

INTERFACIAL REACTIONS BETWEEN SN-58MASS%BI EUTECTIC SOLDER AND (CU, ELECTROLESS NI-P/CU) SUBSTRATE

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ABSTRACT

The growth kinetics of intermetallic compound layers formed between eutectic Sn-58Bi solder and (Cu, electroless Ni-P/Cu) substrate were investigated at temperature between 70 and 120 °C for 1 to 60 days. The layer growth of intermetallic compound in the couple of the Sn-58Bi/Cu and Sn-58Bi/electroless Ni-P system satisfied the parabolic law at given temperature range. As a whole, because the values of time exponent (n) have approximately 0.5, the layer growth of the intermetallic compound was mainly controlled by volume diffusion over the temperature range studied. The apparent activation energies of Cu₆Sn₅ and Ni₃Sn₄ intermetallic compound in the couple of the Sn-58Bi/Cu and Sn-58Bi/electroless Ni-P were 127.9 and 81.6 kJ/mol, respectively.

KEYWORDS

tin-58bismuth solder, growth kinetics, intermetallic compound, time exponent(n), activation energy

1. Introduction

Sn-Bi, Sn-Ag and Sn-Zn[1-3] eutectic and near eutectic alloys are already used in some applications for the specific advantages they offer over eutectic Sn-Pb, such as lower process temperatures, compatibility with particular substrates, or superior reliability under certain conditions[4]. Especially, Sn-58Bi eutectic solder is a low melting point lead free solder developed for step soldering processes. The low melting point of this solder makes it suitable for soldering temperature-sensitive components and substrates. Also, when compared to the Sn-Pb eutectic solder, the Sn-58Bi eutectic solder offers a higher strength and superior creep resistance but a lower ductility[5-9]. During soldering, the solder alloy melts and then reacts with the substrate to form intermetallic compounds at the joint interface. Excessively thick reaction layers which grow between solder and substrate can significantly degrade the physical and mechanical properties of the solder joints, particularly in high impact load environments[10]. Therefore, it is necessary to understand and control the factors that govern the kinetics of interfacial reaction.

Some studies have been performed on the interfacial reactions between Sn-58Bi eutectic solder and (Cu, Ni) substrates. Vianco et al.[11] studied the kinetics of intermetallic compound layer growth by solid state reactions between Sn-58Bi solder and Cu substrate. They found the growth process of intermetallic layers to follow diffusion mechanism. Also, Chen et al.[12] studied the reactions between Sn-58Bi solder and pure Ni substrate, and found that only Ni_3Sn_4 formed. Nevertheless, no other information is yet available on the interfacial reaction between Sn-58Bi solder and electroless Ni-P/Cu substrate.

This study focuses on the growth kinetics of Cu_6Sn_5 and Ni_3Sn_4 intermetallic compounds for Sn-58Bi solder/(Cu, electroless Ni-P/Cu) system during solid-state aging. The growth rate constants of Cu_6Sn_5 and Ni_3Sn_4 intermetallics were measured as a function of time and temperature, and the activation energies for intermetallic growth were calculated by the Arrhenius equation.[13]

2. Experimental Procedures

The Sn-58Bi/Cu and Sn-58Bi/electroless Ni-P/Cu(Ni-P layer thickness : 5~7 μm) couples were prepared by spreading method.[3] Solder joints were cross-sectioned for examination both immediately after being reflowed and after being aged in a furnace at 70, 90, 100, and 120 $^\circ\text{C}$ for times ranging from 1 to 60 days respectively. Isothermal aging of diffusion couples were performed in air furnaces with a temperature stability of $\pm 1^\circ\text{C}$. The interface was examined by the scanning electron microscopy(SEM) and the composition of intermetallic compound was measured by the energy-dispersive X-ray(EDX) analysis. 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

Figure 1 shows the SEM micrographs of intermetallic compound layers for the interface between Sn-58Bi solder and (Cu, electroless Ni-P/Cu) substrate aged at 100 $^\circ\text{C}$ for different aging times. In the as-soldered joints, the layer thickness of the Cu_6Sn_5 and Ni_3Sn_4 intermetallic compound were approximately 0.45 and 0.12 μm , respectively. The interface between the Cu_6Sn_5 and solder displays a scalloped morphology. As evident from the Fig. 1(d)-(f), Ni_3Sn_4 intermetallic compound exhibited the layered structure, and its thickness increased rather slowly with aging time, reaching only 1.12 μm for 60 days of aging at 100 $^\circ\text{C}$.

Figure 2 shows the SEM micrographs of the interface between Sn-58Bi solder and (Cu, electroless Ni-P/Cu) substrate aged at 120 $^\circ\text{C}$ for 50 days. The Bi-rich and Sn-rich phases exhibited extensive coarsening due to isothermal aging. Especially, the growth of the intermetallic compound layers depleted the Sn-rich phase adjacent to the Cu_6Sn_5 intermetallic and led to the formation of a layer of Bi-rich phase across the Cu_6Sn_5 layer/solder interfaces, as shown in Fig. 2(a). In addition, the solder joints exhibited cracking within the intermetallic compound layer. According to the Sn-Bi binary phase diagram[14], the solubility of Bi in the Sn-phase increase rapidly from negligible at room temperature to about 9 at% Bi at 120 $^\circ\text{C}$. The $\text{Cu}_6(\text{Sn},\text{Bi})_5$ intermetallic compound layer in this work contained a Bi content of 1-6 at% by EDS analysis. The source of the Bi containing layers is Bi rejected from the Sn-rich solder phase as it participated in the formation of the intermetallic layer. Therefore, addition of the Bi atoms to the Cu-Sn intermetallic, the interface between Cu_6Sn_5 and the Bi containing Cu_6Sn_5 phase may be disrupt the local atomic arrangement, weaken the interfacial bonding,

and then cause interfacial embrittlement. Similar result was also reported by Liu and Shang[15]. Figure 3(a) and (c) represent the top view of Cu_6Sn_5 and Ni_3Sn_4 intermetallic after the sample was aged for 70 days at 100°C , followed by solder etched away. The Cu_6Sn_5 and Ni_3Sn_4 intermetallic surface shown in Fig. 3(a) and (c) were then used to obtain the X-ray diffraction pattern of Cu_6Sn_5 and Ni_3Sn_4 intermetallic as shown in Fig. 3(b) and (d), respectively. On the Cu substrate, the hexagonal-shape intermetallic can be seen in Fig. 3(a). In contrast, the polygonal-shape intermetallics are formed on the electroless Ni-P/Cu substrate as shown in Fig. 3(c).

Figure 4 shows the thickness of the intermetallic compound layer as a function of the square root of time for various aging temperatures. The intermetallic compound layer thickness increased linearly with the square root of aging time. This is in agreement with previous works[12, 16-18]. If the growth process were controlled by volume diffusion, the increase of the intermetallic compound layer after aging should follow the square root time law, $W = k t^{0.5}$. It is empirically found that n takes the value of 0.5 when the diffusion reaction is mainly controlled by volume diffusion[19]. Vianco[11] and Chen[12] studied the growth kinetics of the Cu_6Sn_5 and Ni_3Sn_4 intermetallic compound in Sn-58Bi solder and reported that the growth of these intermetallic compounds followed diffusion controlled kinetics. In Fig. 4, the results are in good agreement with the diffusion controlled growth kinetics reported by them. The growth of the Ni_3Sn_4 intermetallic is much slower than that of the Cu_6Sn_5 intermetallic. This implies Ni-P deposits will be a very good diffusion barrier for the Sn-58Bi solder.

The growth rate constant was calculated from a linear regression analysis of W versus $t^{0.5}$, where the slope = k . Table 1 lists the growth rate constants calculated for the Cu_6Sn_5 and Ni_3Sn_4 intermetallic at different aging temperatures, respectively. This good linear correlation ($R^2 > 0.96$) suggests that the growth of the intermetallic compound layers is similar diffusion mechanism over the temperature range studied.

The time exponent was evaluated using the equation representing the growth kinetics at each aging temperature as,

$$Y = At^n + B \quad (1)$$

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

$$\ln(Y-B) = n \ln t + \ln A \quad (2)$$

The time exponent(n) was obtained from the slope of $\ln(Y-B)$ versus $\ln t$.(Table 2) 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 following simple Arrhenius relationship was used to determine the activation energy for the layer growth of Cu_6Sn_5 and Ni_3Sn_4 intermetallic compound respectively;

$$k^2 = k_0^2 \exp(-Q/RT) \quad (3)$$

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($8.314\text{J/mol}\cdot\text{K}$); and T is the aging temperature. The activation energies were calculated from the slope of the Arrhenius plot using a linear regression model.

Figure 5 shows the Arrhenius plots for the layer growth of the Cu_6Sn_5 and Ni_3Sn_4 intermetallic layers. The apparent activation energies for the layer growth of Cu_6Sn_5 and Ni_3Sn_4 intermetallic compound are 127.9 and 81.6 kJ/mol, respectively. The activation energies for the layer growth of Cu_6Sn_5 and Ni_3Sn_4 intermetallic compound reported by Vianco and Chen (which the author evaluated from figure 17 in reference [11] and figure 8 in reference [12], respectively) are also shown in Fig. 5. Table 3 lists the values of the activation energy(Q) obtained from the temperature dependence of k^2 , with the data from previous works. The Q -values for the

growth of the Cu_6Sn_5 and Ni_3Sn_4 intermetallic found by Vianco et al.[11] and Chen et al.[12] were 55 ± 7 and 90 kJ/mol, respectively. The diffusion couple of Vianco et al.[11] and Chen et al.[12] was prepared using hot dipping. Also, the diffusion couple of Chen et al.¹²⁾ was assembled from Sn-58Bi solder and pure Ni. Thus, the discrepancy among the activation energies is due to the differences in the diffusion couples, aging conditions and analytical method used. As shown in Fig. 5(a), the lower temperature data(70, 90 and 100 °C) exhibited an apparent activation energy of 84.2 kJ/mol and the higher temperature data(100 and 120 °C) had a value of 203.8 kJ/mol. Combining the two data sets resulted in a value of 127.9 kJ/mol. But the resulting activation energy of 127.9 kJ/mol is considered too high for Sn-58Bi/Cu system. Neglecting the 120 °C data point would have an activation energy of 84.2 kJ/mol, which is a more reasonable number. Further work between 100 °C and 120 °C is required to fully clarify this point.

4. Conclusion

The effect of isothermal aging(70-120 °C) on the microstructure and intermetallic growth of Sn-58Bi solder/(Cu, electroless Ni-P/Cu) substrate were presented in this paper. The following conclusions were obtained:

(1) The aged Sn-58Bi/Cu joint consists of the Cu substrate, the Cu_6Sn_5 intermetallic, the Bi containing Cu_6Sn_5 phase, the Bi-rich and Sn-rich phase. It found that the formation of the double-layer (Cu_6Sn_5 / Bi containing Cu_6Sn_5) was due to the faster growth of Cu_6Sn_5 intermetallic.

(2) There was a linear relationship between the growth of the intermetallic layer thickness and the square root of the aging time. The good linear correlation of the results indicates that the formation of intermetallic compound layer is mainly controlled by volume diffusion. The growth rate of the Ni_3Sn_4 intermetallic is much slower than that of the Cu_6Sn_5 intermetallic. This implies Ni-P deposits will be a good diffusion barrier for the Sn-58Bi solder.

(3) The apparent activation energies calculated for the growth of the Cu_6Sn_5 and Ni_3Sn_4 intermetallic are 127.9 and 81.6 kJ/mol, respectively. The activation energy of Cu_6Sn_5 intermetallic due to the faster growth at high temperature exhibited higher than that of Ni_3Sn_4 intermetallic.

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Table 1 Calculated the square of growth rate constants(k^2) and linear correlation coefficient (R^2).

Solder/Substrate (Intermetallic)	Temp. (°C)	R^2	k^2 ($10^{-19} \text{ m}^2/\text{s}$)
Sn-58Bi/Cu (Cu_6Sn_5)	70	0.85	1.16
	90	0.97	4.50
	100	0.98	13.37
	120	0.96	374.75
Sn-58Bi/Electroless Ni-P/Cu (Ni_3Sn_4)	70	0.85	0.14
	90	0.97	0.75
	100	0.99	1.91
	120	0.96	4.99

Table 2 Time exponent (n)

Solder/Substrate (Intermetallic)	Temp. (°C)	n
Sn-58Bi/Cu (Cu_6Sn_5)	70	0.68
	90	0.47
	100	0.49
	120	0.66
Sn-8Bi/electroless Ni-P/Cu (Ni_3Sn_4)	70	0.48
	90	0.44
	100	0.54
	120	0.33

Table 3 Activation energy for the growth of Cu_6Sn_5 and Ni_3Sn_4 intermetallic compound(IMC) together with values reported in previous works.

Solder/Substrate	Diffusion couple Prep. method	Temp. (°C)/ Time (day)	IMC Layer	Activation energy (Q,kJ/mol)	Ref.
Sn-58Bi/Cu	Spreading	70 - 120°C / up to 60days	Cu_6Sn_5	127.9	This work
	Dipping	55 - 120°C / up to 400days	Cu_6Sn_5	55 ± 7	11)
Sn-58Bi/Ni	Spreading	70 - 120°C / up to 60days	Ni_3Sn_4	81.6	This work
	Dipping	85 - 120°C / up to 150days	Ni_3Sn_4	90	12)

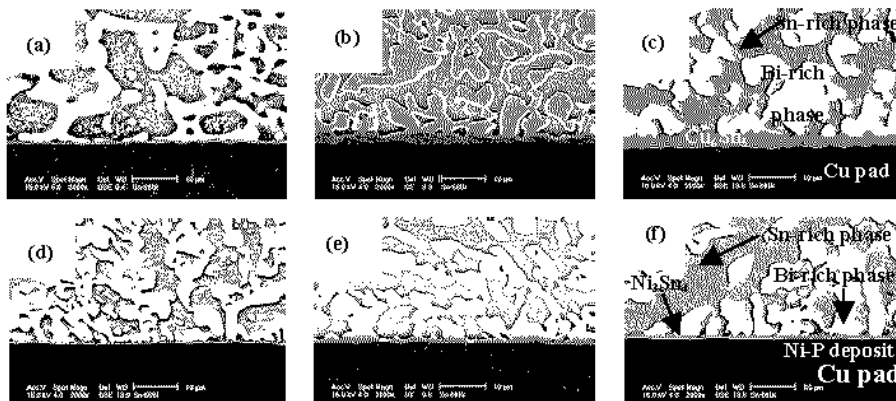


Fig. 1 SEM micrographs of the interface between (a-c) Sn-58Bi solder and Cu substrate, (d-f) Sn-58Bi solder and electroless Ni-P/Cu substrate: as-reflowed (a, d) and after aging at 100°C for 30 days (b, e) and 60 days (c, f).

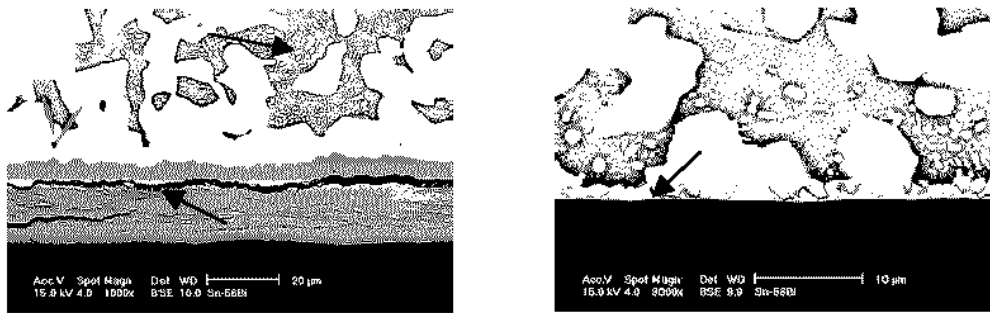


Fig. 2 SEM micrographs of the interface between (a) Sn-58Bi solder and Cu substrate, (b) Sn-58Bi solder and Electroless Ni-P/Cu substrate aged at 120°C for 50 days.

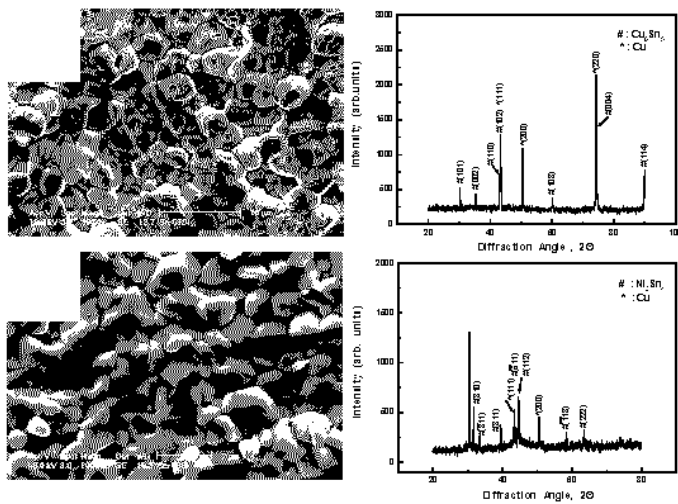


Fig. 3 Top views and X-ray diffraction patterns of the intermetallic compound : Cu₆Sn₅(a, b) and Ni₃Sn₄(c, d)

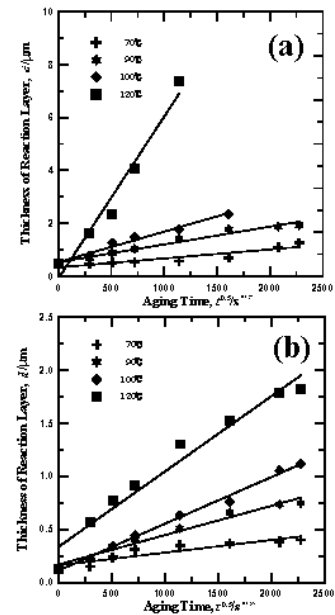


Fig. 4 Thickness of the intermetallic compound layers with aging time : (a) Cu₆Sn₅ and (b) Ni₃Sn₄

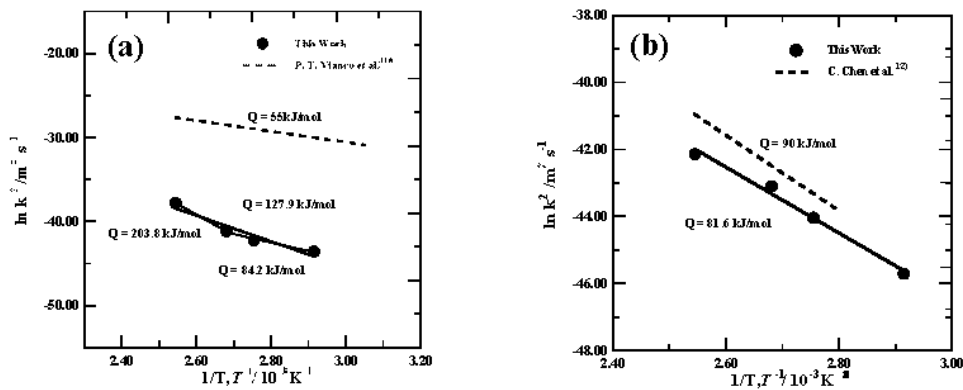


Fig. 5 Arrhenius plot of the intermetallic compound layer growth : (a) Cu₆Sn₅ and (b) Ni₃Sn₄