Gold Embrittlement of Solder Joints

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Introduction

Gold embrittlement of solder joints has been written about for at least four decades [1 – 3]. Nevertheless, gold embrittlement related solder joint failures have been analyzed in this laboratory as recently as July 2009. Gold embrittlement can be avoided by careful solder joint design and knowledge of the causes of this condition. The purpose of this paper is to provide a detailed account of material and process parameters that can lead to gold embrittlement in electronic assemblies.

There are a variety of reasons that designers might want to solder to gold or gold plating. One reason is that some designs involve wire bonding and soldering operations on the same assembly. Another reason would be to include gold contact pads (e.g. for dome keypad contacts) or card edge contacts (e.g. PC cards). The wire bond pads or contact pads can be selectively gold plated, but the selective plating process can be expensive.

The electronics industry currently recognizes a threshold level for gold that can be dissolved into eutectic tin-lead solder above which the solder is likely to become embrittled. This threshold is ~ 3 wt% gold. It will be shown in the paragraphs below that embrittlement of solder joints can develop at significantly lower bulk gold concentrations.

Metallurgical Description of Gold Embrittlement

The most important soldering alloy in the electronics industry is the eutectic tin-lead alloy, $63\%\,Sn - 37\%\,Pb$. This may change in the near future as lead-free soldering takes its hold on the industry. The eutectic tin-lead alloy melts 183°C, which is a low enough temperature to avoid thermal damage of polymer based printed-wiring-board materials and component molding compounds. Soldering temperatures are typically ~ 230°C at which point the molten solder has a low enough viscosity and high enough surface energy to wet all solderable surfaces to which it comes into contact.

Molten eutectic tin-lead solder during solidification separates into two different solids, a lead-rich phase and a tin-rich phase. The resulting microstructure is shown in Fig. 1.
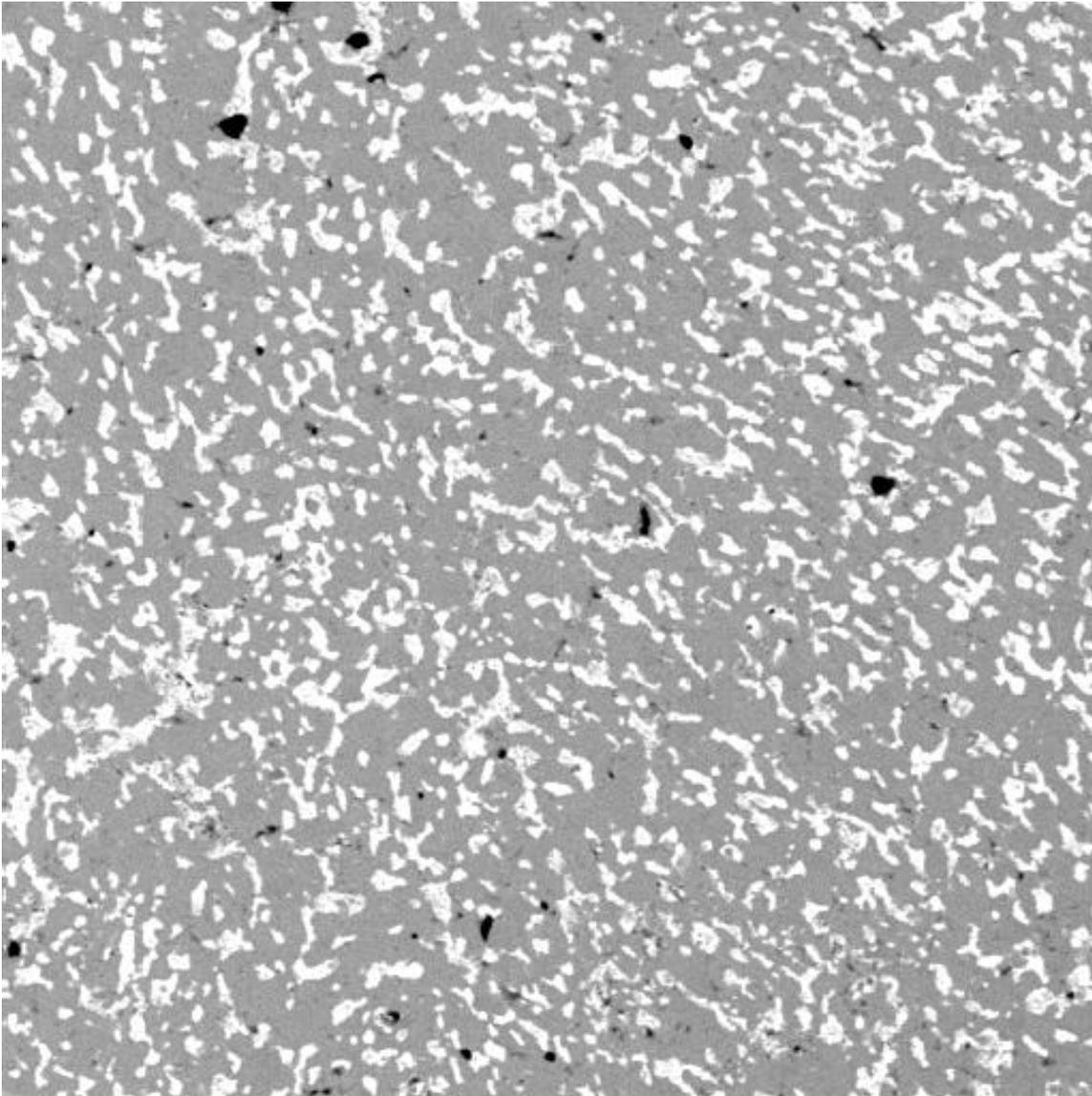
Figure 1: Eutectic tin-lead microstructure [BSE SEM image at 1700X] at moderate to rapid cooling rate. Bright areas are Pb-phase and darker areas are Sn-phase.

Additional phases form when gold is dissolved into the eutectic tin-lead alloy. The most important phases are $AuSn_4$ and $AuSn_2$ intermetallic compound phases. There are several other possible intermetallic phases that can form in this system including $AuSn$, Au_5Sn, Au_2Pb, $AuPb_2$, and $AuPb_3$ [4]. Figure 2 shows the microstructure of a severely embrittled solder joint. The embrittlement is the result of a large volume fraction of hard Au-Sn IMC platelets in the ductile Sn-Pb matrix.
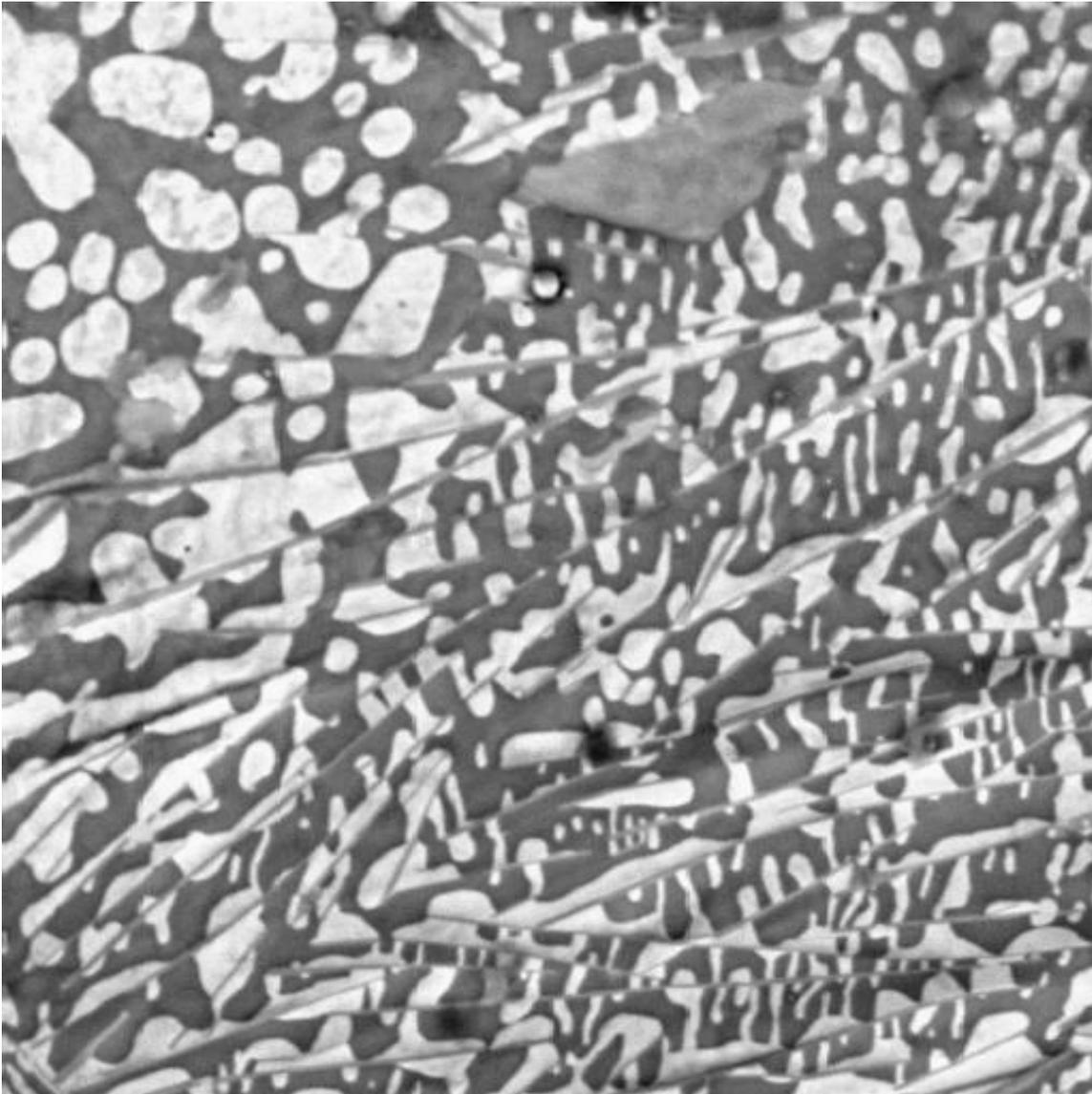
Figure 2: Eutectic tin-lead microstructure with gold embrittlement [BSE SEM image at 3400X]. Bright areas are Pb-phase, darker areas are Sn-phase, and intermediate contrast areas are Au-Sn IMC (primarily $AuSn_4$ and $AuSn_2$). Image processing was used to estimate the area fraction of IMC in this image, which was calculated at 20.5% corresponding to a severely embrittled solder joint.

   The degree of embrittlement could be expected to depend on the morphology of the hard Au-Sn intermetallic phases in the softer Sn-Pb matrix. The Au-Sn IMC platelets in Fig. 2 are very thin, ~ 0.25 microns. At a fixed concentration of gold, thinner plates would have a larger total interface area with the surrounding matrix and therefore a stronger contribution to the overall mechanical behavior of the solder joint. This makes it somewhat precarious to rely on general rules such as the 3 wt% gold threshold for embrittlement.

Calculation of Gold Concentration in Solder Joints

The calculation of gold concentration in solder joints is relatively straight forward and should be performed whenever there is a requirement for soldering to gold plated finishes. The gold concentration in wt% is simply,

$$wt\%Au = \frac{wtAu}{wtAu + wtSnPb} \times 100$$ ……………………………. Eq. 1

The weight of the material can be calculated using,

$$wt = V \times \rho$$ ……………………………………. Eq. 2

where V is volume and ρ is the density of the material. The density of gold is 19.3 g/cc and the density of eutectic tin-lead solder is 8.46 g/cc [2].

These calculations will be illustrated for the following example. A SMT PWB is specified to have 30 microinches of electroplated gold over 100 microinches minimum of nickel. The solder paste stencil is assumed to have apertures that are 80% of the pad dimensions and a 5-mil stencil thickness (*note – the factor 0.64 in the wtSnPb equation is due to 0.8 x W x 0.8 x L = 0.64 x W x L*). The solder paste is SN63 with a solids content of 90% Wt% (or 50 Vol%). The device leads are assumed to contribute no Au or Sn-Pb content for simplicity in this example (though these considerations should be included in most cases). In this case,

wtAu = 30 x 10^{-6} inches x 2.54 cm/inch x W x L x 19.3 g/cm^3 = 1.471 x 10^{-3} g/cm^2

wtSnPb = 0.64 x 0.5 x 5 x 10^{-3} inches x 2.54 cm/inch x W x L x 8.46 g/cm^3 = 0.03438 g/cm^2

wt% Au = 1.471 x 10^{-3} g/cm^2 / (1.471 x 10^{-3} g/cm^{2} + 0.03438 g/cm$^{2)}$ x 100 = 4.1 wt % Au

The calculated gold concentration is above the 3 wt% threshold for gold embrittlement. In at least one case [5], a printed wiring assembly that was similar to this example exhibited gold embrittlement related failures. This will be discussed in more detail in section "Case History #1" below.

SEM/EDS Analysis of Gold Concentration

Microanalysis using SEM/EDS is one method of assessing the gold concentration in solder joints. Ideally, this is performed on metallographically polished cross-sections of the solder joints. The intensities of the x-ray peaks in an EDS spectrum are proportional to the concentrations of the elements contained in the sample. These peak intensities must be corrected for atomic number, absorption, and fluorescence effects (i.e. ZAF corrections). This approach is considered "semi-quantitative", but is very useful for estimating the gold concentration associated with gold embrittled solder joints. Gold concentrations in actual failed solder joints determined using SEM/EDS data by the author have ranged from ~ 5 – 6 wt% Au, which qualitatively supports the 3 wt% threshold discussed previously.

Image Analysis of Gold Embrittlement

Image analysis can be used to examine the area fraction of Au-Sn IMC in metallographic sections or exposed solder surfaces using SEM BSE images. This is

accomplished by selecting a "density slice" of a 256 gray scale image that corresponds to the gray scale range of values for the IMC. Conveniently, this is usually about midway between the gray scale values for Sn-phase and Pb-phase in these images. The area fraction of IMC is computed by counting the number of pixels in the density slice and dividing by the total number of pixels in the image. For example, the image shown in Fig. 2 gave 20.5% by area of IMC.

Case History #1

A failure analysis effort in September 2003 [5] raised some interesting questions regarding the relationship of gold embrittlement to voiding is SMT solder joints. The client reported that SMT components were literally falling off of the PCBA. Examination of the fracture surfaces in the SEM (Fig. 3) revealed that the joints were heavily voided and that the voids contained some entrapped soldering flux. Closer examination revealed that there were thin Au-Sn intermetallic platelets widely distributed over the fracture surface and in the surfaces of the voids. Most of the Au-Sn IMC in these solder joints appeared to be in a very thin (~ 0.1-0.2 microns) plate morphology, which could be expected to exaggerate the embrittlement effect for a given amount of gold compared with coarser plates or needle morphologies. It was hypothesized that the numerous thin Au-Sn IMC plates trapped solder paste volatiles during reflow resulting in the voided condition of the solder joints. It was unclear what specific conditions lead to the observed morphology of the IMC in these joints. Calculation of the gold concentration in these joints based on the 33 microinches measured on unassembled PWBs gave 1.65 wt%Au, which is significantly lower than the 3 wt% threshold for gold embrittlement. This suggests that there may be embrittlement and other process issues for lower concentrations of gold if the IMC segregates to certain areas of the solder joint.

Figure 3:   [Ref. IFN 897A_1, BSE SEM image, 94X] This is a BSE SEM image of the fracture surfaces of failed connector solder joints. There is severe voiding and flux entrapment (dark material) associated with the fracture surface.
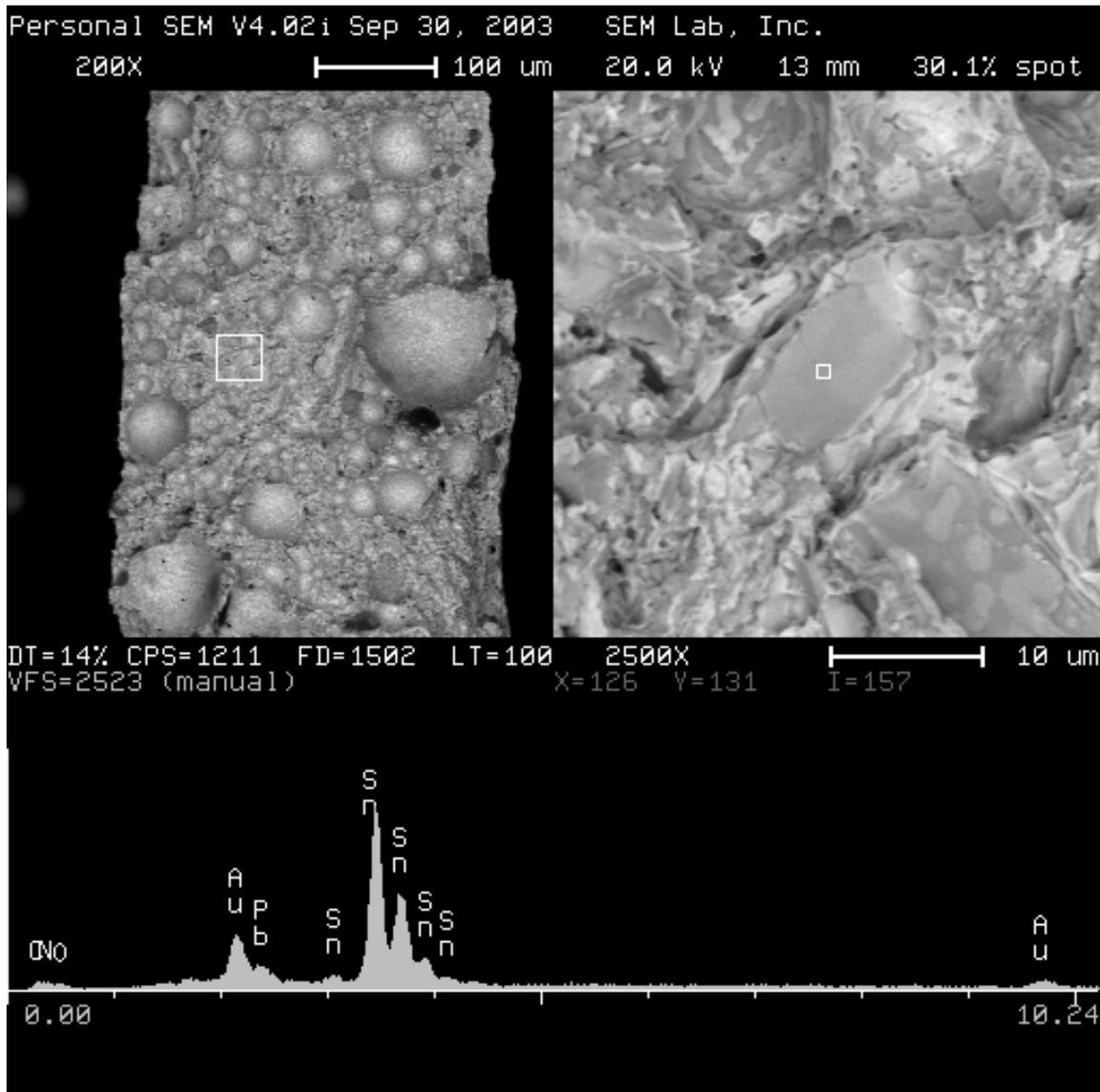
Figure 4: [Ref. IFN 897A_5] This is the elemental spectrum from a Au-Sn IMC plate on the fracture surface. The Au-Sn ratio determined from this spectrum is consistent with $AuSn_2$ IMC.

Case History #2

In this case, solder joint sections of as-soldered joints were provided to determine if a gold embrittlement condition existed. The gold content in the bulk solder joint measured using EDS suggested that there was 10 wt% Au in the solder. The area fraction of Au-Sn IMC in the microstructure was measured using image analysis as ~ 28% This data suggested that the gold content in the subject solder joint was ~3X the accepted limit for gold embrittlement.

The gold plating thickness on the unsoldered leads was measured as ~288 microinches. This is extremely thick electroplated gold. Since the client understood the

possibility of gold embrittlement, it is not clear why such a solder joint design was even considered.
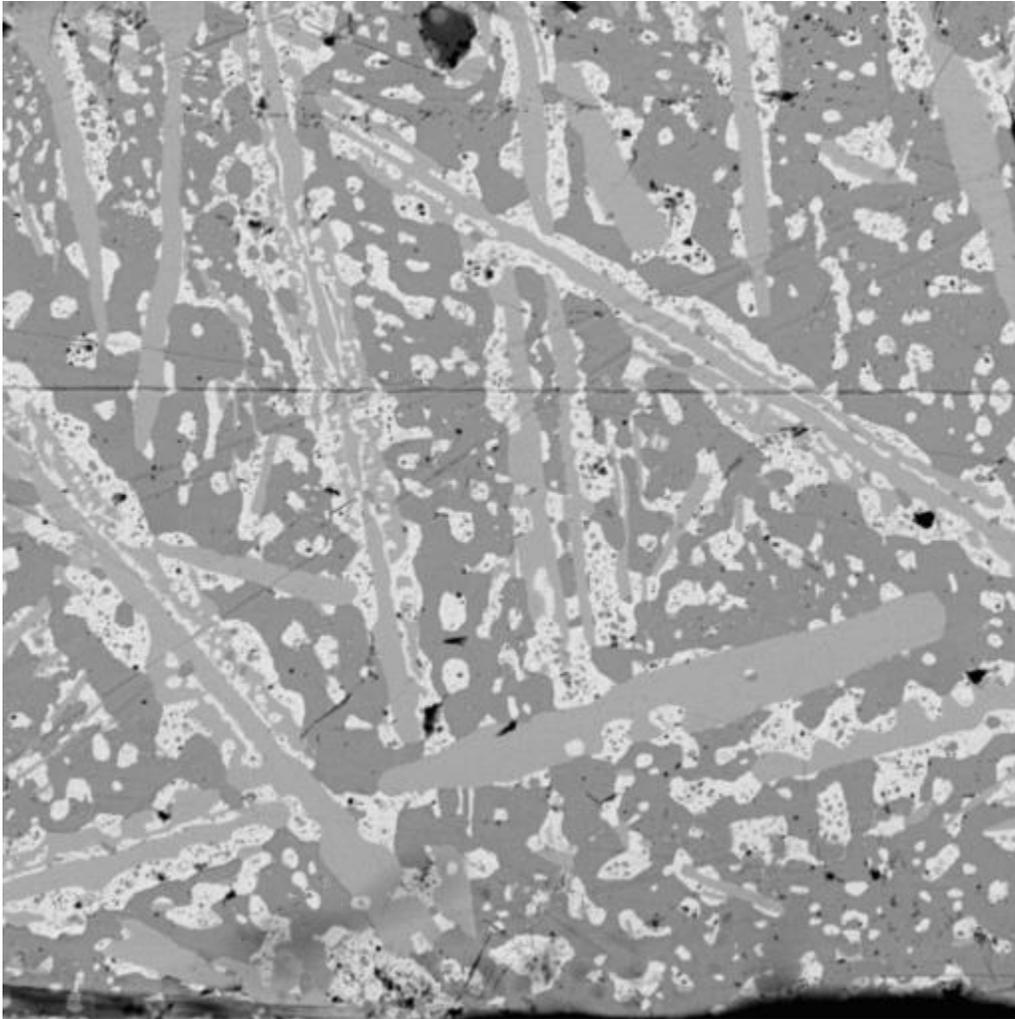

Figure 5: [Ref. IFN 370_5, BSE SEM image, 1513X]. This is the microstructure of the solder joint showing the distribution of Sn-phase (dark gray), Pb-phase (light gray) and Au-Sn IMC (intermediate gray). Image analysis suggests the Au-Sn IMC is ~28% area fraction. EDS results gave ~ 10 wt% Au, which is ~3X the 3 wt% threshold.

Volume of Au-Sn Intermetallics

No literature values for the molar volume of $AuSn_4$ were available when the author last checked, but its theoretical value can be determined from the unit cell and lattice parameters of $AuSn_4$. The compound $AuSn_4$ has an orthorhombic structure with a = 6.51241 Å, b = 6.51621 Å, c = 11.70651 Å [4]. There are 4 Au atoms and 16 Sn atoms in each unit cell [4]. These data produced a molar volume of 75.0 cm3/(mol of $AuSn_4$). In other words, one μm of Au layer will become 7.4 μm of $AuSn_4$ layer. Using the crystal structure data for $AuSn_2$ [4], the ratio of volume expansion from Au to $AuSn_2$ can be

estimated to be 4.2, which is also substantial. These data explain why the $AuSn_4$ and $AuSn_2$ can be so large a fraction of the microstructure at levels of just 3 wt% Au.

Au-Sn Intermetallics in SN62 Solder

The phenomenon of gold embrittlement in SN62 solder (62Sn-36Pb-2Ag, $T_m = 179°C$) is very similar to eutectic tin-lead solder (63Sn-37Pb, $T_m = 183°C$) because of the similarities in these alloys. The 2% of Ag produces some pro-eutectic Ag_3Sn intermetallic phase, but because three silver atoms are consumed for every tin atom consumed in forming the intermetallic, there is very little Ag_3Sn intermetallic phase in the solder microstructure.

A set of equations was developed in order to determine the volume percentage of $AuSn_4$ intermetallic compound versus weight percentage of gold in SN62 solder. Note that the Ag_3Sn intermetallic phase was ignored in order to simplify the calculations.

Given EDS data for wt%Au in SN62 solder what is the Vol% AuSn4 IMC?

$p_{Sn} = 7.3$ g/cm^3

$p_{Pb} = 11.34$ g/cm^3

$p_{AuSn4} = 8.985$ g/cm^3

$AW_{Sn} = 118.71$ g/mole

$AW_{Pb} = 207.2$ g/mole

$AW_{Au} = 196.97$ g/mole

$V\%_{Sn} + V\%_{Pb} + V\%_{AuSn4} = 1$

$V_{Sn} + V_{Pb} + V_{AuSn4} = V_{total}$

$V_{Pb} = M_{Pb}/p_{Pb}$

$V_{Sn} = M^*_{Sn}/p_{Sn}$ … M^*_{Sn} is mass of Sn in primary Sn phase

$V_{AuSn4} = M_{AuSn4}/p_{AuSn4}$

$M_{Sn} + M_{Pb} + M_{Au} = 1$ … as for EDS results

$M^*_{Sn} + M_{Pb} + M_{AuSn4} = 1$

$M_{Sn} = M^*_{Sn} + M^{**}_{Sn}$ … M^{**}_{Sn} is mass of Sn in AuSn4

For $AuSn_4$ phase ….

$M_{AuSn4} = M_{Au} + 4 * M^{**}_{Sn}$

$M^{**}_{Sn} = (M_{AuSn4} - M_{Au})/4$

$M^{**}_{Sn} = M_{AuSn4}*4 * AW_{Sn}/(AW_{Au} + 4 * AW_{Sn})$

$M_{Au} = M_{AuSn4}* AW_{Au} /(AW_{Au} + 4 * AW_{Sn})$

$4 * M_{Au}/AW_{Au} = M^{**}_{Sn}/AW_{Sn}$

$>>> M^{**}_{Sn} = 4 * M_{Au} * AW_{Sn}/AW_{Au}$

For SN62 solder …

$>>> M_{Pb}=0.58 * M_{Sn}$ …

$M_{Au} =$ EDS result

$M_{Sn} =$ EDS result

M_{Pb} = EDS result

V_{AuSn4} = M_{AuSn4}/p_{AuSn4}

M_{AuSn4} = 1 - M^{*}_{Sn} - M_{Pb}

M_{AuSn4} = 1 - (M_{Sn} - M^{**}_{Sn}) - M_{Pb}

M_{AuSn4} = 1 - (M_{Sn} - 4 * M_{Au} * AW_{Sn}/AW_{Au}) - M_{Pb}

>>>>

V_{AuSn4} = (1 - M_{Pb} - (M_{Sn} - 4 * M_{Au} * AW_{Sn}/AW_{Au}))/ p_{AuSn4}

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$V\%_{AuSn4}$ = 100* V_{AuSn4}/(V_{AuSn4}+V_{Pb} + V_{Sn})

The volume percentage of $AuSn_4$ intermetallic compound, primary Sn-phase and primary Pb-phase are shown plotted against weight percentage of gold in SN62 solder in Fig. 6. These calculations suggest that the volume percentage of $AuSn_4$ intermetallic compound is equal to ~ 3.33 X wt% Au in the solder.
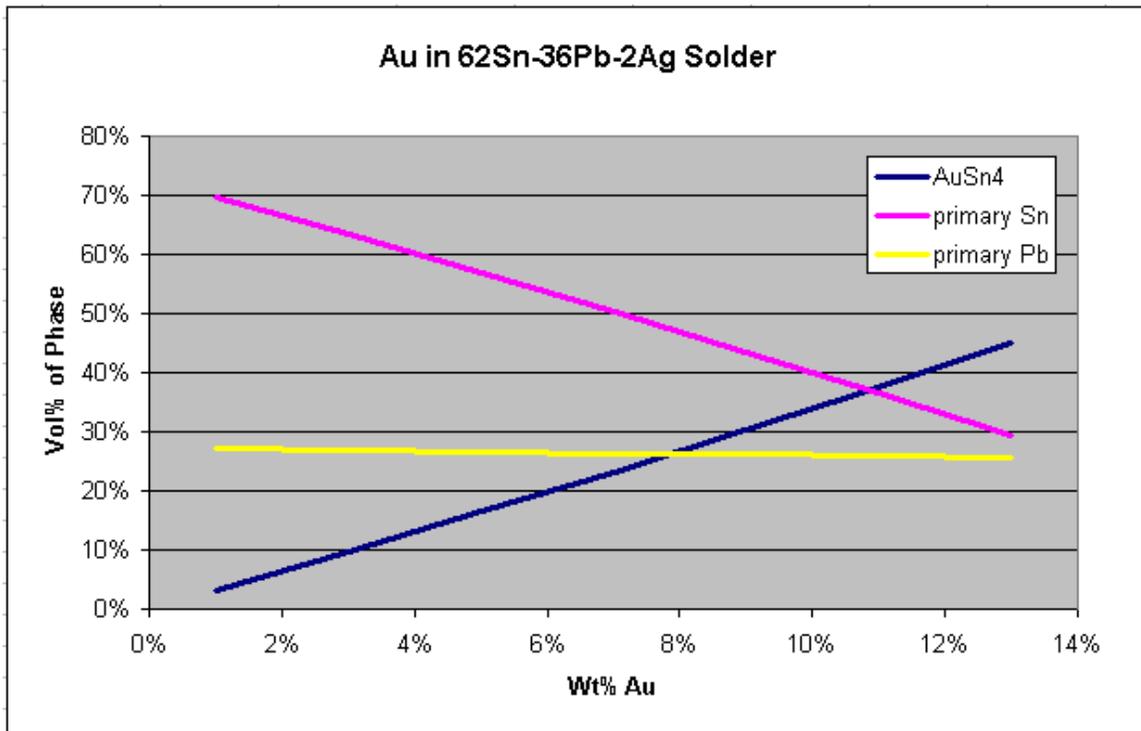

Figure 6: Volume percentage of $AuSn_4$ intermetallic compound, primary Sn-phase and primary Pb-phase versus weight percentage of gold in SN62 solder.

Conclusions

Gold embrittlement continues to appear as a significant reliability issue for soldered assemblies. Reliable products require careful consideration of the solder joint design, which must take into account the potential gold content of the solder joint that is fixed primarily by the design. SEM/EDS analysis and image processing of BSE SEM images are useful tools for assessing the degree of gold embrittlement of actual solder joints.

Careful design and hardware analysis can be used together to ensure gold embrittlement is avoided.

Acknowledgements

Thanks to Scott Nelson at Harris Corporation who pointed out an error where 90% solids content was taken as vol% rather than wt%. A more appropriate vol% for 90 wt% solids is 50 vol%. This resulted in a calculated wt% gold of ~ 4.1 wt% rather than wt 2.3%

References

[1] F. Gordon Foster, "Embrittlement of Solder by Gold Plated Surfaces", Papers on Soldering, ASTM Special Technical Publication, p. 13, 1962.

[2] Howard H. Manko, "Solders and Soldering, McGraw-Hill, 1979.

[3] M. H. Bester, "Metallurgical Aspects of Soldering Gold and Gold Plating", International Electronics Packaging and Production Conference (1st; 1968; Brighton, England), pp. 211 – 231.

[4] ASM Handbook – Vol. 3: Alloy Phase Diagrams, ASM Press, 1992.

[5] SEM Lab report SLI-897, October 4, 2003 (private document).