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Cu_6Sn_5 and Cu_3Sn Intermetallics Study in the Sn-40Pb/Cu System during Long-term Aging

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ABSTRACT

Replacing Sn-Pb solder with lead-free solder is a great challenge in the electronics industry. The presented lead-free solder is Sn based and forms two intermetallic species upon reaction with the Cu substrate, namely Cu_6Sn_5 *and* Cu_3Sn*. The growth of* Cu_6Sn_5 *and* Cu_3Sn *intermetallics have been investigated with respect to Sn-40Pb/Cu solder joints. The joints were aged under long-term thermal exposure using single shear lap joints and the intermetallics were observed using scanning electron microscopy. As-soldered solder joints exhibit a single* Cu_6Sn_5 *phase, however after aging a* Cu_3Sn *layer below the* Cu_6Sn_5 *is observed to manifest. The* Cu_6Sn_5 *layer develops with a scalloped morphology, whereas the* Cu_3Sn *layer always develops an undulating planar shape in phase with the* Cu_6Sn_5*. The* Cu_6Sn_5 *layer begins to transform from a scalloped- to a planar-shape as aging progresses in order to minimize the interfacial energy. The intermetallic layers exhibit a linear dependence on the square root of aging time, which corresponds to diffusion-controlled growth. The activation energy for the growth of the* Cu_6Sn_5 *intermetallic layer has been determined to be 56.16 kJ/mol.*

Keywords: *Intermetallic, Lead-free Solder, Cu-Sn, Growth Kinetics, Solder*

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Introduction

When molten solder wets a base metal (substrate) metallurgical bonds form as the solder solidifies [1, 2]. This metallurgical bonding occurs at the boundary between the solder and the substrate, termed the interface. This interface consists of a thin layer(s) of alloy termed the intermetallic compound (IMC). This intermetallic layer(s) is composed of metals from both the solder and the substrate [1]. Manko [3] defines an intermetallic compound to be a distinguishable homogeneous phase with a relatively narrow range of composition in simple stoichiometric proportions (*i.e.* atomic ratios). The intermetallic layer provides the necessary bonding strength and interfacial continuity between the solder and the substrate.

The formation and subsequent growth of the IMC is a major issue in soldering. The formation of intermetallic compounds is desirable for a good solder joint and in soldering this formation is a consequence of good wetting. The implementation of lead-free solders as new soldering materials enhances the importance of these IMCs, because although their formation is desirable in attaining good bonding between the substrate and the solder, there are some drawbacks. The intermetallics are quite brittle and excessive thickness may degrade the interfacial strength and culminate in a mismatch in the physical properties: such as the thermal expansion coefficient and the elastic modulus [4].

Reliability losses in many electronic systems have been identified to be directly related to the failure of solder joints, as opposed to device malfunction, consequently there is greater focus on solder joint reliability [5]. In order to develop reliable lead-free solder joints, it is desirable to understand the kinetics governing the growth of IMCs.

Lead-free solder is tin-based and the interaction between the solder and the Cu substrate produces Cu-Sn IMCs. In the case of liquid tin/copper and many liquid-tin alloy/copper interconnections; Cu_6Sn_5 IMCs form almost immediately upon contact of the liquid solder with the solid copper [6-9]. After solid state aging at high temperature a Cu_3Sn layer forms below the Cu_6Sn_5 phase [10]; a consequence of a lower growth activation energy for Cu_3Sn as opposed to that for Cu_6Sn_5. Flanders *et al.* [11] reported the activation energies for the growth of ε-Cu_3Sn and Cu_6Sn_5 intermetallic phases in a Sn-3.5Ag/Cu system to be 77.21 and 107.10 kJ/mol, respectively. Yoon and Jung [12] stated that solid state isothermal aging in a Sn-5Bi/Cu system using the reflow method yielded IMC growth activation energies of 90.50 and 98.35 kJ/mol for ε-Cu_3Sn

and Cu_6Sn_5, respectively. Vianco *et al.* [13] studied the effect of solid state aging on the intermetallic growth of Sn-3.9Ag-0.6Cu on a Cu substrate and reported that the activation energy for the growth of the ε-Cu_3Sn phase is 50 and 44 kJ/mol for the Cu_6Sn_5 phase, which is lower than those reported in the aforementioned lead-free solders.

This study investigates the microstructural evolution and growth kinetics of Cu_6Sn_5 and Cu_3Sn IMCs using conventional Sn-40Pb solder on a Cu substrate.

Measurements and Apparatus

The Sn-40Pb solder, $ZnCl_2$ flux and Cu substrate considered and implemented in this study are all commercially available. Before soldering, the Cu surface was polished using SiC coated paper in order to remove the inherent copper oxide layer. The single shear lap tensile specimens were constructed by soldering two dog-bone shaped Cu strips together using approximately 0.2 g of Sn-40Pb solder sandwiched between the two copper substrates. The solder contact area was maintained at 4 × 8 mm^2 and a thickness of 0.5 mm, shown in Figure 1.

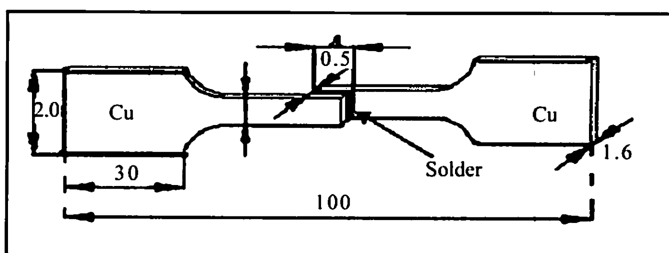

Figure 1: Single Lap Dog-bone Shape (All Dimensions in mm)

After applying $ZnCl_2$ flux to the soldered area of the Cu substrates, the system was placed on a hotplate and heated to a maximum temperature of 240°C as presented in the temperature profile in Figure 2.

After soldering, specimens were left on the hotplate to cool and removed upon attaining 50°C. The samples were then cleaned using dish washing soap to remove any impurities. After allocating some samples for as-soldered IMC reference analysis, the remainder underwent thermal aging. The soldered samples were placed in an oven and heated at 50,

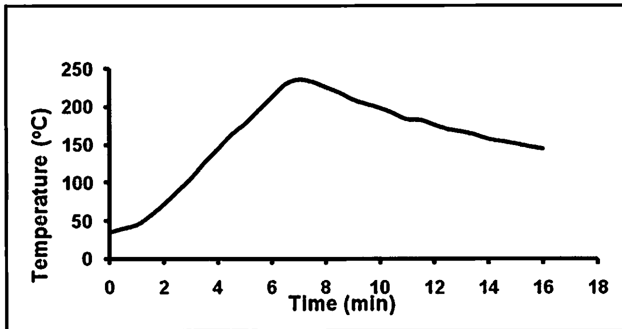

Figure 2: Hotplate Temperature Profile

75, 100, 125 and 150°C with a temperature stability of ± 3°C and aged for 100, 250, 375, 500 and 700 hours.

Cross-sectional samples were taken using a low speed diamond cutter and mounted using epoxy resin. The mounted samples were mirror polished and etched. The Cu/solder/Cu interface was analyzed using a Zeiss-Supra 35VP-24-58 Field Emission Variable Pressure Scanning Electron Microscope (FEVPSEM) operating at 15 kV in backscatter mode. For each sample, 8-10 micrographs were taken and backscatter EDX has been used to identify the elemental composition of the phases. To determine the average thickness of the intermetallic layers, the total area of the layer was calculated using ImageJ and divided by the micrograph length to an accuracy of ± 0.01 mm.

Results and Discussions

Intermetallic Formation

Figures 3-9 show the interface that exists between the Sn-40Pb solder and Cu substrate after 700 hours of aging at different temperatures. The IMC formed between the as-soldered Sn-40Pb solder joint and the Cu substrate is presented in Figure 3. According to Arenas and Acoff [14] the nucleation and growth of IMCs begins when the molten solder at the interface becomes saturated with copper. The interface exhibits a scalloped shape with a 40.6:59.4 (Cu:Sn weight percentage) composition and has been identified to be Cu_6Sn_5 from the Cu-Sn phase diagram.

The Cu-Sn system has been studied extensively by many researchers and the formation of the Cu_6Sn_5 phase has been well documented [7,15-

Figure 3: As-soldered IMC Layer between the Sn-40Pb and Cu Substrate

19]. According to Tu [15] the formation of the Cu_6Sn_5 phase is a consequence of the interstitial diffusion of Cu into Sn at temperatures below 60°C.

The growth of the scalloped Cu_6Sn_5 phase is promoted by exposure to heat over extended time periods. From the SEM image presented in Figure 4 it is evident that after aging at 50°C for 500 hours, the scalloped structures penetrate deep into the solder matrix.

The presence of a ε-Cu_3Sn layer below the Cu_6Sn_5 phase as reported by Arenas and Acoff [14], Tu and Thompson [16], Liu *et al.* [20] and Kim and Tu [21] is evident in Figure 5. Hwang *et al.* [4] used TEM to observe the ε-Cu_3Sn phase in Cu-Sn system soldered at 250°C and reported that Sn-3Ag-6Bi/Cu, Sn-Cu/Cu and Sn-Bi/Cu systems exhibit a ε-Cu_3Sn phase approximately 100 nm thick.

Figure 4: IMC Layer Formed between the Sn-40Pb and Cu Substrate Isothermally Aged at 50°C for 500 Hours

In this study, the formation of a thin layer of ε-Cu_3Sn below Cu_6Sn_5 and closer to the Cu substrate has been identified with respect to EDX compositional analysis; 62:38 (Cu:Sn weight percentage). At higher aging temperatures and longer aging times this ε-Cu_3Sn layer becomes thicker and more distinctive, Figure 6.

No ε-Cu_3Sn phase was observed using FEVPSEM for samples aged at 50°C; however it was observed for those aged at 75°C. Similar results were reported by Tu [15, 22] and Tu and Thompson [16], who discovered using TEM analysis that thin film Cu/Sn diffusion couples annealed below 60°C contained no e-Cu_3Sn phase, whereas those annealed above 60°C did.

The formation of the Cu_6Sn_5 phase at the interface depletes the Sn-rich phase near the Cu substrate and consequently Pb-rich phases begin

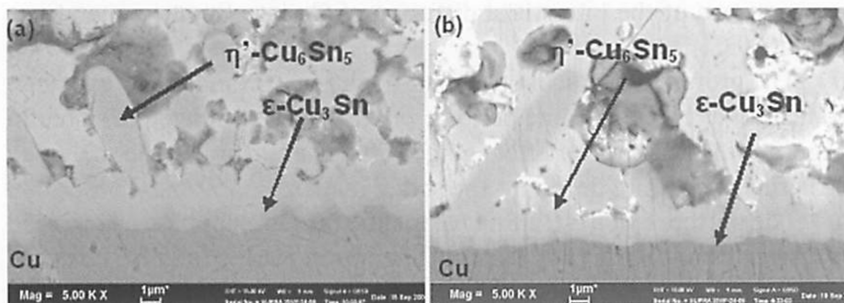

Figure 5: The Formation of the IMC Layer between the Sn-40Pb and Cu Substrate for Samples Isothermally Aged at 75°C for (a) 100 and (b) 700 Hours

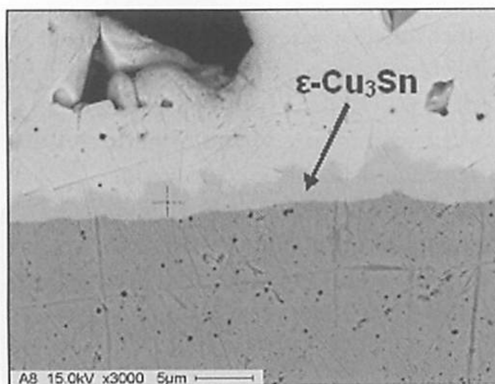

Figure 6: The Manifestation of the ε-Cu_3Sn Below the Cu_6Sn_5 IMC for a Sample Aged at 150°C for 100 Hours

to accumulate at the solder/Cu_6Sn_5 intermetallic layer interface. The formation of this Pb-rich phase near the interface is evident in Figure 7(a) and Figure 7(b) shows the penetration of the scalloped Cu_6Sn_5 phase into the Pb-rich phase.

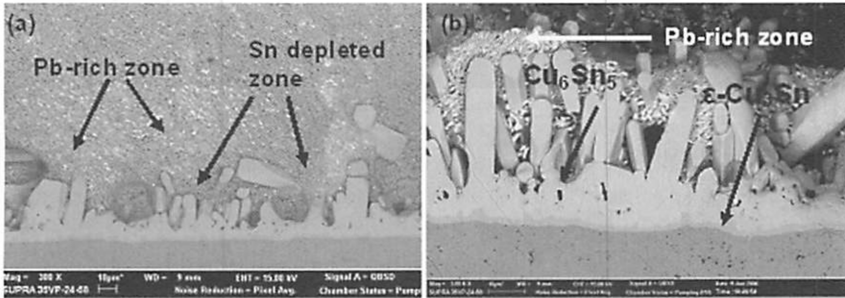

Figure 7: The Reaction between Sn and Cu Creates (a) a Sn Depleted Zone and Results in (b) the Cu_6Sn_5 Intermetallic Penetration into the Pb-rich Zone. Both Images are for Samples Aged at 150°C for 100 Hours

The formation of the Cu_6Sn_5 IMC reduces the Sn concentration near the interface and results in the formation of the Cu-rich ε-Cu_3Sn IMC as explained by Choi *et al.* [23] and Islam *et al.* [24]. They state that the supply of Sn through the Cu_6Sn_5 is more restricted than the supply of Cu from the substrate, hence the Cu_6Sn_5 transforms into the Cu-rich ε-Cu_3Sn phase.

After the formation of the ε-Cu_3Sn layer both the Cu_6Sn_5 and ε-Cu_3Sn IMC layers grow progressively. Figure 8 depicts the evolution of the Cu_6Sn_5 phase changes from a scalloped morphology to a more layered structure and Figure 9 shows the limit of the present experimental work, whereby a flat Cu_6Sn_5 phase is achieved after aging at 150°C for 700 hours. The findings are in good agreement with the works of Tu *et al.* [2], Lee *et al.* [25] and Yu *et al.* [26].

The transformation from a scalloped to a more planar morphology as aging progresses may be attributed to changes in the interfacial energy. According to Tu *et al.* [2] scalloped morphologies have larger interfacial areas than flat interfaces. So the IMC converts to a layered morphology in order to minimize the interfacial energy.

Furthermore, as the aging time increases, neighbouring scallops grow into each other, and the overall thickness of the Cu_6Sn_5 layer increases. Lee *et al.* [25] explained that in solid-state aging, the intermetallic growth at the channels (valleys) between two adjacent scallops is faster than at

Figure 8: Transformation from Scallop to Planar Layer with Aging: (a) 100°C for 250 Hours, (b) 125°C for 100 Hours, (c) 100°C for 500 Hours, (d) 125°C for 375 Hours, (e) 125°C for 700 Hours and (f) 150°C for 375 Hours

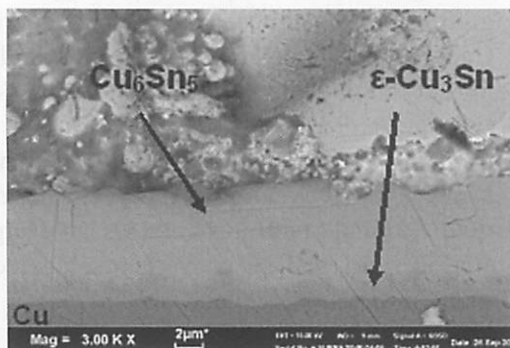

Figure 9: IMC Layer Formed between Sn-40Pb and Cu Substrate Isothermally Aged at 150°C for 700 Hours

the peaks of the scallops. Consequently the Cu_6Sn_5 intermetallic layer is transformed from a scallop-like shape to a layer-type shape. The two Cu-Sn phases described have been observed in other Sn-based lead-free solders on Cu substrates including 100Sn [27], Sn-3.5Ag [28] and Sn-3.9Ag-0.6Cu [13].

Intermetallic Growth

The increase in temperature and time results in growth of the Cu_6Sn_5 and e-Cu_3Sn intermetallics as presented in Tables 1 and 2. At an aging temperature of 50°C Cu_6Sn_5 intermetallic growth is insignificant. The thickness grew from 1.4 mm at room temperature to 2.3 mm after 700 hours. For the same duration, but with aging at 75°C the intermetallic thickness increases to 2.9 mm. At this temperature, after 100 hours of aging, the ε-Cu_3Sn layer has a thickness of 0.44 mm, but the ε-Cu_3Sn phase does not grow significantly, and within the experimental error of around ± 0.15 μm.

For an aging time of 700 hours at 100 and 125°C, the intermetallic thicknesses have increased to 5.0 and 8.0 mm, respectively. However, the ε-Cu_3Sn phase still does not grow significantly at these aging temperatures; only a slight increase from 0.43 mm to 0.57 mm at 125°C.

Aging at 150°C significantly affects the intermetallic thickness. After 250 hours of aging, the scallop structure has become flat and the thickness has increased to 6.1 mm. As the aging time increases, the intermetallic thickness increases further to 10.0 mm and the ε-Cu_3Sn phase thickness increases to 1.83 mm.

Table 1: Cu_6Sn_5 Intermetallic Thickness

Temperature/°C	50 (μm)	75 (μm)	100 (μm)	125 (μm)	150 (μm)
As soldered	1.4±0.1	1.4±0.1	1.4±0.1	1.4±0.1	1.4±0.1
100 hours	2.1±0.2	2.2±0.2	2.5±0.3	2.8±0.3	Nil
250 hours	2.2±0.1	2.4±0.4	3.0±0.2	3.5±0.3	6.1±0.6
375 hours	2.3±0.3	2.5±0.2	3.5±0.1	5.0±0.3	7.0±0.8
500 hours	2.3±0.1	2.6±0.1	4.0±0.2	6.0±0.6	8.0±0.1
700 hours	2.3±0.3	2.9±0.4	5.0±0.5	8.0±0.3	10.0±0.6

Table 2: ε-Cu_3Sn Intermetallic Thickness

Temperature/°C	75 (μm)	100 (μm)	125 (μm)	150 (μm)
As soldered	Nil	Nil	Nil	Nil
100 hours	0.44	Nil	0.43	Nil
250 hours	0.31	Nil	0.56	1.13
375 hours	0.39	0.42	0.67	1.44
500 hours	0.37	0.39	0.65	1.50
700 hours	0.34	0.33	0.57	1.83

According to Choi *et al.* [23], the formation of the Cu_6Sn_5 layer reduces the quantity of Sn available for reaction at the solder/substrate interface. Furthermore, the Cu_6Sn_5 layer may inhibit Sn diffusion towards the solder/substrate interface. This in turns increases the total diffusion distance and thus delays the Sn supply required for IMC growth.

Intermetallic Growth Rate and Activation Energy

If the intermetallic growth process is a volume-diffusion-controlled phenomenon, then the isothermal growth of the intermetallic layer can be described using a square root time law [21]. Generally, the thickness of an IMC layer in diffusion couples can be expressed by a simple parabolic equation, Equation (1);

$$d = (k.t)^n + d_0 \qquad (1)$$

where d is the thickness of the intermetallic layer, d_0 is the initial thickness, k is the growth rate constant (cm^2/s), n is the time exponent (0.5) and t is the reaction time (in s). Equation (1) can be re-written as follows:

$$d - d_0 = k^{\frac{1}{2}}.t^{\frac{1}{2}} \qquad (2)$$

k is strongly related to the diffusion coefficient for the elements comprising the IMC and can be determined by linear regression. Plotting the average measured intermetallic thickness, $d - d_0$, against the square root of the aging time, $t^{\frac{1}{2}}$, yields lines of gradient $k^{\frac{1}{2}}$, Figure 10.

The growth rate constants for all the intermetallic compounds are presented in Table 3, however kinetic analysis of the Cu_3Sn layer cannot be presented in this study due to insufficient data.

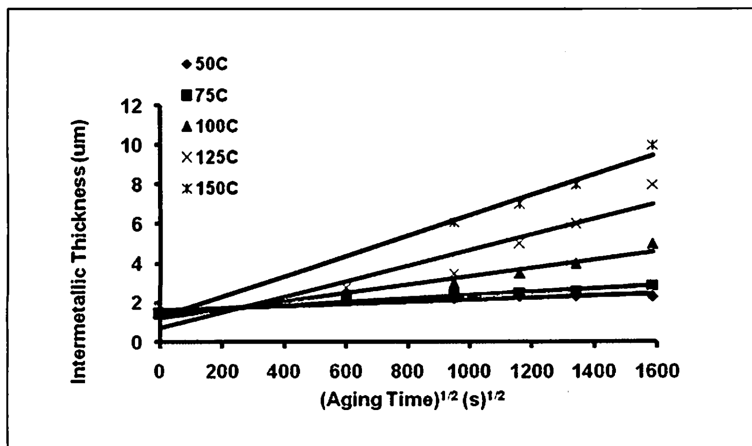

Figure 10: The Relationship between Cu_6Sn_5 Intermetallic Thickness and Aging Time, $t^{\frac{1}{2}}$

Table 3: Growth Rate Constants for Cu_6Sn_5 IMC Growth

Temperature (°C)	$k^{\frac{1}{2}}$ ($cm/s^{\frac{1}{2}}$)	k (cm^2/s)
50	5×10^{-8}	0.25×10^{-14}
75	9×10^{-8}	0.81×10^{-14}
100	10×10^{-8}	4.41×10^{-14}
125	26×10^{-8}	15.2×10^{-14}
150	42×10^{-8}	27.0×10^{-14}

The linearity of the data and the good correlation between the data points and the linear regression fits indicate that IMC layer growth is a diffusion-controlled process and hence the Arrhenius equation can be used to determine the activation energy for intermetallic growth:

$$k = k_0.\exp\left(-\frac{Q}{RT}\right) \qquad (3)$$

which can be rewritten as

$$\ln k = -\frac{Q}{RT} + \ln k_0 \tag{4}$$

where Q is the activation energy for layer growth (J/mol), R is the ideal gas constant (8.314 J/mol.K) and T is the absolute temperature in Kelvin. The activation energy for Cu_6Sn_5 layer growth has been determined to be 56.16 kJ/mol from the gradient of a plot of ln k versus 1/T, Figure 11. This value excludes the intermetallic thickness data for aging at 150°C and 100 hours, because the layers are too irregular to measure the IMC growth rates accurately. Some literature values for the growth of the Cu_6Sn_5 intermetallic are presented in Table 4 for the purpose of comparison.

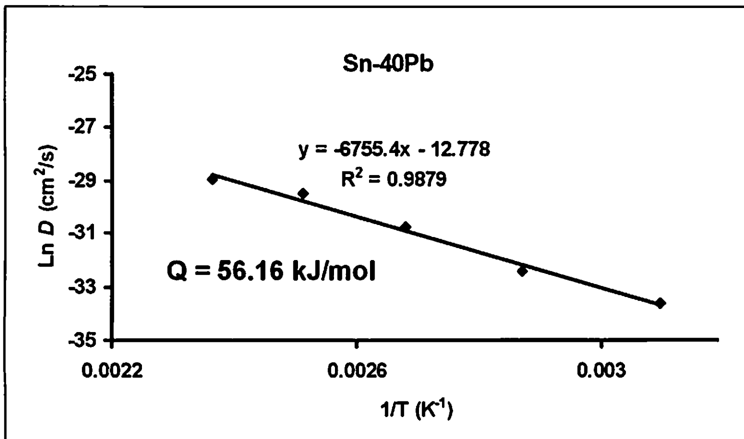

Figure 11: Arrhenius Plot of the Cu_6Sn_5 Intermetallic Layer Growth for the Sn-40Pb/Cu System

The data obtained by Abtew and Selvaduray [29] in which Sn-40Pb solder paste reacted on a single crystal Cu substrate gives a significantly lower activation energy value than that determined in this study. This may be attributed to the form of Cu employed, *i.e.* a single Cu crystal as opposed to a Cu substrate.

Table 4: Activation Energies for Cu_6Sn_5 Intermetallic Growth

Solder/substrate system	Activation energy (kJ/mol)	Temperature range (°C)	Aging time (hours)	Reference
Sn-40Pb solder paste/single crystal Cu	39.64-48.22	90-170	Nil	[29]
Sn-Pb/Cu	45-66	Nil	Nil	[30]
Sn-Pb/Cu	111	50-150	4000	[23]
Sn-37Pb/Cu	77	110-160	1536	[1]
Cu/Sn-40Pb/Cu	42.25	100 and 150	625	[31]
Sn-40Pb/Cu	56.16	50-150	700	This study

Conclusions

The morphology and kinetics of the growth of IMC layers at the Cu-solder interface in Sn-40Pb solder joints during solid state aging has been determined. The IMC layers formed consist of Cu_3Sn, which forms adjacent to the Cu substrate and Cu_6Sn_5, which forms towards the solder. The Cu_6Sn_5 develops with a scalloped morphology, whereas Cu_3Sn grows as an undulating planar layer in phase with the Cu_6Sn_5. The Cu_6Sn_5 layer transforms from a scalloped- to a planar-morphology as aging progresses due to minimization of the interfacial energy. The growth of the IMC is diffusion-controlled and consequently the activation energy for growth of the Cu_6Sn_5 intermetallic layer has been determined to be 56.16 kJ/mol which is in good agreement with the literature values. This finding is of value in that it provides kinetic insight into the formation and progressive growth of IMCs in solder joints, which may impinge on the structural and mechanistic application of Sn-based solders in the electronics industry.

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