COPPER-TIN INTERMETALLICS: THEIR IMPORTANCE, GROWTH RATE, AND NATURE

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ABSTRACT

The formation of copper-tin intermetallics is fundamental to a functional solder joint. In creating most solder joints, two pieces of copper, which melt at 1085°C, are bonded together with solder, at less than 230°C. Most of us, with years of experience in electronic assembly, don't usually think of this technological "miracle" of soldering. We are able to bond two pieces of copper together at a temperature low enough where the bonding can be performed in the presence of polymer material. Without this low-temperature formation of copper-tin intermetallics, the electronic industry might not exist. However, contemporary wisdom is that these intermetallics are brittle and can result in poor thermal cycle or drop shock performance.

This paper will review the formation of copper-tin intermetallics, their growth rate, their effect on thermal cycle life, and drop shock performance. The brittle nature of copper-tin intermetallics will also be discussed. In addition, several graphs of intermetallic growth rate will be presented. Some of the additional ancillary effects of copper-tin intermetallic growth, such as tin whiskers, will also be discussed.

Key words: copper-tin intermetallics, gold embrittlement, tin whisker abatement

INTRODUCTION

Pity Ötzi[i], The Iceman who existed circa 3500 BC and was later discovered in 1991 by German tourists. It is believed that he was involved in copper smelting, as both copper particles and arsenic, a trace element in some copper ores, were found in his hair. Not only was he being slowly poisoned by the arsenic, but to smelt the copper he had to achieve a wood fire temperature of about 1085°C (1985°F.) The arsenic in the copper did have a benefit, as it gave the copper a little more strength than if it were pure.

Shortly after Otzi's time, metal workers discovered that adding 10% tin to copper produced bronze. Bronze is not only markedly harder than copper, but it melts at almost 100°C lower temperature, making metal working much easier. Since it melts at a lower temperature, bronze also fills molds better. The Bronze Age had begun. This period coincided with what scholars would recognize as the beginnings of modern civilizations, such as those in Egypt and Greece.

In my opinion, it is almost certain that the Bronze Age is related to the development of soldering. The first evidence of soldering was about 3000 BC, where the Sumerians, who were arguably the first civilization, assembled their swords with high temperature solders. Since the base metal for most copper to copper soldering is tin, the early metal workers probably learned that tin could be used to join copper or bronze pieces together at much lower temperatures than smelting.

Since tin-based solders melt at temperatures below 232°C, soldering enables the two pieces of copper, which melts at 1085°C, to bond at tin's much lower melting temperature. Without this "miracle of soldering" the electronics industry could not exist. The reason being that we must form the copper conductor supporting structure on low cost materials that are electrical insulators. These materials are typically polymers that can only be exposed to temperatures above 232°C for a minute or so.

But what happens during the soldering process to accomplish this miracle?

THE FORMATION OF INTERMETALLICS

Intermetallics are formed during soldering of copper with a tin-based solder. Since the soldering is performed at about 245°C and copper melts at about 1085°C, the copper must diffuse into the tin. Near the tin, a tin-rich intermetallic, Cu_6Sn_5 is formed. Near the copper, a copper rich Cu_3Sn is created. See Figure 1.

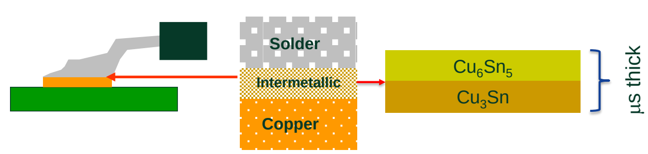

Figure 1. Intermetallic formation in a solder joint.

A micrograph of the intermetallics in a solder joint is shown in Figure 2.

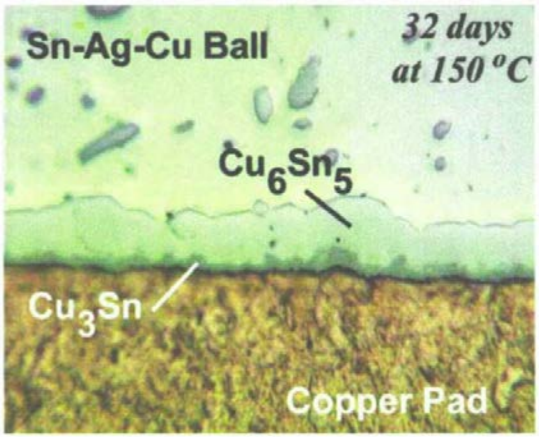

Figure 2. Intermetallic formation at the interface of an SAC405 solder ball at the copper pad after 32 days of aging at 150°C[ii]

The formation rate of intermetallics is highly dependent on temperature. So higher processing times and temperatures will form thicker intermetallics. In addition, on the Kelvin scale, 40°C, a mild operating temperature for electronics, is 313°K. The melting temperature for tin is 232°C or 505°K. So 40°C is (313/505) = 0.62, or 62% of the melting temperature. In comparison, this temperature would be like using steel at a red hot 825°C. So the intermetallics are not stable even at room temperature and the copper can preferentially diffuse into the tin, leaving voids called Kirkendall voids. See Figure 3.

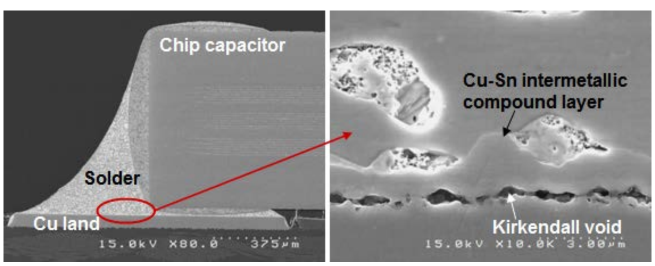

Figure 3. Since copper diffuses into tin more rapidly than tin into copper, Kirkendall voids can occur in the copper near the formation of the intermetallics. This phenomenon can occur even at room temperature.[iii]

INTERMETALLIC GROWTH RATES

By using data developed by Siewert etal[iv] for SAC328 solder, I was able to calculate the kinetics of intermetallic formation between lead-free solder and copper. Both Cu_6Sn_5 and Cu_3Sn were measured for the total intermetallic thickness. Since the process is a diffusion mechanism, I assumed the intermetallic growth distance, X, would be given by the diffusion distance:

$X = (kt)^{0.5}$ equation 1,

where t is time in seconds and k is the growth rate. Since the process is related to diffusion, one would expect that k would be strongly temperature dependent and have an Arrhenius relationship:[v]

$k = A\, e^{-Ea/RT}$ equation 2

or $\ln(k) = -Ea/RT$, equation 3

where Ea is the activation energy, R is the universal gas constant, and T is the temperature in degrees Kelvin.

Applying these equations to Siewert's data yielded the graph in Figure 4. Note that the fit is very good, with a correlation coefficient, R^2, of 0.9981.

The equation for k is then:

$k = 23.995e^{-(10828/T)}$ equation 4.

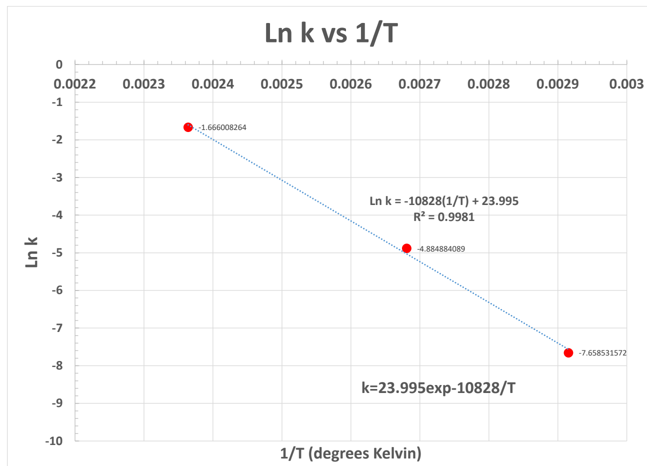

Figure 4. An Arrhenius plot of Siewert's total intermetallic growth data.

Using equations 1 and 4, we can then predict the growth of the total intermetallic at 70°C as in Figure 5. The square root of time dependence is evident.

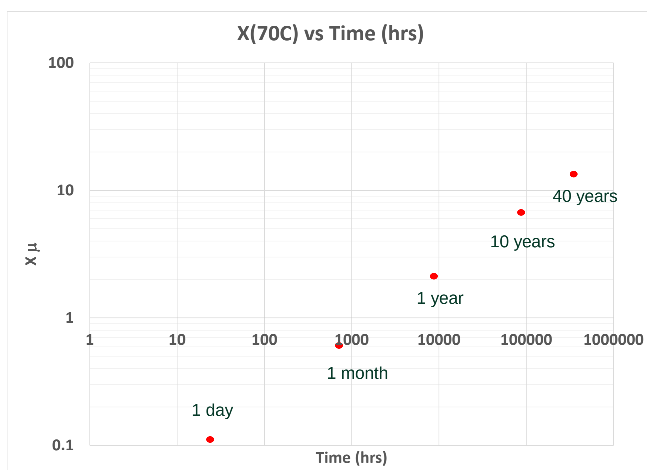

Figure 5. The total intermetallic growth at 70°C versus time.

Performing similar calculations at 200°C results in the graph seen if Figure 6.

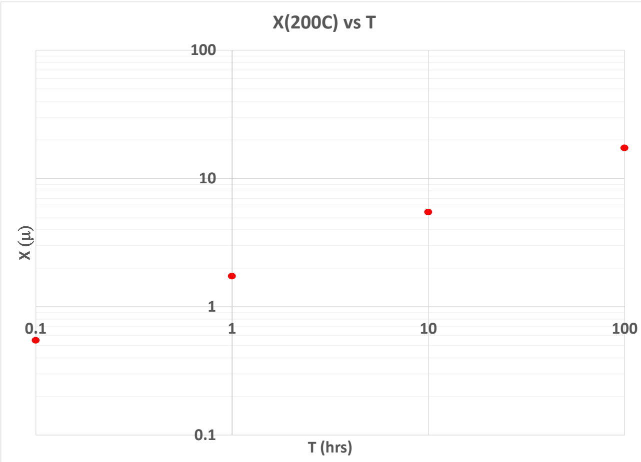

Figure 6. The total intermetallic growth at 200°C versus time.

Notice the profound difference between Figures 5 and 6. The total intermetallic growth at 200°C for 100 hours equals approximately that at 70°C for 40 years.

In another paper[vi], Ma etal. investigated intermetallic growth at 125°C. See Figure 7. Using the equations developed from Siewert's work, we would predict a growth of about 2.2 micrometers. Figure 7 shows that, as soldered, the intermetallic thickness is about 2 microns, after 120 hours of aging, it is about 4 micrometers. The difference of 2 micrometers is close to the prediction of 2.2 micrometers.

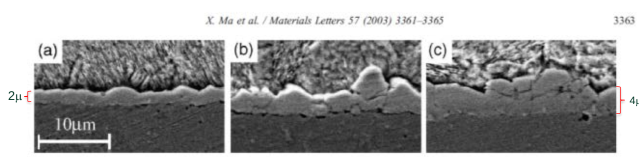

Figure 7. Intermetallic growth in SAC208 (with 0.6 Sb) aged at 125°C: (a) as soldered, (b) 48 hours, (c) 120 hours

COMMON BELIEFS ABOUT INTERMETALLICS

Having been in the electronics assembly industry for more years than I would like to admit, I feel confident sharing what I believe are the common "beliefs" about intermetallics in electronic soldering. These beliefs are:

1. Intermetallics are needed to form the low temperature bond between solder and copper. This asset is good and, in a sense, vital.
2. Unfortunately intermetallics are brittle. This property is bad.
3. Thin intermetallics are OK, but thick intermetallics are bad, as they can negatively impact reliability.
4. Hence, high processing times and temperatures and excessive rework can cause thick intermetallics and should be avoided.

In their well titled paper, *Are Intermetallics Really Brittle*, [vii] Lee etal. performed experiments to measure the physical properties of intermetallics. They also carefully studied fracture micrographs of failed BGA solder joints. Their conclusion, quoted in total below, is striking:

> "We collected and reviewed the properties of Cu_6Sn_5, Cu_3Sn, Ni_3Sn_4, $AuSn_4$, Cu and Sn3.5Ag to first understand whether IMCs are brittle as many believe. Our conclusion seems to indicate otherwise. There is no sufficient scientific data to support the statement of "IMCs are brittle." Fracture along interfaces such as solder/IMC, IMC_1/IMC_2, and IMC/Cu is not related to whether the IMC is brittle or not. Rather, this interfacial fracture is caused by insufficient bond strength along the boundary. To blame brittle fracture in flip-chip solder joints to IMCs being brittle probably needs reconsideration and further assessment."

So they concluded that the failures may not be caused by the intermetallics being brittle, since they argue that few of the failures they studied were in the intermetallic itself. They summarized related materials properties in Table 1 below.

Table 1. The properties of some materials related to soldering. I used Lee's [vii] data and added the fracture toughness for copper in red.

Properties	Copper	96.5Sn3.5Ag	Cu_6Sn_5	Cu_3Sn	Ni_3Sn_4	$AuSn_4$
Melting Point (°C)	1,083	221	415	676	796	252
Density (g/cc)	8.94	7.4	8.28	8.90	8.65	
Thermal Conductivity (watt/cm-K)	3.862	0.78	0.341	0.704	0.196	
Electrical Conductivity (/Ωcm)	$5.88x10^5$	$0.812x10^5$	$0.57x10^5$	$1.12x10^5$	$0.35x10^5$	
Thermal Expansion Coeff. (/°C)	$16.42x10^{-6}$	$22.2x10^{-6}$	$16.3x10^{-6}$	$19.0x10^{-6}$	$13.7x10^{-6}$	$19.3x10^{-6}$
Yield Strength (psi)	10,000	3,600				
Ultimate Tensile Strength (psi)	32,000	5,000 – 7,000				
Fracture Toughness ($MPa/m^{1/2}$)	40-100		2.80	5.72	4.22	2.50
Young's modulus (GPa)	129.8 [32]	52.73	85.56	108.3	133.3	71
Poisson's ratio	0.339	0.36	0.309	0.299	0.330	0.31
*Hardness** (Vickers)*	37 (Brinell)	14.8 (Brinell)	378	343	365	59.2

However, others, such as Pu etal[viii] have found that mechanical failure rates in solder joints increase with aging (hence thicker intermetallics). Pu's work showed a reduction in thermal cycle life of about 50% as intermetallic thickness increases from 1 to 2 micrometers in tin-lead solders. Liu etal[ix] found that thermal cycle fatigue results were not significantly affected by aging at 150°C from 0 to 250 hours for eutectic tin-lead, SAC105, SAC 305, and a low silver SAC alloy with manganese doping. The last alloy (called SACm) actually improved with aging.[x] However, in most cases the drop shock performance, in the JADEC Drop test, was significantly reduced by aging.

Note from Table 1 that the fracture toughness of the different intermetallics is in the 2.5 to 6 ($MPA/m^{1/2}$) range significantly better than window glasses 0.75, but not close to that of copper at about 70. I think Lee's data[vii] supports the notion that the intermetallics in question are not the source of all mechanical failures and may not strictly be brittle, but they have a much lower fracture toughness than copper. The fracture toughness for intermetallics in Table 1 is more in line with that for ceramic materials,[xi] which most people would consider brittle.

Considering all of the data, it appears to be a cautious approach to still support the industry belief that thick intermetallics are less reliable.

INTERMETALLICS AND REWORK

We see in Figure 7 that the as processed intermetallic thickness is about 2 micrometers. This growth occurred in seconds during the reflow process. So and Chan[xii] showed that intermetallic growth rate was about 1 micron in 120 seconds of additional reflow time with eutectic tin-lead solder.

Clearly multiple reworks at high temperatures could result in very thick intermetallics and should be avoided.

OTHER INTERMETALLICS

Nickel forms a Ni_3Sn_4 intermetallic with copper. Tomlinson and Rhodes[xiii] showed that the growth of nickel-tin intermetallic is considerably slower than that of copper-tin intermetallic. This property makes nickel an ideal interface material between copper and tin (see Figure 8) to minimize tin whisker growth as it has been shown that the rapid diffusion of copper into tin creates compressive stresses that enhance tin whisker growth.

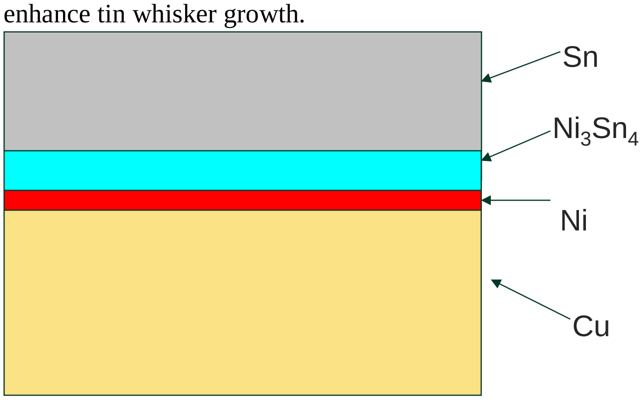

Figure 8. Using nickel as an interface material between copper and tin will minimize the compressive stress that can cause rapid tin whisker growth.

Gold also forms an intermetallic with tin, $AuSn_4$. Because there are four tin atoms for every gold atom, just a small amount of gold can create a considerable amount of intermetallic, although the high density of gold mitigates this concern somewhat. Industry "rules of thumb" suggest that the amount of gold in a solder joint must be less than 4% (some suggest 2% to 3% to be conservative) to avoid producing enough gold-tin intermetallic to cause gold embrittlement. As seen in Table 1, gold-tin intermetallic has a low fracture toughness. Gold might typically be found in ENIG (electroless nickel gold) PWB pad surface finish as seen in Figure 9.

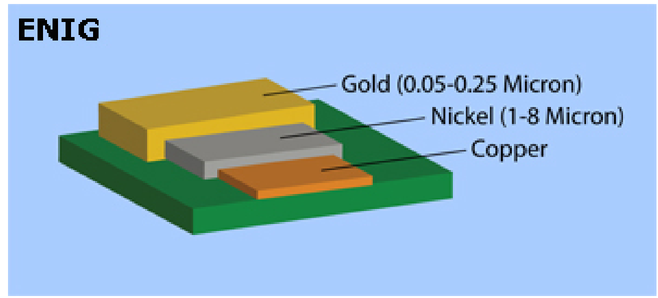

Figure 9. A very schematic depiction of ENIG.

I developed an Excel® based *Gold Embrittlement Calculator*[xiv] to calculate the amount of $AuSn_4$ in a solder joint. As an example, consider an ENIG finished PWB pad that has a gold thickness of 0.25 micrometers. Assume that the pad width is 8 mils, the stencil is 4 mils thick, the solder paste deposit width is 6 mils and the volume fraction of the solder paste is 50% solids. Also assume that SAC305 solder is being used. See Figure 10 from the *Gold Embrittlement Calculator* to observe that the amount of gold in the solder joint is about 2% by weight.

Gold Embrittlement Calculator	
Gold thickness (microns)	0.25
Solder Paste Thickness (mils)	4
Solder Volume Fraction	0.5
Deposit Width (mils)	6
Pad Width (mils)	8
Density gold	19.3
Density tin	7.3
% tin in solder	0.965
Weight of gold	9.8044E-06
Weight of tin	5.4538E-04
Weight fraction of gold	1.7977E-02

Figure 10. Output from the *Gold Embrittlement Calculator* is in the grey cells. Note that the percent gold in this case is a little less than 2%.

CONCLUSIONS

Intermetallics are a miracle of soldering, enabling the bonding of copper to copper at less than 250°C in the presence of polymeric insulators. Without this feature of copper-tin intermetallics, the electronics industry as we know it would not exist.

Intermetallics form immediately during the soldering process, typically at a thickness of one to two micrometers. The intermetallics increase in thickness very slowly over time at temperatures below 100°C. However, intermetallic thickness increases vary rapidly at temperatures above the melting point of solder. Therefore, multiple solder reworks can dramatically increase intermetallic thickness. Most studies show that increasing intermetallic thickness reduces thermal cycle life, but dramatically reduces drop shock life. Considering this information, it is best to minimize the number of reworks and the times of rework soldering.

[i] https://en.wikipedia.org/wiki/%C3%96tzi.

[ii] Roubaud etal, *Impact of IM Growth on the Mech. Strength of Pb-Free Assemblies*, APEX 2001.

[iii] http://www.jfe-tec.co.jp/en/electronic-omponent/case/img/case_solder_02.png.

[iv] Siewert, T. A. etal, *Formation and Growth of Intermetallics at the Interface between Lead-Free Solders and Copper Substrates*, APEX 1994.

[v] https://en.wikipedia.org/wiki/Arrhenius_equation.

[vi] X. Ma etal, *Materials Letters*, 57 (2003) 3361-3365.

[vii] Lee, C. C. etal., *Are Intermetallics Really Brittle,"* IEEE Electronic Components and Technology Conference

[viii] Tu, P. L. etal, *Effect of IMC on Thermal Fatigue of SMT Solder Joints*, IEEE transactions on Components, Packaging and Manf Tech, Part B, Vol 20, No1, Feb 1997.

[ix] Liu, Weiping, etal, *Achieving High Reliability Low Cost Lead-Free SAC Solder Joints via Mn and Ce Doping*, IEEE ECTC, Sn Diego, May 2009

[x] SACm

[xi] https://en.wikipedia.org/wiki/Fracture_toughness

[xii] So, Alex, Chan, Yo, IEE Transactions on Components, Packaging and manufacturing Technology Part B Vol 19, No. 3 August 1996.

[xiii] Tomlinson, W.J., and Rhodes, H. G., *Kinetics of Intermetallic Compound Growth between Nickel, Electroless Ni-P, Electroless Ni-B and Tin at 453 to 493 K*, Journal of Materials Science 22 (1987) 1769-1772.

[xiv] Those interested in a copy of the *Gold Embrittlement Calculator*, send an email to rlasky@indium.com.