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AN INVESTIGATION OF COPPER DISSOLUTION AND THE FORMATION OF INTERMETALLIC COMPOUNDS IN MOLTEN TIN AND Tin-Silver SOLDERS

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ABSTRACT

This paper presents an experimental study of copper dissolution in molten tin and tin-silver (Sn-Ag) solders and the formation and presence of the Cu-Sn intermetallic compound at solder/copper interfaces. During the experiments, copper (99.9% pure) samples, coated with a RMA flux, were dipped vertically in a molten solder for different time periods ranging from 5 seconds to 10 minutes. The molten solder was maintained at temperatures of 232°C, 250°C and 300°C for pure tin and 221°C, 250°C, and 300°C for Sn-3.5%Ag respectively. The samples were then cut, cleaned and cold mounted in epoxy at ambient temperature. Mechanical grinding, finish polishing, etching, and optical metallographic procedures were utilized for examining the microstructures of the polished and etched samples. The average thickness of the intermetallic compound and the amount of copper dissolved was determined. Experimental results indicate the temperature of molten solder to control the rate of dissolution of copper and the formation and presence of intermetallic compounds at the interfaces. At a given temperature of the solder temperature, the rate of dissolution of copper in the solder revealed a rising trend with an increase in dwell time of copper in the solder. For short contact time periods, the dissolution rate is low and the thickness of the intermetallic compound is small. With an

increase in dwell time, the dissolution rate of copper rapidly increases and eventually reaches a plateau. Initiation of dissolution of copper causes a layer of the Sn-Cu intermetallic compound to form around the copper substrate. This in turn prevents direct contact of the copper substrate with the molten solder. The rate of formation of the layer of intermetallic compound reveals a similar trend. Based on experimental results, the kinetic parameters involved in governing the growth of the intermetallic were determined for the two solders. The parameters can be used to estimate the kinetics of copper dissolution and intermetallic compound formation during soldering.

Keywords: Copper dissolution, intermetallic compound, tin, Sn-Ag solder, dipping, reflow

INTRODUCTION

Environmental and health concerns related to the traditional tin-lead solders have provided the much desired impetus for intensive research efforts at developing alternate lead-free solders [6]. Almost all of the potential candidate materials, to include the promising Sn-Ag alloy of eutectic composition, are high tin-containing alloys [6]. Conventional tin-lead solders are prone/susceptible to inferior fatigue

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properties during thermal excursions and/or cycling. A harder alloy with high melting point and enhanced mechanical properties is needed to obtain durable solder joints [4]. The Sn - (3-3.9)% Ag alloy offers improved mechanical properties and good interfacial bonding [9]. During the soldering process, copper dissolves in the molten solder and reacts with tin, to form a layer of the intermetallic compound (IMC) Cu_6Sn_5 , at the solder/copper interfaces. Although formation and presence of the IMC layer is desirable for good wetting and bonding, an excessively thick layer is detrimental due to its intrinsic brittleness that makes it susceptible and/or prone to mechanical failures even at low loads [12]. Also, an excessively thick IMC layer results in a joint having non-uniform physical and electrical properties [9]. In addition, reaction between the high tin containing solder-copper is intense during soldering, which favors quick depletion of copper. Rapid depletion of copper is conducive for dewetting and failure of the joint. Dissolution of copper in lead free solders is observed to be much higher than in lead-containing solders [8]. As the thickness of copper is limited and the rework of a solder joint requires a layer of unreacted copper, the loss of copper during soldering processes must be kept under control [6]. Therefore, the thickness of the IMC layer and the reduction of copper are of particular importance to the integrity of solder joints and the overall reliability of electronic devices [2].

The copper dissolution rate and resultant growth of IMC layer in soldering reaction has been a critical issue in the electronic packaging industry. The growth rate of the IMC layer is determined both by temperature of the solder and dwelling time. In the present study, we have analyzed the average thickness of Cu-Sn inter-metallic compound between pure tin, Sn-3.5%Ag alloy and copper substrate as a function of dwell time and temperature. While the IMC formation between pure tin and copper is of academic importance, the analysis of interface compound between the Sn-Ag alloy solder and copper is of practical significance.

EXPERIMENTAL SET-UP AND PROCEDURES

Around 400 grams of pure Sn and Sn-3.5 wt %Ag were taken and melted separately in a stainless steel crucible. The molten solders were then transferred to a glass container for the two different experiments. Copper samples of size 10 mm × 20 mm × 0.4 mm were cut from a 99.9 % pure copper sheet. The sample substrates were mechanically ground and then finish polished to remove any oxide on the surface and to enhance the wettability. The samples then were rinsed in water and alcohol.

Molten solder was put in an enclosed furnace maintained at the desired experiment temperature. A fine gauge chromel alumel thermocouple was immersed in the middle of the solder bath. The temperature of the bath was maintained in the range of $\pm 2^\circ C$ of the experiment temperature. A thin coating of mildly activated rosin (RMA) was applied to the polished samples prior to dipping the samples vertically in a solder bath. The samples were taken out of the solder vertically at different time intervals ranging from 5 seconds to 10 minutes. The molten solder was maintained at temperatures of: (a) 221°C, 250 °C,

and 300 °C for Sn-3.5 wt %Ag solder, and (b) 232 °C, 250 °C and 300 °C for pure tin.

The samples were cut along the length and perpendicular to the solder copper interface using a diamond-cutting wheel. All samples were cleaned with methanol to remove any dirt and/or grease prior to cold mounting in epoxy at room temperature. The mounted samples were then wet-ground using 320, 600, 800 and 1200 grit SiC impregnated emery paper. After grinding, the samples were fine polished using 5 micron, 1 micron and 0.05 micron alumina based lubricant (aluminum oxide suspended in distilled water). The polished samples were then etched for around 1 to 2 seconds using an etchant (a solution mixture of 5 ml HNO_3 , 2 ml HCl and 93 ml Methanol).

The polished and etched samples were examined in a light optical microscope to analyze the formation, presence and growth of the IMC. The images at the solder copper interface were captured with a digital camera attached to the microscope and stored on a computer. Several images were taken at various sections (top, middle and bottom) along the length of the samples. To calculate the average thickness, the area of IMC, in each micrograph, was manually traced out using a high accuracy digital planimeter (Figure 1). Measurements were repeated three times at each location. Four or five locations were measured for each micrograph.

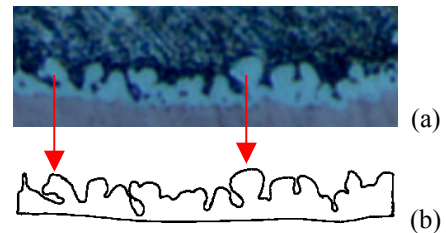


Figure 1. Sample of the optical micrograph showing the IMC layer (a) and its trace (b) used for the measurement of average thickness by a digital planimeter.

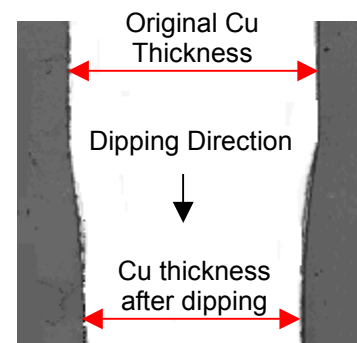


Figure 2. Thickness reduction in the copper substrate after dipped in molten solder.

To calculate the total copper dissolution in the solder, it was assumed that a reduction in the thickness of the copper

substrate is a good measure and directly proportional to total copper dissolution. The reduced thickness of the copper substrate (Figure 2) was measured at three different locations of each sample, namely: top, middle and bottom. Their average was subtracted from the original thickness (Figure 2) of the sample to get the reduction in total thickness. It is noted that in this experiment, the solder tends to attack the substrate from both sides. Consequently, the measured value of decrease in thickness is twice the value in an actual soldering process, and therefore, only half of the measured value is plotted.

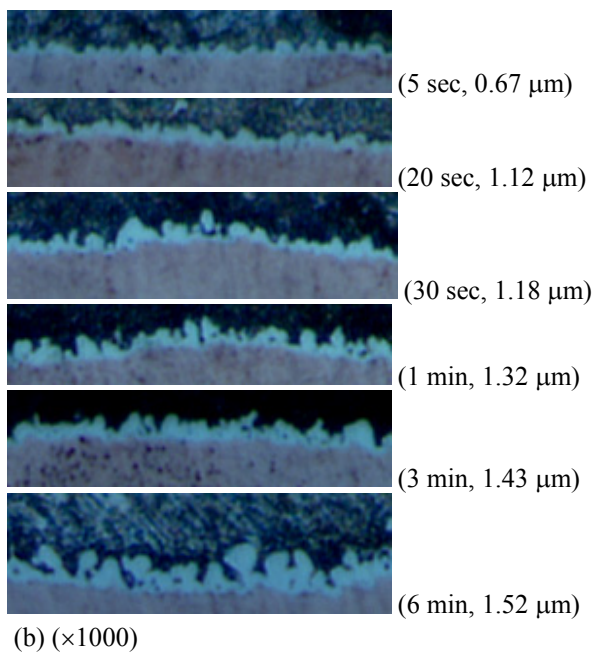
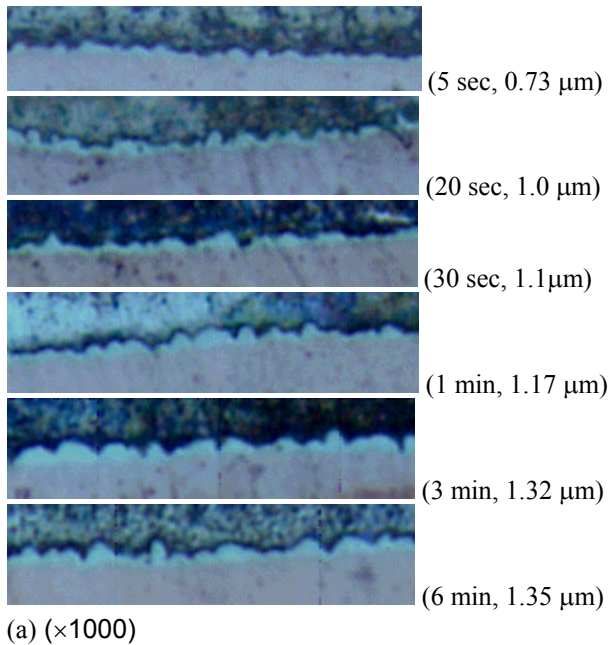


Figure - 3 Optical micrographs showing the intermetallic layer growth with increasing dipping time at 250 °C for (a) pure Sn and (b) Sn-3.5%Ag. Dipping time and average thickness for these micrographs are given by the image as (time, thickness).

RESULTS AND DISCUSSIONS

Growth of Intermetallic Compound Layer

First we examine the growth of intermetallic compound layer at the solder/copper interface. Figure 3 shows typical optical photographs of the IMC layer. In these photographs, the bottom part is the copper substrate and the top part is the solder. The middle light color region is the IMC layer, Cu_6Sn_5 . As is observed, the IMC layer does not grow as a regular layered structure. Rather, the Cu_6Sn_5 phase grows as scallop like grains within the molten solder [4]. Figures 3a and 3b shows the growth of IMC for pure Sn and Sn-3.5%Ag solders on Cu with the molten solder at 250 °C. The corresponding dwell time and the resultant average IMC layer thickness are also given for each photograph. At a given temperature, the thickness of the IMC layer is a strong function of dwell time. The longer the dwell time, the thicker the IMC layer.

The solder material has an important influence on both thickness of the IMC layer and interface morphology. Examining Figure 3 reveals the Sn-Ag alloy can result in a thicker IMC layer, except for a short dwell time (5 seconds). This observation indicates that adding silver can favor IMC growth. Overall, the IMC interface morphology is fairly smooth for pure tin, with IMC being well connected. However, for the Sn-3.5%Ag solder, the interface becomes significantly irregular and rough, particularly for the cases involving a lengthy dwell time.

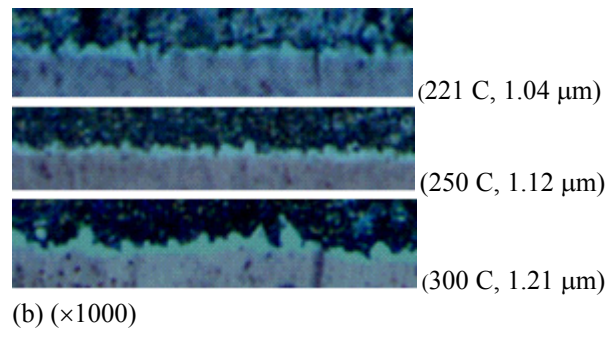
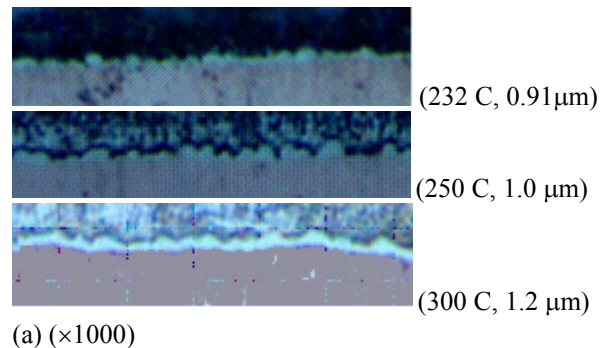
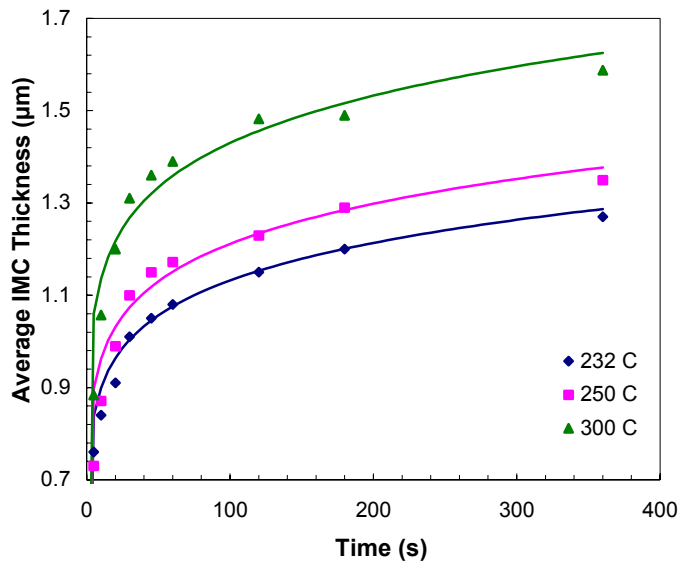
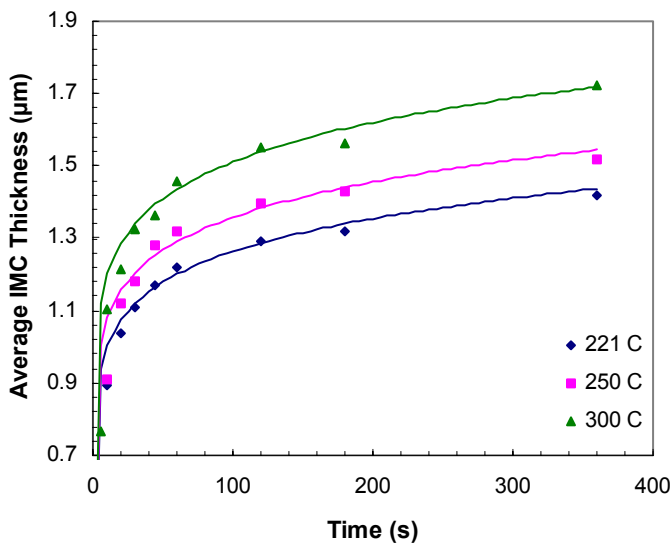


Figure 4. Optical micrographs showing the intermetallic layer growth with increasing temperature for dipping time of 20 seconds for (a) pure Sn and (b) Sn-3.5%Ag. Temperature and average thickness for these micrographs are given by the image as (Temperature, thickness).

Another important parameter to control growth of the IMC layer is temperature of the molten solder. In Figure 4 is shown the end IMC layer structure and thickness for both pure Sn and Sn-3.5%Ag solders at different temperatures and for the same dwell time. It is evident from the figure that a higher solder temperature results in a higher thickness of the IMC, as expected. For the dwell time chosen for Figure 4, i.e., 20 seconds, the two materials reveal an identical IMC layer thickness. Also, the IMC interface morphology for the Sn-3.5%Ag is more irregular than that for pure Sn.



(a)



(b)

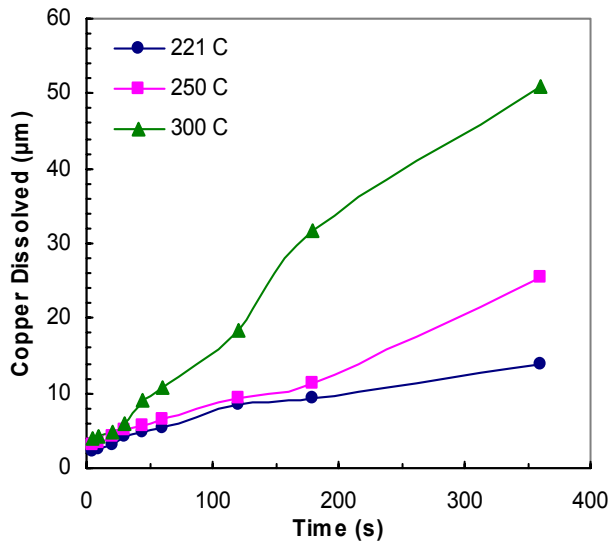
Figure 5. Average IMC thickness as a function of dipping time at different temperatures for (a) pure tin and (b) Sn-3.5%Ag.

The evolution of thickness of the IMC layer as a function of the dipping time, at different temperatures, is shown in Figure 5. It is evident from the curves that IMC growth is a strong function of dipping time and temperature of the solder. The IMC layer thickness increases with dwell time and solder temperature. The IMC growth rate at all temperatures is high during the initial stage and then gradually slows down during the terminal stages. The observed initial high growth rate is attributed to the diffusion of tin along grain boundaries of the fine IMC grains formed at the beginning of IMC growth. As the IMC grains thicken and concurrently coarsened, diffusion of tin to the copper substrate becomes difficult, resulting in an actual decrease in IMC growth rate.

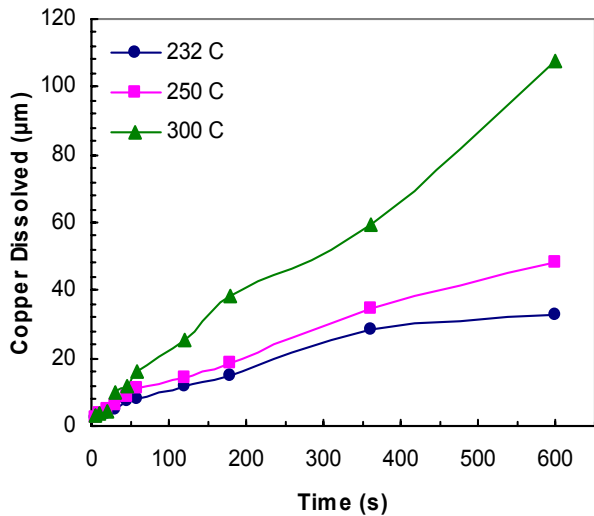
The average intermetallic thickness recorded in the present dipping experiments is smaller than that obtained by normal reflow processes [1,2]. In a reflow process, the amount of solder is limited; and it takes a finite time period for the solder to melt and attain a desired temperature. This has an influence on IMC growth. Cooling rate of the samples after soldering also affects final thickness of the IMC. This study has convincingly shown that slower the cooling rate of the solder joint, the higher is the IMC scallop growth. During normal reflow process, the IMC layer grows significantly due to precipitation during cooling of the joint. In this research study the samples were quenched in cold water immediately after removal from the solder bath, the growth due to precipitation is constrained, resulting in a lesser average thickness of the IMC. In addition, in the present set of experiments, the copper substrates were held in the solder bath placed in an enclosed furnace and the temperature of the solder varied within a range of $\pm 2^\circ\text{C}$, consequently, low current convection can exist in the bath that is conducive for the growth of the IMC.

Dissolution of Copper

Figure 6 shows the dissolution rate of copper in pure tin and Sn-3.5wt%Ag as a function of dwelling time at different solder temperatures for pure Sn (a) and Sn-3.5%Ag solder (b). As is observed, for a given temperature of the molten solder, the dissolution rate of copper in solder shows a rising trend with an increase in dwell time of copper in the molten solder. For a short period of time, at the beginning, the dissolution rate is low and thickness of the resulting intermetallic compound is thin (See Figure 5). As the dwell time increases, the dissolution rate of copper increases. A further increase in dwell time can essentially slow down the dissolution rate. However, if the temperature is high the dissolution rate can pick up. The existence of a non-linear variation in dissolution rate with respect to dwell time suggests the intricate physics governing the dissolution of copper at different stages of the process. At the beginning when copper is in contact with the molten solder, the copper starts dissolving in the molten solder with the concurrent formation of a layer of Sn-Cu intermetallic compound on the copper surface. The latter suppresses further direct contact of the copper substrate with the molten solder. When the solder around copper is saturated with copper, further dissolution of copper is prevented. The dissolution of copper is due entirely to growth of the intermetallic.



(a)



(b)

Figure 6. Reduction in copper thickness as a function of dipping time at various temperatures for (a) pure tin and (b) Sn-3.5%Ag.

It is also observed that the solder around the reinforcing copper gets saturated easily at the low temperatures. This is because at the higher temperatures the intermetallic compound is transported away from the copper substrate than at the low temperatures.

Experimental results also revealed the dissolution rate of copper are more in pure tin than in Sn-Ag at all temperatures (Figure 6). This is because pure tin reacts with copper more readily than Sn-Ag. It is also evident from the present study that the diffusion coefficient (D) for tin is higher than that for Sn-Ag.

Kinetics of Growth of Intermetallic Phase

The kinetics of copper dissolution and growth of IMC can be quantified based on thickness measurements. A simple power law for growth, the IMC thickness can be related to dwell time as follows [1,2],

$$x(T, t) = Dt^n \quad (1)$$

where x is the thickness of the IMC layer, t is the dwelling time, T is the temperature of molten solder, D is the diffusion coefficient, and n is a constant. The diffusion coefficient D is related to temperature through the Arrhenius equation:

$$D = D_0 \exp(-Q/RT) \quad (2)$$

where D_0 is a pre-exponential temperature-independent constant, Q is the activation energy of the solute (copper in this case), and R is the gas constant.

The Equation (1) can be used to fit the IMC thickness data as shown by the solid lines in Figure 3 at each temperature for D and n as a function of T . Then an Arrhenius plot of D versus temperature can be established as shown in Figure 7. The values of D_0 and Q for each solder material can be estimated from Figure 7. The values of D_0 , Q and n for the two solders together with data available in the open literature [1,2] are summarized in Table 1.

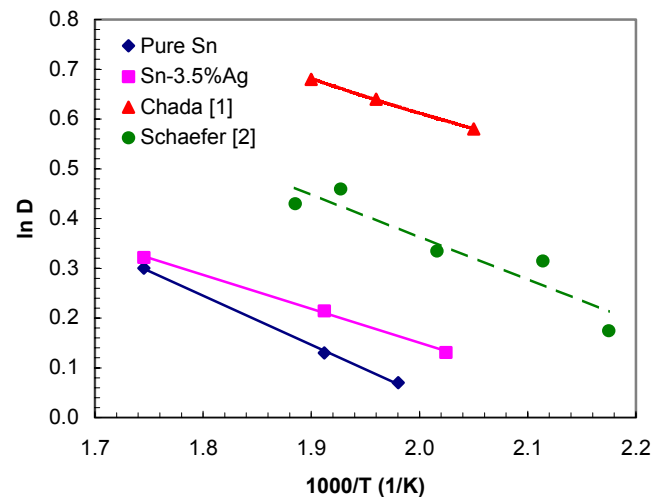


Figure 7. Arrhenius plot of D values obtained from the curve fits in Figure 3.

Although the diffusivity data D shown in Figure 7 seems to be lower than those available in the literature [1,2], the values of the activation energy, Q_0 and pre-exponential constant, D_0 , are comparable with those obtained by Chada et al. [1] for Sn-Ag, and Shaffer et al. [2] for Sn-Pb, using reflow experiments of small solder samples. It is noted that the parameter, n , is important in determining the initial rate of IMC growth. A low value of n as determined in the present study explains the growth rate of IMC to be very high during the initial stages at all temperatures, since the molten solder is held at a constant temperature prior to dipping. This is very different from the reflow process wherein the solder paste has to be initially heated to the melt temperature and subsequently superheated.

Table 1. Estimated values of D_o , Q and n

Solder	Q (kJ/mol)	D_o (m^2/s)	n
Pure Tin*	8.26	7.7	0.10
Sn-3.5wt. % Ag*	6.0	5.1	0.10
Sn-3.5wt%Ag [1]	7.6	11.3	0.33
Sn-Pb [2]	7.04	7.75	0.25

* Present Study

CONCLUSIONS

1. This paper presents an experimental study of copper dissolution and intermetallic compound growth of lead-free solders in contact with a copper substrate using a dipping technique.
2. Pure Sn and eutectic Sn-Ag solder are employed in the study.
3. It is found that during a dipping process, the growth of the IMC is fast during the initial stages and slows down after a short period of time.
4. Most of the intermetallic growth takes place during the first 2 minutes of dipping time in case of pure tin and 3 to 4 minutes for Sn-3.5%Ag.
5. The growth kinetics parameters were determined for the two solders. The activation energy and constant, n were determined to be $Q = 8.26$ kJ/mol and $n = 0.10$ for pure Sn and $Q = 6.0$ kJ/mol and $n = 0.10$ for Sn-3.5%Ag. The activation energies determined in these experiments are well within the range of apparent activation energy for diffusion in liquid metals. The lower activation energy for Sn-3.5%Ag is due to the lower melting point of Sn-Ag when compared to pure Sn. The experimental data fit well with the calculated parameters.
6. It was also observed that copper dissolved more readily into pure Sn than Sn-Ag, implying that the addition of silver aids in retarding the dissolution of copper. The dissolution rate for both solders increases with an increase in solder temperature.

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REFERENCES

1. S. Chada, W. Laub, R. A. Fournelle, and D. Shangguan, An Improved Numerical Method for Predicting Intermetallic Layer Thickness Developed during the Formation of Solder Joints on Cu Substrates, *J. Electron. Mater.* Vol. 28, pp. 1194-1202, 1999.
2. M. Shaefer, W. Laub, J. M. Sabee, and R. A. Fournelle, A Numerical for Predicting Intermetallic Layer Thickness

- Developed During the Formation of Solder Joints, *J. Electron. Mater.* Vol. 25, pp. 992-2003, 1996.
3. M. Shaefer, R. A. Fournelle, and J. J. Liang, *J. Electron. Mater.* Vol. 27, pp. 1167-, 1998.
 4. O. Fouassier, J. Chazeals, and J. Silvan, Conception of a consumables copper reaction zone for a NiTi/SnAgCu composite material, *Composites: Part A*, Vol., 33 pp. 1391-1395, 2002.
 5. D. Ma, W. D. Wang, and S. K. Lahiri, Scallop formation and dissolution of Cu-Sn intermetallic compound during solder reflow, *J. Appl. Phys.*, Vol. 91, pp. 3312 – 3317, 2002.
 6. H. K. Kim and K. N. Tu, Rate of consumption of Cu in soldering accompanied by ripening, *Appl. Phys. Lett.* Vol. 67, pp. 2002 – 2004, 1995.
 7. Y. G. Lee, and J. G. Duh, Characterizing the formation and growth of intermetallic compound in the solder joint, *J. Mater. Sc.* Vol. 33, pp. 5569 – 5572, 1998.
 8. T. M. Korhonen, P. Su, S. J. Hong et. al., Reaction of Lead-Free Solders with CuNi Metallizations, *J. Electron. Mater.*, Vol. 29, pp. 1194 – 1199, (2000).
 9. K. Sukanuma, Advances in lead-free electronics soldering, *Current Opinion in Solid State and Materials Science* Vol. 5, pp. 55 – 64, 2001.
 10. S. W. Chen and Y. W. Yen, Interfacial Reaction in Ag-Sn/Cu Couples, *J. Electron. Mater.* Vol. 28, pp. 1203 – 1208, 1999.
 11. Y. C. Chan, C. K. Alex, and J. K. L. Lai, Growth kinetic studies of Cu-Sn intermetallic compound and its effect on shear strength of LCCC SMT solder joints, *Mat. Sc. Eng. B*, Vol, B55, pp. 5-13, 1998.
 12. K. H. Prakash and T. Sritharan, Interface Reaction Between Copper and Molten Tin-Lead Solders, *Acta Mater.*, Vol. 49, pp. 2481 – 2489, 2001.
 13. Y. G. Lee and J. G. Duh, Interfacial morphology and concentration profile in the unleaded solder/Cu joint assembly, *J. Mater. Sc.* Vol. 10, pp. 33 – 43, 1999.