POSSIBILITY OF PARTIAL MELTING SOLDERING PROCESS WITH OFF-EUTECTIC LEAD FREE SOLDER ALLOYS

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ABSTRACT

This paper introduces the partial melting process for solder application and characterization of its feasibility using Sn-Ag, and Sn-Cu solder alloys. In order to show that the liquid phase in the semi-liquid state maintains the similar wettability as single-phase liquid, the wetting balance tests are conducted with varying temperatures and compositions. Also, as a new soldering technology, the microstructural and mechanical test were investigated. The results from this research indicate that the partial melting can yield satisfactory slder joints as long as the liquid phase acquires sufficient chemical activity. At a condition where the partial melting is effective, a direct correlation between the wettability and the surface tension is found to exist.

KEYWORDS

Partial melting process, wettability, surface tension, Sn-7Ag, Sn-3Cu

1. Introduction

With a rapid progress of electronic devices requiring dense and complex array of solder joints, new types of solder alloys are under great demand. The conventional solder alloys are largely based on the binary combination of a few elements such as Pb, Sn, Ag, and Cu. However, the range of soldering temperatures that these alloys offer are limited and not sufficient to enable the multiple processes involved in modern packaging assembly.[1] As the conventional soldering process utilizes the complete melting of the alloy, the process flexibility can be improved only when a new alloy is introduced. If, however, soldering is achievable without relying on complete melting but partial melting of the alloy, this may provide a simple yet effective way of increasing process flexibility without a need for new alloy design.[2] This has been the main objective behind research presented in this paper. Unlike the eutectic alloys, the alloys with off-eutectic composition do not melt at one temperature but show ranges of temperatures where solid and liquid phase coexists. At these ranges of temperatures, due to the presence of liquid phase whose composition is at or near to eutectic, soldering reaction can take place. The advantage of partial melting, i.e., semi-liquid, for soldering application can be many provided that the resulting quality of solder joint is satisfactory. It not only expands the soldering temperatures, ranging from the solidus to liquidus temperature of the alloy, but also can enhance the mechanical stability of the joint during soldering process because the presence of the solid phase increases the viscosity of the melt and thus prevents unnecessary flow of alloys.

2. Experimental Procedures

Wetting Balance Test

Sn-7Ag, and Sn-3Cu binary alloy systems are chosen for this investigation. Wetting Balance Tests are performed with SAT-5000 with data acquisition software developed by Rhesca Co. As a testing piece, pure Cu (99.9% purity) pad (8×30×0.3mm) is used. Before wetting balance testing, the Cu pad is degreased and etched in a mild acid – 95% ethanol, 3% HNO_3, and 2% H_2SO_4- for 20~30 seconds to expose the contamination-free surface. Immersion speed, immersion depth, and immersion time are normally set to 5 mm/sec, 3 mm, and 10 or

30 seconds, respectively.

Following method is used to extract the apparent surface tension and the contact angle from the wetting balance testing. The wetting balance test produces two physical quantities of importance: the tension force at equilibrium state of wetting and the maximum withdrawal force that resists against any force in the equilibrium wetting condition. The equilibrium wetting force is related to the surface tension of the liquid, contact angle and the buoyancy force, and it is given as

$$F_{eq} = p\gamma \cos\theta - \rho g V_b \qquad \text{Eq. (1)}$$

where, F_{eq} means the equilibrium wetting force, p is the sample perimeter, γ is surface tension, and V_b is buoyancy volume.[3,4] Contrast to the equilibrium force, the maximum withdrawal force is not dependent on the contact angle because the contact angle is known to be nearly zero at the state where the maximum withdrawal force occurs. The buoyancy volume in eq.(1) also should be replaced with the solder volume risen under the sample bottom.[5]

$$F_{wd} = p\gamma + \rho g V_u \qquad \text{Eq. (2)}$$

where, F_{wd} denotes the maximum withdrawal force, while V_u is the solder volume risen under sample bottom[6]. Combining Eqs. (1) and (2), the surface tension and the contact angle can be uniquely estimated:[7]

$$\gamma = \frac{(F_{wd} - \rho g V_u)}{p} \qquad \text{Eq. (3)}$$

$$\theta = \cos^{-1}\left(\frac{F_{eq} + \rho g V_b}{F_{wd} - \rho g V_u}\right) \qquad \text{Eq. (4)}$$

Surface Tension Calculations

In order to compare the surface tension of the semi-liquid state with the values predictable from the liquid phase alone, thermochemical calculation of the surface tension is carried out following method introduced by Butler[8]. The surface tension of A-B binary liquid can be estimated with assumption that an equilibrium holds between a bulk phase and a monolayer at the surface, and that the partial molar surface area of components in an alloy is equal to the molar surface area of pure elements. The surface tension then can be expressed as

$$\begin{aligned} \sigma &= \sigma_A + \frac{RT}{S_A}\ln\left(\frac{x'_A}{x_A}\right) + \frac{1}{S_A}\{\Delta^{XS}\overline{G'_A}(T, x'_B) - \Delta^{XS}\overline{G_A}(T, x_B)\} \\ &= \sigma_B + \frac{RT}{S_B}\ln\left(\frac{x'_B}{x_B}\right) + \frac{1}{S_B}\{\Delta^{XS}\overline{G'_B}(T, x'_B) - \Delta^{XS}\overline{G_B}(T, x_B)\} \end{aligned} \qquad \text{Eq.(5)}$$

where, σ_i and S_i are surface tension and surface area, respectively in a monolayer of pure liquid i, x'_i and x_i are mole fraction of i in the monolayer and the bulk; $\Delta\overline{G'_i}$ and $\Delta\overline{G_i}$ are partial excess Gibbs energy of i in the monolayer and the bulk as a function of temperature and composition, and R is gas constant, and T is absolute temperature. The surface area, S_i in eq. (5) can be calculated from molar volume, V_i of the element I, using a usual relation. [9,10]

$$S_i = b \cdot (N_A)^{1/3} \cdot V_i^{2/3} \quad , \qquad \text{Eq.(6)}$$

where, b is a geometric factor (1.091 for close packed structures) and N_A is an Avogadro number. Since the excess Gibbs energy in the surface phase can be assume to take the same form as that in the bulk phase except the coordination number, Z[11,12], the partial excess Gibbs energy in the surface phase is given as

$$\Delta^{XS}\overline{G'_i}(T, x'_B) = (Z^{surface} / Z^{bulk})\Delta^{XS}\overline{G_i}(T, x'_B) \qquad \text{Eq. (7)}$$

Tanaka and Iida[13] have investigated the $Z^{surface} / Z^{bulk}$ and suggested that it ranges from 0.5 to 1. In the present case, ¾ is chosen as the value. Table 2 presents the summary of thermodynamic data used in the present calculation.[14,15,16,17]

Table 1 Liquidus and Eutectic Temperatures of Alloys Used in This Study

Alloy System	Liquidus temperature (°C)	Eutectic Temperature (°C)
Sn-7wt.%Ag	262	221
Sn-3wt.%Cu	303	227

Table 2 Data Used for the Calculation of Phase Density and the Surface Tension[14,15,16,17]

Element	T_M(K)	V_m($10^{-6}m^3$/mol)	Σ (mN/m)
Ag	1235.08	$11.54\ (1 + 0.97\times10^{-4}\times(T - T_M))$	$903 - 0.16\times(T - T_M)$
Cu	1358.02	$7.94\ (1 + 1.00\times10^{-4}\times(T - T_M))$	$1285 - 0.13\times(T - T_M)$

Microstructures and Mechanical Properties

Sn-7Ag and Sn-3Cu solder alloys were melted in vacuum induction furnace for 1 hour at 1200°C and maintained for 6 hours at 500°C for homogenization. After this, the solders were quenched in a water bath. Using a disc-making device, we fabricated solder discs of 6.5mm in diameter and 0.35mm in thickness. Solders mounted on the Cu substrate were reflowed in a conventional reflow furnace. A reflow machine for this experiment was the hot air and IR hybrid type. Reflow conditions are displayed in table 3. All the temperature conditions were set to be between the liquidus and eutectic temperatures of each alloy, i.e. the partial melting zone. During the soldering process, all the samples stayed at least over 10s in the peak temperature region. Reflowed samples were mounted with epoxy, and polished with 2000 grit emery paper and 0.04 ㎛ alumina powder. Polished samples were etched by 5㎖ HNO, 3㎖ HCl, and 92 ㎖ ethanol etchant for 20 seconds. Microstructures of cross section were observed using optical microscope and scanning electron microscope. Phases and composition were investigated using EDX, Auger Electron Microscope and Electron Probe X-ray Microanalysis.

For evaluation of mechanical properties of soldered joint, hardness test and shear test were conducted. The MVK-H1 micro Vickers hardness tester was used. The load was 10g, the loading time was 15 s. Tests were conducted seven times for each sample After the maximum and the minimum values were ruled out, the average of five results were used as the mean value. The PTR-1000 Bonding Tester was adopted for the shear tester. The distance between stylus and substrate was 10 ㎛ and speed was set to 200 ㎛/sec.

Table 3 Reflow Conditions

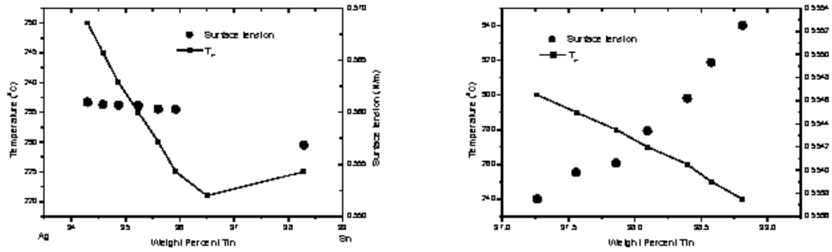
Solder	Reflow Temperature(°C)			
Sn-7Ag	230	240	250	260
Sn-3Cu	240	260	280	300

3. Results and Discussions

Wetting Properties

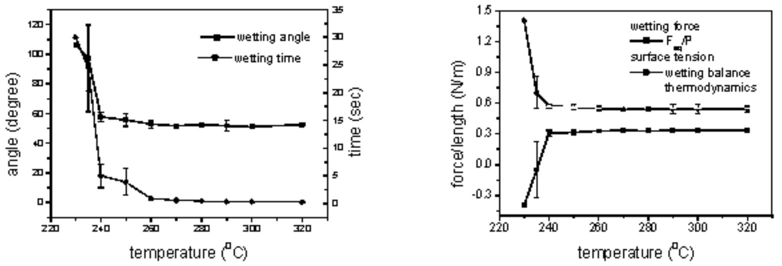
The wettability results of Pb-free solders examined in this investigation are less conclusive. Figure 1 (a)-(b) presents the calculated surface tension of liquid phase in two alloy systems considered (a) Sn-7Ag, and (b)

Sn-3Cu in comparison with liquidus temperature of the alloy as a function of temperature and Sn content. It can be seen that the surface tension of the liquid phase in Sn-3Cu is sensitive to the Sn content and increases with Sn content, while it is less sensitive in Sn-7Ag alloys. Figure 2(a) and (b) shows the wetting characteristics of Sn-7Ag alloy, (a) the wetting force/surface tension and (b) the wetting angle, as a function of temperature.. A reasonable level of wettability becomes apparent at temperature higher than 250°C. Note also that the surface tension, especially the one measured, follows the general trend of the wettability, indicating the close correlation between the surface tension and the wettability. As the liquidus temperature of this alloy is 262°C, the occurrence of a good wetting at temperature above 250°C suggests that the alloy can produce sound solder joints with the partial melting method. A similar result is also found from Sn-3Cu alloys. Figure 3 (a) and (b) show the testing results obtained from Sn-3Cu alloys. Much the same way as the Sn-7Ag behaves, this alloy exhibits good wettability at semi-liquid state. These results shown in this investigation reveals that the soldering through partial melting process can be effective in achieving quality joint with greater process flexibility, provided that a proper solder alloy is chosen.



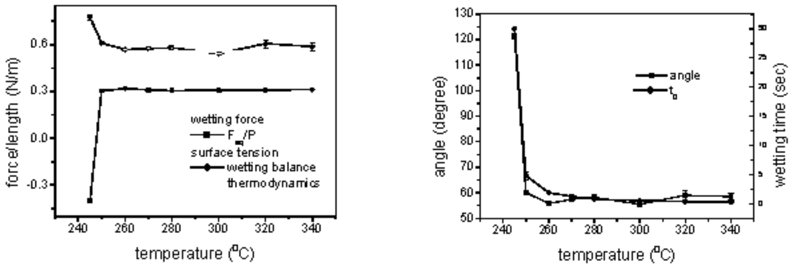
(a) (b)

Figure 1 Calculated surface tension of Pb-free alloys used in this study: (c)Sn-Ag, (d)Sn-Cu



(a) (b)

Figure 2 Wetting characteristics of Sn-7Ag alloys; (a)wetting force, and (b)wetting time and angle

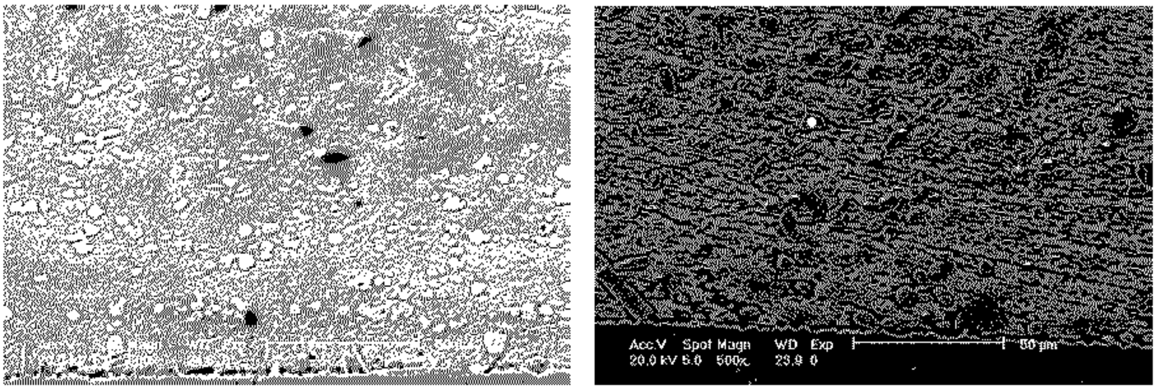


(a) (b)

Figure 3 Wetting characteristics of Sn-3Cu alloys; (a)wetting force, and (b)wetting time and angle

Microstructure and Mechanical Properties

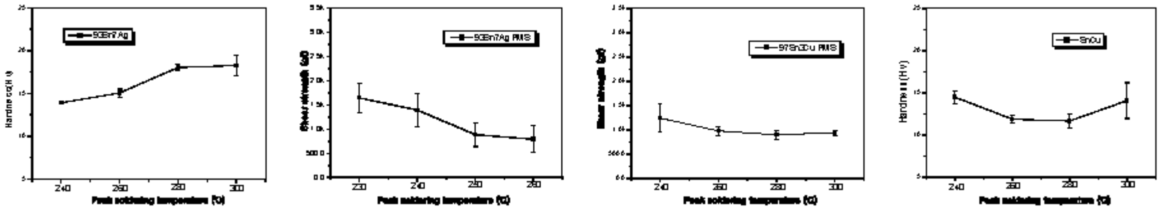
Figure 4 is a photo focused on the primary phases in the solder bulk of (a)Sn-7Ag, and (b)Sn-3Cu. In two cases, the intermetallic compounds are formed soundly through all the interfaces between substrate and partial melting solders. Also, in the matrix, there are approximately 5-6 ㎛ size intermetallics which are dispersed uniformly over the entire area in the matrix. It is thought to be that theses phases can strengthen the matrix just like the role of reinforcement ingredients in the composite alloys.



(a) (b)

Figure 4. SEM microstructure of (a)Sn-7Ag and (b)Sn-3Cu soldered interface in partial melting state

Figure 5 presents the results of micro-Vickers hardness test and shear strength for the partial melted solders. In all cases, the hardness value deceases as the peak soldering temperature increases. Increase in reflow temperature results in both growths of the intermetallics and weakening of the solder matrix. Therefore, the hardness results indicate the mechanical property of the matrix, not the joint. The hardness values are in the range of 1 to 2. It is reported that the hardness of fully melted Sn-Pb solders lies between 1.2 and 1.5, showing that the hardness of the Sn-Ag solder is similar to that of Sn-Pb. In all cases, shear strength has a tendency to decrease as peak soldering temperature increases. However, the values of shear strength is almost same as that of full melting process. So, we can know that the reaction area was bonded firmly with these partial melting state process.



(a) (b) (c) (d)

Figure 5 Mechanical properties (a)Hardness of Sn-7Ag (b) Shear Strength of Sn-7Ag (c) Hardness of Sn-3Cu and (d)Shear Strength of Sn-3Cu

4. Conclusion.

In this study, we proposed a new soldering process in the partial melting state. To verify the possibility of the process, Sn-7Ag, and Sn-3Cu solders were fabricated, calculated and reflowed on the Cu plate in their partial melting state. When a sufficient chemical activity of the liquid phase is available, the wettability is directrly related to the surface tension of the alloy irrespective of the liquid phase fraction. This is the case of Sn-3Cu, and Sn-7Ag alloys. While the wetting becomes better as temperature increases, it reaches its maximum well below the liquidus temperature, making the partial melting process feasible. From the microstructural point of view, we can get soundly soldered joints of Sn-7Ag at 230°C. In the cases of the Sn-Cu, 260°C is the lowest possible temperature condition for partial melting soldering. The solid phase of the partial melting state shows the reinforcement effect by such as particles in a composite solder. The liquid phase wets on Cu resulting in the intermetallic formation at the interfaces. The hardness values of partial melted off eutectic solders were similar or higher than that of full melting process. Shear stress was almost 80% of those of fully melted joint strengths.

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