Growth and Selection of Intermetallic Species in Sn-Ag-Cu No-Pb Solder Systems based on Pad Metallurgies and Thermal Histories

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Abstract
The adoption of Pb-free solders will affect manufacturing processes and joint reliability for electronics packages. Since SAC solder has a higher melting temperature than eutectic Pb-Sn solder, higher processing temperatures will be required. The higher processing temperatures allow for increased solubility of some elements, such as Ni, within the solder melt. The specific selection of pad metallurgies can influence both the type of intermetallics that form at the pad interfaces, and the age related evolution of those intermetallics. In joints where both Ni and Cu pad metallurgies are present, the fast diffusing Cu species can allow the intermetallic compound, (Cu,Ni)6Sn5, to form at the opposite, Ni, interface. The absence of a Cu pad can starve the system of Cu and effectively stop the growth of this (Cu,Ni)6Sn5 intermetallic compound.

The Ag component of the SAC solder can, under proper conditions, result in the growth of Ag3Sn plates in the solder melt before the Sn phase nucleates. This is controlled by the specific concentration of Ag in the solder, by the cooling rate of the solder, and by the tendency of the solder joints to undercool by a typical 30°C before the Sn phase nucleates. The critical cooling rate for the onset of this phenomenon is between 3°C/sec. and 0.3°C/sec., within the range of normal reflow practices of the electronics industry.

Introduction
Sn is the major constituent for most Pb-free solders of interest (e.g. eutectic Sn-Cu, Sn-Ag, and Sn-Ag-Cu, where Sn is found at concentrations greater than 90 atomic percent). [1-10] Relatively small amounts of additional elements such as Cu or Ag are added to Sn to reduce the melting point of the solder alloy, and improve its mechanical and wetting properties. These constituents dramatically affect the mechanical properties of the solder, and possibly the reliability as well. Therefore it is important to understand the evolution of the distribution of these constituents during reflow and long term aging, including changes in the morphology of the intermetallic compounds (IMC's) formed along with Sn by these elements. In Sn-Ag-Cu alloys, Cu6Sn5 and Ag3Sn form in the equilibrium state, with different morphologies, platelets for Ag3Sn and hollow, hexagonal rods for Cu6Sn5. [1-7] We consider the evolution of IMC's during reflow, particularly Ag3Sn, including cooling to the solid state, and during long term aging.

Both the composition, and the cooling rate from the melt, of Sn-Ag-Cu alloys profoundly affect their morphologies. Within this context, it is interesting to note that NEMI has selected a relatively Ag rich composition Sn-3.9Ag-0.6Cu,
while the Japan Electronics and Information Technology Industries Association (JEITIA) has proposed alloys less rich in Ag: Sn-3.0Ag-0.5Cu and Sn-3.5Ag-0.7Cu. As indicated in Fig. 1, the primary crystallization product is changed from Ag₃Sn in the case of the NEMI alloy [Sn-3.9Ag-0.6Cu], to Sn in the case of the JEITIA alloys: Sn-3.0Ag-0.5Cu, and Sn-3.5Ag-0.7Cu.[1,7] This difference is significant because of the large undercooling of the Sn phase observed for these alloys, which allows the Ag₃Sn compound to grow to relatively large length scales (tens of microns) in Ag rich SAC alloys (e.g. SACO, Fig. 1) before the nucleation and growth of solid Sn. Some insight into this phenomenon is provided by a sketch of the metastable Ag₃Sn liquidus line (Fig. 2).[1,7] This sketch is produced by a simple extrapolation below the eutectic temperature. The suppression of the nucleation and growth of Sn allows the growth of Ag₃Sn to extend to a larger fraction of the sample, to larger dimensions, as illustrated in Fig. 3. [1,7] The extent of the growth of Ag₃Sn plates depends upon the time below the liquidus before the nucleation of the Sn phase, which depends monotonically on the inverse cooling rate, as reflected in Fig. 3 for the Ag rich SAC alloy, SACO. We examined such phenomena in control samples, isolated Sn-Ag-Cu solder balls of various compositions, prepared under highly controlled conditions. We also studied the evolution of the microstructure of Sn-Ag-Cu balls in Sn-Ag-Cu solder joints prepared by commercial vendors. We found similar phenomena in both systems, with strong dependences on cooling rate from the melt, and upon solder composition.

The melting event was recorded during the heating phase of these solder alloys and was characterized by the temperature of the onset of melting. The solidification event is recorded during the cooling phase. The temperature at the onset of solidification characterizes the solidification event. It is typical to see a larger super cooling of the melt at larger cooling rates.

A commercial vendor provided the second sets of samples. These samples consisted of a silicon chip attached to an organic chip carrier with a near eutectic Sn-Ag-Cu (SAC) solder. The upper pad, on the silicon side, was finished with a Ni layer. The lower pad was finished with either a copper OSP bump or a copper bump finished with a Electroless Nickel Immersion Gold (ENIG) finish. The solder was reflowed at a peak temperature of 235°C and 60 seconds above the liquidus. The nominal reflow profile temperature decreases at approximately 2.4°C/sec until the temperature is at least as low as 180°C. After reflow some of these samples were aged at 125°C for up to 1000 hours.

After any heat treatment, samples were sectioned, mounted and polished for metallographic analysis. Metallography included optical and scanning electron microscopy along with energy dispersive spectroscopy (EDS) and electron probe microanalysis (EPMA). Optical metallography examinations were performed with a Nikon metallograph with digital high-resolution color camera and integrated image processing. Finally the samples were taken for electron microscopy on an SEM. Using composition mode Back Scattered Electron Imaging (Comp BSEI) and spot mode EDS, most of the IMCs can be identified. The same general metallography route was used for the vendor-supplied samples with the addition of an EPMA step to more quantitatively identify the composition of some IMCs.
Experimental Results and Discussion

**Observation of the Microstructure of Control Samples**

The effect of cooling rate on the microstructure was examined in control samples of SAC solders (Figures 4 - 7). In addition to varying the cooling rate, the temperature at the onset of initial melting was measured, and the temperature at the onset of tin phase solidification was also measured (Table 2). Figure 1, above, shows a portion of the Sn-Ag-Cu ternary phase diagram. Five of the alloys investigated in this study are plotted on that diagram. Metallography was performed on many of these samples and the micrographs can be compared with the measured cooling rate and solidification temperatures.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Melt T.</th>
<th>Solid T</th>
<th>Solid T</th>
<th>Under-cool AT</th>
<th>Under-cool AT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate</td>
<td>0.3°C/s</td>
<td>0.1°C/ s</td>
<td>1.0°C/ s</td>
<td>0.1°C/s</td>
<td>1.0°C/s</td>
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<tr>
<td>Sn</td>
<td>231.5</td>
<td>172.1</td>
<td>152.8</td>
<td>59.4</td>
<td>78.7</td>
</tr>
<tr>
<td>Sn/Pb</td>
<td>183</td>
<td>158.9</td>
<td>149.3</td>
<td>24.1</td>
<td>33.7</td>
</tr>
<tr>
<td>Sn3.5Ag</td>
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<td>199.1</td>
<td>185.7</td>
<td>21.9</td>
<td>35.3</td>
</tr>
<tr>
<td>SAC1</td>
<td>216</td>
<td>185.6</td>
<td>182</td>
<td>30.4</td>
<td>34</td>
</tr>
<tr>
<td>SAC2</td>
<td>217</td>
<td>182.3</td>
<td>162.5</td>
<td>34.7</td>
<td>54.5</td>
</tr>
</tbody>
</table>

Table 2. Table shows measured values for the onset of melting and the onset of tin phase solidification, derived from DSC runs on the respective alloys.

A consequence of the rapid growth of the tin phase is that all other nucleation and growth is suppressed during and for an interval after the onset of tin phase solidification. This is in part because the tin phase solidification reaction is exothermic. As the tin phase grows, it raises the temperature of the joint, even if only briefly, making other nucleation events less likely. Finally, the tin phase grows so rapidly that no significant time period remains for growth of any other nucleated phases.
The effect of cooling rate on microstructure was examined for a near eutectic Sn-3.5Ag-0.9Cu wt% alloy (SAC1, see Figure 4). Larger primary Ag₃Sn precipitates form at the lower cooling rate of 0.1 °C/s. But SAC1 has a relatively large amount of Cu, so we begin to see a large number of primary Cu₆Sn₇ rods, especially in the 0.1°C/sec cooling rate sample. Note that both these samples suffered similar amounts of undercooling, 30.4°C at 0.1°C/sec and 34°C at 1.0°C/sec, so the time below the eutectic temperature is primarily responsible for the microstructure differences manifest here.

Figure 6. Sn3.5Ag solder cooled at 1.0°C/sec, at top, and at 0.1°C/sec, at the bottom. The large precipitates visible in these bright field optical micrographs are primary Ag₃Sn plates precipitated in the melt.

The SAC2 alloy, Sn-2.6Ag-0.9Cu, is hypoeutectic in silver, and is not expected to produce any primary Ag₃Sn plates (Figure 5). No primary Ag₃Sn plates are present within our cross sections at either cooling rate. This is an even more remarkable observation given that our 1.0°C/sec SAC2 sample undercooled 54.5°C. The SAC2 alloy is near eutectic in copper and we find many primary Cu₆Sn₇ rods at both cooling rates. The rods are more numerous, and smaller, at 1.0°C/sec than at 0.1°C/sec.

The Sn3.5Ag solder alloy was used as one of three reference standards for our DSC study, since it is a true eutectic alloy. The Sn3.5Ag solder provides a rich resource for microstructural studies (Figure 6). As discussed above, primary Ag₃Sn plates form as result of entering the metastable Ag₃Sn liquidus region of the phase diagram. As expected, larger Ag₃Sn plates grow at the lower cooling rate (Figure 6).

The extremely rapid growth of the crystalline Sn phase (> 20 cm/s) from the undercooled Sn melt [11] not only limits the nucleation and growth of other phases, it suppresses nucleation of other Sn crystals. As a result, very few grains can be expected within a typical SAC solder ball (Figure 7). Some solder balls may even be formed as single crystals, at least before they experience any deformation. The paucity of separate Sn crystals is illustrated in Fig. 7, a cross polarizer image of the same sample seen in Figure 4. The cross polarizer image allows the establishment of the locations of the grain boundaries (since tin is birefringent, variations in crystal orientation provide optical contrast when viewed with crossed polarizers). Within Figure 7, only 4 separate grains, or crystal orientations, are revealed. Furthermore, all of these crystals are apparently radiating from a common nucleation site. This structural evidence illustrates the suppression of the formation other nucleation sites by the rapidly growing Sn crystals.

Observation of the Microstructure of Commercially Prepared SAC Solder Joints

The microstructural evolution phenomena that were observed in the control samples were also observed in the vendor samples. Figure 8 shows a group of four images showing SAC joints joining a silicon chip to a substrate. These are all very small joints, processed through a commercial reflow profile, and each shows, in proportion, relatively large primary Ag₃Sn plates. The nominal reflow profile has a cooling rate through the melting temperature of about 2.4°C/sec. At this rate one might reasonably expect small or nonexistent primary Ag₃Sn plates. But the actual cooling rate of the solder mass can be expected to be slower
than the programmed oven profile. The cooling rate of the actual solder mass may be retarded by the shielding effect of the over layers and the thermal mass of the adjoining components. The retarding effect will depend on the thermal mass and thermal conductivity of the adjoining components and PCB. In any event, as the presence of these plates has been shown by others to affect the mechanical properties of the solder [3-5], thus their presence in these commercial SAC solder joints of nominal high cooling rate may be of interest to those interested in reliability.

Figure 8. SEI micrographs of near eutectic Sn/Ag/Cu solder joints supplied by a vendor. Lower pad is Ni metallurgy on a silicon chip. Upper pad is as designated within the images.

Within the vendor-supplied joints, we have SAC solder on either Cu/OSP or Ni/Au pads. In each case a Ni UBM pad is also present. This difference turns out to be significant; it is emphasized that in one case we have SAC solder with both a Ni metallization, and a Cu/OSP metallization, while in the other case the SAC solder is only in contact with two Ni metallizations.

Let us consider first the case when soldering to a Cu/OSP pad. In the as reflowed condition, Cu$_6$Sn$_5$ forms at the Cu interface as expected. The morphology is characterized by a scallop shaped intermetallic layer growing off of the Cu pad surface into the solder (Figure 9). On the Ni interface the IMC morphology is much more complex. The surface is decorated with a fine dispersion of precipitates, among them are found Cu$_6$Sn$_5$, Ni$_3$Sn$_4$ and (Cu,Ni)$_3$Sn$_5$. Many of these precipitates are nearly too small to probe with EPMA. Copper containing intermetallics would not normally be expected at such a Ni interface in a Sn-Pb solder, but as has been previously reported [8], Cu in the SAC solder can combine with Ni and Sn to form the ternary compound. Cu diffuses at very high rates in the Sn matrix, so that the (Cu,Ni)$_3$Sn$_5$ compound can grow relatively quickly.

Figure 9. SEI micrograph of near eutectic Sn/Ag/Cu solder joint in the as reflowed condition. Cu pad (1), Cu$_6$Sn$_5$ (2), Ag$_3$Sn (3), fine dispersion of Cu$_6$Sn$_5$, Ni$_3$Sn$_4$ and (Cu,Ni)$_3$Sn$_5$ precipitates (4) and Ni UBM layer (5).

After 1000 hours at 125°C, the microstructure of the sample originally portrayed in Figure 9 has matured and coarsened as seen in Figure 10. The Cu$_6$Sn$_5$ on the copper pad has thickened substantially and has lost much of its original scalloped shape. Instead the layer has more uniform thickness, and has several large IMCs growing out of the Cu$_6$Sn$_5$ layer. The IMCs on the Ni pad have developed a continuous thin layer with many spiky precipitates attached to it or protruding through it. All of these precipitates are found to be (Cu,Ni)$_3$Sn$_5$. No Ni$_3$Sn$_4$ can now be found. The primary Ag$_3$Sn plates are now coarser, thicker and less smooth. Again the plates are quite large relative to the solder ball size.

Figure 10. SEI micrograph of near eutectic Sn/Ag/Cu solder joint aged at 125°C for 1000 hrs. Cu pad (1), Cu$_6$Sn$_5$ (2), Ag$_3$Sn (3), (Cu,Ni)$_3$Sn$_5$ (4) and Ni UBM layer (5).
In contrast, consider the case when both the pad interfaces in the solder joint are composed of nickel. Figure 11 shows that after reflow, the SAC solder has formed \((\text{Cu},\text{Ni})_2\text{Sn}_5\) IMCs at both pad interfaces. The original gold coating of the upper pad has dissolved into the solder and precipitated out throughout the bulk of the solder as fine \((\text{Au},\text{Ni})\text{Sn}_4\) intermetallics. The increased solubility of Ni at the higher reflow temperatures needed for SAC alloys helps explain the presence of Ni within the bulk solder. A very large flat plate of \(\text{Ag}_3\text{Sn}\) can be seen which nearly cuts the ball in half.

After 1000 hours at 125°C, the thicknesses of the Cu-Ni-Sn IMCs at both pad interfaces are largely unchanged (Figure 12). They have not grown thicker or coarser to any large extent. This too is consistent with our previous observations that the growth of the \((\text{Cu},\text{Ni})_2\text{Sn}_5\) abates upon its consumption of all of the Cu in the SAC alloy. In the case of the samples with a Cu/OSP metallization interface, a constant supply of Cu was available, and the growth of \((\text{Cu},\text{Ni})_2\text{Sn}_5\) could continue at the Ni metallization. Without such a source of Cu atoms, the growth is limited. It is also observed that the \((\text{Au},\text{Ni})\text{Sn}_4\) IMCs have coarsened significantly and many have lost their characteristic as sections of flat plate like structures. These \((\text{Au},\text{Ni})\text{Sn}_4\) IMCs are observed to have formed structures like pearls on a string.

Similar observations of the importance of the chemical identity of the pad metallization [Cu/OSP or Ni] to the growth of intermetallic compounds on the chip side (Ni) were made for samples prepared by a different vendor (Figure 13). When Ni is present at both the upper and lower pads of the solder joint, no source of additional copper is available to the solder during aging. We have seen in the past, the IMC species that is most kinetically favored tends to be the one that forms first. Since \((\text{Cu},\text{Ni})_2\text{Sn}_5\) tends to grow faster than \((\text{Cu},\text{Ni})_2\text{Sn}_5\), it tends to grow first at the pad interfaces. However, further growth is inhibited due to the finite supply of copper within the SAC solder joint.

**Conclusions**

We observed the influence of SAC solder composition, cooling rate from the melt, and solder joint pad metallurgies on the evolution of the microstructure of SAC Pb free solder joints. As the morphology and distribution of intermetallic compounds in SAC solder joints affects the mechanical properties of these joints [3-5], this evolution must be better understood in order to ensure Pb free solder joint reliability.

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References


