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Effect of isothermal aging on intermetallic compound layer growth at the interface between Sn-3.5Ag-0.75Cu solder and Cu substrate

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Intermetallic compound (IMC) growth during solid-state isothermal aging at temperatures between 100 and 200°C up to 60 days for Sn-3.5Ag-0.75Cu solder on Cu substrate was investigated. A quantitative analysis of the IMC layer thickness as a function of aging time and temperature was performed. Diffusion couples showed a composite IMC layer comprised of Cu_6Sn_5 and Cu_3Sn. After isothermal aging at temperature over 120°C, the solder/Cu interface exhibited a duplex structure of Cu_6Sn_5 and Cu_3Sn intermetallics. The growth of IMCs followed diffusion-controlled kinetics and the layer thickness reached 13 μm after 60 day of aging at 170°C. The apparent activation energies calculated for the growth of the total IMC ($Cu_6Sn_5 + Cu_3Sn$), Cu_6Sn_5 and Cu_3Sn intermetallic are 62.6, 49.1 and 80.1 kJ/mol, respectively. © *2004 Kluwer Academic Publishers*

1. Introduction

Recently, many different solder alloys have been proposed as potential Pb-free solder replacements, owing to environmental and health concerns [1–8]. Among several candidate alloys, the Sn-Ag-Cu alloy family is believed to be the first choice with the combination of other alloys such as Sn-Ag-Bi, Sn-Bi, Sn-Zn-Bi and Sn-Cu [6–16]. In 2000, NEMI (National Electronics Manufacturing Initiative) recommended to replace eutectic Sn-Pb alloy by eutectic Sn-Ag-Cu alloy in reflow soldering and eutectic Sn-Cu alloy in wave soldering. The benefits of Sn-Ag-Cu alloy are its relatively low melting temperature compared with Sn-Ag eutectic alloy and its superior mechanical properties, as well as relatively good solderability [17].

During soldering, the solder alloy reacts with the substrate to form IMCs at the joint interface. While forming a thin IMC layer, by the reaction between solder and substrate, it is desirable to achieve a good metallurgical bond. However, excessive IMC growth may have a deleterious effect [17–19]. In other words, the thick intermetallic growth degrades interface integrity, owing to the brittle nature of IMCs and also the mismatches in physical properties such as thermal expansion coefficient and elastic modulus. Therefore, it is necessary to understand the factors that control the kinetics of interfacial reaction.

Many studies have been performed on the Sn-Ag and Sn-Ag-Cu system Pb-free solder alloys such as microstructures, mechanical properties and interfacial reactions [7, 13, 17, 21]. However, a growth kinetics evaluation on the interfacial reaction between Sn-Ag-Cu solder and Cu substrate has not been sufficiently performed. Lee *et al.* [15] studied the kinetics of intermetallic growth at the Sn-3.8Ag-0.7Cu solder/electroplated Cu substrate interface during solid-state aging at 125, 150 and 170°C up to 1500 h. They found the grow rates of IMC layers to follow parabolic kinetics. The activation energy value for the growth of total Cu-Sn IMC found by them was 92.6 kJ/mol (which the author calculated from Table I in reference [15]). But, the resulting activation energy of 92.6 kJ/mol is considered too high when compared with other Pb-free solder/Cu system [13, 20, 21]. Therefore, the objective of this study focuses on the kinetics of the Cu-Sn IMCs growth for the Sn-3.5Ag-0.75Cu solder/Cu system during solid-state aging. And, the activation energy for intermetallic phase growth was determined from the temperature dependence of the square of the layer growth rate.

2. Experimental procedures

The substrates used in this study were pure Cu sheets measuring 10 × 10 × 0.2 mm. These Cu substrates were then cleaned with acetone and etched in a 10% H_2SO_4–90% CH_3OH solution to remove surface oxide and contaminates. Also, the Sn-3.5Ag-0.75Cu solder used in this study was prepared from high purity materials (Sn, Ag and Cu; 99.99 mass%). The Sn-3.5Ag-0.75Cu/Cu joint samples were prepared by reflowing solder on Cu substrates. Solder sheets and Cu plates were ultrasonically cleaned in ethanol before soldering. Rosin mildly activated (RMA) flux was used in this test. The substrates were heated on a hot plate to 40°C above the melting temperature of the solder and the temperature was kept stable within ±3°C. Each reaction couple was then placed in an oven maintained at a constant aging temperature. The temperature homogeneity and stability for each oven was better than ±1°C. The aging temperatures were 100, 120, 150, 170 and 200°C. The time periods were 0 to 60 days with a tracking error of ±30 min.

Upon completion of the aging step, the samples were then mounted in epoxy and metallographically polished in preparation for characterization. First, the epoxy-mounted samples were cut by a diamond saw and abraded by coarse sandpapers. Then, the samples were finished by 0.3 μm Al_2O_3 powder polishing. Before scanning electron microscopy (SEM) observation, samples were slightly etched by the use of 4% HNO_3–1% HCl–95% CH_3OH solution for several seconds to delineate the morphology of the compound layer. In

TABLE I The square of growth rate constants (k^2) and linear correlation coefficients (R^2)

Temperature (°C)	Intermetallic	k^2 (10^{-19} m²/s)	R^2
100	Cu_6Sn_5	16.4	0.99
	Total ($Cu_6Sn_5 + Cu_3Sn$)	38.61	0.99
120	Cu_6Sn_5	21.57	0.99
	Cu_3Sn	2.56	0.95
	Total ($Cu_6Sn_5 + Cu_3Sn$)	116.26	0.99
150	Cu_6Sn_5	39.81	0.98
	Cu_3Sn	21.93	0.99
	Total ($Cu_6Sn_5 + Cu_3Sn$)	259.98	0.99
170	Cu_6Sn_5	89.37	0.98
	Cu_3Sn	45.1	0.98
	Total ($Cu_6Sn_5 + Cu_3Sn$)	1375.64	0.99
200	Cu_6Sn_5	570.56	0.98
	Cu_3Sn	172.46	0.99

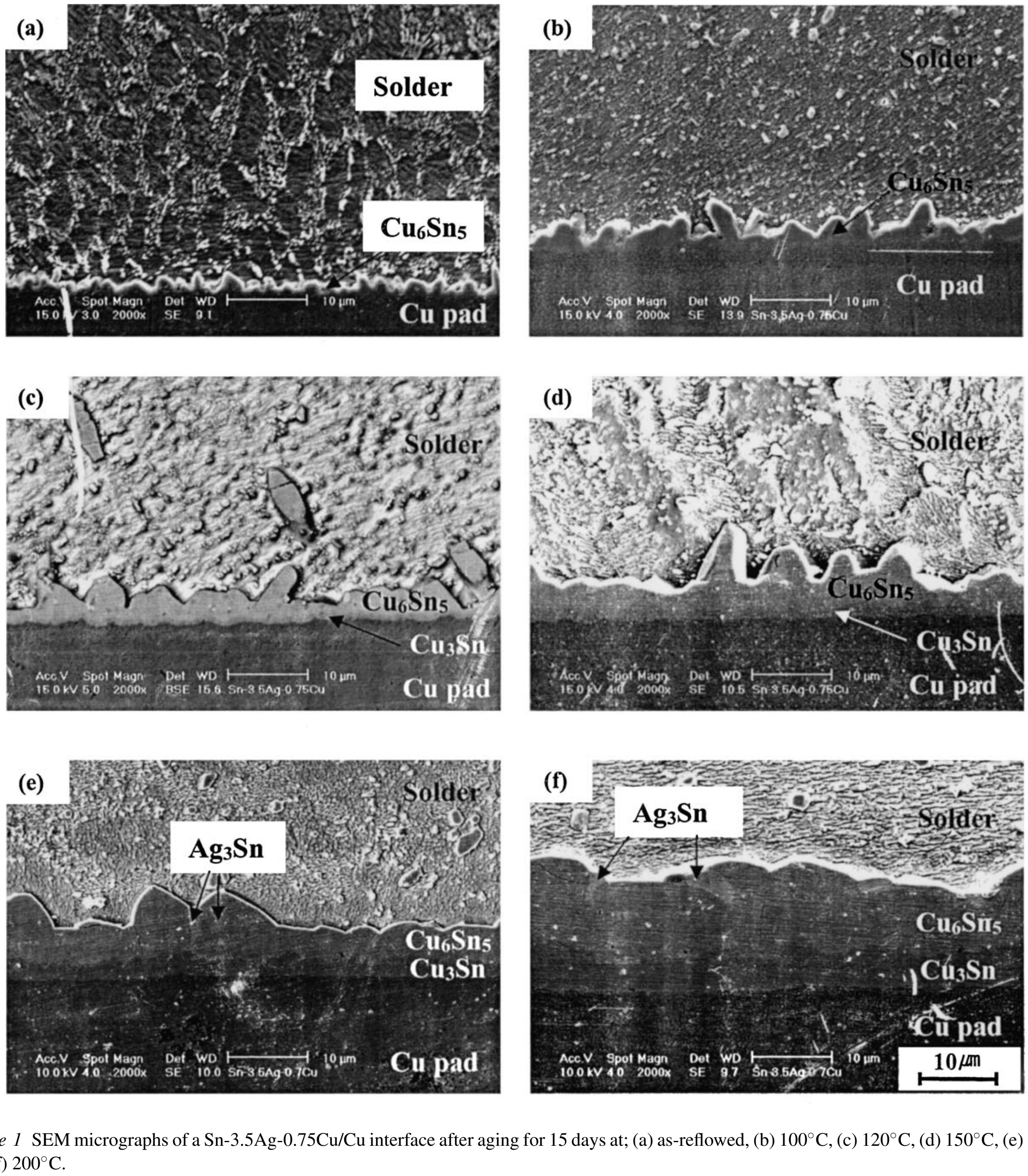

Figure 1 SEM micrographs of a Sn-3.5Ag-0.75Cu/Cu interface after aging for 15 days at; (a) as-reflowed, (b) 100°C, (c) 120°C, (d) 150°C, (e) 170°C and (f) 200°C.

order to examine the growth kinetics of IMCs during interfacial reactions, the cross sections of all specimens were observed with SEM. Energy dispersive X-ray spectroscopy (EDS) analysis of each intermetallic phase were performed. The thickness of IMC layer was defined as the total area occupied by that phase divided by the length. The phases at the interface were identified using the X-ray diffraction (XRD) analysis. The specimens for XRD were prepared by mechanically removing the solder and etching away the remaining solder part.

3. Results and discussion

Fig. 1 shows the SEM micrographs of Sn-3.5Ag-0.75Cu/Cu reaction couples after 15 days of aging at various temperatures (100–200°C). During the reflow, the solder was in the molten state and the formation of Cu_6Sn_5 IMC had a round scallop-type morphology. In solid-state aging, all these scallops changed to a layered-type morphology. Fig. 1a is an SEM micrograph of the intermetallic phases formed at the solder/Cu interface during the initial soldering operation (no aging). In the as-soldered joints, the Cu_6Sn_5 IMC located at the solder/Cu interface was identified by means of EDS analysis and the thickness of the intermetallics was approximately 0.7 μm, but Cu_3Sn IMC was not found as shown in Fig. 1a. The Cu_3Sn layer was absent at all time periods for the aging temperature of 100°C. After isothermal aging at temperature over 120°C, the solder/Cu interface exhibited a duplex structure of Cu_6Sn_5 and Cu_3Sn intermetallic as shown in Fig. 1c–f. A similar result was also reported by Tu and Thompson [22]. They studied the phase transformation between Cu_3Sn and Cu_6Sn_5 with increasing aging temperature, and reported that Cu_3Sn formed and grew at higher temperature (115–150°C). Generally, below about 350°C, Cu_6Sn_5 and Cu_3Sn are the main reaction products. Most Sn-based solder alloys form these two reaction layers at the interface between solders and Cu. Intermetallic growth in this solder system is consistent with intermetallic growth in other solders previously studied [7, 13, 15, 21]. Although Cu_3Sn was not observed at the low temperatures, Cu_3Sn is known to form during soldering, based on previous TEM study of Sn-3Ag-(0,3,6)Bi solder/Cu system [23]. The Cu_3Sn layer is probably not observed for short aging times and low temperatures due to the limited spatial resolution of the SEM. Reaction at such an elevated temperature for a longer time caused the appearance of a very thick and uniform IMC layer (Fig. 1e and f). The total IMC thickness was approximately 13 μm in joint aged at 170°C for 60 days.

Fig. 2 shows the SEM micrographs of IMC layers for the interface between solder and Cu substrate aged at 200°C for different aging times. Two IMC layers, Cu_6Sn_5 and Cu_3Sn, formed at the interface between solder and Cu substrate in all the reaction couples after isothermal aging at 200°C. And, total IMC thickness increased with aging time. The aged solder joint comprises the Cu substrate, the Cu_3Sn intermetallic layer, the Cu_6Sn_5 intermetallic layer, the Ag_3Sn particles embedded with the Cu_6Sn_5 intermetallic layer, the Ag_3Sn particles in the solder, and the solder. With increased aging time, the Ag_3Sn particles became more prevalent in the Cu_6Sn_5 intermetallic layer. This observation is

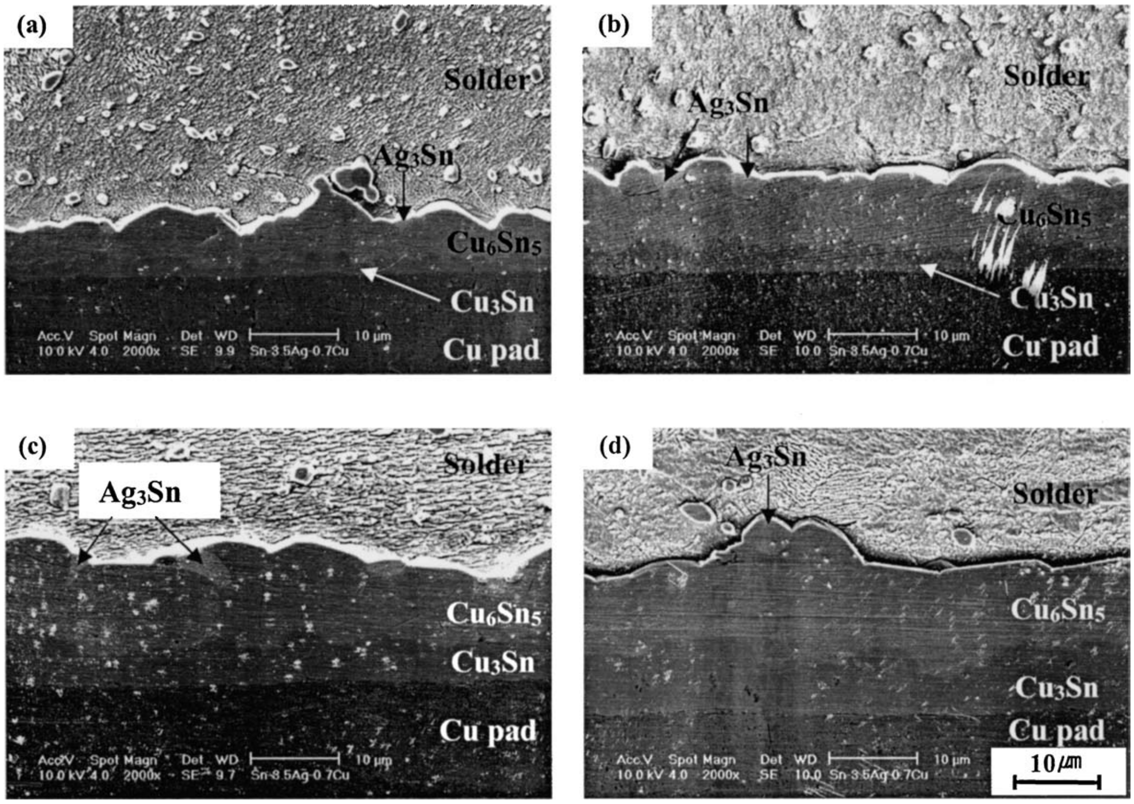

Figure 2 SEM micrographs of a Sn-3.5Ag-0.75Cu/Cu interface aged at 200°C with various aging times; (a) 3 days, (b) 6 days, (c) 15 days and (d) 30 days.

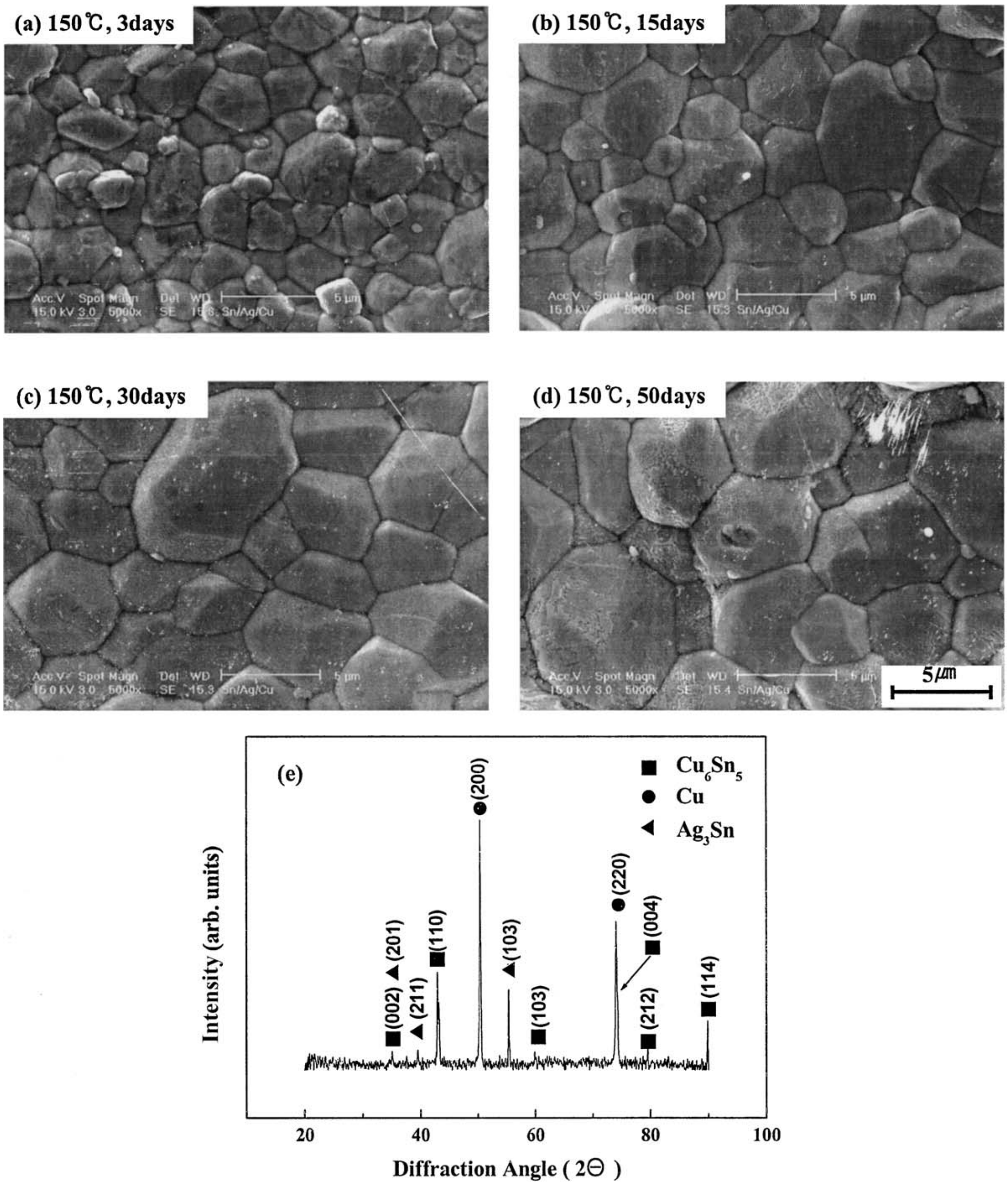

Figure 3 (a–d) Top views of IMCs and (e) X-ray diffraction pattern of (d).

consistent with a previous study on the intermetallic growth in the eutectic Sn-Ag/Cu diffusion couple [7, 24]. Also, this is in agreement with the suggestion that Sn diffuses the intermetallic layers to react with the Cu substrate. The existence of Ag_3Sn particles within the Cu_6Sn_5 intermetallic layer is related to the depletion of Sn close to intermetallic layer. The thickness of the total Cu-Sn, Cu_6Sn_5 and Cu_3Sn reached 15.3, 10.6 and 4.7 μm after 15 days of aging at 200°C, respectively (Fig. 2c). As shown in Figs 1 and 2, the thickness of the IMC layer increased with aging temperatures and times.

Fig. 3a–d represent the top views of Cu_6Sn_5 intermetallics after the samples were aged for various aging times at 150°C, followed by solder etched away. On the Cu substrate, the hexagonal-shape intermetallic can be seen in Fig. 3. These Cu_6Sn_5 grain size increased with increasing aging times. The Cu_6Sn_5 intermetallic surface shown in Fig. 3d was then used to obtain the X-ray diffraction pattern of Cu_6Sn_5 intermetallic (Fig. 3e).

Generally, the thickness of a reaction layer in the diffusion couples can be expressed by the simple parabolic equation;

$$W = kt^n \tag{1}$$

where W is the thickness of the reaction layer; k is the growth rate constant; n is the time exponent; and t is the reaction time.

The thickness of the IMC layer as a function of the square root of time for each of the aging temperatures is shown in Fig. 4. The mean thickness of interfacial IMC layer was found to increase linearly with the square root of aging time and the growth was faster for higher aging

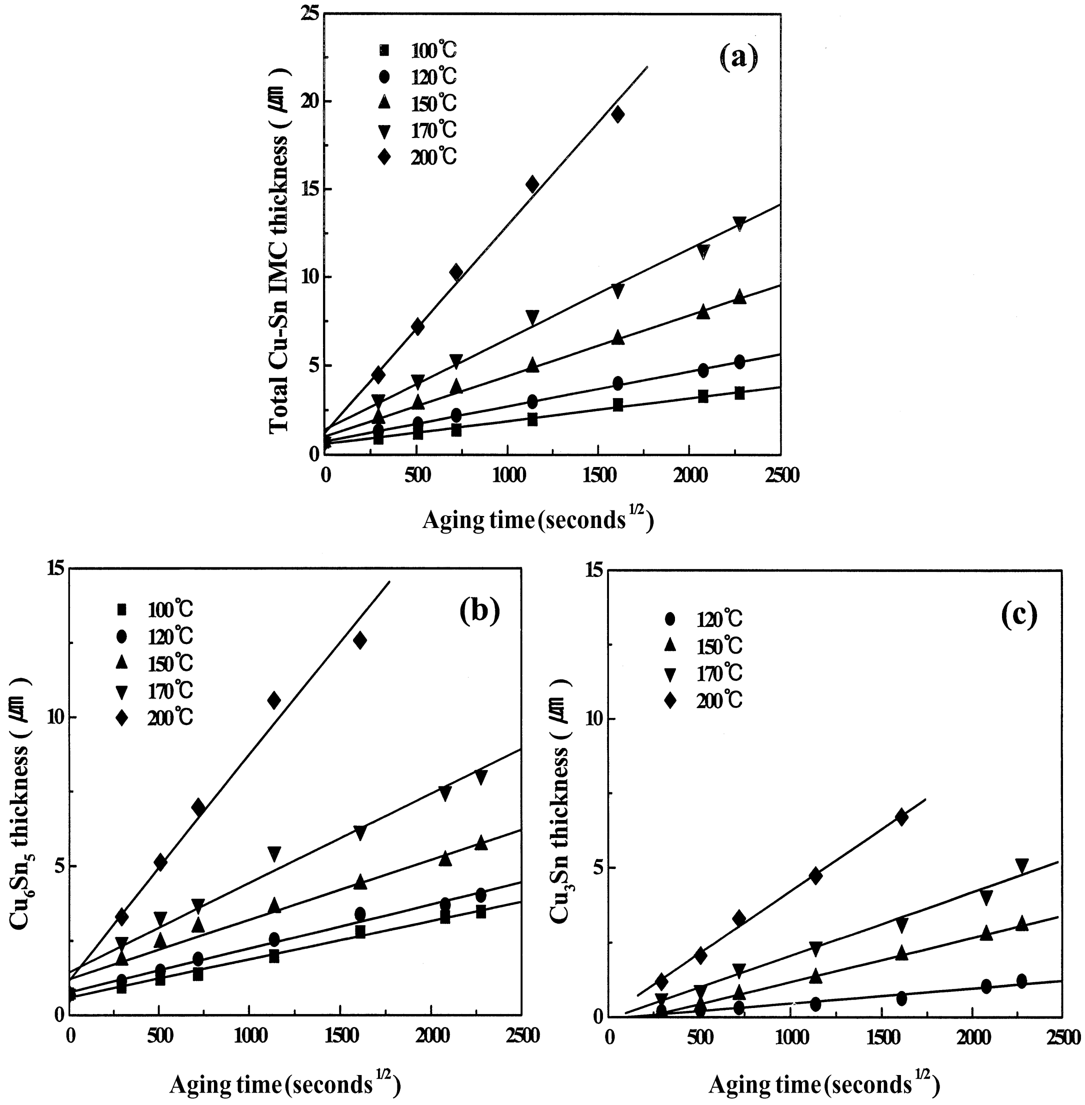

Figure 4 Intermetallic compound layer thickness with various times and temperatures; (a) Total ($Cu_6Sn_5 + Cu_3Sn$) IMC, (b) Cu_6Sn_5 and (c) Cu_3Sn.

temperatures. This means that these layers growth is controlled by the volume diffusion mechanism. Fig. 4b and c shows the IMC layer thickness (W) of Cu_6Sn_5 and Cu_3Sn phases as a function of the square root of the reaction time ($t^{1/2}$). The layer growth of the Cu_3Sn was slower than that of the Cu_6Sn_5. And, the Cu_3Sn intermetallic layer was not observed in the micrographs of samples aged at 100°C.

The growth rate constant was calculated from a linear regression analysis of W vs $t^{0.5}$, where the slope $= k$. Table I lists the growth rate constants calculated for total IMC ($Cu_6Sn_5 + Cu_3Sn$), Cu_6Sn_5 and Cu_3Sn at different aging temperatures. Most of the linear correlation coefficient values (R^2) for these plots were greater than 0.98. This confirms that the growth of the IMC layers is diffusion-controlled over the temperature range studied.

To evaluate the time exponents, the growth kinetics at each temperature was represented by Equation 2;

$$Y = At^n + B \tag{2}$$

where Y is the layer thickness; t is reaction time; n is the time exponent; B is the layer thickness at $t = 0$; and A is a constant. This equation was converted into a logarithmic expression;

$$\ln(A - B) = n \ln t + \ln A \tag{3}$$

The time exponent (n) was obtained from the slope of the plot of ln (Y-B) vs. ln t Listed in Table II shows the time exponents determined by the linear regression analysis of each aging temperature using Equation 3. The diffusion processes appeared to be largely responsible for growth of the intermetallic compound layer, although the time exponents were not exactly 0.5.

The temperature variations of k^2 for the IMC layer growth can be expressed by the following Arrhenius

TABLE II Time exponent (n) as a function of aging temperature

Temperature (°C)	n
100	0.60
120	0.49
150	0.43
170	0.40
200	0.48

TABLE III Activation energy (Q) for the growth of Cu-Sn IMC layers together with values reported in previous work

Solder/substrate	Temperature range (°C)	Reaction time (day)	Intermetallics	Activation energy (kJ/mol)	Diffusion couple method	Reference
Sn-3.5Ag-0.75/Cu	100–200	0–60	$(Cu_6Sn_5 + Cu_3Sn)$	62.6	Spreading	
	100–200	0–60	Cu_6Sn_5	49.1		This work
	100–200	0–60	Cu_3Sn	80.1		
Sn-3.8Ag-0.7Cu/Cu	125–170	0–1500 h	$(Cu_6Sn_5 + Cu_3Sn)$	92.6	Flip-chip	Lee *et al.* [15]
	125–170	0–1500 h	Cu_6Sn_5	83.9		
	125–170	0–1500 h	Cu_3Sn	102		
Sn-3.5Ag/Cu	70–170	0–100	$(Cu_6Sn_5 + Cu_3Sn)$	64.82	BGA type	Lee *et al.* [21]
Sn-3.5Ag/Cu	343–478	0–400	$(Cu_6Sn_5 + Cu_3Sn)$	59	Dipping	Vianco *et al.* [13]
Sn-3.5Ag/Cu	383–481	0–32	Cu_6Sn_5	107.06	Sandwich type	Flanders *et al.* [7]
	403–481	0–32	Cu_3Sn	70.41		

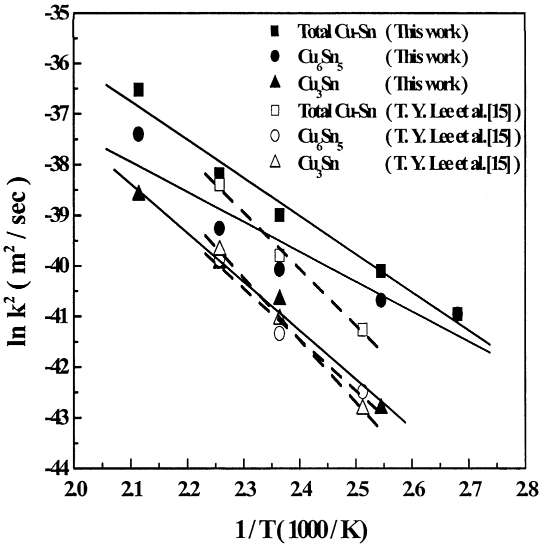

Figure 5 Arrhenius plot of the intermetallic compound layer growth (closed symbol: this work and opened symbol: Lee *et al.* [15]'s result).

Equation 4.

$$k^2 = k_0^2 \exp\left(\frac{-Q}{RT}\right) \tag{4}$$

where k^2 is the square of growth rate constant (m^2/s); k_0^2 is the frequency factor; Q is the activation energy; R is the gas constant (8.314 J/mol-K); and T is the aging temperature (absolute units). The activation energies were calculated from the slope of the Arrhenius plot using a linear regression model.

Fig. 5 shows the Arrhenius plots for the growth of the total IMC ($Cu_6Sn_5 + Cu_3Sn$), Cu_6Sn_5 and Cu_3Sn intermetallic layers with the data from previous work [15]. Although some scatter does occur in the data, it follows the Arrhenius equation. The apparent activation energies calculated for the growth of the total IMC ($Cu_6Sn_5 + Cu_3Sn$), Cu_6Sn_5 and Cu_3Sn intermetallic are 62.6, 49.1 and 80.1 kJ/mol, respectively. Table III lists the values of the activation energy (Q) obtained from the temperature dependence of k^2, with the data from previous works [7, 13, 15, 21]. The Q-values for the growth of the total Cu-Sn, Cu_6Sn_5 and Cu_3Sn IMC found by Lee *et al.* [15] were 92.6, 83.9 and 102 kJ/mol, respectively (Fig. 5 and Table III). They used a diffusion couple of Sn-3.8Ag-0.7Cu/electroplated Cu and the solder bumps were reflowed twice. Also, the temperature profile of their study had a peak temperature of 240°C, 60 sec above the melting temperature of the solder. And then, the samples were annealed at three different temperatures (120, 150 and 170°C) for 500, 1000 and 1500 h. The thickness of the Cu-Sn intermetallics formed during the initial soldering operation (no aging) found by us and Lee *et al.* [15] were 0.7 and 2.72 μm, respectively. Therefore, their results had a low growth rate constant (k) at low temperature due to the higher initial IMC thickness (Fig. 5). Vianco *et al.* [13] studied the growth kinetics of the Cu-Sn IMC in the eutectic Sn-Ag/Cu system. The Q-value for the growth of the total Cu-Sn intermetallic found by them was about 59 kJ/mol. Their diffusion couples were prepared using hot dipping. Our rsults are in good agreement with the results of them. However, the Q-value for the growth of the Cu_6Sn_5 IMC found by Flanders *et al.* [7] was 107.06 kJ/mol. The diffusion couple of them was a sandwich type sample using double reflow processes and the reflow temperature was 230°C (reflow time: 60–90 sec). And, one of the important aspects of measuring the IMC layer thickness and comparing the data of the IMC growth kinetics is the method utilized. Lee *et al.* [15] and Lee *et al.* [21] measured the thickness by using digital images in which the area in the IMC image was divided by the interface length. On the other hand, Vianco *et al.* [13] and Flanders *et al.* [7] measured the thickness by one dimensional measurements of the IMC layer at different positions along the interface and reported the averages of IMC thickness. In the result, the discrepancy among the activation energies is due to the differences in the solder, diffusion couple method, aging conditions (temperatures and times) and analytical method used.

4. Conclusion

IMC layer growth between Sn-3.5Ag-0.75Cu solder and Cu substrate was examined as a consequence of solid-state isothermal aging. The isothermal aging conditions ranged from 100 to 200°C and time period of from 0 and 60 days. After isothermal aging at temperature over 120°C, the solder/Cu interface exhibited a duplex structure of Cu_6Sn_5 and Cu_3Sn intermetallics. Cu_6Sn_5 forms adjacent to the solder matrix and Cu_3Sn forms adjacent to the Cu substrate. After isothermal aging, the interface between the IMC and bulk solder becomes smoother. A quantitative analysis of the total IMC layer thickness as a function of time and temperature was performed. The increase of IMC thickness during aging follows parabolic relationship with time. In addition, the good linear correlation of the results indicates that the formation of IMC layer is mainly controlled by diffusion mechanism. The apparent activation energies calculated for the growth of the total IMC ($Cu_6Sn_5 + Cu_3Sn$), Cu_6Sn_5 and Cu_3Sn intermetallic are 62.6, 49.1 and 80.1 kJ/mol, respectively.

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