Growth kinetic studies of Cu–Sn intermetallic compound and its effect on shear strength of LCCC SMT solder joints

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Received 25 September 1997; received in revised form 30 January 1998

Abstract

Growth kinetics of interfacial Cu–Sn intermetallic (IMC) layer and its effect on the shear strength on practical LCCC surface mount solder joints were studied for isothermal aging at 70, 120, 155 and 170°C. Only normal Cu6Sn5 (η-phase) intermetallic was found in the interfacial IMC layer of as-soldered solder joint, whereas the duplex structure of both η-phase and ε-phase Cu3Sn existed in all annealed joints. The growth kinetics of the overall interfacial IMC layer can simply be described by classical kinetic theory for solid-state diffusional growth with an activation energy of 1.09 eV and interdiffusion coefficient of 1.61 × 10⁻⁴ m² s⁻¹. The relatively higher activation energy, as compared with that found for bi-metallic couple of eutectic Sn–Pb solder on copper, is attributed to the dissolution of Ni from the component metallization into the bulk Sn–Pb solder. In addition, the shear fractures in all the solder joints investigated are shown to be ductile in nature and confined in the bulk solder rather than through the interfacial IMC layer. A linear reduction in shear joint strength was observed with an increase in intermetallic layer thickness up to ~ 5.6 μm. Such a reduction in joint strength is due to a continuous removal of Sn from the bulk solder for the growth of interfacial IMC layer and flattening of the solder/IMC layer during isothermal aging of the solder joint. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Intermetallic compound; Solder joints; Kinetic studies

1. Introduction

One of the critical factors that greatly affects surface mount solder joint reliability is the formation of Cu–Sn intermetallic compound (IMC) [1–9] that evolves at the solder/Cu interface between the molten Sn–Pb solder and the copper pad of a printed circuit board (PCB). Basically, the presence of a thin interfacial Cu–Sn IMC layer is essential for the bondability of the copper pad because the IMC layer promotes good wetting between solder and copper. However, too thick an interfacial IMC may weaken the joint. Due to its brittle nature and lattice mismatch with that of copper and Sn–Pb solder, interfacial Cu–Sn IMC layer is probably a preferential crack initiation site in a surface mount solder joint, especially when subjected to thermal or mechanical fatigue cycling.

Interfacial Cu–Sn IMC layer becomes thicker during the reflow soldering. It also grows in thickness during the operation life of the solder joint (even at room temperature). Previous studies have focused on the formation and growth of Cu–Sn intermetallic compounds in a bimetallic Cu–Sn system [5,10–21]. It is generally reported that an interfacial Cu–Sn IMC layer composed of only η-phase Cu6Sn5 exists in as-solidified solder/Cu bimetallic couple while both the η-phase and the copper-rich ε-phase (Cu3Sn) are found in annealed samples. Our previous work [1] shows that interfacial Cu–Sn intermetallic compounds in leadless ceramic chip carrier (LCCC) surface mount solder joints thicken linearly with increasing soldering time and its formation process is faster for higher soldering temperature. Kay and Mackay [10] studied the growth kinetics of Cu–Sn intermetallic compounds in Sn–Pb solder (with various composition) on various substrates. They report that
the growth of Cu–Sn IMC layer at the interface between eutectic 63Sn–37Pb solder and copper substrate shows a $t^{1/2}$ dependence with aging time ($t$). Tu and Thompson [11] propose that the growth rate of Cu$_6$Sn$_5$ in bimetallic Cu–Sn thin film is linear and the reduction rate of Cu$_6$Sn$_5$ due to the growth of Cu$_3$Sn is parabolic. Nevertheless, almost all of them are performed on bimetallic Cu–Sn couple. Such configuration is different from a practical surface mount solder joint in a number of ways such as the effect of component metallization, small amount of solder involved and the finite dimension of SMT solder joints.

The effect of Cu–Sn intermetallic compounds on joint strength has drawn considerable attention in recent years [6,7,19,20,22–25]. Pratt et al. [22,6] observe that mode I fracture occurs within the interfacial Cu–Sn IMC layers in a Cu/63Sn–37Pb solder joint upon reaching a critical IMC layer thickness of ~5–7 μm. Dirnfeld and Ramon [5] investigated the effect of Cu–Sn IMC on the shear strength of a solder joint by using a plug-and-ring sample. They show that the shear strength of a solder joint increases with increasing interfacial Cu–Sn IMC layer thickness below 1.3 μm, at which the joint strength is maximum. When the thickness is larger than this, the joint strength decreases. However, such investigations done on bimetallic samples of Cu–Sn cannot reflect the real stressing conditions of a practical surface mount solder joint, which is much more complex than a simple tensile condition (as in the mode I fracture toughness studies [20,22]) as well as a plane-strain condition (as for a plug-and-ring sample [24,25]).

Realizing the deficiencies of previous investigations mentioned above, this work has focused on the growth kinetics of Cu–Sn intermetallic compound in practical surface mount solder joints. Its effect on the shear strength of such joints has also been investigated.

2. Experimental procedures

The surface mount solder joints of LCCC resistor were studied in this work. Sample boards containing LCCC resistors of different sizes (0805, 1206, 1210 and 1812) were assembled and infra-red reflowed using standard surface mount technology (SMT) process as mentioned in our previous paper [1]. For statistically significant results, four resistors (i.e. a total of eight solder joints) of each size were assembled on each sample board [19]. The amount of solder paste (Multicore SN63 RM92 with solder composition 63Sn–37Pb) printed on each copper land pad was carefully monitored to be within 150–170 μm so that the availability of Sn for the growth of interfacial Cu–Sn IMC layers were roughly similar for all samples being investigated.

To study the solid state growth kinetics of the Cu–Sn intermetallic compounds in surface mount solder joints, sample boards were isothermally annealed at 70, 120, 155 and 170°C for 0–25 days in an oven. Annealed solder joints were cross-sectioned and prepared for thickness measurement of the interfacial IMC layer and metallographic inspection by the procedure as mentioned in our previous paper [1]. Thickness measurements were done by means of a Nikon microscope in conjunction with an image analyzing software, Optimas, capable of measuring the area fraction of the Cu–Sn IMC layer in the real-time image of the cross-section of a surface mount solder joint.

Another set of sample boards aged at 155°C for 0–16 days were used to study the effect of interfacial Cu–Sn
IMC layer on the shear strength of the solder joint. Before mechanical testing, normalization was done by re-melting all the annealed solder joints so that any change in shear strength of the solder joint due to change in microstructure of the bulk solder (which occurred simultaneously during isothermal aging) can be eliminated. Mechanical testing was performed by an Instron Mini 44 Universal Testing Machine using a load cell of 500 N specially designed for low loading condition as in testing electronic assembly. The load weighting accuracy of the machine was within 0.5% of the load reading. The LCCC SMT solder joints under testing were loaded as shown in Fig. 1. This configuration provides a fast and convenient way to test the mode III shear strength of a practical LCCC surface mount solder joint. Besides, the length-to-width ratio of most surface mount passive devices is normally as large as 2:1 and the length-to-thickness ratio is only 5.5:1, mode III shear deformation (where the loading direction is parallel to the interfacial IMC layer) is believed to be more dominant than tensile deformation (where loading direction is perpendicular to the interfacial IMC layer) when the assembly is subjected to thermal fatigue condition, which is the most common failure mode for surface mount solder joints. Moreover, the test was performed at two extreme loading-rate, 0.05 and 0.0006 mm min\(^{-1}\) in order to investigate the effect of strain rate on the test results.

3. Results and discussions

3.1. Morphology of Cu–Sn interfacial IMC in SMT solder joint

Cross-sectional morphologies of the interfacial Cu–Sn intermetallic layers in LCCC 0805 surface mount solder joint annealed for 0, 9 and 16 days at 155°C are shown in the series of SEM micrographs in Fig. 2. Back-scattered electron imaging (BEI) was used to obtain the micrographs to produce better contrast among various layers of material. The unique phase (appeared dark) at the bottom is the Cu-pad. The bi-metallic Sn–Pb solder (appeared as dark and bright) can be found on the top of all micrographs. In the middle portion, the interfacial Cu–Sn intermetallic layers are located, with only the \(\eta\)-phase \(\text{Cu}_6\text{Sn}_5\) (appeared as white) found in as-solidified sample while both the \(\eta\)-phase and the \(\varepsilon\)-phase \(\text{Cu}_3\text{Sn}\) (appeared as dark gray) are found in all annealed samples. Composition of both phases are verified by EDX microprobe analysis. Such microstructures of Cu–Sn interfacial intermetallic compounds described above are similar to what others researchers [5,10–13,15,16,19,20] have found in bimetallic couples of Sn–Pb solders on copper. The formation of \(\eta\)-phase \(\text{Cu}_6\text{Sn}_5\) intermetallic layers in solder

Fig. 2. SEM BEI micrographs showing the cross-section of interfacial Cu–Sn IMC layer in 0805 LCCC surface mount solder joint annealed at 155°C (a) 0 day, (b) 9 days and (c) 16 days.
joint during the reflow process arises by interfacial reactions between its constituting species, Sn from the solder and Cu from the copper land pad. The absence of Cu₃Sn ε-phase in as-solidified solder joint can be explained simply by the equilibrium phase diagram of the Cu–Sn system [15], indicating that the Cu₃Sn ε-phase forms only when the crystallization temperature of the system reaches 415°C or above. During isothermal aging, the Cu₆Sn₅ h-phase in the layer grows by interdiffusion of Cu and Sn and reaction with each other, while the Cu₃Sn α-phase forms and grow by reactions between the Cu substrate and Cu₆Sn₅ ε-phase IMC layer. This is manifested by the micrographs in Fig. 2, showing a thickness increase of the interfacial IMC layer from 1 μm in as-solidified solder joint to ~7 μm in solder joint annealed at 155°C for 16 days. Apart from thickening of IMC layer, the solder/Cu–Sn IMC boundary also flattens during isothermal aging. Furthermore, it is observed in Fig. 2 that the growth of Cu₃Sn α-phase intermetallic in the layers is accompanied by the formation of micropores in the interfacial IMC layer. This is probably due to the difference in microstructure between copper (FCC) and that of the ε-phase (pseudohexagonal) intermetallic, micropores forms during the conversion of the η-phase Cu₃Sn₃ intermetallic into the ε-phase Cu₃Sn.

3.2. Growth kinetic of Cu–Sn IMC during isothermal aging

In order to study quantitatively the growth kinetics of interfacial Cu–Sn intermetallic compound layers in annealed surface mount solder joint, the thicknesses of IMC layer in 0805 LCCC surface mount solder joints annealed isothermally at 70, 120, 155 and 170°C for various times were measured and plotted against the square root of aging time, \( t^{1/2} \), as shown in Fig. 3. Due to the limited resolution of the Nikko optical microscope in resolving the ε-phase Cu₃Sn layer in solder joints annealed for very short period of time, the total IMC layer (including both the η-phase and ε-phase) thickness instead of thickness for individual phase was measured. From Fig. 3, it is seen that the total IMC layer thickness increases linearly with \( t^{1/2} \) and the growth rate is faster for higher aging temperature. According to the classical kinetic theory, such a \( t^{1/2} \) dependence for the growth of interfacial Cu–Sn IMC layer in LCCC surface mount solder joint provides good evidence that the growth is controlled by diffusion.

However, a comparison between Fig. 3 and others researchers [10,12–15] work in bi-metallic couple of eutectic solder on copper substrate reveals that the growth of interfacial Cu–Sn IMC layer in LCCC surface mount solder joint has been suppressed for all aging temperatures. To study this phenomena further, the activation energy, \( Q \), for the growth of interfacial Cu–Sn intermetallic layer is evaluated by means of an Arrhenius plot of \( \ln(D) \) against \( 1/T \), where \( D \) is the interdiffusion coefficient (given by the slope of each line in Fig. 3) for the IMC growth and \( T \) is the respective aging temperature, as shown in Fig. 4. From this, the activation energy and the pre-exponential factor, \( D_0 \), for interfacial Cu–Sn IMC layer growth in LCCC surface mount solder joint is determined to be ~1.09 eV and \( 1.61 \times 10^{-4} \text{ m}^2 \text{ s}^{-1} \), respectively.

This higher activation energy found for the growth Cu–Sn intermetallic in SMT solder joint is probably due to the diffusion of Ni from the component metallization to the bulk solder fillet. According to Wu et al.
[13], the addition of only 4 wt.% Ni particles in eutectic solder drastically reduces the $\varepsilon$-phase Cu$_3$Sn IMC layer thickness and increases the $\eta$-phase Cu$_6$Sn$_5$ thickness at the interface of bi-metallic couple of Sn–Pb solder on copper. Pinizzotto et al. [14] did their experiment with 4.5 wt.% of Ni particles in eutectic solder on copper substrate and found that the resulting activation energy for the growth of Cu$_3$Sn in the interfacial IMC layer increases from 1.69 eV (for eutectic solder alone) to an unmeasurable value (with Ni particles being added). The growth of Cu$_3$Sn$_3$ in the layer increases from 0.8 to 2.17 eV. Unfortunately, the measurement technique employed in our study is unable to resolve the $\varepsilon$-phase Cu$_3$Sn from the interfacial IMC layer. Nevertheless, the 1.09 eV activation energy for the growth of overall interfacial Cu–Sn IMC layer in LCCC surface mount solder joint as calculated from the Arrhenius plot shown in Fig. 4 is higher than that for the growth of the $\eta$-phase Cu$_6$Sn$_5$ intermetallic (which has a large portion of the interfacial IMC layer in our experiment) in bi-metallic couple of eutectic solder and copper.

3.3. Shear fracture surface morphology of failed surface mount solder joint

The 1206 LCCC surface mount solder joints were pulled in a shear manner (Fig. 1) until failure occurred. Figs. 5 and 6 show the SEM micrographs for the fracture surfaces of the copper side of the failed solder joints annealed at 155°C for 1 and 16 days, respectively. Fig. 5(b) and Fig. 6(b) are the respective enlarged views of Fig. 5(a) and Fig. 6(a). From these fractographs, it is observed that the joints annealed for 1 and 16 days failed in a ductile manner, as manifested by the dimples revealed on both fracture surfaces. The only difference between the two fractures is that dimples on the fracture surface of the solder joint annealed for 1 day shows evidence of a great deal of plastic deformation along the loading direction. This is not found on the fracture surface for joints annealed for a longer time. Such large amount of plastic deformation on the shear fracture surface for as-soldered solder joint in Fig. 5 indicates that the shear fracture in as-soldered LCCC surface mount solder joint can occur through Sn–Pb solder by microvoid nucleation and coalescence. This is usually not the case in solder joints annealed for a longer time.

To locate the fracture paths, failed joints were cross-sectioned and inspected by optical microscopy, as shown in Figs. 7 and 8 for joints annealed for 1 and 16 days, respectively. Regardless of the interfacial IMC layer thickness, it is clearly seen that the fracture path is initiated underneath the component and developed towards the solder fillet. Upon reaching the vicinity of the component corner, it bent towards the surface of the solder fillet at $\sim 45^\circ$ to the interfacial IMC layer although it encountered a macropore there. Nevertheless, the crack path in the solder joint annealed for 16 days is seen to travel a longer distance before it bent towards the surface of the solder fillet. A close look at Fig. 7(b) Fig. 8(b) also reveals that the fracture path underneath the component occurs in the solder for the solder joint with thinner interfacial IMC layer, whereas fracture path for the joint with thicker IMC layer is found to be along the solder/IMC layer interface.
In as-soldered conditions, the interfacial Cu–Sn IMC layer in the solder joint may be too thin (~1 μm) to cause a significant effect on the shear fracture of the solder joint [7,9,19,20]. As the interfacial IMC layer thickens during isothermal aging, the increasing thickness causes the failure path to switch from inside the bulk Sn–Pb solder to the solder/IMC layer interface (Fig. 8). Besides, the flattened solder/IMC layer interface in annealed solder joint is also believed to be responsible for the failure path in annealed solder joint [7]. All solder joints investigated were normalized by re-melting the solder after annealing for various times. The Sn-depleted (Pb-rich) layer, normally found between solder and the interfacial Cu₆Sn₅ IMC layer in all Sn–Pb solder/copper system and proved to be responsible [6,8,9,15,19,20] for the interfacial separation between solder and interfacial IMC layer, should not be the reason for such change of failure path as mentioned above.

3.4. Shear strength of surface mount solder joint—effect of interfacial Cu–Sn IMC layer

Fig. 9 shows the effect of Cu–Sn interfacial IMC layer thickness on the mechanical properties of LCCC surface mount solder joint, as a plot of the ultimate shear load (or the fracture load) of the joints as a function of IMC layer thickness. Unlike the simple tensile test (mode I fracture) on bi-metallic couples of Cu–Sn/Pb solder joints done by Frear [18,20] and the plain shear strain conditions (mode II fracture) in Dirnfeld’s [5] and Shawki’s [24] experiments on the plug-and-ring sample of Cu–Sn/Pb solder joints, the complex shear loading conditions in our experiment...
makes it difficult to determine the ultimate shear strength of the LCCC surface mount solder joint. However, the ultimate shear load can be readily recorded and should be adequate for a comparative analysis if the same type of LCCC solder joints are adopted throughout the range of aging time. It is seen that the ultimate shear load of two 1206 LCCC surface mount solder joints (for detaching one LCCC surface mount component) decreases linearly with increasing interfacial Cu–Sn IMC layer thickness for both fast (0.05 mm min\(^{-1}\)) and slow strain rates (0.0006 mm min\(^{-1}\)), with slower decreasing rate for slower strain rate.

The linear decrease in ultimate shear load with increasing thickness of interfacial Cu–Sn intermetallic layer for LCCC surface mount solder joint in Fig. 9 indicates that no fracture occur through the interfacial Cu–Sn IMC layer even for the thickest one (\( \sim 5.6 \) µm) obtained by annealing the joint for 16 days. Pratt et al. [22,6] investigated the mode I chevron notch fracture toughness of Cu/63Sn–37Pb solder joints as a function of solid-state Cu–Sn intermetallic growth at the solder/copper interface and observed a significant drop in the fracture toughness for the Cu/63Sn–37Pb solder joints as the total intermetallic layer thickness increases from 5 to 7 µm. They also show that such a drop in the fracture toughness for solder joints is associated with a change in fracture mechanism from microvoid nucleation and coalescence in the bulk solder of the joint to cleavage within the interfacial IMC layer. Therefore, the shear fracture of LCCC surface mount solder joints with the range of interfacial IMC layer thickness being studied is believed to be confined inside the Sn–Pb solder despite the fact that the fracture path for solder joint annealed for the longest time at the solder/Cu\(_6\)Sn\(_5\) interfacial.

However, the growth of interfacial Cu–Sn intermetallic layer is indeed undesirable as having an ‘indi-
rect’ effect on the shear strength of LCCC surface mount solder joint—a 20% drop in the ultimate shear load of the joints as the IMC layer increases from ~1 μm in as-soldered joints to 5.6 μm in joints annealed at 155°C for 16 days. The effect is termed ‘indirect’ because such a reduction in joint strength is attributed to the loss in strength of the bulk solder. As the interfacial IMC layer grows, Sn is being depleted continuously from the Sn–Pb solder of the joint. As a consequence, the solder composition has a lower tin content and the joint strength decreases accordingly as long as the fracture path is confined in the solder.

Finally, similar linear reduction in joint strength corresponding with the interfacial Cu–Sn IMC layer growth is also observed for lower shear strain rate (0.0006 mm min$^{-1}$) as shown in Fig. 9. However, the drop in joint strength is very small and within the variation of the data recorded. Here, it is proposed that a higher strain rate would be more appropriate for evaluating the effect of interfacial Cu–Sn IMC layer on the strength of surface mount solder joint using an eutectic Sn–Pb solder and copper substrate.

4. Conclusion

The growth kinetics of interfacial Cu–Sn IMC layer in practical LCCC surface mount solder joints and its effect on the joint strength were investigated. It is observed that only $\eta$-phase Cu$_6$Sn$_5$ intermetallic compounds are revealed in the interfacial Cu–Sn IMC layer in as-soldered joint while both the $\eta$-phase and $\varepsilon$-phase Cu$_x$Sn$_y$ intermetallic are found in all annealed solder joints. Its growth follows closely with the classical kinetic theory for diffusional growth of bi-metallic compound, with an activation energy of ~1.09 eV and interdiffusion coefficient of $1.61 \times 10^{-4}$ m$^2$ s$^{-1}$, respectively. However, the growth of interfacial Cu–Sn IMC layer in LCCC surface mount solder joint has been suppressed when comparing our results with those of other researchers using bi-metallic couples of Sn–Pb solder on copper substrate. Such a suppression in growth rate is probably due to the dissolution of Ni from the component metallization to the bulk solder.

From the study on the effect for the growth of interfacial Cu–Sn IMC layer in LCCC surface mount solder joint on the joint strength had been investigated, it is observed that the shear fracture in both as-soldered and annealed joints are both ductile in nature with a large amount of plastic deformation associated with the fracture surface for as-soldered joint. Moreover, cracks are found to propagate through the Sn–Pb solder rather than the interfacial IMC layer, despite the fracture path in solder joints annealed at 155°C for 16 days is found to be at the solder/Cu$_6$Sn$_5$ IMC interface. Linear reduction in ultimate shear load for the solder joints is recorded with increasing thickness of interfacial Cu–Sn IMC layer. This is due to two reasons. Firstly, the growth of interfacial Cu–Sn IMC layer during isothermal aging of the solder joint continuously depletes Sn from the bulk Sn–Pb solder. This will lead to a lower tin content and hence lower the joint strength as long as the fracture crack is confined in the bulk solder. Secondly, flattening of the solder/Cu$_6$Sn$_5$ IMC interface during isothermal aging should also be responsible for the reduction in shear joint strength. Finally, our shear test results confirm that higher strain rate is more appropriate for examining the effect of the interfacial Cu–Sn IMC layer growth on the shear strength of LCCC surface mount solder joints.

Acknowledgements

The authors would like to thank the Universities Grants Council of Hong Kong for financial support (project nos. 9040109 and 9040212).

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