated at the extreme end of some of the larger Cu₆Sn₅ particles, consistent with a solidification catalyst effect.

The nucleation enhancement effect of Co also was supported by the calorimetric measurements, as indicated by the collection of heating and cooling thermograms of Fig. 4. The onset of the endothermic melting event for each alloy
of the AFPB shear strength measurements that compare as-
retained strength by modification of the coarsening behavior
that Co also may promote microstructural stability and permit
increased microstructural refinement, it was hypothesized that Ag3 Sn and Cu6Sn5. This near-eutectic joint microstruc-
ture is distinct from the coarse Sn dendrites with interden-
sified eutectic (Sn + Ag3Sn) of the Sn–Ag solder joint. The
solder joints with the Co addition have a more complex, 3-
phase morphology with additional strengthening from larger
dispersed Cu6Sn5 phases. One reason for the complex micro-
structure of the Sn–Ag–Cu–Co alloys appears to be the soli-
dification catalyst effect of Co that promotes reduced un-
dercooling and seems to enhance the nucleation site density
for the Cu6Sn5 phase. The occurrence of these effects is
supported by evidence from both the calorimetry measure-
ments of Fig. 4 and the Auger elemental mapping results of
Fig. 3.14) The substitution of a minor amount of Fe for Cu in
a near-eutectic Sn–Ag–Cu solder also appeared to produce
a catalytic effect and microstructural refinement in the re-
results of some recent studies on solder joints made in a similar
manner.15) Additional measurements with these techniques,
as well as high resolution microstructural studies are needed
to more firmly establish these mechanisms and the generality
of this type of catalytic action.

In addition to an apparent solidification catalyst effect that
increased microstructural refinement, it was hypothesized that Co also may promote microstructural stability and permit
retained strength by modification of the coarsening behavior
of a solder joint during high temperature aging. A summary
of the AFPB shear strength measurements14) that compare as-
solidified solder joints to aged specimen behavior after expo-
sure to 150°C for 72 hours is contained in Table 1, for the NE,
NE + 0.15Co, NE + 0.45Co and Sn–3.5Ag alloy joints. Some
replication of the measurements was performed, as indicated
in Table 1, showing close agreement. SEM micrographs of
equivalent as-solidified solder joints, prior to testing were
provided in Fig. 2. As Table 1 shows, the Sn–3.5Ag joints
exhibit a decrease of about 21% in maximum shear strength
after aging. The NE alloy experiences a more moderate de-
crease (12%) in the maximum shear strength upon aging.
The higher Co addition, 0.45Co, seems to suppress completely a
reduction in strength from this level of aging.14) However, the
aging-induced strength reduction of the NE + 0.15Co solder
joint appears very similar to the NE alloy. SEM analysis of
the joint samples that were aged at 150°C is still in progress
to identify the persistent microstructural characteristics of the
Co-modified joint samples that promote strength retention.

4. Discussion

As an initial benefit for strengthening over the baseline Sn–
Ag eutectic solder, the Sn–Ag–Cu near-eutectic alloy exhibits
Cu6Sn5 primary phase particles dispersed in a ternary eute-
ictic microstructure of highly refined intermetallic particles of both Ag3Sn and Cu6Sn5. This near-eutectic joint microstruc-
ture is distinct from the coarse Sn dendrites with interden-
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The influence of the solder joint interface and matrix micro-
structure characteristics should be reflected in the shear
strength of the joints, assuming a high level of reproduc-
ibility of the results. Unfortunately, our experience7) with the sensitivity of shear strength measurements to extrinsic vari-
ables, e.g., joint porosity and joint gap, appears, at this point,
to restrict our comparisons of shear strength to relative mea-
surements within a set of AFPB bars that are cut from a sin-
gle butt joint sample. With this limitation on the data in this
report, relative comparisons of the heat treatment effects on
the same alloy are more useful than absolute comparisons be-
tween alloys. Thus, the results from the limited set of data
in Table 1 do indicate that a ranking of shear strength aging
stability can be established with the NE + 0.15Co alloy most
stable, the NE and the NE + 0.15Co with moderately enhanced
stability, and the Sn–3.5Ag alloy the least stable. Of course,
Effects of Alloying in Near-Eutectic Tin-Silver-Copper Solder Joints

As part of recent studies, the soldering procedure was further refined to reduce porosity problems which promoted increased data reproducibility and permitted at least seven repeat tests for each condition. The major parameter changes were a reduction in the total flux addition and the restriction of flux application to only once, before heating. This procedure and the resulting mechanical properties are reported in detail, elsewhere. In addition, an improvement of the previous quaternary alloying design was incorporated that involved a direct replacement of a portion of the Cu content in a Sn–3.7Ag–0.9Cu alloy by either Co or Fe. Following more closely a substitutional alloy design assumption, this was accomplished by the direct substitution of either 0.3 mass%Co or 0.2 mass%Fe for the same mass%Cu in the alloys. This would limit the total content of “equivalent Cu” to be available for formation of Cu₆Sn₅ intermetallic in the as-solidified solder joint microstructure. Such a change was suggested by the results in this paper that showed an excess of blocky Cu₆Sn₅ phase in the solder matrix regions of Figs. 2(c) and (d). The excess Cu₆Sn₅ in the joint microstructure for additions of Co to Sn–3.6Ag–1.0Cu, was consistent with the Sn–Ag–Cu phase diagram assessment, where the Cu₆Sn₅ phase certainly would be a primary solidification product. Modification of the joint solidification microstructure in Fig. 5(b) by Fe or Co additions also is observed clearly in Figs. 5(c) and (d), respectively.

To study the aging effects, more quantitative microstructural analysis is needed to characterize the differences in coarsening and diffusion processes that occur, along with some systematic variation of the aging parameters. A new study of aging will incorporate 100 h and 1,000 h aging at 150°C for the alloys in Fig. 5, along with Sn–3.0Ag–0.5Cu, Sn–3.9Ag–0.6Cu, and Sn–3.5Ag. Also, an extended series of thermal-mechanical fatigue studies are underway with some industrial partners to give an enhanced understanding of the reliability of solder joints made with this new family of Pb-free solders, beyond the encouraging shear strength results.

5. Summary

In this study, the microstructure and shear strength of Cu/solder/Cu solder joints made from Sn–Ag–Cu and Sn–Ag–Cu–Co alloys were characterized and compared to results for joints made from Sn–3.5Ag to provide a baseline. Shear strength was employed as a microstructure-sensitive mechanical property measurement to provide an indication of joint reliability. Microstructural analysis revealed that the Sn–Ag–Cu near-eutectic alloy exhibits a more highly refined microstructure containing intermetallic particles of both Ag₃Sn and Cu₆Sn₅, compared to the coarser Sn dendrite/eutectic structure of the Sn–Ag solder joint, containing Ag₃Sn intermetallics. The solder joints with the Co additions appear to have a more complex, 3-phase morphology with additional strengthening from larger dispersed Cu₆Sn₅ phases.
Calorimetry measurements and Auger elemental mapping results suggest that the microstructure of the Sn–Ag–Cu–Co alloys is influenced by a solidification catalyst effect from Co that promotes reduced undercooling and seems to enhance the nucleation site density for the Cu₆Sn₅ phase. Some recent additional results with Co and Fe additions are consistent with this catalysis effect, where a reduced total solute level was tested. Shear strength results indicate that a ranking of high temperature aging stability can be established with the NE⁺₀.₄₅Co alloy most stable, the NE and the NE⁺₀.₁₅Co with moderately enhanced stability, and the Sn–3.5Ag alloy the least stable.

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REFERENCES