Sn-Ag-Cu Solders and Solder Joints: Alloy Development, Microstructure, and Properties

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Slow cooling of Sn-Ag-Cu and Sn-Ag-Cu-X (X = Fe, Co) solder-joint specimens made by hand soldering simulated reflow in surface-mount assembly to achieve similar as-solidified joint microstructures for realistic shear-strength testing, using Sn-3.5Ag (wt.%) as a baseline. Minor substitutions of either cobalt or iron for copper in Sn-3.7Ag-0.9Cu refined the joint matrix microstructure, modified the Cu_6Sn_5 intermetallic phase at the copper substrate/solder interface, and increased the shear strength. At elevated (150°C) temperature, no significant difference in shear strength was found in all of the alloys studied. Ambient temperature shear strength was reduced by large-scale tin dendrites in the joint microstructure, especially by the coarse dendrites in solute poor Sn-Ag-Cu.

INTRODUCTION

Depending on whether one is traveling in an automobile during a commute to work or in an aircraft on a long distance trip, the consequences of premature electronic joint failure can be either inconvenient or disastrous. Thus, electronic joining methods must become more robust and tolerant of extreme operating temperatures and high stress levels. Some current high-temperature automotive joining demands have been met by Sn-Ag eutectic solder (T_e = 221°C), where the soft second phase of traditional Sn-Pb eutectic solder (T_e = 183°C) is replaced by a hard intermetallic Ag_3Sn phase to impart strength and creep resistance.[1] A more general drive toward such lead-free solders now has begun to mitigate the threat of ground-water pollution by lead toxins, where leaching of Sn-Pb solders in discarded electronics could play some role.[2,3] Recent lead-free solder development programs promoted by electronics trade organizations appear poised to make broad replacement of Sn-Pb solders a reality.[4,5]

As an improvement over the previous Sn-Ag eutectic solder in lead-free electronic assembly applications, the Sn-Ag-Cu eutectic[6] and near-eutectic solders offer a reduced melting temperature (about 4°C lower) and additional tolerance for variations in cooling rate after reflow.[7] Prior calorimetric studies[8] revealed the very similar melting behavior of several closely related Sn-Ag-Cu alloys, consistent with the phase diagram studies[9] on this system. Compared to other common choices, the copper alloy addition to Sn-Ag is abundant and low cost, is compatible with common no-clean paste fluxes[10], and, unlike bismuth and antimony, is not a by-product of lead mining.

In comparison to Sn-Pb solders, a successful Sn-Ag-Cu alloy solder should exhibit enhanced shear strength at ambient temperatures. Perhaps more importantly, the Sn-Ag-Cu solder should display improved creep strength and resistance to thermal-mechanical fatigue during temperature excursions up to about 150°C, the current maximum

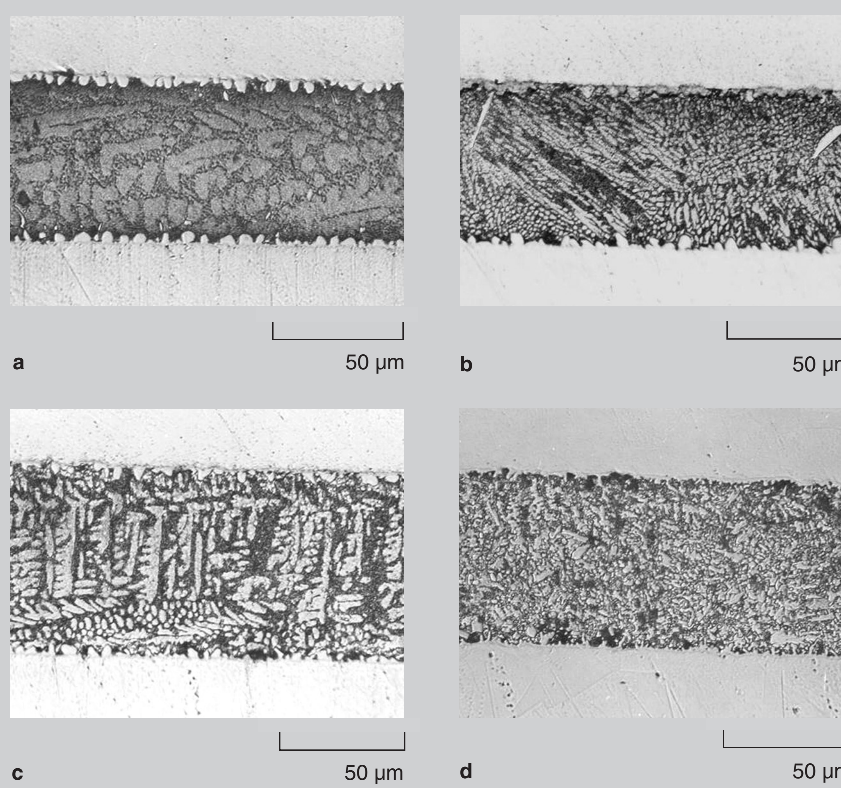

Figure 1. Optical micrographs of as-solidified solder joints made from (a) Sn-3.0Ag-0.5Cu, (b) Sn-3.9Ag-0.6Cu, (c) Sn-3.7Ag-0.9Cu, and (d) Sn-3.6Ag-1.0Cu.

operating temperature limit of under-the-hood automotive electronics.[10] This can be accomplished by microstructural strengthening for the solder matrix and the matrix/intermetallic interface regions of the solder joint that bond to the conductors on either side. Essentially, the matrix-strengthening strategy is to avoid or refine tin dendrites, to refine any pro-eutectic intermetallic phases, and to increase the fraction of fine eutectic in the as-solidified joint.[11] For strengthening the interface regions, a refined scale of non-faceted interface intermetallic growth is desired. While most Sn-Ag-Cu solder joints have improved coarsening resistance,[12] a fourth-element alloying approach with cobalt or iron substituting for a portion of the copper is being developed to further suppress coarsening[13,14] of the matrix and interface regions.

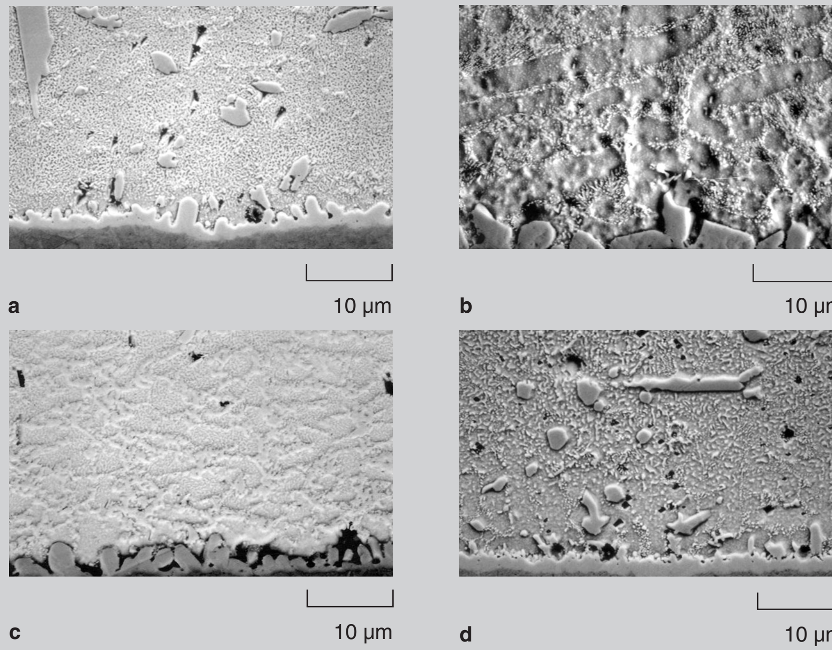

Figure 2. SEM micrographs (BEI) of as-solidified solder joints made from (a) Sn-3.6Ag-1.0Cu, (b) Sn-3.7Ag-0.9Cu, (c) Sn-3.7Ag-0.7Cu-0.2Fe, and (d) Sn-3.7Ag-0.6Cu-0.3Co.

EXPERIMENTAL PROCEDURE

Sn-3.5Ag (wt.%) solder alloy wire (1.57 mm) came from a commercial vendor. Other wires were fabricated from 99.99% purity Sn, Ag, Cu, Co, and Fe by Ames Laboratory in 100 g chill-cast ingots that were drawn into 1.57 mm wire. The nominal ingot compositions consisted of Sn-3.7Ag-0.9Cu (wt.%), Sn-3.7Ag-0.6Cu-0.3Co, Sn-3.7Ag-0.7Cu-0.2Fe, Sn-3.0Ag-0.5Cu, Sn-3.9Ag-0.6Cu, and Sn-3.6Ag-1.0Cu.

Samples for shear-strength testing and microstructural analysis were made by hand soldering copper blocks at about 255°C in a butt-joint geometry with a 76 μm controlled joint gap, similar to many types of electronic solder joints.[7] After solder application and a dwell time of 30 s, each sample was slow cooled (1–3°C/s) to ambient temperature, simulating the cooling rate in a conventional reflow oven on typical surface-mount solder joints.[15]

An asymmetric four-point bend (AFPB) test[16] determined the shear strength of each solder-joint specimen at a strain rate of 0.1 mm/min. and at 22°C and 150°C. The microstructure of the as-solidified solder joints was analyzed by scanning electron microscopy (SEM) on metallographic specimens that were polished and lightly etched with 0.25 vol.%HCl in methanol.

RESULTS

The micrographs of Figure 1 show the effect on the as-solidified joint microstructure of fairly minor variations in silver and copper content in the near-eutectic Sn-Ag-Cu solder alloys used to make the joints. The rather coarse tin dendrites in Figure 1a, with an SDAS of about 6–10 μm, can be compared to the extremely fine tin dendrites in Figure 1b, with an SDAS of about 2 μm. Also, the tin dendrite pattern associated with Sn-3.7Ag-0.9Cu of Figure 1c has a very similar spacing to the tin dendrites associated with Sn-3.5Ag.[17] In contrast, the solidification morphology associated with Sn-3.6Ag-1.0Cu in Figure 1d does not appear dendritic, certainly not with any extended tin dendrites. Moreover, Figure 1b is distinguished from the others in Figure 1 by the Ag_3Sn "needle" phases that project from the upper intermetallic layer into the solder matrix, as confirmed by energy dispersive spectroscopy (EDS) in the SEM.

The higher magnification and atomic number contrast of the scanning electron microscopy-backscattered electron image (SEM-BEI) micrographs in Figure 2 provide additional information on the as-solidified joint microstructures shown in Figure 1c and 1d, along with joint microstructures made from iron and cobalt modifications of Sn-3.7Ag-0.9Cu. In Figure 2a and 2d, for example, it seems that Cu_6Sn_5, rather than tin, is the primary phase in the solidification of Sn-3.6s-1.0Cu and Sn-3.7Ag-0.6Cu-0.3Co solders, as confirmed by EDS in the SEM, followed by solidification of an extremely fine ternary eutectic. An interesting difference in the intermetallic at the copper/solder interface is also apparent, where the finely-spaced rounded stubs of Figure 2a and 2c contrast with the partially faceted Cu_6Sn_5 fingers of Figure 2b and the finer interfacial Cu_6Sn_5 intermetallic in Figure 2d, which has a continuous 1–2 μm thick Cu_6Sn_5 layer on the copper substrate. Actually, the intermetallic interface in Figure 2d is very similar to that in a solder joint made from a Sn-3.6Ag-1.0Cu-0.45Co solder alloy under equivalent solidification conditions in an earlier study.[7,18]

A summary of the ambient temperature shear test results for all of the alloys studied are shown in Figure 3. The repeatability of the maximum shear-strength values is indicated by the narrow range (± 2.5–5 MPa) of the standard deviation of the measurements, where at least seven specimens were tested for each type of solder joint. The weakest of the solder joints was made from the Sn-3.0Ag-0.5Cu, while the strongest joints were made from Sn-3.7Ag-0.7Cu-0.2Fe. The shear strength of the baseline Sn-3.5Ag solder joints fell in the middle of the range of values, stronger than previously reported.[7] This apparent strengthening may have resulted from a minor increase in cooling rate over the previous study due to the sensitivity of the Sn-3.5Ag solder microstructure to solidification conditions.[7,11,15] The difference between the maximum shear strength and the apparent yield strength is an indication of the reasonable ductility exhibited by these samples, although the yield-strength values had an increased standard deviation. The results of elevated-temperature (150°C) testing indicated a drop of at least half of the shear strength of the ambient temperature measurements.[17] Due to the increased standard deviation of the measurements, no significant differences can be reported between the elevated-temperature shear strengths of the solder joints made from any of the alloys tested. The microstructural response to elevated-temperature aging of all of the experimental alloys remains to be characterized in a subsequent report.

DISCUSSION

To implement the matrix-strengthening approach, four Sn-Ag-Cu solder alloys were selected that fall in a composition region that includes and closely surrounds the calculated ternary eutectic composition[9] of Sn-3.7Ag-0.9Cu (wt.%), as shown in Figure 4. Two alloy choices, Sn-3.0Ag-0.5Cu (outlined by a triangle in Figure 4) and Sn-3.9Ag-0.6Cu (outlined by a circle in Figure 4), were chosen to correspond to alloys being studied actively by the Japanese Electronic Industry Development Association[5] and the National Electronics Manufacturing Initiative,[5] respectively. Another alloy, Sn-3.6Ag-1.0Cu (outlined by a hexagon in Figure 4), was included to provide a correspondence to previous studies by the authors.[7,18] In addition, an improvement of the previous quaternary alloying design[7] was incorporated that involved a direct replacement of a portion of the copper content in the Sn-3.7Ag-0.9Cu alloy by either cobalt or iron. This was accomplished by the direct substitution of either 0.3 wt.%Co or 0.2 wt.%Fe for the same volume of copper in the alloys. This limited the total content of "equivalent copper" to be available for formation of Cu_6Sn_5 intermetallic in the as-solidified solder-joint microstructure and was suggested by previous work[7] that showed an excess of coarse Cu_6Sn_5 phase. Previously, excess Cu_6Sn_5 was observed in the joint microstructure for additions of 0.15Co and 0.45Co to Sn-3.6Ag-1.0Cu, made by decreasing the tin content.[7] As Figure 4 suggests, Cu_6Sn_5 phase would be a primary solidification product when the equivalent copper content is moved to the right of the hexagon composition.

To analyze the near-eutectic Sn-Ag-Cu alloy selections, the as-solidified joint matrix microstructures of the ternary solder alloys in Figure 1 can be compared to that predicted from the phase-diagram calculations.[9] As shown by mapping of the four selected solder compositions on the Sn-Ag-Cu liquidus surface in Figure 4, under equilibrium solidification conditions the Sn-3.9Ag-0.6Cu alloy would be expected to form Ag_3Sn as a primary phase prior to completion of solidification. Also, under equilibrium conditions, the Sn-3.6Ag-1.0Cu alloy should form Cu_6Sn_5 primary phase and the Sn-3.0Ag-0.5Cu alloy should form tin primary phase prior to completion of solidification. Evidence for each prediction is exhibited in the micrographs of Figure 1. Of course, the microstructure in Figures 1c and 2b of the joint made from Sn-3.7Ag-0.9Cu, the calculated ternary eutectic composition, also reveals tin primary dendrites with a fine uniform ternary eutectic structure in the interdendritic regions. If the calculated ternary eutectic composition is correct, the appearance of primary tin dendrites in this alloy is evidence for some significant undercooling of the solder joint,[9] where the tin phase may have solidified at a temperature beneath the coupled eutectic-growth region.[18] Actually, a similar amount of undercooling may be expected to affect the solidification processes of the other near-eutectic alloys, but, perhaps, not to the extent that it would change the observed primary phases. Thus, these solidification microstructure observations provide a preliminary correlation with some features of the calculated phase diagram.[9] It should be noted also that the effect of copper dissolution from the substrates on the solder-matrix alloy composition is not included in this discussion, although its influence might add roughly 0.5Cu to the solder-joint alloy composition, depending on the reflow conditions.[8]

As given in Figure 2, minor substitutions of cobalt or iron for copper in the Sn-3.7Ag-0.9Cu alloy refine the joint matrix microstructure and modify the growth mode of the matrix/substrate

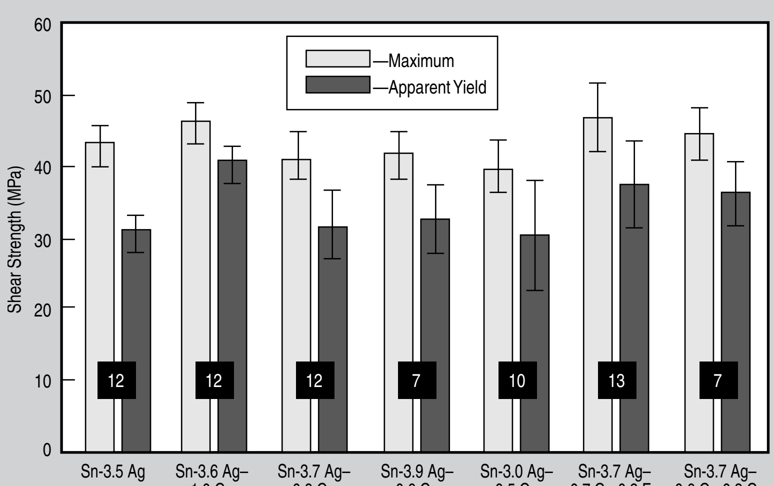

Figure 3. A summary of asymmetric four-point bend tests at ambient temperature on solder joints made from the alloys listed along the y-axis. The number of repeat samples for each alloy is indicated in light contrast on each set, along with the standard deviation of the values at the top of each bar.

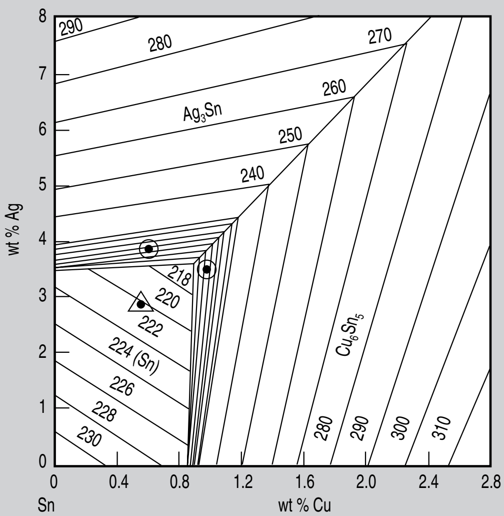

Figure 4. The composition region that closely surrounds the calculated ternary eutectic composition[9] of Sn-3.7Ag-0.9Cu (wt.%), as seen from the calculated liquidus surface adapted from Reference 9.

interface, most profoundly in the case of cobalt, as shown in Figure 2d. A previous study of the cobalt effect[7] in a more solute-enriched alloy, Sn-3.6Ag-1.0Cu-0.45Co, indicated that this transition metal had a solidification catalysis effect on Cu_6Sn_5 phase in the solder matrix. The microstructural results in Figure 2d suggest that the same effect operates in the lower solute alloy, but a more desirable (reduced) volume fraction and size (smaller) of primary Cu_6Sn_5 phase results from solidification of the joint made from Sn-3.7Ag-0.6Cu-0.3Co. A significant effect was also observed from the minor substitution of iron for copper, as seen in Figure 2c, promoting highly refined tin dendrites in the solidified solder matrix.[17] Further studies are needed about this effect.

The maximum shear strength of the as-solidified lead-free solder joints at ambient temperature, given in Figure 3, appears to follow some predictable patterns based on joint microstructure observations. The ambient-temperature shear strength of the joints made from Sn-Ag-Cu solders is weakened by large-scale tin dendrites in the joint microstructure, especially by the coarse tin dendrites in the solute-poor Sn-Ag-Cu, (i.e., Sn-3.0Ag-0.5Cu). Consistent with many studies, the joints with the most highly refined tin dendrites (made from Sn-3.7Ag-0.7Cu-0.2Fe) exhibited the highest shear strength of all the samples tested. The shear strength results for Sn-3.6Ag-1.0Cu and Sn-3.7Ag-0.6Cu-0.3Co followed closely, where Figure 2a and Figure 2d reveal a ternary eutectic joint matrix microstructure, without tin dendrites. The collapse of all of the 150°C shear-strength values to a single range clustered between about 15 MPa and 20 MPa suggests that the high-temperature mechanical properties of these Sn-Ag-Cu solders probably are controlled by the decreased strength of the tin phase in the solder matrix.[17] On the other hand, a complete suppression of microstructural aging effects on ambient-temperature shear strength[7] has been demonstrated for joints made from Sn-3.6Ag-1.0Cu-0.45Co after exposure to 150°C for 72 hours, while the results for Sn-3.6Ag-1.0Cu exhibited a 12% decline. The potential benefit of the cobalt and iron additions for strength retention in Sn-Ag-Cu-X solder alloys of this study (with lower copper equivalence) remains to be tested. The thermal-mechanical fatigue response of solder joints made from the current set of alloys by surface-mount technology is included in a continuation of this study that will be presented in a future report.

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