Aging Studies of Cu–Sn Intermetallic Compounds in Annealed Surface Mount Solder Joints

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***Abstract*— Our previous investigation [1], revealed the formation kinetics and characteristics of copper-tin (Cu–Sn) intermetallic compounds (IMC) in leadless ceramic chip carrier (LCCC) surface mount solder joints during infrared (IR)-reflow soldering. The present study focuses on the solid state growth of the interfacial Cu–Sn IMC in LCCC surface mount solder joints under prolonged annealing at elevated temperature. A thick Cu–Sn IMC layer at the Sn–Pb solder/Cu interface of a surface mount solder joint (which can be achieved by prolonged aging at high temperature or after long term operation of surface mount technology (SMT) electronic assemblies) makes the interface more sensitive to stress and may eventually lead to fatigue failure of all SMT solder joint. The microstructural morphology of the Cu–Sn IMC layer at the solder/Cu pad interface in all annealed LCCC surface mount solder joints is duplex and consists of η-phase Cu_6Sn_5 and ε-phase Cu_3Sn IMC. Both Cu–Sn IMC phases thicken as the aging time increases. On the other hand, at the interface close to the component metallization, the growth of both the η- and ε-phase were shown to be suppressed, with more a pronounced effect on ε-phase, by Ni originating from the metallization. The mean total layer thickness was found to increase linearly with the square root of aging time and the growth was faster for higher annealing temperature. The activation energy for the growth of interfacial Cu–Sn IMC layers and the pre-exponential factor, D_o, for diffusion were found to be 1.09 eV and 1.68×10^{-4} m^2/s, respectively, for the 0805 LCCC surface mount solder joint using eutectic Sn–Pb solder. The pad size and quantity of Sn–Pb solder employed in LCCC surface mount solder joints were shown to have little effect on the solid state growth rate of interfacial Cu–Sn IMC layers.**

***Index Terms*—Cu_6Sn_5, Cu_3Sn, intermetallic compounds, reliability, solder joint, surface mount technology.**

I. Introduction

COPPER–TIN (Cu–Sn) intermetallic compounds (IMC), which serve as the mechanical bonding between tin-lead solder and the copper land pad in surface mount (SMT) solder joints, form instantly when Sn–Pb solder melts on the Cu land pads and thickens rapidly to a few microns due to the high soldering temperature and molten state of the solder. Because of its brittle nature and microstructural mismatch between Sn–Pb solder and copper, too thick a Cu–Sn IMC layer at the solder/Cu interface causes the interface in the solder joint to be more sensitive to stress [4], [8], [11]–[13], [15], especially under the action of cyclic loading. The effect is much more marked in a surface mount solder joint due to its small dimension.

A thick interfacial Cu–Sn IMC layer in surface mount solder joints is not only caused by the long reflow time and high reflow temperature during soldering, but also by prolonged storage and long term operation of the electronic assembly even at room temperature. Although numerous investigations on the solid state growth of Cu–Sn IMC have been done previously, almost all of them are performed on bulk samples of Sn–Pb solder and copper which differ from a surface mount solder joint in a number of ways, including the amount of solder in the joint, dissolution of materials from the component leads or metallization, and geometry of the solder joint. All of these are potential factors affecting the growth of interfacial Cu–Sn IMC in a surface mount solder joint under isothermal aging. This investigation is aimed at understanding the growth kinetics of Cu–Sn IMC in real surface mount solder joint under isothermal aging.

II. Background

When Sn–Pb solder melts on the Cu substrate of a printed circuit board (PCB) during soldering, Cu–Sn IMC form instantly at the interface and serve as the bonding materials between the bulk solder and the Cu pad. Such layer of interfacial Cu–Sn IMC will continue to grow, even at room temperature, after the solder joint has solidified. The relationship between the thickness of IMC layer and aging time is generally considered to have the usual form [19]

$$d = \sqrt{Dt} \tag{1}$$

where d is layer thickness, D is the interdiffusion coefficient and t is the aging time. Layer growth is faster for higher aging temperature with the interdiffusion coefficient being given by the Arrhenius equation [19]

$$D = D_o \exp^{-(Q/kT)} \tag{2}$$

where D_o is the interdiffusion constant, Q is activation energy for the growth of interfacial Cu–Sn IMC layer, k is the Boltzmann constant, and T is the absolute temperature.

Various investigations [2]–[11], [16]–[20] have been done on growth of Cu–Sn IMC's in different configurations. It is generally observed that both the η-phase Cu_6Sn_5 and ε-phase Cu_3Sn IMC are found in annealed interfacial Cu–Sn IMC layers. A. J. Sunwoo *et al.* [2] aged samples of eutectic Sn–Pb solder on Cu substrate at 70 and 170 °C. The interfacial intermetallic layer was found to be essentially unaffected by aging at 70 °C for as long as 13 weeks. At 170 °C, the η-phase

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TABLE I
EFFECT OF COMPOSITE SOLDERS ON THE ACTIVATION ENERGY FOR THE GROWTH OF Cu_6Sn_5 AND Cu_3Sn IMC (PINIZZOTTO [13])

Composite Solder (62Sn-37Pb)	Q, Cu_6Sn_5, eV	Q, Cu_3Sn, eV
No Addition	0.80	1.69
20 wt.% Cu_6Sn_5	1.18	0.95
20 wt.% Cu_3Sn	1.42	0.80
4 wt.% Ni	2.17	very large

IMC layer thickened and the ε-phase nucleated at the Cu/η-phase interface and grew to a thickness comparable to that of the η-phase. They also illustrated that the η-phase could be converted into ε-phase after short periods of aging for a pretinned (thin layer of solder) Cu substrate at 170 °C. R. F. Pinizzotto *et al*. [3], reflowed composite Sn–Pb solder, with addition of different particles, on Cu and revealed that particle additions had a dramatic effect on the growth patterns of the intermetallic layers. Their results are summarized in Table I. None of them was done using real surface mount solder joints in which the component metallization, trace amount of solder used, and geometry of solder joint could be potential factors affecting the growth of interface Cu–Sn IMC layers.

III. EXPERIMENTAL PROCEDURE

Surface mount passive components of four different sizes, 0805, 1206, 1210, and 1812 [21], were assembled on FR-4 PCB's using standard infra-red reflow. The number of components for each size were chosen to be four so that a total of eight surface mounted solder joints of each pad size were made. This was done in order to make the thickness measurements statistically significant. The solder paste employed was MULTICORE SN63 RM92 of eutectic solder composition (63Sn–37Pb). Care was taken to keep the quantity of solder paste printed on each copper pad constant so that effect of variation in Sn availability for the formation and growth of the Cu–Sn intermetallic layers was minimized. The assemblies were preheated at 100 °C for 100 s and then reflowed at 230 °C for 100 s. As suggested by our previous work, such soldering conditions can minimize the formation of pores [15], which are commonly found in the solder/IMC interface of the solder joint and can affect the formation, as well as the growth kinetics, of the interfacial IMC.

Surface mounted assemblies were then aged isothermally in an oven at 70, 120, and 155 °C for various times up to about 400 h. Metallographic preparation for all surface mounted solder joints were done according to the method described in our previous work [1]. Scanning electron microscopy (SEM) and optical microscopy were used to study the microstructural morphology of the Cu–Sn IMC layers in solder joints before and after annealing. Energy-dispersive x-ray (EDX) and ZAF-4 analysis were employed to characterize the various phases in the interfacial Cu–Sn intermetallic layer. The mean thickness of the interfacial intermetallic layers in joints annealed for various times were measured with the aid of a powerful image processing system, OPTIMAS, used in conjunction with a Nikon optical microscope.

IV. RESULTS AND DISCUSSION

A. Microstructural Morphology

High magnification SEM micrographs showing the cross sectional views of the solder/Cu interface in 0805 surface mounted solder joints annealed at 155 °C for various times are illustrated in Fig. 1. Backscattered electron imaging of SEM is used to provide more distinguishable boundaries of the interfacial IMC layer. The globular, single layer structure of η-phase Cu_6Sn_5 interfacial IMC found in the as-solidified surface mounted solder joint was reported and explained in our previous work [1]. Duplex structure, with η-phase Cu_6Sn_5 IMC next to the solder and the ε-phase Cu_3Sn at the η-phase/copper interface (as labeled in the SEM micrograph), of the interfacial Cu–Sn intermetallic layer was observed in all annealed surface mount solder joints [Fig. 1(b)–(e)]. The composition of each Cu–Sn intermetallic layer was verified by EDX and ZAF-4 analysis as shown in Fig. 2(a) and (b), respectively. Such duplex structure of interfacial Cu–Sn IMC in annealed surface mount solder joint is similar to the results obtained elsewhere [2]–[10], [15]–[19].

Fig. 1 also reveals that both the η-phase Cu_6Sn_5 and the ε-phase Cu_3Sn interfacial Cu–Sn intermetallic layers thicken, from about 1 μm of η-phase and no ε-phase in as-solidified solder joints to about 5 μm of η-phase and 1 μm ε-phase in joints aged at 155 °C for 16 days, and the solder/η-phase boundaries flatten as the aging time increases. The solid state growth of the η-phase is attributed to interdiffusion of the constitutive species, Cu from the copper pad and Sn from the eutectic Sn–Pb solder, which react to form the IMC while the growth of ε-phase Cu_3Sn consumes η-phase Cu_6Sn_5. Moreover, the η-phase IMC layer was observed to grow in a faster rate then the ε-phase, which is the reverse of what previous researchers found using bulk samples of solder on copper. This can be explained by the presence of small amount of Ni in the bulk solder of the solder joint. According to Pinizzetto *et al*. [3], the addition of small amount (4 wt.%) of Ni in eutectic 63Sn–37Pb solder would increase the activation energy for the solid state growth of both η-phase (from 0.8 to 2.17 eV) and ε-phase (from 1.69 eV to a very large value) Cu–Sn IMC. This in turn suppresses their growth with a much more pronounced effect on the ε-phase Cu_3Sn IMC than the η-phase Cu_6Sn_5. In the present study, the terminal metallization of surface mount passive components is the most probable source of Ni.

Fig. 4(a) and (b) show cross sectional views of interfacial Cu–Sn IMC layers taken from different parts of the solder/Cu interface in a 1206 surface mount solder joint aged for 12 days at 155 °C. It is found that closer the interfacial Cu–Sn IMC layer [Fig. 4(a)] is to the component metallization, the slower is the growth of ε-phase Cu_3Sn IMC without too much change in the total thickness of the IMC layer. As the distance from the component metallization increases, the amount of Ni in the bulk solder of a surface mount solder joint decreases because of the long diffusion distance from the component terminal metallization. As a result, the suppression of interfacial IMC growth due to the present of Ni in bulk

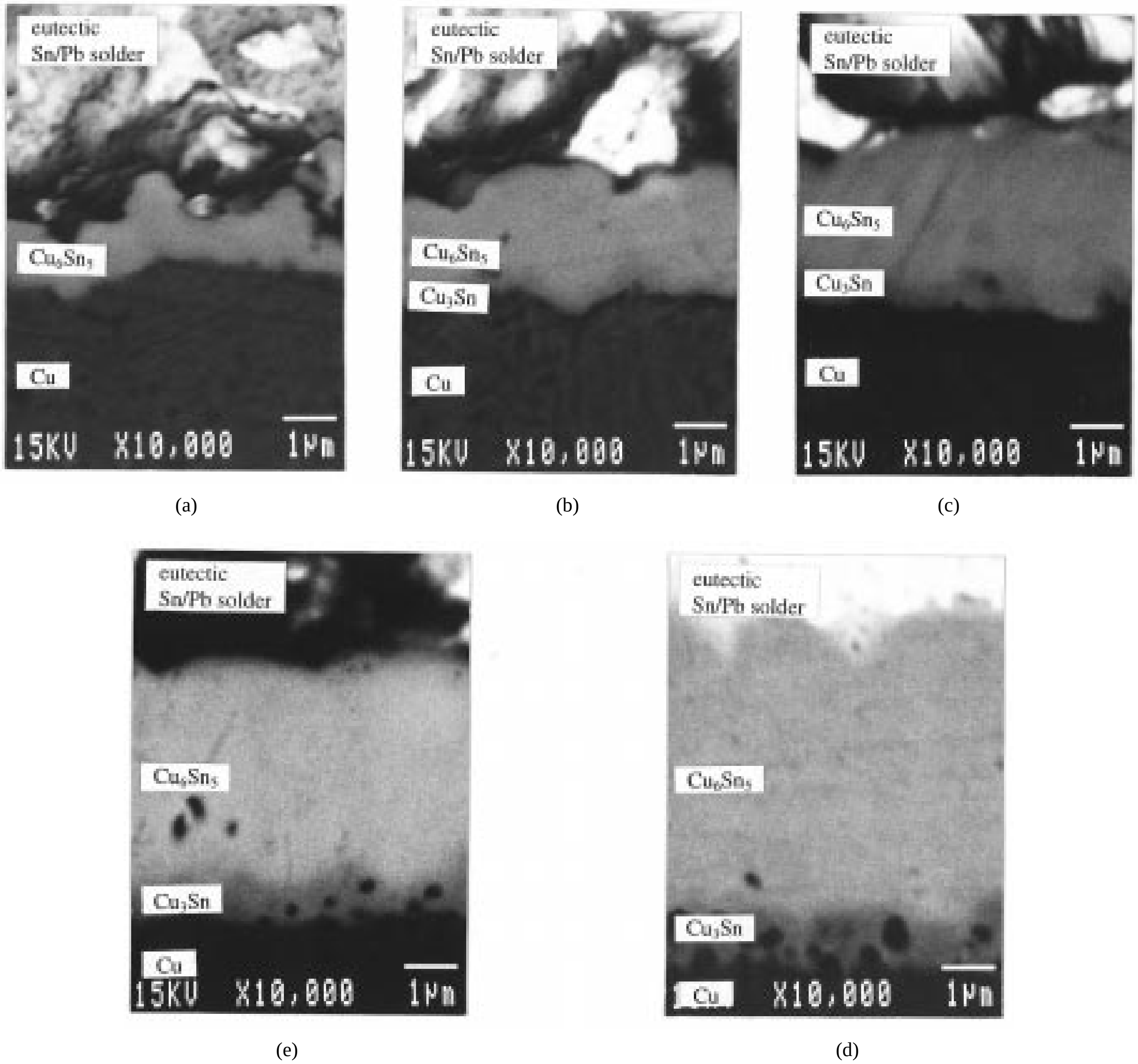


Fig. 1. High magnification SEM micrographs showing Cu–Sn IMC layers at the interface of 0805 surface mount solder joints annealed for various days at 155 °C (Backscatter, X10000).

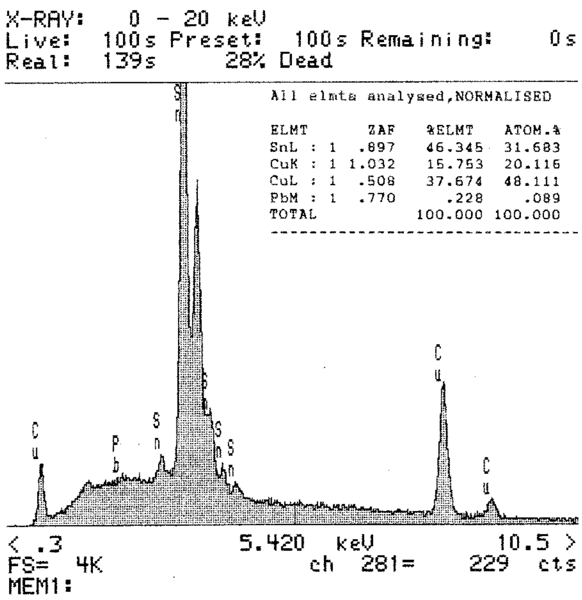
solder is less pronounced as the distance from the component metallization increases.

D. Grivas *et al*. [11], concluded from their observations that solder of less tin content (5Sn–9SPb) favors the formation of Cu_3Sn at the solder/Cu interface. Therefore, the availability of Sn in solder just above the interfacial Cu–Sn IMC layer may also be a cause of the enhanced growth of ε-phase Cu_3Sn IMC as shown in Fig. 4(b), since the height of bulk solder in a LCCC surface mount solder joint is decreased as the distance from the component increases (Fig. 3).

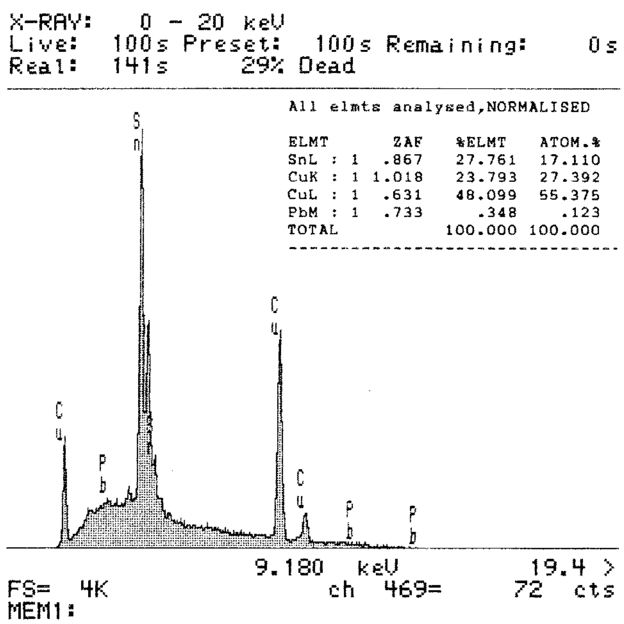
To investigate this effect, eutectic solder was reflowed on copper pads for 1206 surface mount solder joint (without component) using the same reflow conditions as above and was then annealed at 155 °C for six days. Another set of 1210 surface mount solder joints was made with component using Cu as terminal metallization and was annealed at 155 °C for 12 days. Optical micrographs of interfacial Cu–Sn IMC taken at different parts of the solder "joints" are illustrated in Figs. 5 and 6, respectively. Neither of the two samples shows the relatively enhanced growth of Cu_3Sn at the edge of the solder joint. This indicates that the terminal metallization material of SMT passive device is more significant in affecting the growth pattern of interfacial Cu–Sn IMC than the bulk solder height.

B. Growth Kinetics Studies of Interfacial Cu–Sn IMC in 0805 LCCC Surface Mount Solder Joints

The thicknesses of interfacial Cu–Sn IMC in 0805 LCCC surface mount solder joints aged at 70, 120, and 155 °C for 1, 2, 4, 6, 9, 12, and 16 days were measured using an image analyzer which processes images captured directly from a Nikon optical microscope. All measurements made were confined to that half of the solder joint closest to the component so that the effect of Ni from the component terminal metallization mentioned above is in operation. This was done in order to reflect the situation in a real surface mount solder joint. Since the magnification of optical microscopy is limited, the



(a)



(b)

Fig. 2. EDX and ZAF-4 analysis of: (a) η-phase Cu_6Sn_5 and (b) ε-phase Cu_3Sn.

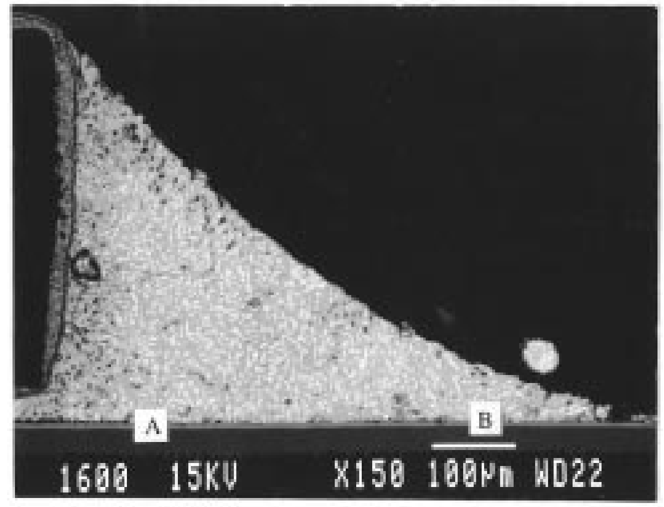


Fig. 3. Cross sectional view of a 1206 surface mount solder joint.

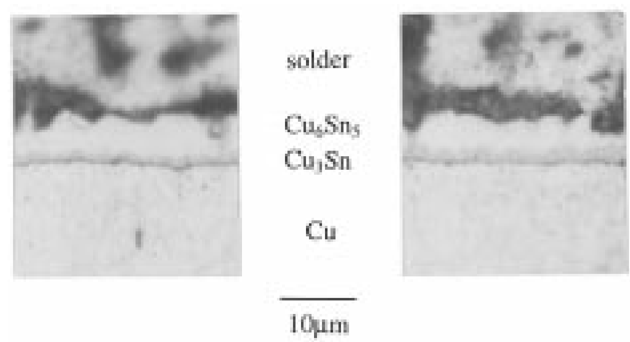


Fig. 4. Interfacial Cu–Sn IMC layers at point: (a) A and (b) B of Fig. 3 in a 1206 solder joint (Ni metallization) aged for at 155 °C 12 days.

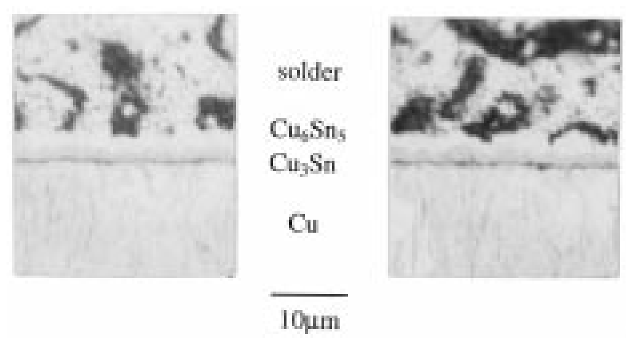


Fig. 5. Interfacial Cu–Sn IMC layers at point: (a) A and (b) B of Fig. 3 in a solder plated 1206 Cu-pad aged at 155 °C for six days.

thickness of the ε-phase Cu_3Sn IMC layer, smaller than 1 μm in the present study, cannot be resolved independently with acceptable accuracy. As a consequence, the mean total thickness of the interfacial Cu–Sn IMC layer, including both η- and ε-phase, in all solder joints was measured. The results are plotted as a function of the square root of aging time in Fig. 7.

The mean thickness of the interfacial Cu–Sn IMC layer in 0805 surface mount solder joints is found to increase linearly with the square root of aging time, with faster growth rate for higher aging temperature, indicating that the growth of interfacial Cu–Sn IMC in solid state surface mount solder joints is an ordinary diffusional growth described by classic kinetic theory and the rate is controlled by the interdiffusion of, rather than reaction between, the constitutive species (i.e., Cu and Sn). This is in good agreement with what other researchers' [2]–[10] findings in bulk Sn–Pb solder/Cu couples. However, closer study of Fig. 7 reveals that the growth rate of interfacial Cu–Sn IMC is slower in real surface mount solder joints than in bulk Sn–Pb solder/Cu couples [2]–[5], [7]–[9], [16], [19], for all aging temperatures studied This is due to the presence of Ni in the bulk solder of real LCCC surface mount solder joints as mentioned above.

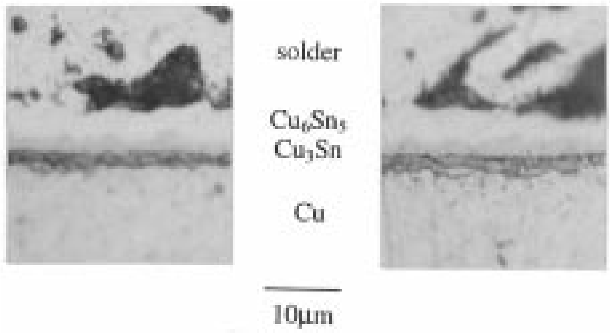


Fig. 6. Interfacial Cu–Sn IMC layers at point: (a) A and (b) B of Fig. 3 in a 1210 solder joint (Cu metallization) aged for 12 days at 155 °C.

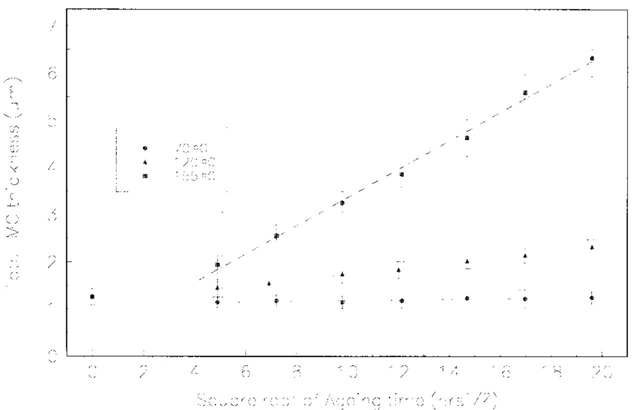


Fig. 7. The total interfacial Cu–Sn IMC layers growth in 0805 LCCC surface mount solder joints aged at 70, 120, and 155 °C for various times.

The interdiffusion coefficient in the interfacial Cu–Sn IMC layer for various aging temperatures is determined from the slopes of the lines shown in Fig. 7. Note that the zero-time IMC layer thickness obtained experimentally is not employed in the determination of slopes since the zero time thickness is the result of reaction between Cu and Sn while the solder is in its molten state. The formation rate of Cu–Sn IMC at the interface of molten solder/Cu is much faster than its growth rate at the solid solder/Cu interface, which is illustrated by the lower zero-time intercept of the lines shown in Fig. 7. The activation energy for the growth of interfacial Cu–Sn IMC in 0805 solder mount solder joints was found to be about 1.09 eV by plotting the Arrhenius curve, in D against $1/T$, shown in Fig. 8. The pre-exponential factor, D_o, for diffusion in the interfacial Cu–Sn intermetallic layer in the surface mount solder joint being studied was found to be 1.68×10^{-4} m^2/s. These values may be used to predict the thickness of interfacial Cu–Sn IMC layers in SMT solder joints. Hence, the influence of interfacial Cu–Sn IMC layer on the reliability of real 0805 surface mount solder joints after electronic assembly operated under different thermal conditions may be evaluated.

C. Effect of Pad Size

Fig. 9 shows the variation of the mean total thickness of interfacial Cu–Sn IMC layers with aging time for surface mount solder joints of different pad size annealed at 155 °C. The results illustrate that the pad size of LCCC surface mount

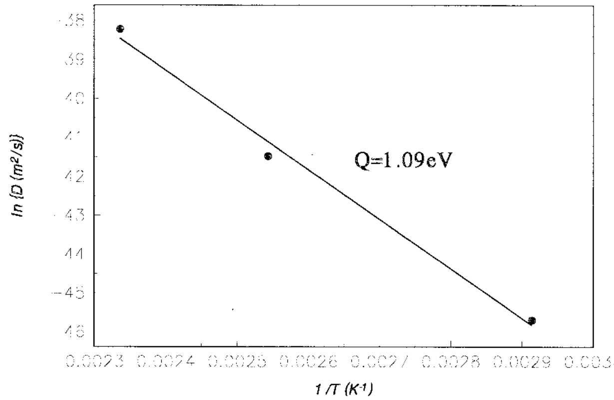


Fig. 8. Arrhenius plot for the growth of the total interfacial Cu–Sn IMC layers in 0805 LCCC surface mount solder joint.

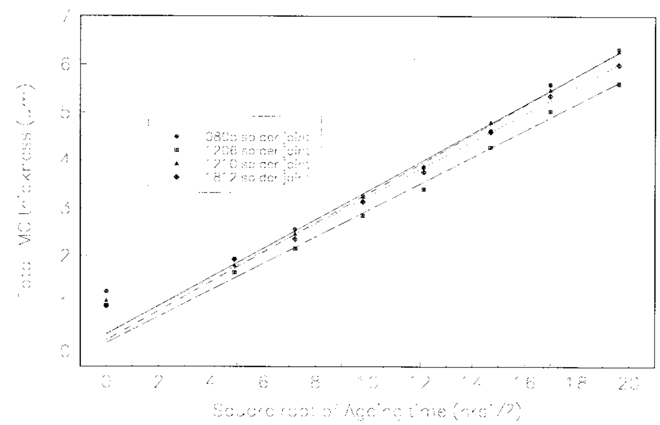


Fig. 9. Thickness of the total interfacial Cu–Sn IMC layers as a function of aging time for 0805 LCCC surface mount solder joints of different pad size aged at 155 °C.

solder joint has no effect on the growth rate of interfacial Cu–Sn IMC. This can be explained by the diffusion-controlled nature of solid state growth of the interfacial Cu–Sn IMC layer. If its growth is a reaction-controlled process, the total number of reactions between Cu and Sn, and hence time required to form a unit thickness of interfacial Cu–Sn IMC is greater for a large pad size. However, this is not the case in present study. This observation further confirms the diffusion-controlled nature of solid state growth of interfacial Cu–Sn IMC in LCCC surface mount solder joints.

V. CONCLUSION

Following on from our previous investigation [1], the solid state growth of Cu–Sn IMC in LCCC surface mount solder joints annealed isothermally at 70, 120, and 155 °C for various times were studied in the present work. It is generally observed in all annealed solder joints that the interfacial Cu–Sn IMC layer is duplex, consisting of η-phase Cu_6Sn_5 next to the solder and ε-phase Cu_3Sn at the η/Cu pad interface. The thickness of both phases was observed to increase, with the ε-phase being nucleated during the initial stage of aging, as the aging time increases. It is also verified that the growth of both η- and ε-phases in interfacial Cu–Sn IMC layers near the component terminal metallization is suppressed predominantly by the presence of Ni, originating from the component terminal metallization, in the bulk solder of the solder joint. This suppression is more pronounced for the ε-phase Cu_3Sn than the η-phase Cu_6Sn_5.

The total thickness of interfacial Cu–Sn IMC layers in 0805 LCCC surface mount solder joints was found to increase with the square root of aging time over the range of aging temperatures studied. This confirms the diffusion-controlled nature of its growth kinetics. The activation energy for growth and the pre-exponential factor, D_o, for diffusion were found to be 1.09 eV and 1.68×10^{-4} m^2/s, respectively, for the configuration of surface mount solder joint studied. These values are useful in predicting the total thickness of interfacial Cu–Sn IMC layer in 0805 LCCC solder joints operated under different thermal conditions for various times and hence the contribution of interfacial Cu–Sn IMC to the reliability factor of SMT solder joints. The size of Cu land pad for different LCCC surface mount solder joint was found to play little role on the growth of interfacial Cu–Sn intermetallic layers.

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J. K. L. Lai, for a photograph and biography, see this issue, p. 151.