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Wettability Analysis of Liquid Phase in Partial Melted Solders Using Wetting Balance

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Abstract

To evaluate the possibility of the partial melting soldering, wettability of partial melted solders was measured using wetting balance. 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. It is found that wettability increases over 200℃ regardless of composition, liquid fraction and phases of the original alloy. Sn-7Ag alloy showed good wettability in their partial melting zone, while Sn-65Bi alloy was non-wettable under their melting points.

Keywords: Partial melting state, wettability, off-eutectic solder, Sn-Ag, Sn-Bi, Sn-Pb

1. INTRODUCTION

The major trends in SMT technology can be summarized as follows: fine and ultra-fine pitch technology, area array packaging, and materials development for more environmentally friendly materials and process.[1] Development of Pb-free solders and the fluxless soldering process are the most urgent parts of this trend; development of environmentally friendly materials and process. In these trends, one of the major issues is development of Pb-free solder. In conventional soldering process, however, which melts the solder alloy completely over its melting temperature, there exists a strong limitation; low melting points at its eutectic composition. Therefore, we developed a new technology which doesn't have such a limitation, that is, the soldering technology in partial melting state.[2]

Partial melting state is a state of which solid and liquid phases coexist in the same time. In this state, composition of liquid phase depends not on the original but on the liquidus line at each temperature. And the relative fraction of these two phases is defined by lever rule. This state, so called semi solid state, is used for semisolid forging, or semi solid metal forming for their viscous behavior.

But, why do we have to think about partial melting for soldering? Because this process has several merits compared to conventional soldering process. First, you can expand alloy system for soldering. Conventional soldering is conducted under relatively low temperature, for example around 200℃, our choice for new solder material is limited to the alloy with low eutectic temperature. But, if one can apply partial melting process into soldering, high melting point material can be used as a solder if its eutectic temperature is low enough. In other words, what we have to consider is the eutectic temperature not the melting point. Second, similar to the first merits, we can lower the process temperature compared to conventional soldering, because we don't have to melt the alloy completely. Third, viscous behavior of mixed states can give us a stable joint geometry. However, in this point, viscous behavior can lead to poor or non-wetting. Therefore, wettability is the key point of possibility of this process.

In this research, we focused on the wettability of soldered joint in partial melting state. Major assumption for wettability analysis is that wettability depends only on the liquid phase. On this base, we calculated surface tension and density of liquid phase. Also, wetting balance tests were conducted. For solder materials, we chose off-eutectic composition of Sn-Pb, Sn-Ag, and Sn-Bi alloys.

2. THEORETICAL BACKGROUND

Through wetting balance, we can obtain two major wetting forces; one is the force at the equilibrium state, and the force at the maximum value in the withdrawal force curve, namely the maximum withdrawal force. In case of equilibrium wetting force, forces exerted on the sample consist of force by surface tension and buoyancy force, and this relationship can be expressed as follows.

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

Where, F_{eq} means the equilibrium wetting force, p is sample perimeter, γ is surface tension, and V_b is buoyancy volume.[3]

Contact angle at the maximum withdrawal force is known to be zero.[4] Thus, the maximum withdrawal force is sum of solder weights risen under sample above the horizontal line and surface tension force.

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

Where, F_{wd} means the maximum withdrawal force, and V_u is solder volume risen under sample bottom.[5]

From eq. (1) and (2), following equations about surface tension and contact angle can be drawn.

$$\gamma = \frac{F_{eq} - \rho g V_u}{p} \tag{3}$$

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

So, with these two equations, we can calculate surface tension and contact angle between sample and solder.

3. EXPERIMENTAL PROCEDURES

For solder materials, we chose three binary alloy systems; Sn-Pb, Sn-Ag, and Sn-Bi. For Sn-Pb alloy, Sn weight percent varied from 30 to 90 weight percent by 10 percent increase. Melting points of each alloy are displayed in Table 1. When consider toxicity of Pb, it would be better to rule out the Pb-rich alloy system, but, what is important in this research is just wettability of these alloy systems. Moreover, for experimental convenience, Pb-rich alloys are easy to treat; because these systems have high melting

TABLE 1 Melting and Eutectic Temperature Summaries.

Alloy system		Melting point (℃)	Eutectic point (℃)
Sn-Pb	Sn-70wt.%Pb	257.8	183
	Sn-60wt.%Pb	234.3	
	Sn-50wt.%Pb	210.8	
	Sn-30wt.%Pb	190.3	
	Sn-20wt.%Pb	201.5	
	Sn-10wt.%Pb	215.9	
Pb-free	Sn-65wt.%Bi	152	139
	Sn-7wt.%Ag	262	221

temperature, so we can vary the process temperature more than Sn-rich alloy systems. For lead free solders, we chose Sn-65Bi, and Sn-7Ag binary alloys. In case of Sn-Ag alloy, it is recommendable to lower the expensive Ag composition, however, in that case, melting point and eutectic point is too close. Thus, 7 weight percent Ag tin alloy was chosen. And melting point of this alloy is 263.4℃ and eutectic point is 221℃.

Wetting Balance Tests were performed with SAT-5000. Computer control of the wetting balance and acquisition and analysis of data were performed using Wettability tester software by Rhesca Co. The test samples were 99.9% pure Cu vertical flat plates (8 × 30 × 0.3mm). They were degreased and etched in a mild acid for a few seconds.

Immersion speed, immersion depth, and immersion time were set to 5 mm/sec, 3 mm, and 10 or 30 seconds, respectively.

4. RESULTS & DISCUSSIONS

Results of wetting balance are shown in Fig. 1. Fig. 1(a) shows the equilibrium wetting forces divided by sample perimeter, or normalized wetting forces. Black rectangles indicate 40wt%Sn, hollow circles are eutectic alloy, and dotted triangles 80wt.%Sn alloy. Wetting forces of 80wt%Sn are higher than those of eutectic and 40wt%Sn alloy at all temperatures. But, considering melting point, results turned out to be on the contrary. Melting point of 80wt.%Sn-Pb alloy is 201.5℃, so, only the point at 200℃ indicates partial melting states and the others are results at full melting range. In case of 40wt.%Sn-Pb alloy, however, melting point is 234.3C, and results under 230℃ indicate wetting properties of partial melting state. All the values of 40wt.%Sn-Pb alloy except 200℃ are higher than the first point of 80wt.%Sn-Pb alloy, or results in partial melting state. Moreover, normalized wetting forces of 40wt.%Sn-Pb are very similar to those of

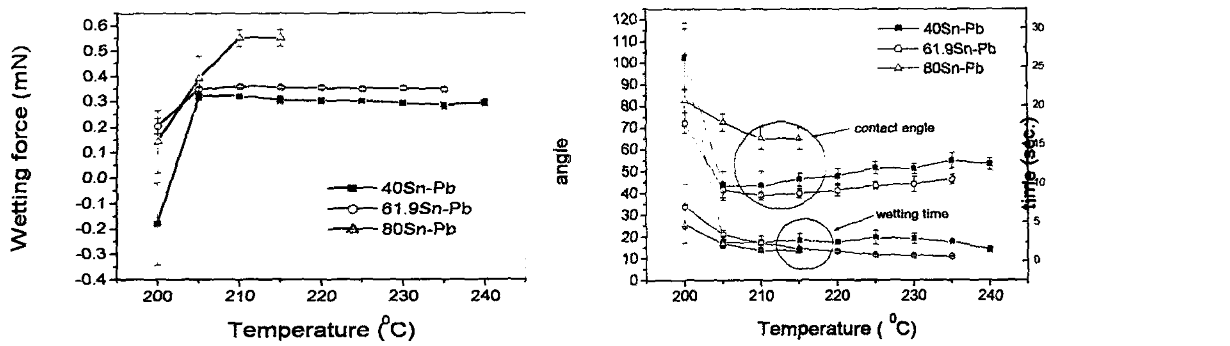

Fig. 1 Wetting results for Sn-Pb alloys; (a) Normalized wetting force vs. temperature, (b) Wetting time and angle vs. temperature.

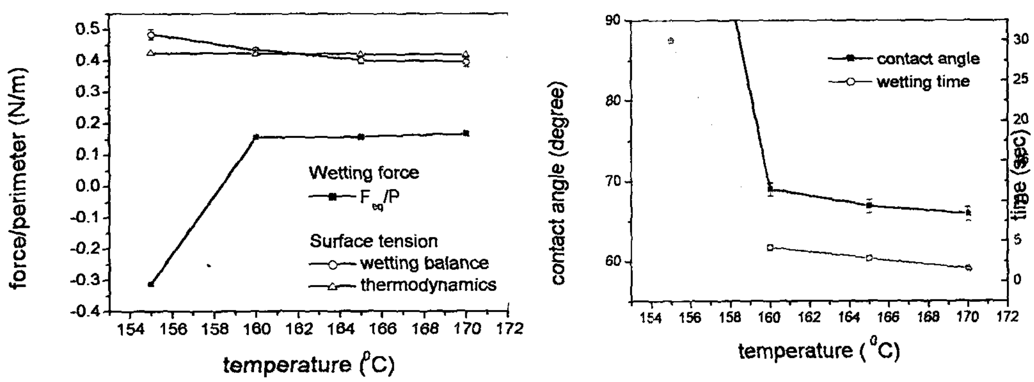

Fig. 2 Wetting results for Sn-65Bi alloys; (a) Normalized wetting force vs. temperature, (b) Wetting time and angle vs. temperature.

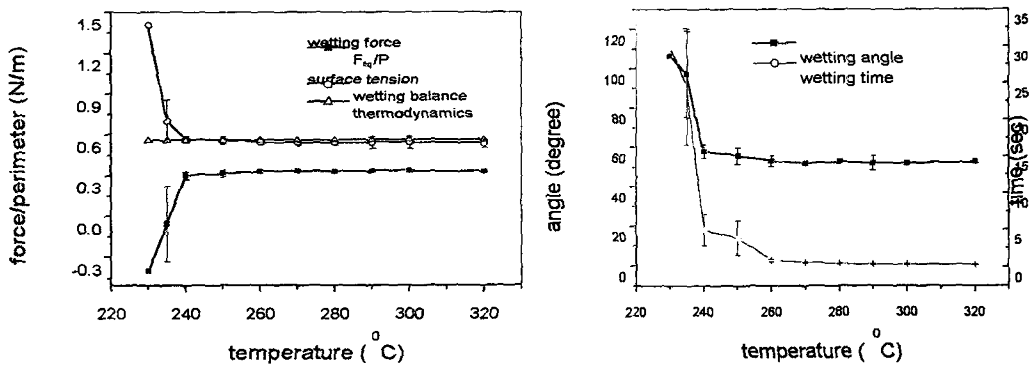

Fig. 3 Wetting results for Sn-7Ag alloys; (a) Normalized wetting force vs. temperature, (b) Wetting time and angle vs. temperature.

eutectic solders at their full melting temperature. Therefore, wetting property of partial melting state of 40wt.%Sn-Pb is superior to that of 80wt.%Sn-Pb.

For contact angle in Fig. 1(b), we can get same tendency with the normalized wetting force. Contact angle of 80wt.%Sn-Pb alloy shows high angle value compared to low Sn alloy, 40wt.%Sn-Pb. However, for wetting times, Fig. 1(b), all the values and tendency of three alloy systems to the temperatures are almost same.

In Fig. 2, wetting results of Sn-65Bi alloy are shown. Melting point of this alloy is 152℃, so, we can get reasonable wettability only above the full melting temperature region. In spite of similar values in surface tension with off-eutectic Sn-Pb alloys, wetting force, wetting angle and wetting time in their partial melting state show almost non-wetting behavior.

However, in case of Sn-7Ag alloy system in Fig. 3, wettability in partial melting zone was quite good over 240℃, where melting temperature is 262℃. So, good wettability of this alloy in partial melting state can be obtained.

To summarize these results about wettability, we can draw two maps about wettability criteria. Mapping results about (a) Sn-Pb alloys, and (b) Pb-free solders are shown in Fig. 4.

The black line connecting black rectangles is melting temperature at each composition. Area under hollow circles means non-wetting, and area over dotted triangles means good wetting. Area between circle-line and triangle-line means adequate or poor wetting region. Numbers at each point indicate relative fraction of liquid phase to solid phase at each temperature.

Good wetting line of low Sn alloys lays under their melting points, while melting points of high Sn alloys lay between circle-line and triangle-line, or adequate or poor wetting region. In case of 70wt.%Sn-Pb, melting point is under poor wetting line. Therefore, low Sn alloys (40wt.%Sn-Pb, 30wt.%Sn-Pb, 50wt.%Sn-Pb) show good wettability in their partial melting zone; while, high Sn alloys (80wt.%Sn-Pb and 90wt.%Sn-Pb) show adequate or poor wetting property. And 70wt.%Sn-Pb alloy is

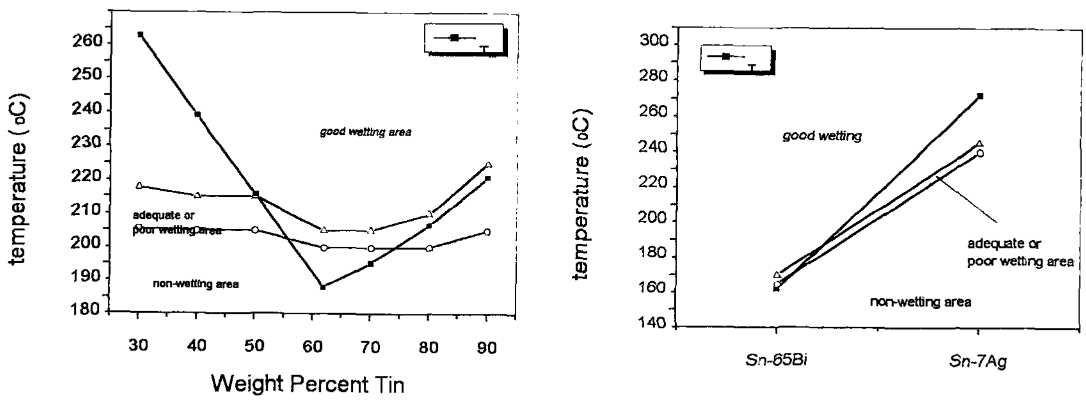

Fig. 4 Mapping graph for wettability criteria; (a) Sn-Pb, (b) Pb-free alloys.

non-wettable.

In Fig. 4 (a), one can find a peculiar thing that good wetting region begins over 210℃ regardless of their composition, liquid fraction, and phase. Even though wetting results of eutectic Sn-Pb alloy were conducted under full melting region, good wetting points appear at 210℃. Thus, it is found that liquid fraction is not major factor that controls wettability of partial melting state.

Fig. 4 (b) shows another wettability map of lead free alloys. Wettability of Sn-Bi alloy was poor or non-wettable under their melting point, so these alloys don't look suitable for partial melting soldering process. But, in cases of Sn-7Ag alloy, good wettability can be obtained in their partial melting state, and wettability is almost same with their full melting liquid.

5. CONCLUSIONS

To evaluate the possibility of the new soldering process called partial melting soldering, surface tension and density were calculated using thermodynamic data, and wettability was measured using wetting balance. From the results, following conclusions can be obtained.

1. About 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. In case of Sn-Pb alloy, it is found that wettability increases over 210℃ regardless of composition, liquid fraction and phases of the original alloy.
3. Sn-7Ag alloys showed good wettability in their partial melting zone, while Sn-65Bi alloys were non-wettable under their melting points.

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, 1999.
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.