WETTING PROPERTIES AND INTERFACIAL REACTIONS OF INDIUM SOLDER

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Abstract

The reliability of the solder joint is affected by type and extent of the interfacial reaction between solder and substrates. Therefore, understanding of intermetallic compounds produced by soldering in electronic packaging is essential. In-based alloys have been favored bonding devices that demand low soldering temperatures. For photonic and fiber optics packaging, In-based solders have become increasingly attractive as a soldering material candidate due to its ductility.

In the present work, the interfacial reactions between indium solder and bare Cu Substrate are investigated. For the identification of intermetallic compounds, both Scanning Electron Microscopy(SEM) and X-Ray Diffraction(XRD) were employed. Experimental results showed that the intermetallic compounds, such as $Cu_{11}In_9$ was observed for bare Cu substrate. Additionally, the growth rate of these intermetallic compounds was increased with the reaction temperature and time. We found that the growth of the intermetallic compound follows the parabolic law, which indicates that the growth is diffusion-controlled.

Key words

Lead(Pb)-free solder, Intermetallic Compound, Interfacial Reaction, Activation energy

1. Introduction

The tin-lead (Sn-Pb) solder is widely used by the electronic industry for packaging applications. This solder has been used for years and meet the performance requirements very well. However, the traditional uses of lead(Pb) in solders have been regulated of food, health and environmental problems.[1-3] In response to the Pb-free trend in the electronic industry, many effort have been made to develop Pb-free solder, with eutectic Sn-Ag being a prospective alloy.

Compared to Sn-base solders, In-base solders have been shown to possess certain advantageous properties such as better wettability, lower melting point and longer fatigue life.[4-7] Indium has been a choice for bonding many photonic devices such as laser diodes and photonic switches, where some creep movement in the joint can be tolerated. Indium is quite ductile and can endure large plastic strain without breakage.

During soldering, the solder alloy melts and reacts with the substrate to form intermetallic compounds at the joining interface. Intermetallic compounds increase in thickness with time in a thermally activated manner. The brittle nature of the intermetallic layer as well as extensive intermetallic growth can be damaging to reliability and solderability of solder joints.[8-9] The interfacial phenomena may be directly related with the solder joint reliability in the electronic packages. Therefore, a knowledge of intermetallic compounds produced by soldering in electronic packaging is essential. However, metallurgical behavior in indium solder joint with different surface finishes has not been sufficiently studied yet.

Therefore, the present study was carried out to investigate wetting properties and interfacial reactions between indium solder and bare Cu Substrate. The growth rate constants for Cu-In was measured as functions of time and temperature, and the activation energies for intermetallic growth were calculated by the Arrhenius equation.[10]

2. Experimental Procedures

2.1 Wetting balance test

Wetting balance test has been widely used in evaluation of soldering material. The wetting test was performed using a wetting balance tester (Rhesca Co. Ltd., SAT-5100), which is a system widely used for controlling the soldering process and assessing and improving soldering performance, since it is provided with an assessing function developed on basis of the principles of meniscography (MIL-STD-883D) as a standard accessory. Prior to the test, the specimen was dipped in flux. These specimens were tested for each condition. For each test condition, a total of ten samples were made in this manner

2.2 Interfacial reaction

In this study, substrates used were bare Cu substrate. Both solder sheets and substrates were ultrasonically cleaned in ethanol before soldering. A piece of solder (approximately 0.18 ~ 0.2g) were laid on the substrates. they were reflowed by using a IR reflow oven. The peak reflow temperature, the highest temperature a package experiences, was 470 K and reflow time at which solder melt was 60 s. Each reaction couples were then placed in an oven maintained at a constant reaction temperature. The temperature homogeneity and stability for each oven was better than ±1K. The aging temperatures were 343, 373, 383 and 393 K for 0 to 4×10^6 sec.

In order to examine the growth kinetics of intermetallic compounds, the cross sections of all specimens were observed with a scanning electron microscope (SEM). Intermetallic compounds were identified with EDX analysis and X-ray diffractometry (XRD). To prepare for the XRD analysis, the chosen specimens were selectively etched with a solution of 10ml HF, 10ml H_2O_2 and 40ml H_2O, so that indium solder would dissolve and the intermetallic compounds would remain.

The layer thickness in the scanned micrographs was evaluated from the total area of intermetallic layer measured using image analysis software. The thickness of a phase is defined as the total area occupied by that phase divided by the length.

3. RESULTS AND DISCUSSION

3.1 Wetting balance test

To evaluate the wettability, wetting balance tests were carried out. For each data point shown in Fig. 1 and 2, at least ten measurements were made and the average value was reported. Fig. 1 shows the relationship between wetting force and wetting time according to test temperatures and flux types. Table 1 lists the characteristics of this flux. There is a tendency for wetting force to increase with an increased temperature, while wetting time shows a tendency to decrease with increasing temperature. That is, in the case of using flux with a relatively high solid content, flux B type(solid content : 12%) compared to flux A type(solid content : 3.3%) has a high wetting force.

Fig.2 shows the relationship of the wetting force and wetting time according to test temperatures and various types of substrate metal finishes (Bare Cu, Ni/Cu and Au/Ni/Cu substrate). In the case of temperature at 483 K, the wetting force is 3.7 and 3.0 mN for Cu substrate and Au/Ni/Cu substrate, respectively. But the Ni/Cu substrate is not full wetting.

3.2 Interfacial reaction

Fig. 3 shows the scanning electron micrographs for reaction couples aged for 4×106 sec at different aging temperatures. A continuous layer of $Cu_{11}In_9$ intermetallic compound located at the solder/substrate interface was identified by means of EDS analysis. In all the reaction couples, only the intermetallic compound $Cu_{11}In_9$ was detected. The thickness of $Cu_{11}In_9$ is increased with the increasing aging temperature.

Fig. 4 show the thickness of the total intermetallic compound layer as a function of the square root of time for each of the aging temperatures. The thickness of a reaction layer in the diffusion couples can be generally expressed by the simple parabolic equation;

$$W = k\,t^{n} \qquad (1)$$

Where, W is the thickness of the intermetallic layer; k, the growth rate constant; n, the time exponent; t, the reaction time.

The atomic diffusion of Cu and In through the intermetallic compound layer is the main controlling process for the IMC growth during aging. In general, the solid state growth for intermetallic compound can follow a linear or parabolic growth kinetics. Linear growth implies that the growth rate was limited by the reaction rate at the growth site. In contrast, Parabolic growth implies that layer growth was mainly limited by volume diffusion. If the layer growth process were controlled by volume diffusion, the increase of the IMC layer after isothermal aging should follow the square root time law, $W \fallingdotseq k\ t^{1/2}$. It is empirically found that n takes the value of 0.5 when the diffusion reaction is mainly controlled by volume diffusion.

Fig.4 shows the growth of intermetallic compounds followed a parabolic law, implying that the growth of the intermetallic layer was controlled by volume diffusion. The growth rate constant was calculated from a linear regression analysis of the plot W versus $t^{1/2}$, where k is the slope.

A simple Arrhenius relationship was used to determine the activation energies for IMC, $Cu_{11}In_9$ intermetallic growth:

$$k^2 = k_o^2 \exp(-Q/RT) \qquad (2)$$

where k^2 is the growth rate constant ; k_o^2 , the frequency factor ; Q, the activation energy ; R, the gas constant (8.314J/mol-K) ; T, the aging temperature. The activation energy was calculated from the slope of the Arrhenius plot using a linear regression model.

Figure 5 shows the Arrhenius plots for the growth of the $Cu_{11}In_9$ intermetallic layers. The activation energy for $Cu_{11}In_9$ growth is 34.14 kJ/mol. The activation energies obtained in this study are generally of the same order as those from the literature when compared with Cu-In intermetallic compound growth with indium base solders during aging. The discrepancy among the activation energies is due to the differences in the diffusion couples, aging temperature and analytical method used.

4. CONCLUSION

The wettability of Indium solder increased with soldering temperature and solid content of flux. The wettability of Indium solder was affected by the substrate finish used, i.e, nickel, gold and copper. On the bare Cu substrate, Indium solder easily wet better than any of the substrate metal finishes tested. Intermetallic compound formed between the liquid solder and substrate reduced the interfacial energy and improved wettability.

The layer of intermetallic compound formed between indium solder and bare Cu substrate was examined with various isothermal aging conditions. A quantitative analysis of the total intermetallic compound layer thickness was performed; T, range from 343 to 393 K; t, periods of from 0 and 4×10^6 sec. 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 growth is mainly controlled by volume diffusion process. The growth rates for intermetallic layers increased with time and temperature.

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Table 1. Characteristics of flux used in the experiment.

Type	Specific gravity(25℃)	Solid content(%)	Cleaning method
Flux A (R)	0.795	3.3	Non-clean
Flux B (R)	0.836	12	Non-clean

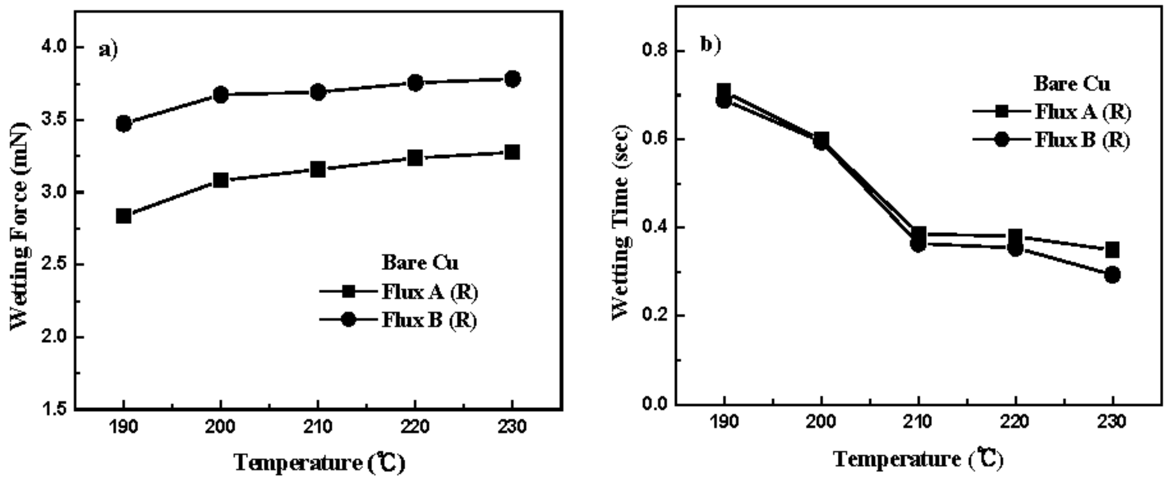

Fig. 1 Temperature dependency on a) wetting force, b) wetting time for flux A and B.

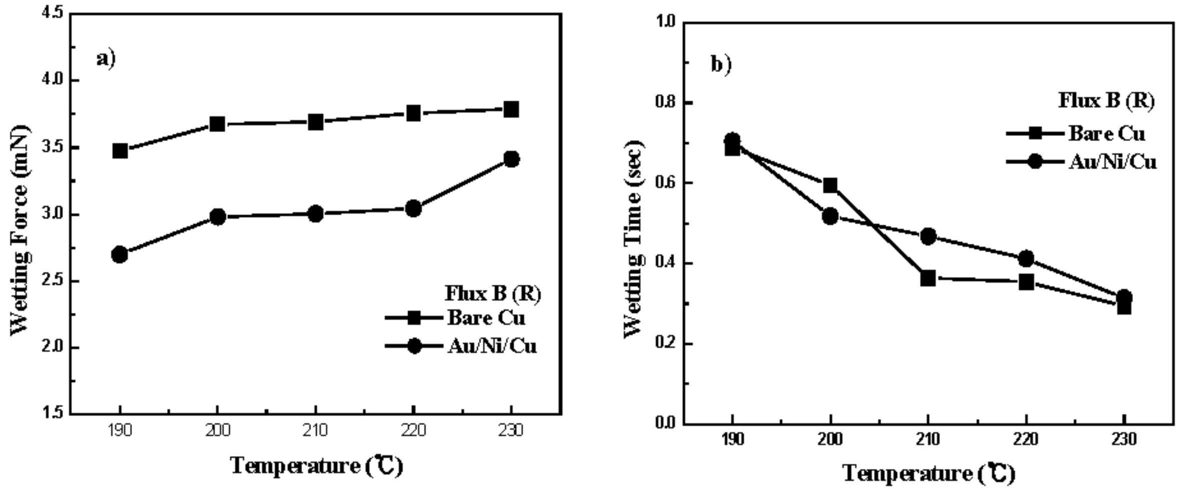

Fig. 2 Temperature dependency on a) wetting force, b) wetting time for various substrate types.

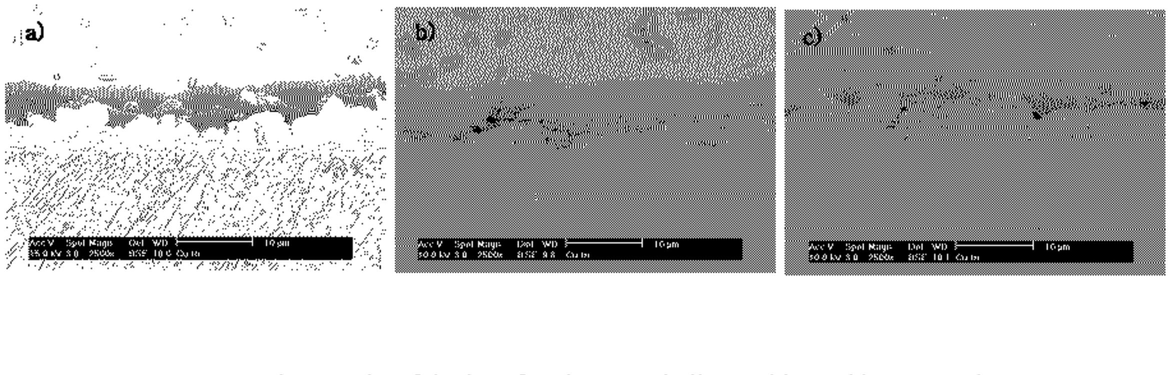

Fig. 3 SEM micrographs of the interface between indium solder and bare Cu substrate :

after aging for 4×106 sec at 343 K(a), 373 K(b), 393 K(c)

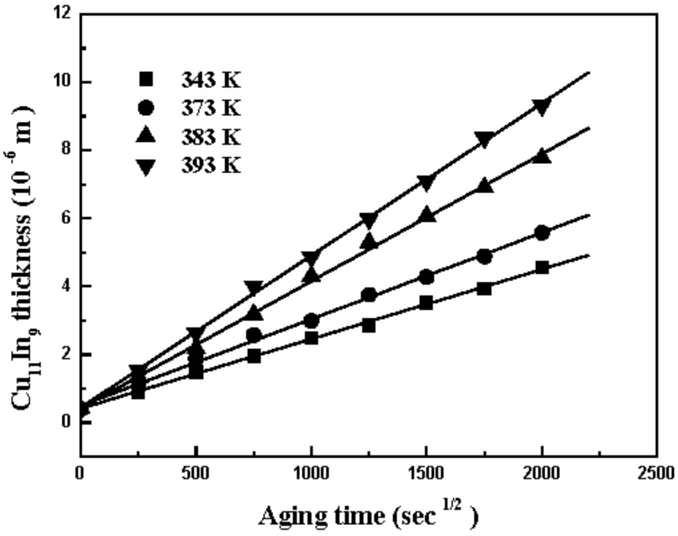

Fig. 4 Thickness of intermetallic compound layers formed at interface between indium solder and bare Cu substrate

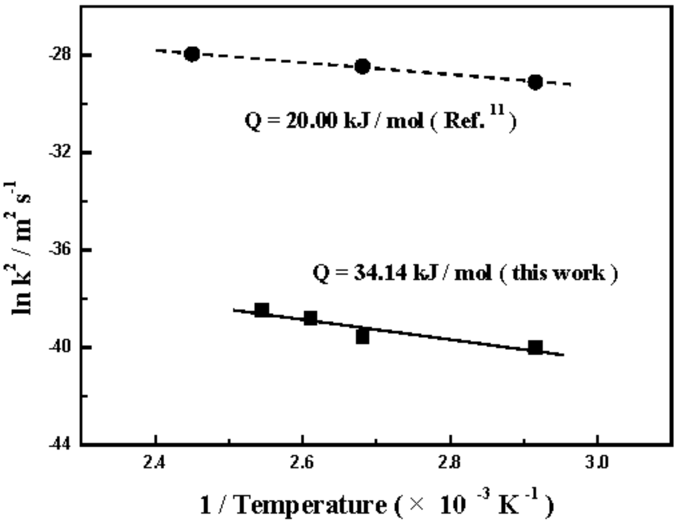

Fig. 5 Arrhenius plot of $Cu_{11}In_9$ intermetallic compound layer growth.