Effect of Soldering and Aging Time on Interfacial Microstructure and Growth of Intermetallic Compounds between Sn-3.5Ag Solder Alloy and Cu Substrate

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The formation and the growth of the intermetallic compound (IMC, hereafter) at the interface between the Sn-3.5Ag (numbers are all in wt.% unless otherwise specified) solder alloy and the Cu substrate were investigated. Solder joints were prepared by changing the soldering time at 250°C from 30 sec to 10 h and the morphological change of IMCs with soldering time was observed. It resulted from the competition between the growth of IMC and the dissolution of Cu from the substrate and IMCs. They were further aged at 130°C up to 800 h. During aging, the columnar morphology of IMCs changed to a more planar type while the scallop morphology remained unchanged. It was observed that the growth behavior of IMCs was closely related with the initial soldering condition.

Key words: Intermetallic compound growth mechanism, soldering and aging, lateral growth, Gibbs-Thompson effect, Sn-Ag-Cu system

INTRODUCTION

Nowadays, there is a great need for the high circuit density device chips having a larger number of input and output leads. Thereby the interconnection by the solder joint is essentially important in the electronic packaging. In the solder Joint, IMCs form and grow at the interface, however, the excessive growth or the unexpected morphological change of IMCs may undermine the joint performance and eventually the reliability.

The formation and the growth of IMCs in various solder joints have been studied.[1–8] Vianco et al.[5,6] observed the growth behavior of IMCs at the interface between the various Sn-based solders and the Cu substrate, and the growth kinetics was explained using the solid/solid state diffusion flux. Schaefer et al.[7] reported that the IMC growth was affected mainly by the grain boundary diffusion during soldering. Kim and Tu[8] explained the growth of IMC through the ripening effect during soldering. Most of the previous works showed that the interfacial morphology between the solder and the substrate changed during the growth of IMCs, and the interfacial change by the growth of IMCs can be a source of mechanical and electrical weakness. As a result, the interfacial phenomena may be directly related with the solder joint reliability in the electronic packages. In this sense the interface needs to be studied more systematically from the soldering stage to the service condition of aging.

In general, the interfacial morphology of the joint is closely dependent on the soldering condition because the soldering condition determines the initial interface morphology right after soldering and the morphological change of the interface during aging is also based on the initial morphology.[9] In case of the Sn-based solder joint with the Cu substrate, the layer of the η-Cu_6Sn_5 phase forms first at the interface.[10] This layer is composed of scallop-shaped grains, of which the size increases or the shape may change with further soldering. When the solder joint is being aged or annealed during operation or service, the interface also changes.

In this study, the interfacial phenomena in the Sn-3.5Ag solder joint on the Cu plate are thoroughly investigated during soldering and aging with a focus on the growth behavior of IMCs, which will be explained by the diffusional flux.

EXPERIMENTAL PROCEDURES

Solder alloys were prepared from pure metals (purity higher than 99.9%). Samples were encapsulated in quartz tubes under vacuum, melted and held at 800°C for 30 min for mechanical mixing. As-cast alloys were obtained by cooling each melt into water.

(Received February 22, 2000; accepted April 6, 2000)

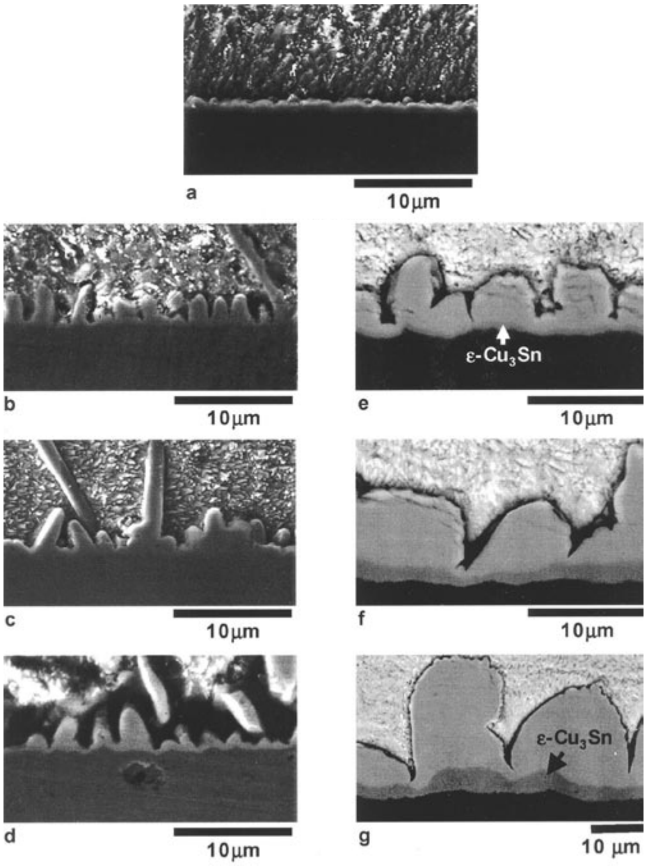

Fig. 1. SEM micrographs of the interface between Sn-3.5Ag solder and Cu substrate at 250°C with increased soldering time: (a) 30 sec, (b) 60 sec, (c) 90 sec, (d) 120 sec, (e) 10 min, (f) 1 h, and (g) 10 h. From 10 min, ε-Cu_3Sn appears between η-Cu_6Sn_5 and substrate.

Then they were cold-rolled into a 0.1 mm thick sheet and punched in the form of a disk-type specimen (3 mm in diameter, 0.3 g in weight). Soldering was performed in the molten state at 250°C from 30 sec to 10 h using rosin mildly activated (RMA) flux. The oxygen-free high conductivity Cu plates (0.5 mm in thickness) were polished with 1 μm diamond paste, then cleaned with acetone and alcohol. Each solder joint was aged at 130°C from 100 h to 800 h in air.

The interface in the cross section of the solder joint was examined by the scanning electron microscopy (SEM) operated at 25 kV. To observe clearly the morphology of IMC at the interface, the solder matrix was etched away using a $5HNO_3$-3HCl-$92CH_3OH$ solution for several seconds. The layer thickness of IMCs was calculated as the average value of more than ten height measurements of adjacent grains with weight factors to the horizontal direction. The composition of IMC was measured by the energy-dispersive x-ray (EDX) analyses. The spatial resolution was 1 μm diameter area about the target point and the compositions were determined by an average of ten center point measurements. The phases at the interface were identified by the x-ray diffraction (XRD) analyses. The specimens for XRD were prepared by mechanically removing the solder and etching away the remaining solder with a HCl solution for 30 sec.

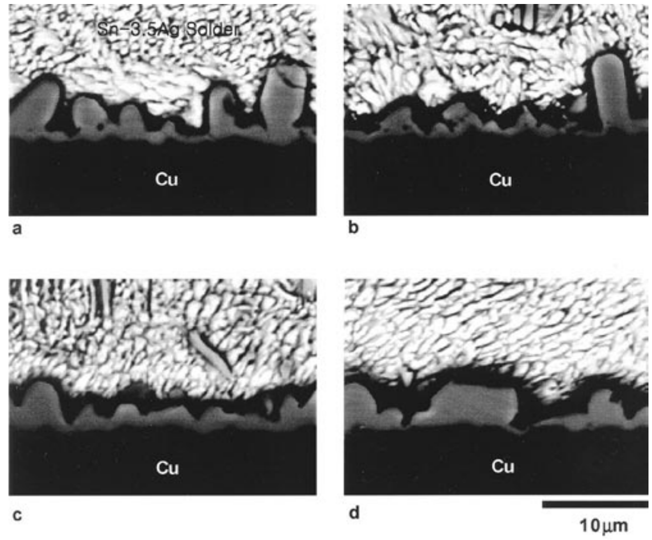

Fig. 2. SEM micrographs of the cross section of the solder joint after repeated soldering at 250°C for 60 sec: (a) once, (b) twice, (c) three times, and (d) four times.

RESULTS

Interfacial Microstructure during Soldering

The interface morphology of the Sn-3.5Ag alloy soldered on the Cu plate at 250°C for 30 sec through 10 h at different intervals is shown in Fig. 1. The first forming IMC was identified as the η-Cu_6Sn_5 phase in all the specimens. When they were soldered longer than 10 min, the second type of IMC was observed between the preformed η-Cu_6Sn_5 phase and the Cu plate as seen in Fig. 1e–g and it was identified as the ε-Cu_3Sn phase. It is illustrated as a dark gray region below the η-Cu_6Sn_5 phase. The IMC layer generally thickened with the increased soldering time and its morphology gradually changed from the initial columnar type in the early stage of soldering as in Fig. 1a–d into the scallop type in the later stage of soldering as in Fig. 1e–g. Grains of IMCs that were seemingly separated in the early stage of soldering approached one another after prolonged soldering. The thickness of IMC increased little from 90 sec to 120 sec. During this interval, several IMC grains were observed to be detached from the interface going inside the solder.

Schaefer et al.[11] reported using the Sn-37Pb solder/Cu joint. Here, there exists a stage in which the copper element is dissolved into the molten solder from IMCs formed initially in order to reach the solubility of Cu in the solder matrix. In this stage, the thickness of IMCs is said to be almost constant. They also confirmed the dissolution of Cu observing the rough and irregular boundary between IMCs and the solder. It has also been reported that the dissolution from the preformed IMCs to the liquid solder has little effect on the growth behavior of IMCs since the liquid solder is saturated with Cu within several seconds at the soldering temperature.[8,12] In order to determine which mechanism is applicable in the current work, the time when the solder is saturated with Cu needs to be known quantitatively.

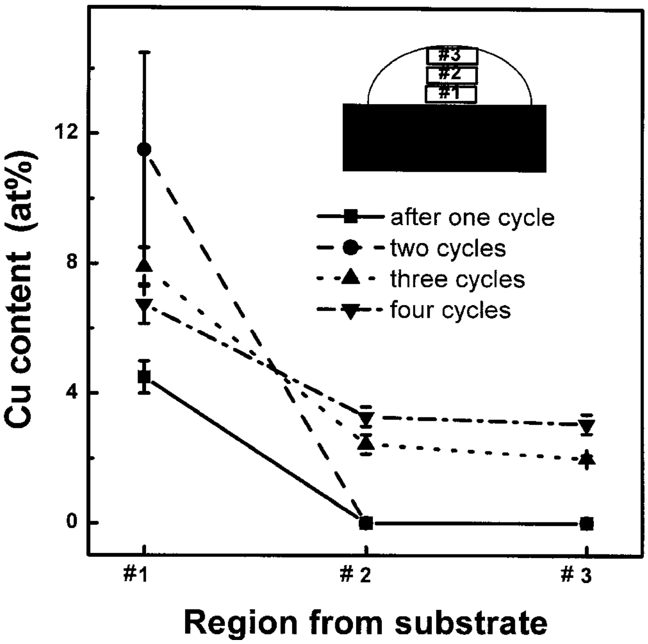

Fig. 3. Cu concentration measured in liquid solder vs. distance from original substrate with repeated soldering.

The thermal cycling of short period was chosen instead of isothermal experiments to observe the morphological change and the Cu dissolution at the very early soldering stage. Figure 2a–d shows the morphological change of the interface after the repeated soldering. One cycle of the soldering process is to raise the temperature to 250°C, holding for 60 sec and then cool down to room temperature. This cycle was repeated up to four times. Until the soldering is repeated three times, the interface between IMCs and the liquid solder is irregular and faceted, and its thickness tends to decrease a little. However, when the soldering is repeated four times, the IMCs grow again.

The Cu concentration in the solder matrix was measured using the EDX analyses in three regions of the solder, at the bottom, in the middle, and at the top from the original Cu substrate. The composition distribution is shown in Fig. 3. Until soldered two times, Cu was not detected at the top. After being soldered three times, Cu was detected and its value was measured as about 3 at.%. A similar concentration distribution was obtained when soldered four times. The solubility limit of Cu in the Sn-3.5Ag solder at 250°C is calculated as 2.03 at.%.[13] There is a slight discrepancy between the detected and calculated contents of Cu. It may be due to the experimental or calculation error and it does not override the current observation. From this result, it is found that the solder is saturated with Cu after being soldered three times and therefore the dissolution of Cu from IMCs does not take place and IMCs grow more when soldered four times. This implies that the liquid solder is not saturated in the Cu content within a very short time and the interfacial phenomena during soldering may be divided into several stages as suggested by Schaefer et al.[11] The first stage is the formation of IMCs and the second stage is that both the growth of IMCs and the dissolution of Cu from IMCs occur simultaneously. IMCs grow again after saturation in the third stage.

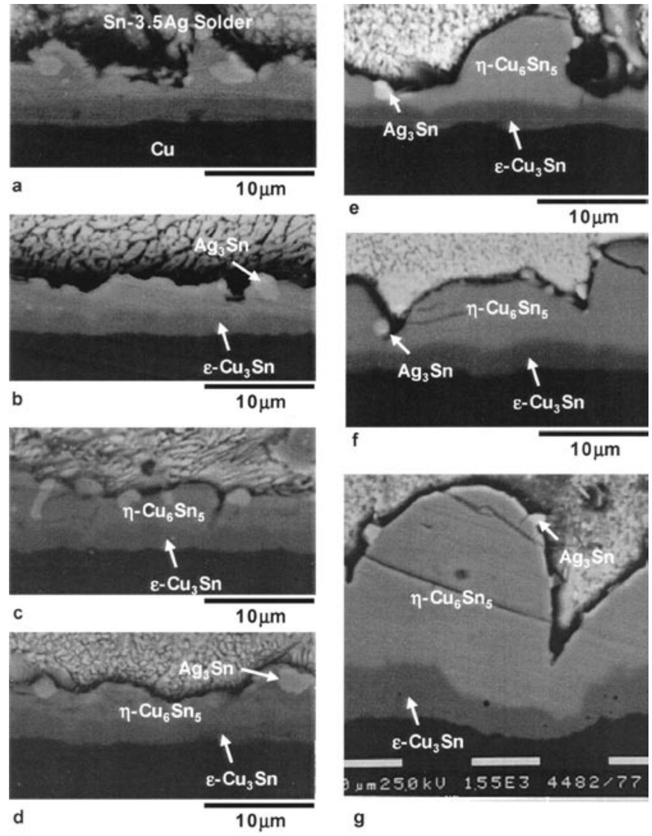

Fig. 4. SEM micrographs of IMCs after aging at 130°C for 800 h when initially soldered for (a) 30 sec, (b) 60 sec, (c) 90 sec, (d) 120 sec, (e) 10 min, (f) 1 h, and (g) 10 h. Note the presence of Ag_3Sn after aging.

Interfacial Microstructure during Aging

The IMCs formed after soldering continue to grow at the service temperature by interdiffusion between the elements of the solder and the substrate. Thus the interface takes on a more complicated microstructure. The interfacial microstructure depends on the initial state before aging determined by the soldering condition. The same specimens that were soldered in the previous section for 30 sec through 10 h were aged at 130°C for 100 h, 400 h, and 800 h, respectively. With an increase in aging time IMCs grew in all the specimens. However, the growth of IMCs showed a different behavior depending on the initial morphology. Figure 4 represents a typical interfacial morphology on aging at 130°C for 800 h. When the specimens soldered for shorter than 120 sec are aged in the solid state, the morphology of IMCs changed into a layer type from the initial columnar type while the grains of IMCs maintain a scallop type after aging when the soldering time was longer than 10 min.

The ε-Cu_3Sn phase that was detected only in the early soldering stage was observed in all the aged specimens. It is also notable that the Ag_3Sn particles precipitated near the interface between the η-Cu_6Sn_5 phase and the solder but not found inside IMCs. This

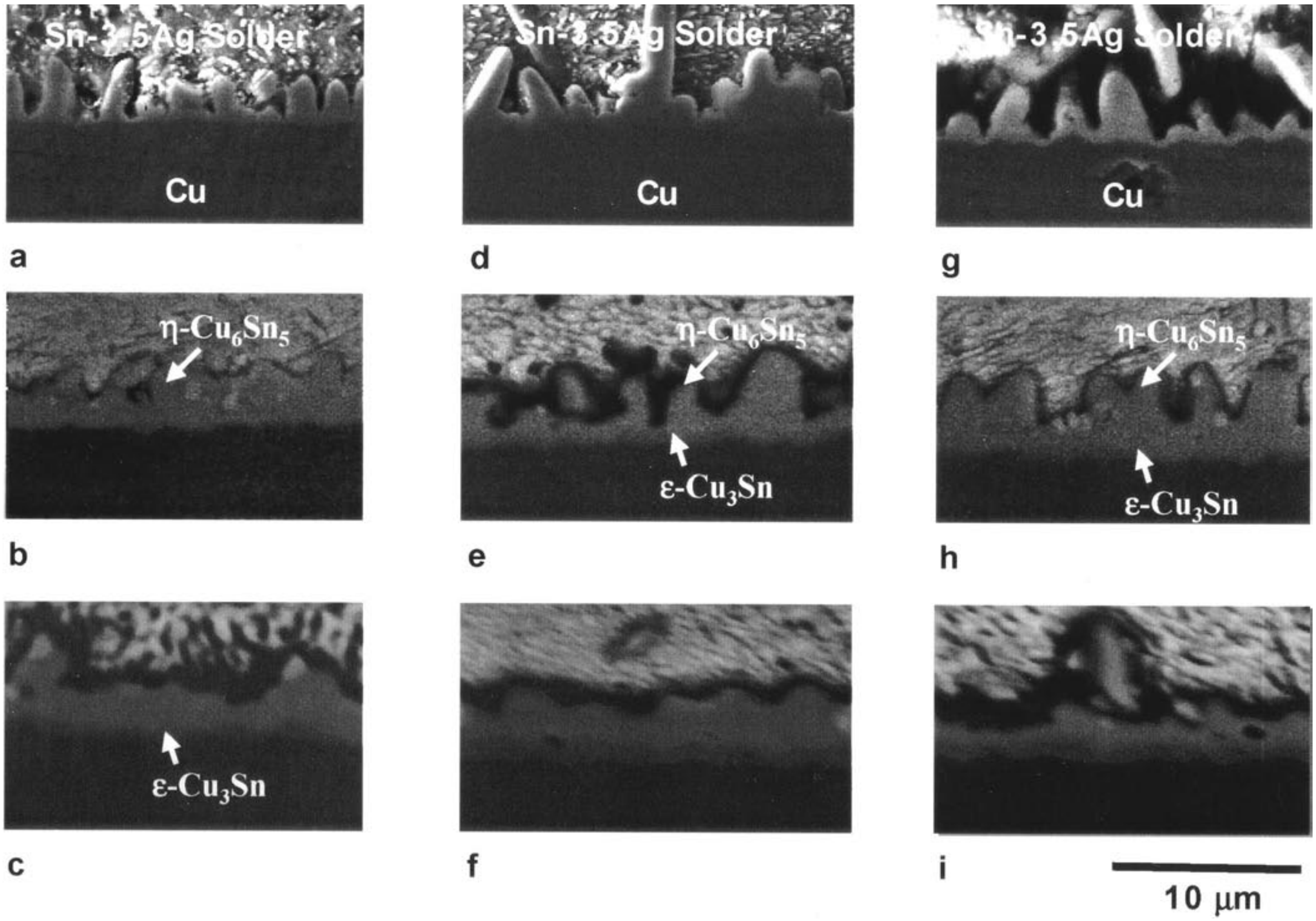

Fig. 5. Morphological change of interface with aging time: (a) 0 h, (b) 100 h, (c) 400 h after soldering for 60 s; (d) 0 h, (e) 100 h, (f) 400 h after soldering for 90 s; and (g) 0 h, (h) 100 h, (i) 400 h after soldering for 120 s. Aging at 130°C and soldering at 250°C.

has been observed in all the specimens aged for even different times of 100 h and 400 h. During aging, IMCs are observed to grow with a different morphology. The specimens having now a layer type of IMCs are those soldered shorter than 120 sec. The specimens keeping a scallop-type morphology are those soldered for a longer time. The morphological change during aging is caused by the solid/solid interfacial energy. Generally, the solid/solid interfacial energy is higher than the liquid/solid interfacial energy.[14] Thus in all the specimens, the interface between IMCs and the solder has a tendency to decrease its area during aging. It decreases the absolute area by a morphological change from columnar to layer in the case of Fig. 4a–d or by coarsening of IMC grains in the case of Fig. 4e–g. In the former case, the change is observed clearly in Fig. 5 where three sets of specimens soldered for 60 sec, 90 sec, and 120 sec, respectively, are aged for 100 h and 400 h. They show that the growth of IMCs is accompanied by growth of the layer in the region between separate columnar IMC grains rather than by coarsening of each IMC grain during aging. Thus the total thickness of the IMC layer is almost unchanged and it maintains a layer type on further aging for 800 h.

The schematic diagram of two types of growth is illustrated in Fig. 6. Figure 6a represents the growth behavior of IMCs in the aged specimens that were soldered for a short period of time, that is, from 30 sec to 120 sec, which is based on the micrographs of Fig. 5. The growth kinetics of IMCs in the region between grains is faster than the growth rate of each columnar grain. As a result, the morphology becomes a layer type from the columnar one. Figure 6b holds true for aging after the prolonged soldering. In this case, the growth of IMCs proceeds through coarsening of the grains. Thus the shape of IMC grains is preserved. The two types of growth is determined by the initial morphological difference whether the IMC grains are close enough to touch one another or not.

Growth Behavior of IMCs

The change of the thickness of IMCs in the liquid soldering is shown in Fig. 7a. The analysis of these data shows that the isothermal growth kinetics may be adequately modeled with a power law and the time exponent is calculated as about 0.4. It is important to remember that the growth was retarded around the time frame of 90 sec and 120 sec as pointed out earlier. Fig. 7b shows the total thickness change of IMCs including both η-Cu_6Sn_5 and ε-Cu_3Sn layers when the specimens were aged at 130°C up to 800 h after being

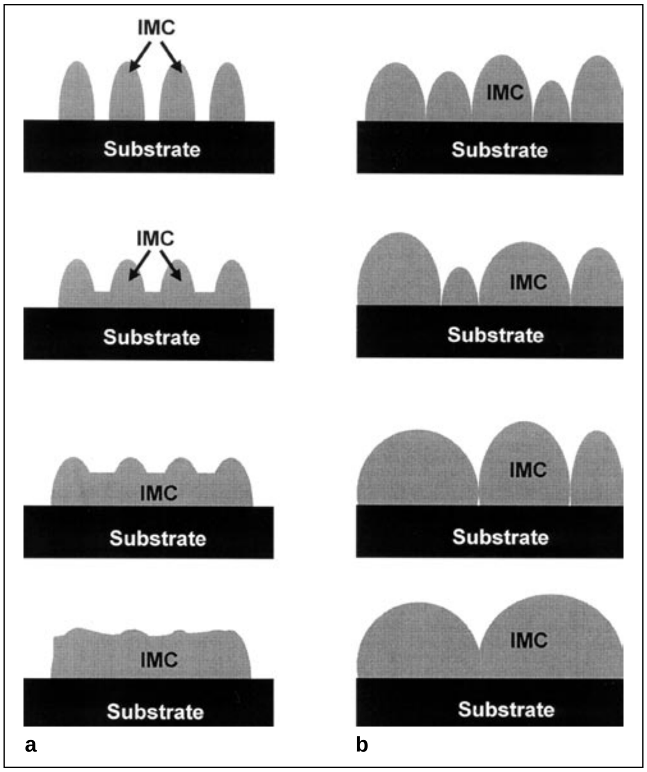

Fig. 6. Schematic diagram of two types of IMC growth mechanism during aging. Time scale increases from top to bottom. (a) is for specimens soldered for shorter than 120 s, and (b) is for specimens soldered for longer than 10 min.

soldered for different time intervals. The growth rate in aging was generally reduced because of the solid state diffusion compared with that of liquid soldering. After aging for 400 h, the total IMC thickness reached almost the same value in the specimens soldered less than 120 sec as shown in Fig. 5. The aging time up to 400 h corresponds to that of the interfacial morphological change from a columnar type to a layer type. The retarded growth kinetics of IMCs is notable, especially, during this time interval. In the specimens soldered longer than 10 min, the growth was observed to be continuous. In this case, IMCs coarsened by the ripening effect of the grains.

DISCUSSION

The reason the growth rate of IMCs is reduced during the morphological change is not clearly known yet. Here is the simple suggestion. It may result from the difference of diffusion path of Cu and the curvature between regions A and B as described in Fig. 8, where it was assumed that the diffusion of Cu is the rate-controlling step for growth of IMCs. Two kinds of fluxes, J_1 and J_2 exist. J_1 is the flux of Cu supplied from the substrate and J_2 is that from the region A into the region B by the concentration gradient due to the curvature difference. In the region A, the supply of Cu is made from the substrate (J_1) and also copper diffuses into the region B ($-J_2$). Therefore the total flux in the region A will be

$$J_A = J_1 - J_2 \quad (1)$$

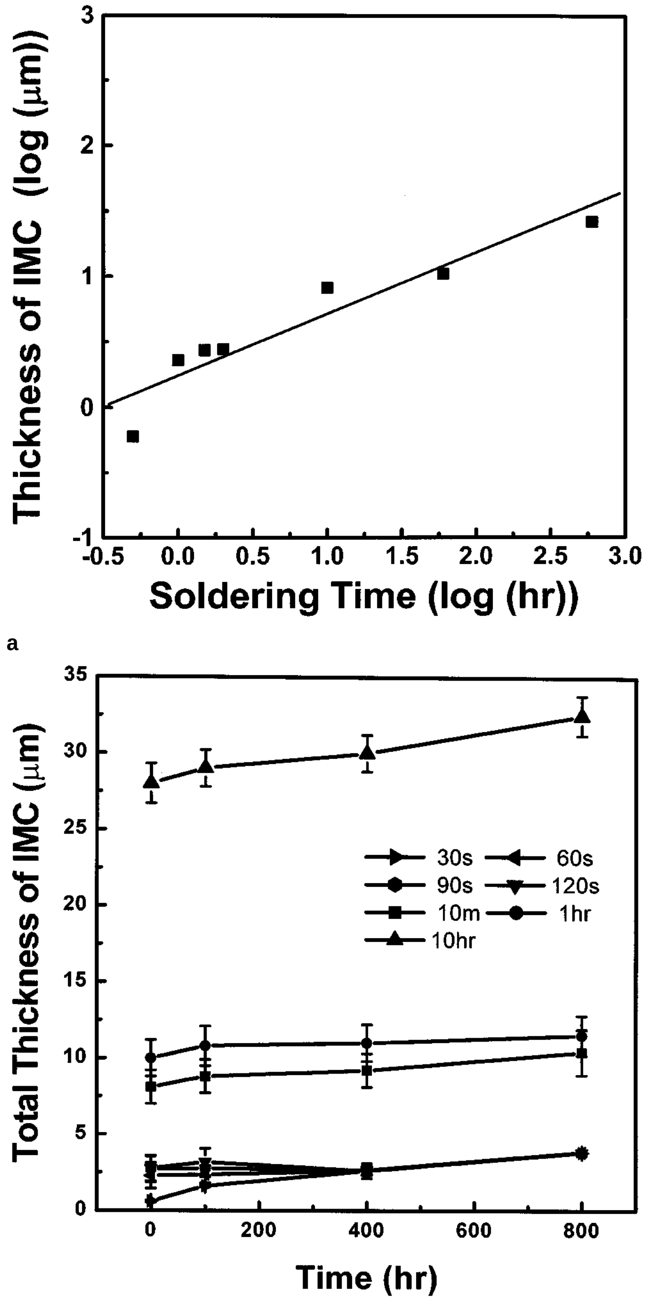

Fig. 7. (a) Change of thickness of IMC with soldering time; and (b) variation of total thickness of IMC during aging at 130°C. Initial soldering time is 30 sec, 60 sec, 90 sec, 120 sec, 10 min, 1 h, and 10 h.

while the total flux in the region B is expressed as follows:

$$J_B = J_1 + J_2 \quad (2)$$

According to the Fick's first law, the flux of Cu to the perpendicular direction of the substrate is

$$J = -D\frac{dC}{dx} \quad (3)$$

where D is an appropriate diffusion coefficient. The flux from IMCs occurs both through the grain bound-

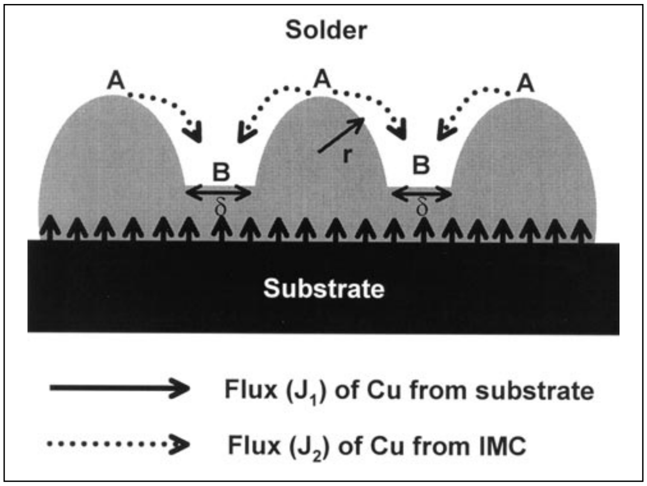

Fig. 8. Schematic model of Cu flux during aging when soldered for a short time less than 120 sec.

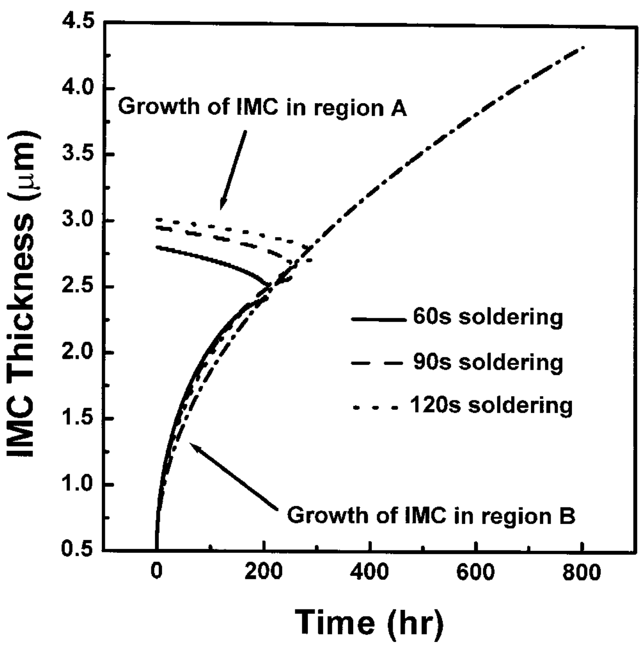

Fig. 9. Effect of initial soldering time at 250°C on thickness of IMC calculated with aging time at 130°C.

ary diffusion and through the volume diffusion. However, the diffusion through the grain boundary is dominant in this study. The model of the growth of IMCs in the solder joint has been made using the grain boundary diffusion. In this work, the flux equation through the grain boundary diffusion proposed by Schaefer et al.[7] is applied to flux J_1:

$$J_1 \approx \left\{ D^{GB} \left(\frac{\delta \Delta C}{\sqrt{3}k} \right) \right\} \frac{1}{x^2} \quad (4)$$

where D^{GB} is a diffusivity of Cu through the grain boundary of IMCs, δ is a distance between grains, k is a variable scallop shape ratio dependent on positions of A and B, and x is an average thickness of IMCs. The concentration difference, ΔC, in this flux is obtained from the diffusion couple of solder/η-Cu_6Sn_5/Cu.

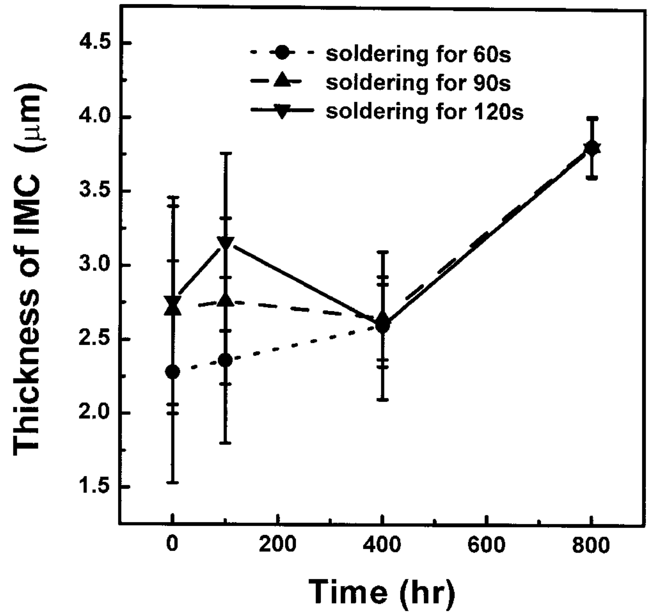

Fig. 10. Variation of total thickness of IMC during aging at 130°C. Initial soldering time is 30 sec, 60 sec, 90 sec, and 120 sec.

The flux J_2 can be obtained from the Gibbs Thompson equation.[14,15] The radius of curvature in the region A is smaller than that in the region B and thus the flux J_2 flows from the region A to B. And the concentration of Cu in the surface of IMC grains is expressed as follows:

$$C = C_0 \exp\left(\frac{2\gamma\Omega}{rRT} \right) \quad (5)$$

with

$$C \cong C_0 \left[1 + \frac{2\gamma\Omega}{rRT} \right] \text{ if } \frac{2\gamma\Omega}{rRT} << 1 \quad (6)$$

where C_0 is the equilibrium concentration of Cu with respect to a flat interface of IMCs, γ is the interfacial energy per unit area between IMCs and the solder, Ω is the molar volume of IMCs, and RT have their usual meanings. The radii in A and B are assumed as r and infinite, respectively. Therefore the concentration difference, ΔC_r, between A and B can be written in the following way.

$$\Delta C_r \approx -\frac{2\gamma C_0 \Omega}{rRT} \quad (7)$$

Because the distance for the movement from A to B is δ/2, J_2 is expressed as follows:

$$J_2 = -D^{vol} \frac{4\gamma C_0 \Omega}{\delta rRT} \quad (8)$$

Therefore, if Eqs. 4 and 8 are substituted for fluxes of J_1 and J_2, respectively, then J_A and J_B can be obtained. Using Eqs. 1 and 2, the growth behavior in A and B is predicted with aging time. In this calculation, the parameters used are as follows. The concentration difference, ΔC, in Eq. 4 is calculated as 0.539 and the equilibrium concentration of Cu in the η-Cu_6Sn_5 phase, C_0 is calculated as 0.006 at 130°C. The activation energy for the grain boundary diffusion, D^{GB}, of Cu in the η-Cu_6Sn_5 phase is taken as one third of the activation energy in the apparent volume diffusion coefficient published by Onishi and Fujibuchi.[1] Then, the value of D^{GB} is obtained as 9.792×10^{-13} cm²/s at 130°C. The interfacial energy between the solid η-Cu_6Sn_5 and the solid solder is hard to know and therefore an approximate value of 1000 erg/cm² has been assumed as with the incoherent solid/solid interfacial energy.[16] The volume diffusion coefficient of Cu, D^{vol}, in the Sn-based solder matrix is 1.2×10^{-11} cm²/s at 130°C.[4] The molar volume of the η-Cu_6Sn_5 phase is taken as 117.87 cm³/mole.[8] Therefore, each flux in the region A and the region B can be calculated and compared quantitatively, though not entirely accurate.

The variation of IMC thickness in regions of A and B is calculated in Fig. 9 with aging time. The variation of IMC thickness in region of A agreed well with the measured thickness variation shown in Fig. 10. The thickness of IMCs in region B increases abruptly but it is almost constant in region A. The specific time when the radius of curvature in A becomes almost equal to that in B has been calculated: about 211 h when soldered for 60 sec, 253 h in the case of 90 sec, and finally 292 h in the case of 120 sec. After this specific time, IMCs grow as a layer type because the radii of curvature in both regions of A and B are now equal. Therefore, when aged longer than 400 h, all IMCs are supposed grow in the same manner.

SUMMARY

The formation and the growth of IMCs at the interface between the Sn-3.5Ag solder alloy and the Cu substrate was investigated both in soldering and in aging. The interfacial morphology changed during soldering with increased time up to 10 h. The interface maintained a columnar type in the early stage of soldering but transformed to the scallop type in the later stage of soldering. The morphological change resulted from the competition between the growth of IMCs and the dissolution of Cu from the substrate and the IMCs. Initially, the growth of IMC was dominant. In the second stage, the growth of IMCs and the dissolution of Cu from IMCs took place simultaneously. And, in the third stage, IMCs started to grow again. When the soldered specimens were aged at 130°C up to 800 h, the morphology of IMCs also changed depending on the initial soldering condition. The morphology of IMCs changed to a layer type from the columnar type or to a more coarsened scallop type. It was revealed by calculation of fluxes that the growth in aging showed a different behavior depending on the initial soldering condition.

ACKNOWLEDGEMENTS

This study has been financially supported by the Korea Science and Engineering Foundation (No. 1999-2-301-007-4).

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