Journal of the Microelectronics & Packaging Society
Vol. 7, No. 2, p. 63-68. 2000

Study on the Soldering of Off-eutectic Pb-Sn Solders in Partial Melting State

Jae Yong Park, Jun Seok Ha, Choon Sik Kang, Kyu Sik Shin, Moon Il Kim and Jae Pil Jung

School of Materials Science & Engineering, Seoul National University, Seoul, 151-742, Korea
Department of Materials Science & Engineering, Univ. of Seoul, Seoul, 130-743, Korea

Abstract: This paper introduces the partial melting process for solder application and characterization of its possibility using off-eutectic Pb-Sn alloy. In order to show that the liquid phase in the semi-liquid state maintains the wettability as the single-phase liquid, the wetting balance test are conducted with varying temperatures and compositions. The results are then compared with the surface tension of liquid, both measured and calculated, to examine the correlation. The results from this investigation indicate that the partial melting can yield satisfactory solder 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. All alloys are found to show a reasonable wettability in semi-liquid state.

Keywords: Partial melting, partial melting soldering, semi-liquid, wettability, surface tension, Sn-Pb

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, In and Bi. 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.

One of the most important properties that solder alloys should show is the sufficient wettability to joining substrate. While the wettability is affected primarily by the chemical reaction between substrate and the liquid phase in the solder, it is also influenced by the properties of liquid itself, such as surface tension. At a given reactivity of the liquid phase, the surface tension has a direct impact on the wettability as it changes the wetting angle following the Young's equation. In case when the alloy is at complete melt-state, the correction between the surface tension and the wettability is direct and easy to predict. However, the situation may differ considerably when the liquid phase exists in the two-phase equilibrium condition due to the presence of the solid phase. The solid phase may add considerable change in the overall surface tension of the liquid phase and thus may result in wettability substantially different from what is predicted from the single-phase state. The present paper examines the correlation between wettability and the surface tension of semi-liquid by conducting the wetting balance experiment on several selected alloys. The wetting behaviors of semi-liquid alloys are compared with the its surface tension, both measured and calculated, in order to establish the correlation and also to investigate the feasibility of partial melting technique. The observations resulted from this investigation reveal that the theoretical surface tension, calculated with an assumption that it is primarily determined by liquid phase alone, matches reasonably well with the experimental data and that the surface tension is useful in predicting the wettability alloys even with partial melting process. It is also shown that the partial melting can be equally effective in achieving a qualilty solder joint.

2. Experimental Procedures

Wetting balance test

Sn-Pb off-eutectic binary alloys are chosen for this investigation; the composition is varied from 40 to 90%Sn with 10% increment (weight percent). Liquidus temperatures of these alloys are displayed in Table 2. The use of Pb-Sn alloy is extensive in this investigation because it enables the needed experiments with significant variation in semi-liquid properties.

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 ×0.3 mm) 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.[3] The equilibrium wetting force is related to the surface tension of the liquid, contact angle and the buoyancy force, and it is given as

$$F_{eq} = p\gamma\cos\theta - \rho g V_b, \tag{1}$$

where, F_{eq} means the equilibrium wetting force, p is the sample perimeter, γ is surface tension, and V_b is buoyancy volume.[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]

$$F_{wd} = p\gamma - \rho g V_u, \tag{2}$$

where, F_{wd} denotes the maximum withdrawal force, while V_u is the solder volume risen under sample

Table 2. A list showing the liquidus and Eutectic Temperature of alloys used in this study

Alloy system	Liquidus temperature (°C)
40 wt.%Sn-Pb	234.3
50 wt.%Sn-Pb	210.8
70 wt.%Sn-Pb	190.3
80 wt.%Sn-Pb	201.5
90 wt.%Sn-Pb	215.9

Table 1. A list showing data used for the calculation of phase density and the surface tension. [8-11]

Element	T_M (K)	V_m (10^{-6} m^3/mol)	Σ (mN/m)
Cu	1358.02	$7.94\ (1+1.00\times10^{-4}(T-T_M))$	$1285-0.13(T-T_M)$
Pb	600.65	$19.4\ (1+1.23\times10^{-4}(T-T_M))$	$413-0.13(T-T_M)$
Sn	505.12	$16.96\ (1+0.88\times10^{-4}(T-T_M))$	$554-0.07(T-T_M)$

bottom. Combining Eqs. (1) and (2), the surface tension and the contact angle can be uniquely estimated:[6]

$$\gamma = \frac{(F_{wd} - \rho g V_u)}{p} \tag{3}$$

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

Thermochemical Calculation of surface tension

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[7]. 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

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

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. (3) can be calculated from molar volume, V_i of the element I, using a usual relation

$$S_i = b \cdot (N_A)^{1/3} \cdot V_i^{2/3}, \tag{6}$$

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, the partial excess Gibbs energy in the surface phase is given as

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

Tanaka and Iida[8] have investigated the $Z^{\text{surface}}/Z^{\text{bulk}}$ and suggested that it ranges from 0.5 to 1. In the present case, ¾ is chosen as the value. Table 1 presents the summary of thermodynamic data used in the present calculation.

As a supplementary work, we estimate the density of each phase in the semi-liquid alloy following the method proposed by Poirier.[9] Since the density of the solid and the liquid phase can be different, segregation of solid phase, either at surface or bottom of solder joint, is expected. It is therefore necessary to calculate the density difference to predict the direction and degree of the solid phase segregation. Due to a limited availability of necessary data needed for the density calculation, the estimation is carried out only for Pb-Sn alloys.

Prior studies suggest that the density of liquid phase is a linear function of temperature:

$$\rho_L = c_1 + c_2 T \tag{8}$$

where the constants c1 and c2 are determined to be

$$c_1 = 11.071 - 3.184X_{Sn} - 1.481X_{Sn}^2 + 0.751X_{Sn}^3 \tag{9}$$

$$\begin{aligned}c_2 = {} & (-12.777 + 2.675X_{Sn} + 8.025X_{Sn}^2 - 4.997X_{Sn}^3) \\ & -4.997X_{Sn}^3) \times 10^{-4}\end{aligned} \tag{10}$$

The prediction of the solid phase density is a little more complex than the liquid phase because it involves the prediction of the lattice constant. In case of the Pb-rich phase, Fecht and Perepezko[10] reported twenty-five sets of possible lattice parameters, depending on the composition and temperature, though they can be approximated in a single relation as

$$\begin{aligned}a = {} & 0.49446 + 1.962471 \times 10^{-5}T(^{\circ}\mathrm{C}) \\ & -0.0141542X_{Sn}\end{aligned} \tag{11}$$

where a denotes the lattice parameter in nm scale and T °C. Then the density of Pb-rich solid phase (fcc) is determined by

$$\rho = (4/N)(X_{Pb}M_{Pb} + X_{Sn}M_{Sn})a^{-3} \tag{12}$$

where ρ is density, N is Avogadros number, M_{Pb} and M_{Sn} are the atomic weights, and X_{Pb} and X_{Sn} are the atom fractions of *Pb* and *Sn*, respectively. The density of *Sn*-rich solid phase is estimated following the similar method:

$$\overline{\alpha_{Sn}} = (22.59 + 0.9205 \times 10^{-2}T) \times 10^{-6} \qquad (13)$$

$$\rho_{Sn} = 7.305[1 + \bar{a}_{Sn}(T-20)] \qquad (14)$$

$$a^{0}_{Sn} = [7.332 M_{Sn}/\rho_{Sn}N]^{1/3} \qquad (15)$$

$$a = a^{0}_{Sn} + pX_{Pb} \qquad (16)$$

$$\rho = (7.332/N)(X_{Pb}M_{Pb} + X_{Sn}M_{Sn})a^{-3} \qquad (17)$$

3. Results & Discussions

Figs. 1(a)-(b) present the composite plots showing the phase diagram of Pb-Sn alloy system (a) and the calculated surface tension of liquid phase along with its corresponding liquidus temperature of the alloy (b). As is shown in this figure, the theoretical calculation predicts that the surface tension increases with Sn content. Since wettability increases with decreasing surface tension of the liquid phase, if other metallurgical factors in wetting mechanism is the same, thess results indicate the possibility that the wettability of semi-liquid Pb-Sn alloy would be better in alloys with lower Sn contents. This prediction is confirmed by wetting balance measurements of the Pn-Sn alloys. Figs. 2(a)-(b) displays the measured wetting force (a) and the wetting angle (b) as a function of temperature taken from alloys with three different Sn concentrations. It can be seen that the wettability decreases as Sn concentration increases. The alloy with 80%Sn shows the worst wettability as the required wetting force and the wetting angle is the highest, and also because the wetting takes the longest time to occur. Notice the fact that the 40Sn-Pb alloy shows the best wetting characteristics even at partial melting state. The liquidus temperature of this alloy is 234.3°C. Therefore, this alloy exists in a semi-liquid state at any temperature

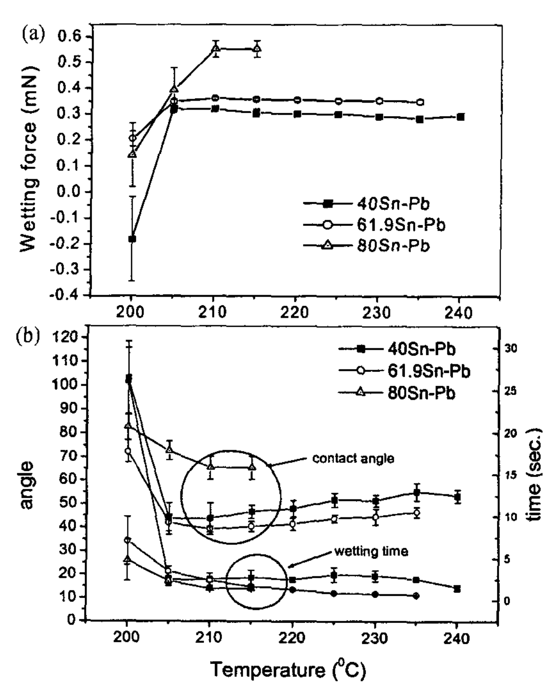
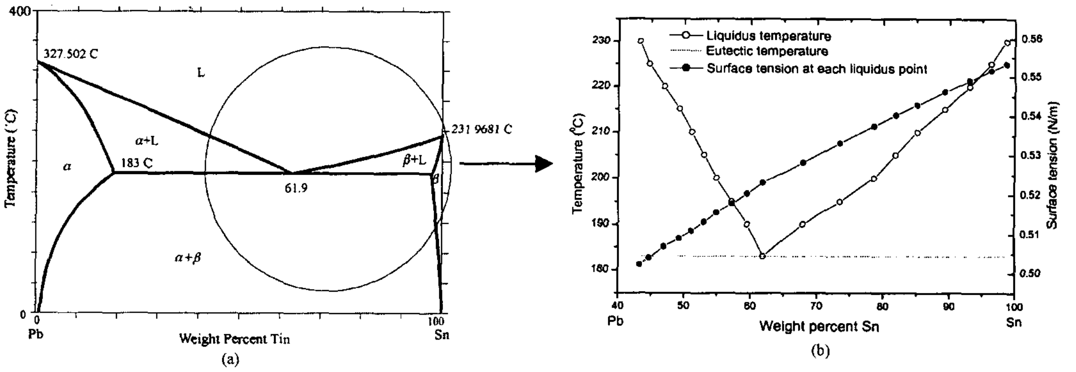


Fig. 2. Plots showing the wetting characteristics of Pb-Sn alloys; a) normalized wetting force vs. temperature, (b) Wetting time and angle vs. temperature.



(a) (b)

Fig. 1. Plots showing the phase diagram of Pb-Sn system (a) and the surface tension of the Pb-Sn alloy calculated from thermodynamic data (b).

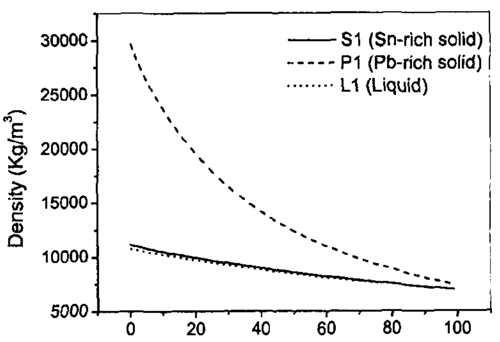


Fig. 3. A plot showing the density of Pb-rich, Sn-rich and liquid phase in Pb-Sn alloys as a function of composition.

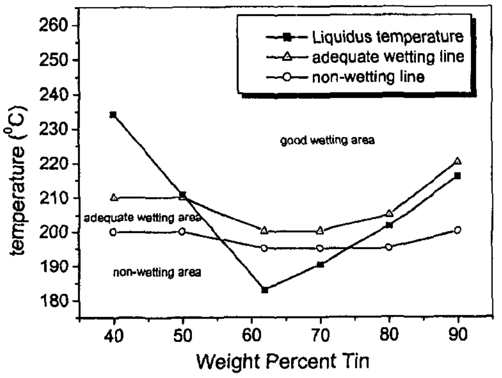


Fig. 4. Composite plots showing the boundary of wettability as function of temperature for alloys tested in this study for Sn-Pb

eutectic alloy (61.9Sn-Pb) becomes a single phase liquid at the same temperature ranges because it melts completely at 183°C. If the presence of the solid phase obscure the wetting mechanism in the semi-liquid alloy, the wettability should ideally be better in the eutectic alloys. The exact opposite result, a better wettability of 40Sn-Pb at all temperatures, does indicate that the surface tension, irrespective of liquid phase fraction and its temperature, is the primary parameter affecting the wetting mechanism in Pb-Sn solder

The 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 care is however necessary because the partial melting process may result in inhomogeneous microstructure due to density difference in the solid and liquid phase. As shown in Fig. 3, the density of Pb-rich phase in Pb-Sn semi-liquid is significantly greater than that of liquid phase. This inevitably results in a segregation of Pb-rich phase at the bottom of the solder joint, creating highly inhomogeneous microstructure across the solder joints. The impact of such segregation is presently unknown and may need a careful investigation, especially in relation to the reliability of the solder joint. Finally, the wettability map is constructed and presented in Fig. 4 to assist the utilization of alloys tested in this investigation for practical application. This figure displays the boundary that separates the different wetting behavior in the space of temperature and alloy composition. A desirable process condition, including the one for partial melting, can be selected from these maps for an alloy under interest.

4. Summary

In this investigation, wetting behavior of off-eutectic Sn-Pb solder alloys are characterized in order to test the feasibility of the use of partial melting process. The results from the wetting balance test are compared with the theoretical estimation of the surface tension. An attempt to correlate the wetting characteristics and the surface tension of the semi-liquid has yielded following conclusions:

1. As to wettability, off eutectic Sn-Pb alloys are wettable in their partial melting zone. Especially, Pb rich alloys showed excellent wettability while wettability of Sn rich alloys were adequate or poor.
2. The theoretical estimation of the surface tension indicates that the surface tension is more sensitive to composition than liquidus temperature. A comparison with the measured surface tension also indicates that it is not significantly affected by the presence of solid phase in the semi-liquid state.
3. It is found that wettability increases over 210°C regardless of composition, liquid fraction and phases of the original alloy. While the wetting becomes better as temperature increases, it reaches its maximum well below the liquidus temperature, making the partial melting process feasible.

References

1. Y.C. Lee and W.T. Chen, *Manufacturing Challenges in Electronic Packaging* (London: Chapman & Hall, 1998), p. 82.
2. Korea patent No. 1999-0444000-3.
3. R.J. Klein-Wassink, *Soldering in Electronics* (Scotland: Electrochemical Publications, 1984), p.45, 303.
4. J.Y. Park, J.P. Jung, and C.S. Kang, *IEEE Trans. CPT,* vol. 22, No.3, 1999, pp.372-377.
5. J.Y. Park, C.S. Kang, and J.P. Jung, *JEM*, vol. 28, No.11, 1999, pp.1256-1262.
6. J.Y. Park, doctorate theses, Seoul National University, 2000, pp.69.
7. J. A. V. Butler, *Proc. Roy. Soc.*, A-135, 1932, pp 348.
8. T. Tanaka, K. Hack and S.Hara, *Mrs Bulletin*, April 1999, pp. 45.
9. D.R. Poirier, *Metallurgical Transactions A*, vol.19A Sept., 1988, pp. 2349-2354.
10. H.J. Fecht and J.H. Perepezko: University of Wisconsin-Madison, Madison, WI, unpublished research 1987.