Effect of In Addition on Wetting Properties of Sn-Zn-In/Cu Soldering

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In this study, trace amounts (0.5–2 mass%) of indium (In) are added to the binary Sn-9Zn alloy to examine the effect of such addition on wetting properties of Sn-9Zn-In soldering. Results show that addition of In to Sn-9Zn alloy leads to decrease in eutectic temperature; and the greater the amount of In added, the larger the decrease is. On the other hand, the maximum wetting force, an indicator of wettability and solderability, increases with increasing mass% of In added. In addition, the higher the eutectic temperature, the better the wettability of solder is. Increasing In content in the solder also enhances the dissolution of Cu. Moreover, the higher the In content, the faster the dissolution rate is. At wetting temperatures of 220°C and 240°C, the wetting time achieved is shorter than 3 s, which can meet practical needs for industrial applications. In sum, the addition of 0.5 mass% of In is optimal in that it can achieve good wettability while maintaining low dissolution rate, which would also enhance solderability. [doi:10.2320/matertrans.MJ2010041]

Keywords: lead-free solder, solder, wetting behavior, maximum wetting force, dissolution rate

1. Introduction

With rapid advances in technology around the world, development of the electronic industry has become an important indicator of a country’s competitiveness. In Taiwan, traditional labor-intensive industries have gradually declined and been replaced by those engaged in manufacturing semi-conductors and electronic packaging products. High-technology industries contribute the most to Taiwan’s gross domestic product. Following silicon wafers, electronic packaging products have been predicted to enjoy rapid growth and expansion. Electronic packaging aims to protect electronic goods against impact from the external environment, thus enhancing their reliability over a longer stretch of time. Generally speaking, electronic packaging of a product serves the functions of (1) protection, (2) transmission of power and electronic signals, (3) thermal treatment, and (4) interconnection of components and the entire electronic system. In all these various functions, the solder used for joining different materials must be able to provide good electric property and solderability. In the past, Pb-Sn solders were used to be the most widely employed. However, with growing concern for the environment and greater awareness of Pb as a toxic heavy metal that poses serious threat to human health, developed countries have all been trying to switch to using Pb-free solders, such as Sn-Ag, Sn-Cu, Sn-Ag-Cu, Sn-Zn and Sn-Bi alloys.1 Among them, Sn-Zn alloy is a low-temperature solder with melting point closest to that of traditional Sn-Pb-based solders. In addition, it has steady mechanical properties. However, joints soldered with Zn are likely to corrode with time because Zn is oxidized easily. This drawback can be overcome by adding other elements to Sn-Zn-based solders. Indium (In) has been found to possess high thermal creep resistance and good wetting properties.2 Nevertheless, In is a rare element not readily available. Moreover, adding too much of it will increase soldering cost enormously. Besides material properties, wettability of solder is an important determinant of soldering results. That is, good wetting characteristics facilitate bond formation, thus ensuring effective and efficient soldering. Much research has been done on examining the melting behavior of solid metal substrates and molten solders.

In actual practice, during every soldering process, the Cu element in both PCB and dual in-line pins of the electronic components will melt into the solder pot. Hence, repeated soldering will change the elemental composition of the molten solder. With continuous increase in Cu content, more IMC layers will be formed. This would in turn undermine the wetting property of solder, as evidenced by increase in defects at the solder joints. Hence, in electronic industries with soldering as an indispensable manufacturing process, control of Cu content in the solder pot is a key technology that determines the final product quality.

In this study, trace amounts (0.5, 1 and 2 mass%) of indium (In) are added to the binary Sn-9Zn alloy. The effect of such addition on wetting properties of Sn-9Zn-In/Cu soldering is then examined. Microstructural observation of Sn-9Zn-In alloy soldered on Cu substrate and analysis of its wetting behavior, dissolution rate and thermal physical properties are also studied to shed light on solderability of the Sn-9Zn-In solder.

2. Experimental Design

High-purity Sn (99.95%, SHOWA, Japan), Zn (99.95%, Alfa Aesar, U.S.A.) and In (99.9%, Alfa Aesar, U.S.A.) were weighed using a precise balance (Mettler Toledo AL104; U.S.A.) and mixed at different weight percentage (mass%) into three eutectic alloys, namely Sn-9Zn-0.5In, Sn-9Zn-1In, and Sn-9Zn-2In, with deviation in weight proportion of less than 1%. The chemical compositions of these eutectic alloys are shown in Table 1. To prevent oxidation, the alloy specimens were vacuum sealed in quartz glass tubes with internal pressure below $1.0 \times 10^{-4}$ N/m². The alloys were then put inside a 250°C furnace for 48 h for complete melting.
and mixing, followed by quenching with cold water. The following experiments were all conducted under 1 atmospheric pressure and 25°C.

2.1 Microstructural observation

After reaction and treatment, the alloy specimens were cut with a low-speed diamond saw (Buehler IsoMet, U.S.A.) and then cold mounted using both epoxy and hardener. Rough polishing of the specimens was conducted using silicon carbide (SiC) abrasive paper #200, 400 and 800, followed by fine polishing with abrasive paper #1000 and #2000, and finally with 0.3-μm Al₂O₃ powder. The Al₂O₃ powder on the specimen surface was removed by an ultrasonic cleaner and the specimens were then immersed in an etching solution containing CH₃OH : HCl : HNO₃ = 9 : 3 : 2 for 60–90 s, followed by observation under scanning electron microscope (SEM; JEOL, JSM-6500F, Japan) and optical microscope (OM; Olympus BX51M, Japan).

2.2 Wetting properties

Wettability of a solder is often evaluated by measuring the wetting angle or using the wetting balance test. Two values, wetting time and maximum wetting force, can be obtained using the wetting balance test.

2.2.1 Wetting angle measurement

The extent of wetting is measured by the wetting angle θ formed at the solid-liquid juncture, which is the contact point between the solid substrate and the molten solder; as shown in Fig. 1. The smaller the wetting angle or the closer it is to 0°, the better the wettability; and vice versa. The wetting angle can be determined from the balance of surface tensions at the juncture according to the Young-Dupre equation as follows:

\[ \gamma_{gl} \times \cos \theta = \gamma_{sg} - \gamma_{sl} \]

where \( \gamma_{gl} \) is the surface tension of the gas-liquid interface, \( \gamma_{sg} \) and \( \gamma_{sl} \) are the surface tension of the solid-gas and solid-liquid interface, respectively.

2.2.2 Wetting balance test

A balance of high accuracy and sensitivity is employed in the wetting balance test. Copper rods (Seriyiku company, Taiwan) of 1 mm in diameter are first degreased in alcohol and then washed in de-ionized (DI) water. They are immersed in an HCl solution of 15 mass% for 30 s to remove the oxides on the Cu surface, washed again in DI water, and finally dried in air.

Figure 2 illustrates the experimental setup and Fig. 3 summarizes the experimental procedures of the wetting balance test. In brief, specimens are securely clamped and dipped slowly at a fixed speed into a pot of molten solder. After remaining at a certain depth inside the solder pot for a pre-set duration, the specimens are then removed from the pot at the same speed as before. The wetting balance test yields two values: maximum wetting force and wetting time, which would shed light on the impact of In additions (0.5–2 mass%) on the wetting behavior of the Cu substrate and Sn-9Zn-In alloy.

Wetting time has two definitions. Firstly, it refers to the moment when the substrate metal overcomes the surface tension of the solder and wetting reaction begins under the resultant force. As specified in ANSI/J-STD-003, the acceptable wetting time for a printed circuit board (PCB) soldering layer is 2 s. As stated in EIAJ ET-7401, at 240°C, a wetting time of 3 s would be considered satisfactory. However, in view of the need for mass production in industries, shorter wetting time is preferred. Secondly, wetting time is also defined as the time taken to reach two thirds of the maximum wetting force. Maximum wetting force refers to the force measured by the wetting balance, under which the specimen, after being dipped into the solder
pot, is coated with the maximum amount of molten solder. The greater the force, the smaller the surface tension of the solder, and the easier the bonding between the substrate and solder pad. Hence, this force is indicative of solderability. In terms of wetting behavior, the shorter the wetting time and the larger the maximum wetting force, the better the solderability is.

The parameters employed in the wetting balance test are as follows:
(1) Amounts of In added: 0.5, 1 and 2 mass%.
(2) Dipping temperature: 200°C, 220°C and 240°C.
(3) Dipping rate: 15 mm/s.
(4) Dipping depth: 1.2 mm.

2.3 Dissolution rate
Experimental conditions and specimen preparation for testing dissolution rate are the same as those of the wetting balance test. With temperature set at 220°C, the Cu specimens are dipped into pots of molten solder with different In contents for 1, 3, 5, 7 and 9 min. The reacted Cu substrate specimens are then observed under optical microscope for changes in diameter of copper rods. The dissolution rate can be calculated using the following equation:

\[
\text{Dissolution rate} = \frac{d_o - d_f}{\text{time}}
\]

where \(d_o\) denotes the original diameter and \(d_f\) denotes the final diameter.

2.4 Thermal physical properties
Thermal physical properties of the alloy specimens were examined using different thermal analysis (DTA). Under heating, the appearance of endothermic peaks indicates the melting of precipitates while exothermic peaks can be observed when precipitation occurs. The area under the peak value represents the volume ratio of the precipitation reaction.

3. Results and Discussion

3.1 Metallurgical microstructure
Figure 4 shows SEM images of Sn-9Zn alloys without and with different amounts of In added. As seen in the alloy microstructure of Sn-9Zn shown in Fig. 4(a), crystallization of needle-shaped Zn-rich phases occurs in the Sn substrate. This is consistent with the findings of Mayappan et al., who mentioned that the eutectic structure of Sn-9Zn is the co-existence of the β-Sn substrate phase and the needle-shaped Zn-rich phase. Compared with the In-free Sn-9Zn alloy, those with In additions show lower concentration and smaller quantity of Zn-rich phases. Examining Fig. 4(b)–(d) also reveals that crystallization of Zn-rich phases in the Sn substrate decreases with increase in mass% of In added. Moreover, when In addition exceeds 1 mass%, the needle-shaped Zn-rich phases become longer in length. In sum, In-free Sn-9Zn alloy has the greatest concentration of needle-shaped Zn-rich phases, whose length is the shortest, while Sn-9Zn-2In shows the lowest concentration of needle-shaped Zn-rich phases of the longest length. Furthermore, increase in amount of In added will lead to increase in length but decrease in concentration and quantity of Zn-rich phases crystallized.
Tables 2 and 3 show the wetting time and maximum wetting force, respectively obtained by the wetting balance test for Sn-9Zn-In/Cu soldering at different dipping temperatures. As can be seen, non-wetting behavior is observed at dipping temperature of 200°C. As the temperature increases from 220 to 240°C, wetting time is found to decrease with the largest reduction observed in Sn-9Zn-1In. Among the three alloy specimens, Sn-9Zn-2In requires the shortest wetting time. In other words, adding 2 mass% of In can help achieve the greatest reduction in wetting time required.

As for the maximum wetting force, increase in temperature from 220 to 240°C raises the maximum wetting force of all three alloys, with the largest increase observed in Sn-9Zn-1In and the least increase in Sn-9Zn-2In. Among the three alloy specimens, Sn-9Zn-2In achieves the highest maximum wetting force. In other words, both temperature and amount of In added shows a positive relationship with maximum wetting force. That is, the higher the temperature and the larger the amount of In added, the higher the maximum wetting force achieved.

Combining the results of both wetting time and maximum wetting force reveals that higher dipping temperature and proper In content advance wetting properties of the Sn-9Zn system with shorter wetting time and higher maximum wetting force.

The wetting time achieved by different specimens at different temperatures in our study are all less than 2 s, which meets the acceptable wetting time of 2 s and 3 s as specified in ANSI/J-STD-003 and EIAJ ET-7401, respectively. This also implies that the three alloy specimens have better wetting properties than the specified requirements. According to Lin et al., adding In of 5 mass% or more while reducing the Zn content in Sn-9Zn alloy can improve wettability although it incurs a higher cost. In this study, the amount of In added is lower and the addition of 2 mass% In has shown to enhance wetting properties. In sum, adding optimal trace amount of In can improve wettability of solder; and the more the In added, the shorter the wetting time and the higher the maximum wetting force achieved.

### 3.3 Wetting angle

Figure 5 shows changes in wetting angle of the three alloy specimens at dipping temperature of 220°C after different reaction times. As can be seen, there exists a negative relationship between wetting angle and reaction time. That is, the longer the reaction time, the smaller the wetting angle is. As mentioned above, smaller wetting angle implies better wetting properties, which facilitate metallurgical bonding between substrate and solder. However, long reaction time is a drawback of on-site soldering process, not to mention the higher cost incurred.

Among the three alloy specimens, Sn-9Zn-2In has the smallest wetting angle and the largest reduction over time. This reveals that the larger the amount of In added and the longer the reaction, the smaller the wetting angle can be achieved. According to Zang et al., wetting angle of 0°, 0°–55°, 55°–90°, 90°–135°, and 135°–180° denotes best, good, average, poor, and worst wetting properties, respectively. Our results show that after 9-min reaction, the wetting angle of Sn-9Zn-0.5In and Sn-9Zn-1In are 60° and 56°, respectively; indicating only average wettability. On the contrary, after the same reaction time, the wetting angle of Sn-9Zn-2In dropped to 52°, showing good wettability and better wettability than that of the other two alloy specimens.

As seen in the results shown in Fig. 5, the largest variation in wetting angle occurs within the first 5 min, with Sn-9Zn-0.5In showing the greatest reduction. All three alloy specimens have similar wetting angle at reaction time of 5 min. As seen in the experimental results, increasing In content will cause reduction in wetting angle and surface tension of the solder, both of which can enhance wettability and solderability. This finding is in line with the result obtained by Lin et al. that wetting properties between Cu substrate and solder become better with addition of In.

In sum, adding In to the Sn-9Zn solder can reduce the wetting angle obtained. This would in turn enhance wettability and solderability, which help shorten production time.

### 3.4 Dissolution rate

Figure 6 shows changes in dissolution rate of the Cu...
substrate at dipping temperature of 220°C after different reaction times. As can be seen, there exists a positive relationship between dissolution rate and reaction time. In other words, the longer the reaction time, the higher the dissolution rate is. A similar relationship is also observed between dissolution rate and amount of In added, showing an order of 2In > 1In > 0.5In. As seen in the figure, dissolution of Sn-9Zn-0.5In rises rapidly in the first 5 min but show no further increase thereafter. On the contrary, the dissolution rate of both Sn-9Zn-1In and Sn-9Zn-2In show steady increase with time, revealing that the amount of In added to the solder has a definite impact on dissolution rate of Cu substrate. As mentioned above, higher dissolution rate of Cu substrate would mean poor wetting property. In actual soldering, when using Pb-based solder, the Cu content in the solder pot must be maintained at less than 0.3%, while that for soldering with Pb-free solder, less than 1.5%.

During soldering, the Cu substrate and molten solder come in contact and are bonded together. There exists a concentration gradient of elements at the solder-Cu interface. With increase in reaction time, the Cu substrate will dissolve quickly into the solder. IMCs will nucleate and grow at the interface when the Cu concentration of the substrate exceeds the corresponding equilibrium Cu concentration in the molten solder. Further nucleation of IMCs and their continuous growth in volume will form an IMC layer at the solder-Cu interface. Cu element in the substrate would mean poor wetting property. In actual soldering, when using Pb-based solder, the Cu content in the solder pot must be maintained at less than 0.3%, while that for soldering with Pb-free solder, less than 1.5%.

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Tseng reported that at dipping temperature of 240°C, the dissolution rate of Cu substrate in the Sn-9Zn solder after 10-min reaction was 0.32 μm/min. In comparison, the dissolution rate of Cu substrate in Sn-9Zn-0.5In after 9-min reaction was 0.23 μm/min. Such slow dissolution rate can help maintain a low Cu content in the solder pot, which would imply longer operation time for the solder pot. As can be seen, the temperature peaks at 197°C, 193°C, and 191°C for Sn-9Zn-0.5In, Sn-9Zn-1In, and Sn-9Zn-2In, respectively. Lin et al. has mentioned that the eutectic melting temperature for the binary Sn-9Zn alloy is 198°C. Furthermore, the weight of the alloy specimen reduces with rising temperature and decreasing heat flow. According to this, the peak temperature is determined to be exothermic and precipitation will occur.

Comparing the three curves reveals that with increase in amount of In added, the eutectic melting temperature drops from 197 to 191°C. Moreover, it is also lower than the eutectic melting temperature for the binary Sn-9Zn alloy, which is presented by Lin et al. to be 198°C. Moreover, the exothermic peak temperature shifts leftward and becomes smaller in size with increasing amount of In added, indicating that at lower exothermic value, addition of In can reduce the melting temperature of alloy, thus lowering the latent heat of phase change. This echoes the findings of Lin et al. that melting temperature decreases with addition of In to Sn-9Zn alloy.

4. Conclusions

From the results above, the following conclusions on wetting properties of Sn-9Zn-In/Cu soldering with different mass% of In added can be drawn.

(1) Exothermic heat temperatures appear at 197°C, 193°C and 191°C for Sn-9Zn-0.5In, Sn-9Zn-1In, and Sn-9Zn-2In, respectively, indicating that addition of In can help reduce melting temperature.
(2) At dipping temperatures of 220°C and 240°C, the wetting time achieved by the alloy specimens are all less than 3 s, which not only meets the specified requirement, but also the practical need for achieving better wetting properties.

(3) Dissolution rate of Cu substrate in solder increases with longer reaction time and increasing amount of In added to the Sn-9Zn alloy. Though increased, the dissolution rate is still lower than that of Pb-free solder with other elements added. Hence, the addition of In can still be beneficial. In terms of overall effect, the addition of 0.5 mass% of In is optimal in that it can achieve good wettability while maintaining low dissolution rate, which would also enhance solderability.

(4) As for wetting property, the shorter the wetting time, the higher the maximum wetting force and the better the solderability will be. Adding appropriate amount of In to the Sn-9Zn solder can reduce wetting time and increase wetting force, which in turn contribute to better solderability.

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