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The effects of flux on the wetting characteristics of near-eutectic Sn-Zn-In solder on Cu substrate

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The effects of flux on the wetting characteristics of the near-eutectic Sn-Zn-In solder alloy [composition: 86Sn-9Zn-5In] on Cu substrate have been studied by using dimethylammonium chloride (DMAHCl), stearic acid (SA), lactic acid (LA) and oleic acid (OA) as fluxes. Wetting time and maximum force were estimated from the wetting experiments. According to the wetting curves obtained by wetting balance apparatus, the SA and OA are not suitable as flux for the near-eutectic Sn-Zn-In solder on Cu substrate. However, the LA and DMAHCl provide a good wetting behavior. The lowest wetting time (0.27 s) was obtained with 3.5 wt% DMAHCl as flux as-dipped at 300°C. When the dipping temperature increased from 250 to 300°C, the wetting time decreased obviously from about 0.6 to 0.4 s while the LA and DMAHCl were used as flux. When the content of LA was less than 5.0 vol% at 250°C and 2.5 vol% at 300°C, non-wetting or partial wetting was observed as determined by wetting curves. In addition, for the content of DMAHCl less than 1.5 wt% at 250 and 300°C, non-wetting or partial wetting was also observed. Quite different from the most tin-based solders for Cu substrate, intermetallic compound γ-Cu_5Zn_8 was found by the X-ray diffraction (XRD) and selected area electron diffraction (SAED) analyses at the interface of solder and substrate after etching out the unreacted solder layer. The Zn element was enriched at the interface between solder and Cu substrate as analyzed by line scanning. © *2000 Kluwer Academic Publishers*

1. Introduction

Lead-tin (Pb-Sn) solders are the most prominent material for the interconnection and packaging of modern electronic components and devices. The wide-spread usage of Pb-Sn solders is due primarily to the combination of low cost and convenient material properties. However, there are environmental and health issues concerning the toxicity of Pb present in these Pb-Sn solder alloys. These concerns have stimulated substantial effort in research and development of substitute solder alloys during the past several years, most of which has been directed toward Sn-containing binary or ternary alloys.

Flux is needed for most soldering processes, which provides tarnish cleaning, heat transfer, and wetting enhancement functions. The efficiency of wetting depends on the degree of surface cleanness as well as on the interfacial tensions of the solid/liquid contact systems. The solid/flux and liquid/flux interfacial tensions vary with respect to flux type, composition, and temperature. On the other hand, the solid/liquid interfacial tension depends on the materials and temperature. Furthermore, the wetting process is dynamic, that is, nonequilibrium [1], the solid/liquid interfacial tension would vary as the wetting proceeds, especially for the soldering process that encounters reaction between the solder and substrate.

Currrent manufacturing technologies are based upon the 183°C melting point of the eutectic 40Pb-60Sn, and the search for a suitable Pb-free solder alloy with an equivalent melting point has posed a considerable challenge. The 87Sn-8Zn-5In [2, 3] and 86Sn-9Zn-5In [4] solders with melting point about 188°C were reported to be comparable to that of the widely used eutectic Pb-Sn solder. McCormack *et al.* [3] had reported that the addition of indium to the Sn-Zn binary system improves the wetting characteristics of the alloy and lowers the melting temperature. However, the effects of flux on the wetting characteristics of the near-eutectic Sn-Zn-In solder on Cu substrate have not been elaborated. The objectives of this investigation are : (1) to evaluate the wetting characteristics of various flux for the near-eutectic Sn-Zn-In solder on Cu substrate, (2) to determine the structure of intermetallic compound formed at the interface of solder and Cu substrate, and (3) to evaluate the schematic diagram of reaction path.

2. Experimental procedures

2.1. Wetting test

The wetting experiment was conducted by a wetting balance, which will produce a wetting curve as shown in Fig. 1 to delineate the wetting force variation on the specimen. In the experiment, a positive force denoted repellent force acting on the specimen. At the point where only buoyancy was acting on the specimen, i.e. point B, the time was referred as the wetting time. Afterwards, the liquid solder kept reacting with the specimen until the maximum wetting force was encountered, i.e. point C. then, the wetting curve may remain unchanged up to the end of the experiment if no other interaction occurred during the contact than the initial wetting reaction.

The wetting behaviors of 86Sn-9Zn-5In solder were investigated on Cu wire (1 mm diameter) using a wetting balance to measure the wetting time. The Cu wire was degreased in an alkaline solution of NaOH (5 wt%) for 15 s, followed by rinsing in de-ion (DI) water for 10 s. Then it was pickled in the HCl solution (5 vol%) for 10 s, followed by rinsing in DI water again. The wire was then dipped in different flux solution including dimethylammonium chloride (DMAHCl), stearic acid (SA), lactic acid (LA) and oleic acid (OA) for 10 s after the pretreatment mentioned above. The wetting experiment was performed at a dipping depth of 5 mm at 250 and 300°C, respectively.

2.2. Microstructure analyses

The samples were cross-sectioned and one segment was mounted and prepared for metallographic analysis. The phase of intermetallic compound exposed by etching out the unreacted solder with a solution consisting of 10% 100g/l $FeCl_3/6H_2O$, 10% 100g/l CrO_3, 40% ethanol, 10% HNO_3, and 30% HCl was analyzed by X-ray diffraction (XRD). The microstructure was observed by scanning electron microscope (SEM) and transmission electron microscope (TEM) while selected area electron diffraction (SAED) was used to examine the intermetallic compound (IMC) phase.

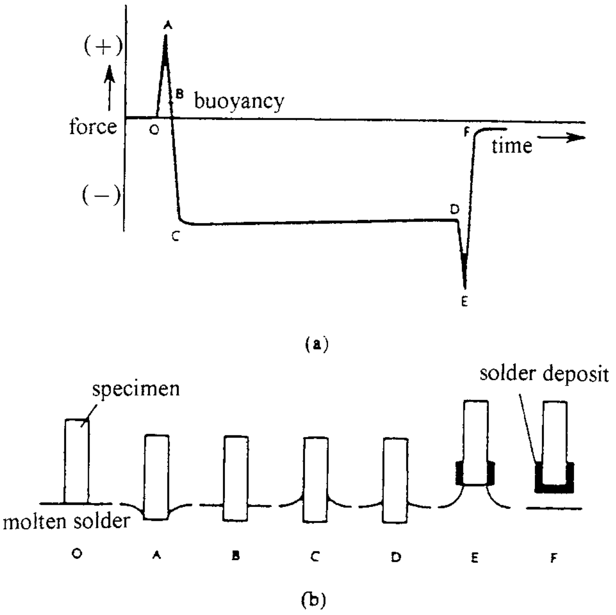


Figure 1 (a) A typical sketch of wetting curve, (b) various moments in dipping experiment corresponding to the points of wetting curve.

3. Results and discussion

3.1. Wetting characteristics

The basic properties of four fluxes utilized to investigate the wetting behaviors are listed in Table I. The wetting time measured through the wettting curve can be regarded as the kinetics index of solderability. Fig. 2

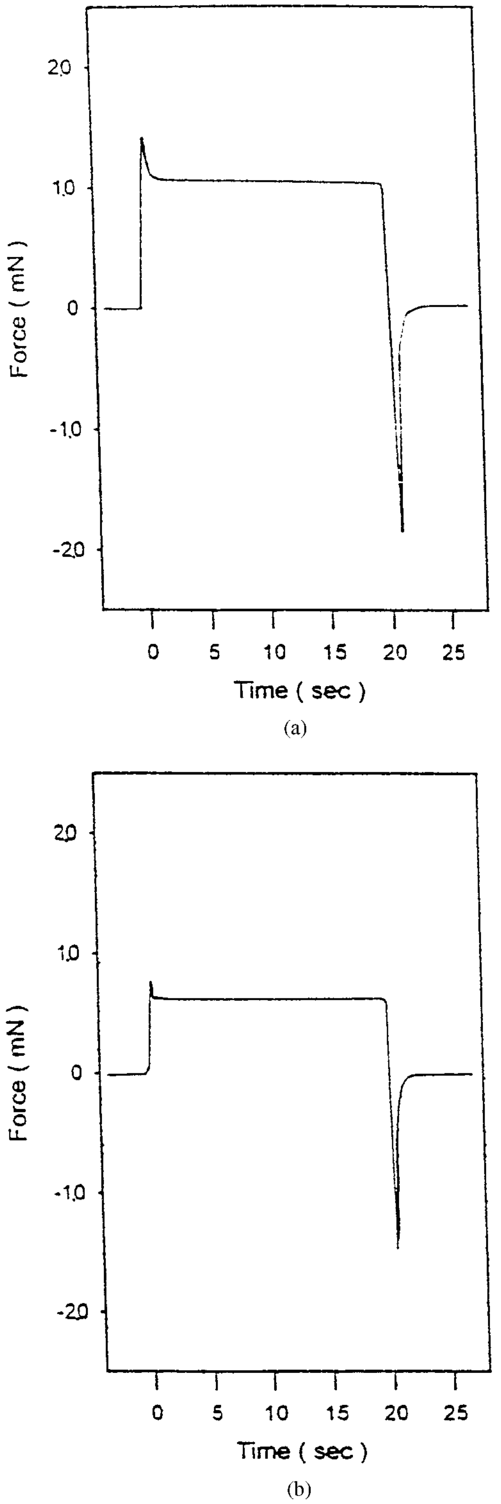


Figure 2 The wetting curves of the near-eutectic Sn-Zn-In solder on Cu substrate at (a) 250°C and (b) 300°C using 2 wt% SA flux.

TABLE I Basic properties of four fluxes utilized

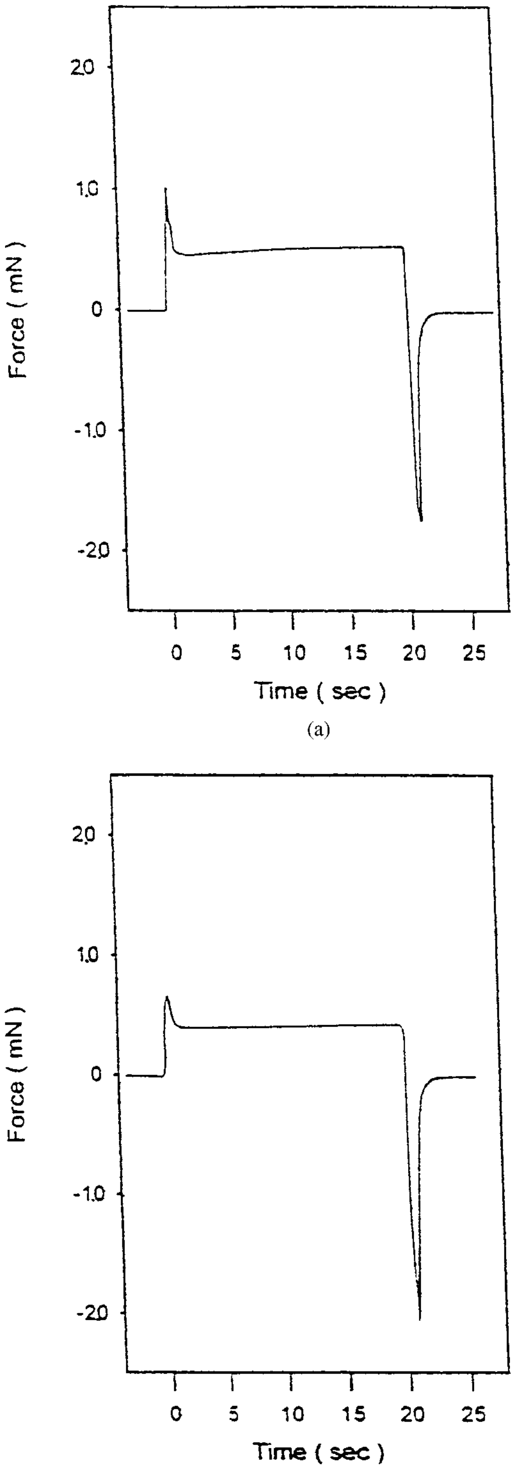
Scientific name	Dimethylammonium chloride (DMAHCl)	Stearic acid (SA)	Oleic acid (OA)	Lactic acid (LA)
Chemical formula	C_2H_8ClN	$C_{18}H_{36}O_2$	$C_{16}H_{34}O_2$	$C_3H_6O_3$
Molecular weight (g/mol)	81.54	284.461	282.47	90.08
Melting point (°C)	170 ~ 173	64 ~ 70	—	—
Boiling point (°C)	—	232	286	119

shows the wetting curves of the near-eutectic Sn-Zn-In solder on Cu substrate at 250 and 300°C respectively by using 2 wt% SA as flux. The forces acting at point A (in Fig. 1) at 250 and 300°C are shown in Fig. 2a and b, respectively. It indicates that the repellent force at 300°C (0.79 mN) is lower than that at 250°C (1.45 mN) because the viscosity of solder alloy decreases with temperature increasing. However, no matter at 250 or 300°C, the wetting curves cannot attach the point where buoyancy is the only force acting on the specimen. Wetting time cannot be obtained for this system indicating the poor wetting. Only repellent force was applied on the specimen instead of attractive force before the specimen was pulling out away from the smelting solder. Consequently, stearic acid was not a suitable flux for dipping the 86Sn-9Zn-5In solder on Cu substrate.

Fig. 3 shows the wetting curves of the near-eutectic Sn-Zn-In solder on Cu substrate at 250 and 300°C respectively by using 10 vol% OA as flux. The repellent forces acting at point A (in Fig. 1) for 250°C and 300°C are shown in Fig. 3a and b, respectively. From Figs 2 and 3, it is observed that the repellent force at point A (in ig.1) using 10 vol% OA flux was lower than that using 2 wt%SA flux at 250 or 300°C. It indicates that OA is more wettable than SA as a flux for the Sn-Zn-In solder dipping on Cu substrate. However, both OA and SA are not suitable flux for the Sn-Zn-In solder system on Cu substrate because of poor wetting as shown in their wetting curves.

Fig. 4 shows the wetting curves of the near-eutectic Sn-Zn-In solder on Cu substrate at 250 and 300°C respectively by using 5 vol% LA as flux. It indicates that the repellent force acting at point A (in Fig. 1) at 300°C (Fig. 4b) is lower than that at 250°C (Fig. 4a), in which the wetting time is less than 1 second, and can be defined as highly wettable [5]. The attractive forces obtained at point C (in Fig. 1), defined as the maximum wetting force, are 0.13 and 0.38 mN as shown in Fig. 4a and b, respectively. In addition, the repellent force at point A (in Fig. 1) at 300°C (0.52 mN) is also lower than that at 250°C (1.02 mN).

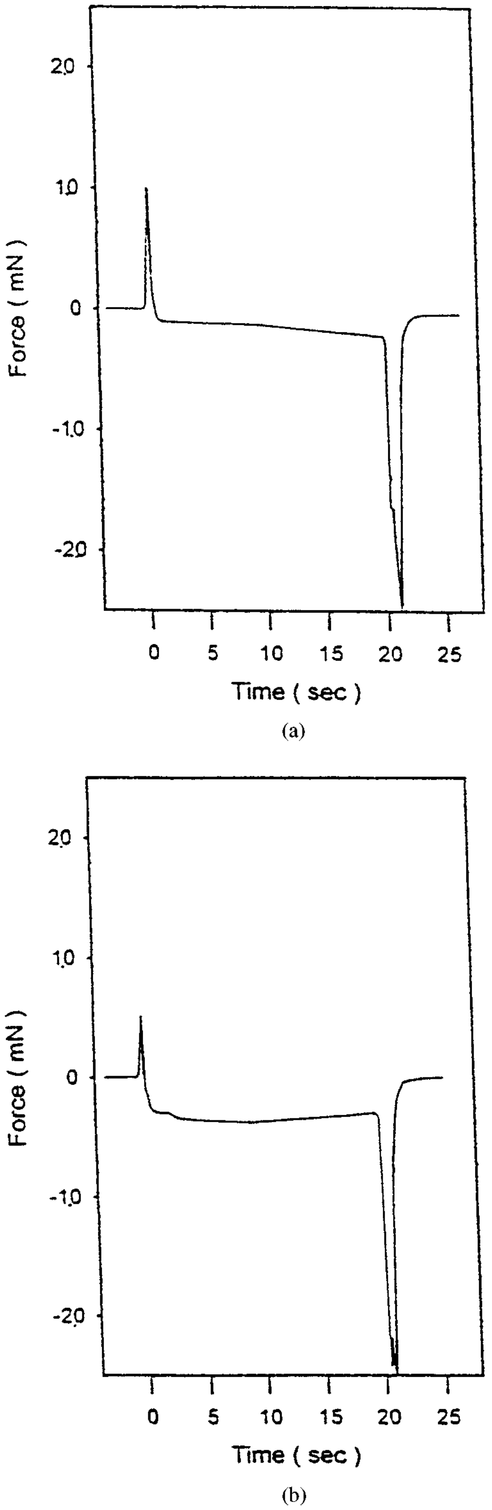
Fig. 5 shows the wetting curves of the near-eutectic Sn-Zn-In solder on Cu substrate at 250 and 300°C respectively using 2.5 wt% DMAHCl as flux. According to Figs 4 and 5, it indicates that the maximum wetting forces by using 2.5 wt% DMAHCl flux are larger than that of 10 vol% LA flux. It shows that DMAHCl is more suitable than LA, OA, and SA as flux for the Sn-Zn-In solder on Cu substrate. The lowest wetting time (0.27 s) was obtained for 3.5 wt% DMAHCl as flux at 300°C. The wetting times with various contents



(a)

(b)

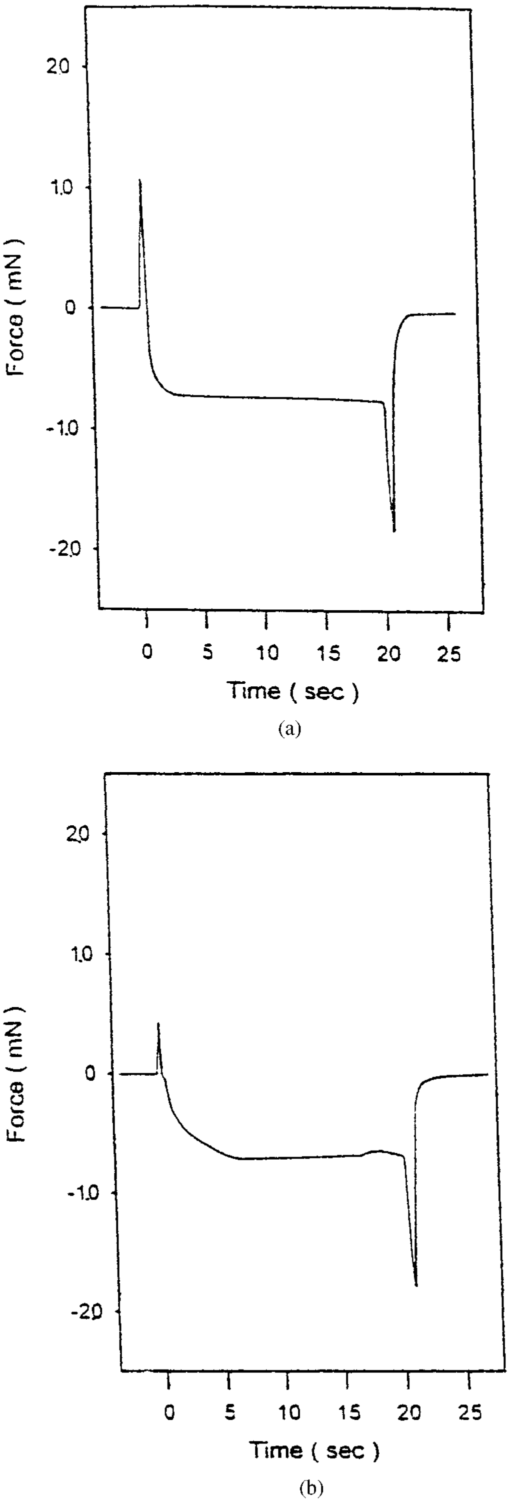
Figure 3 The wetting curves of the near-eutectic Sn-Zn-In solder on Cu substrate at (a) 250°C and (b) 300°C using 10 vol% OA flux.



(a)

(b)

Figure 4 The wetting curves of the near-eutectic Sn-Zn-In solder on Cu substrate at (a) 250°C and (b) 300°C using 5 vol% LA flux.

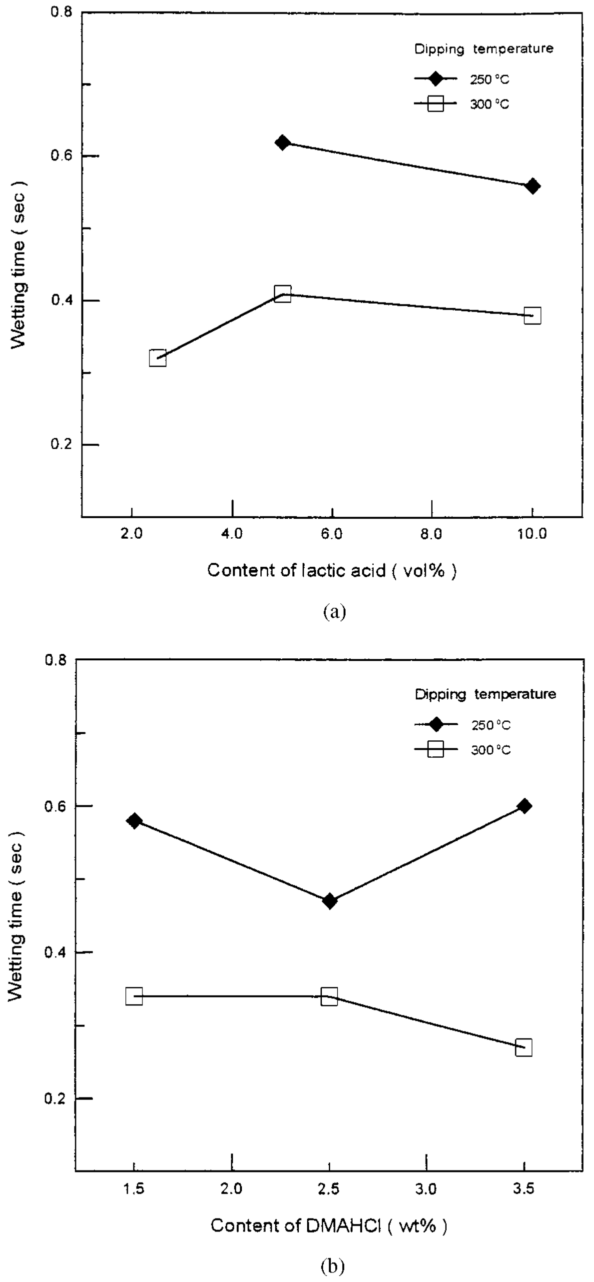


(a)

(b)

Figure 5 The wetting curves of the near-eutectic Sn-Zn-In solder on Cu substrate at (a) 250°C and (b) 300°C using 2.5 wt% DMAHCl flux.

of LA and DMAHCl at 250 and 300°C are shown in Fig. 6a and b, respectively. When the dipping temperature increased from 250 to 300°C, the wetting time decreased obviously from 0.6 to 0.4 s with LA and DMAHCl as flux. The wetting time shown in Fg. 6a at 300 and 250°C varies with the content of LA flux, respectively. For the content of LA less than 5.0 vol% at 250°C and 2.5 vol% at 300°C, non-wetting or partial wetting was observed by wetting curves. In addition, for the content of DMAHCl less than 1.5 wt% at 250 and 300°C, non-wetting or partial wetting was also observed by wetting curves. Fig. 7a is the representative curve for non-wetting case by using 1.5 vol% LA as flux at 250°C. On the other hand, the partial wetting curve by using 3.0 vol% LA is shown in Fig. 7b. Simultaneously, the repellent forces acting on the specimen at point A (in Fig. 1) for using 1.5 and 3.0 vol% LA flux at 300°C are 2.18 and 1.38 mN, respectively. Both LA and DMAHCl with enough amount are the suitable fluxes for the Sn-Zn-In solder wetting on Cu substrate for the wetting time less than 1 s. From Table I, the molecular weights of LA and DMAHCl are larger than that of SA

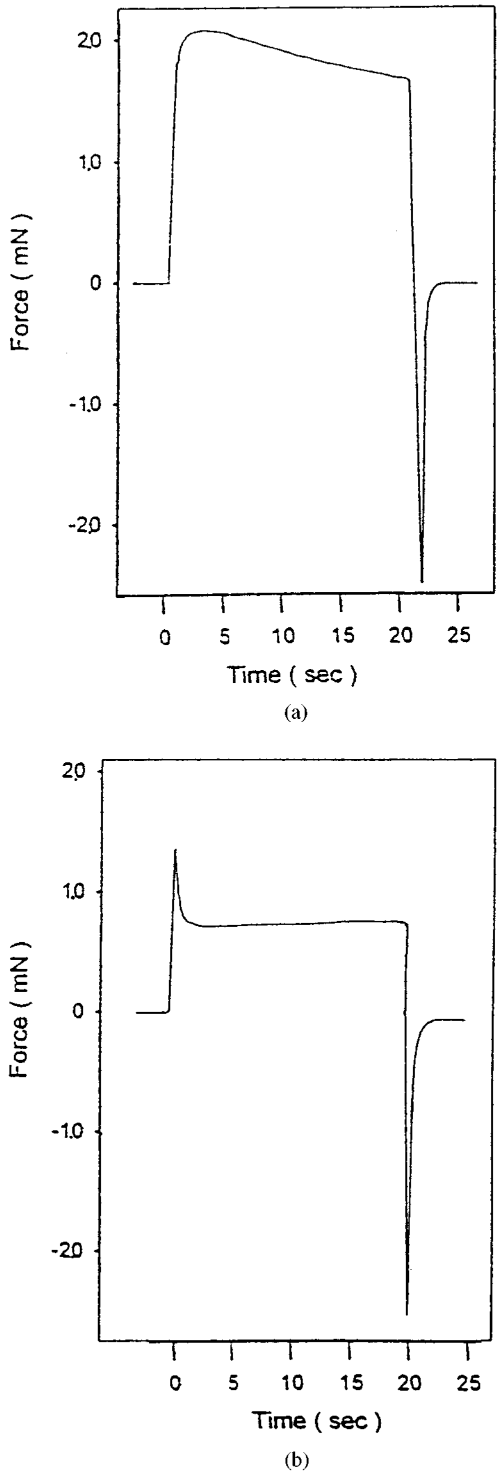


(a)

(b)

Figure 6 The wetting time with respect to content of flux for different temperature and flux of (a) LA, (b) DMAHCl.

and OA, therefore the higher viscosity makes the LA and DMAHCl more wettable than SA and OA for the Sn-Zn-In solder on Cu substrate.



(a)

(b)

Figure 7 The wetting curves of the near-eutectic Sn-Zn-In solder on Cu substrate at 300°C with fluxes of (a) 1.5 vol% LA and (b) 3.0 vol% LA.

3.2. Microstructure analyses

Fig. 8 shows the cross-sectional SEM micrographs and line scanning analyses for the near-eutectic Sn-Zn-In solder as-dipped on Cu substrate at 250° with 2.5 wt% DMAHCl as flux. The Cu and Sn line scanning analyses are shown in Fig. 8a. An interaction layer was formed between Cu substrate and the Sn-Zn-In solder as shown in Fig. 8a. Furthermore, the Zn element was enriched in the interacting layer as shown in Fig. 8b. Bailey and Watkins [6] pointed out that molten metal will wet solid metal better if mutual solubility or intermetallic formation exists. The Zn element diffused forward Cu substrate to form γ-Cu_5Zn_8 IMC as examined by XRD analysis and SAED analyses shown in Figs 9 and 10, respectively.

Fig. 9 shows the XRD pattern of sample dipped at 250°C with 2.5 wt% DMAHCl flux and then etched for eliminating the unreacted solder alloy on the surface. The γ-Cu_5Zn_8 was found at the near-eutectic Sn-Zn-In/Cu interface in this work. Fig. 10 shows the TEM photomicrograph and SAED patterns of the near-eutectic Sn-Zn-In solder as-dipped on Cu substrate with 2.5 wt% DMAHCl flux at 250°C, showing the BF image and SAED patterns along various zone axes. The IMC of γ-Cu_5Zn_8 was formed in the Sn-Zn-In/Cu system,

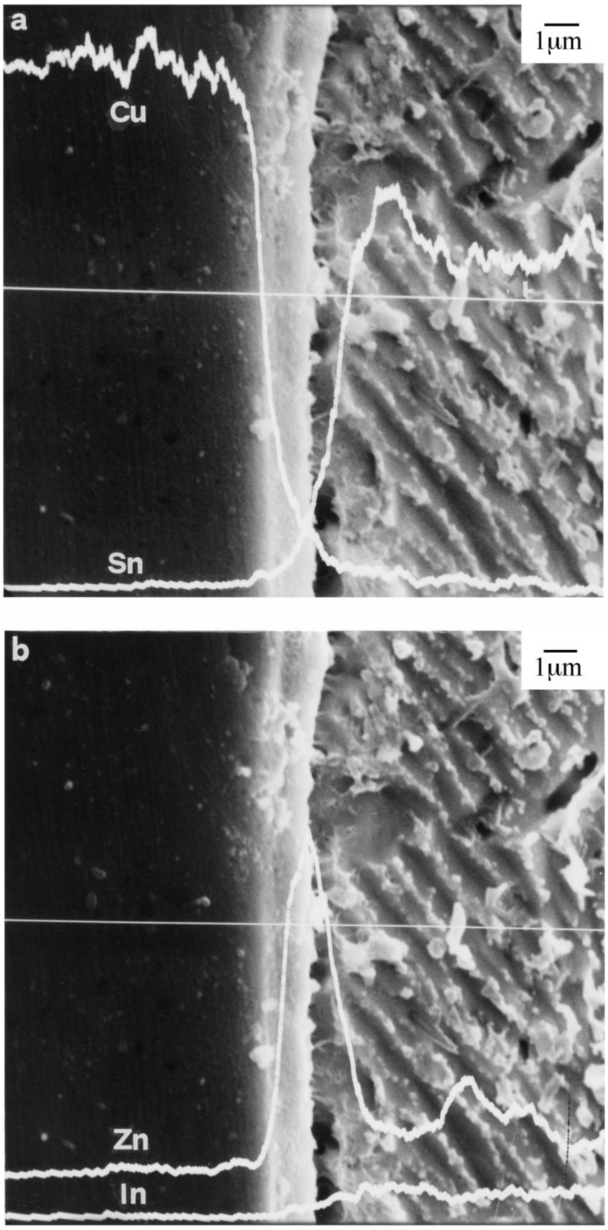


Figure 8 Cross-sectional SEM micrographs and line scanning analysis of the near-eutectic Sn-Zn-In solder as-dipped on Cu at 250°C with 2.5 wt% DMAHCl flux for elements of (a) Cu and Sn (b) Zn and In.

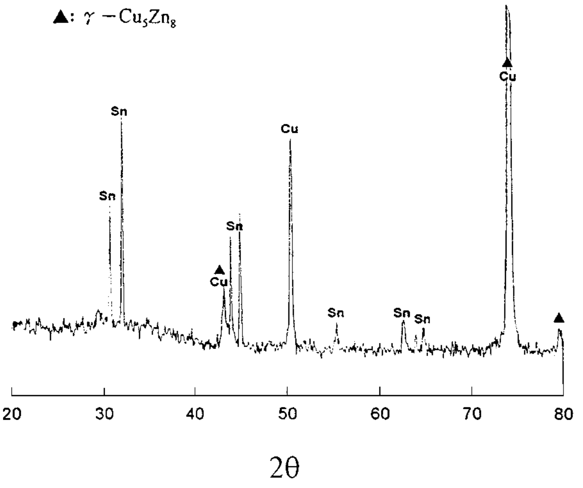


Figure 9 XRD pattern of sample dipped in the near-eutectic Sn-Zn-In solder at 250°C with 2.5 wt% DMAHCl flux and then etched for eliminating unreacted solder alloy.

like in Sn-Zn-Al [7, 8] and Sn-Zn [9] solders with Cu substrate. There was no Cu-Sn alloy or compounds formed at the interface between the Sn-Zn-In solders and Cu substrate, which is quite different from the previous reports [10–18] that indicating the intermetallic phases, Cu_6Sn_5 and Cu_3Sn were observed in the most Sn-base solder systems. In addition, the reasons for γ-Cu_5Zn_8 IMC formation instead of Cu-Sn IMCs were investigated in our previous study by concerning the thermodynamics and diffusivity [8].

3.3. The schematic diagram of reaction path

The flux should have the effect of decreasing the dihedral angle, the angle θ formed between the liquid solder and solid substrate, thus enabling the solder to wet the solid metal better. In addition, the flux should be able to wet the base metal, replacing any vapor phase adsorbed on the surface and making the surface available for total contact with the solder, thus promoting wetting. In the soldering process, where flux is applied, the wetting equation can be presented by Young's equation as follows:

$$\gamma_{\mathrm{SF}} = \gamma_{\mathrm{LS}} + \gamma_{\mathrm{LF}} \cos\theta \qquad (1)$$

where γ_{SF} is the interfacial tension between the metal (solid) and the flux, γ_{LF} is that between the solder (liquid) and the flux, and γ_{LS} is the interfacial tension between the solder (liquid) and the metal (solid).

If the content of flux is not enough to affect the interfacial tension like γ_{SF} and γ_{LF}, poor wetting occurs as shown in Fig. 7. Furthermore, the temperature of the system affects the surface tension to make the wetting behaviors different. Fig. 6 shows that no matter what flux was used, the wetting time decreased as the temperature increased from 250 to 300°C. That is to say that the rate of wetting increased with the rise of temperature as shown in Figs 2–5.

The schematic diagram of reaction path shown in Fig. 11 [19] explains the thermodynamic and kinetic behaviors of the Sn-Zn-In/Cu system with various fluxes. Path (1) represents the reaction path of the Sn-Zn-In/Cu system utilizing SA or OA, while path (2) delineates the path utilizing LA or DMAHCl as the flux. The components participated in the initial state include the Cu substrate and the liquid solder, while in the final state the wetting reaction product of γ-Cu_5Zn_8 IMC is formed. The wetting reaction is described by the following processes:

$$\text{Sn-Zn-In}_{(1)} + \text{Cu}_{(s)} \rightarrow \text{Cu-Zn}^{*} \rightarrow \gamma\text{-Cu}_5\text{Zn}_{8(s)} \qquad (2)$$

The reaction proceeds through the activated state Cu-Zn* and the solid/liquid reaction begins when the solid substrate is in contact with the liquid solder. Consequently, the wetting occurs at the moment of $\gamma_{\mathrm{SF}} = \gamma_{\mathrm{LS}}$, when the wetting reaction proceeds very much close to the activated state which is determined by γ_{SF}. Accordingly, for any solid/liquid contact, the activated state is determined by the flux which governs γ_{SF}, and, thus the wetting time. $\Delta G^{*}_{(1)}$ and $\Delta G^{*}_{(2)}$ are the activation

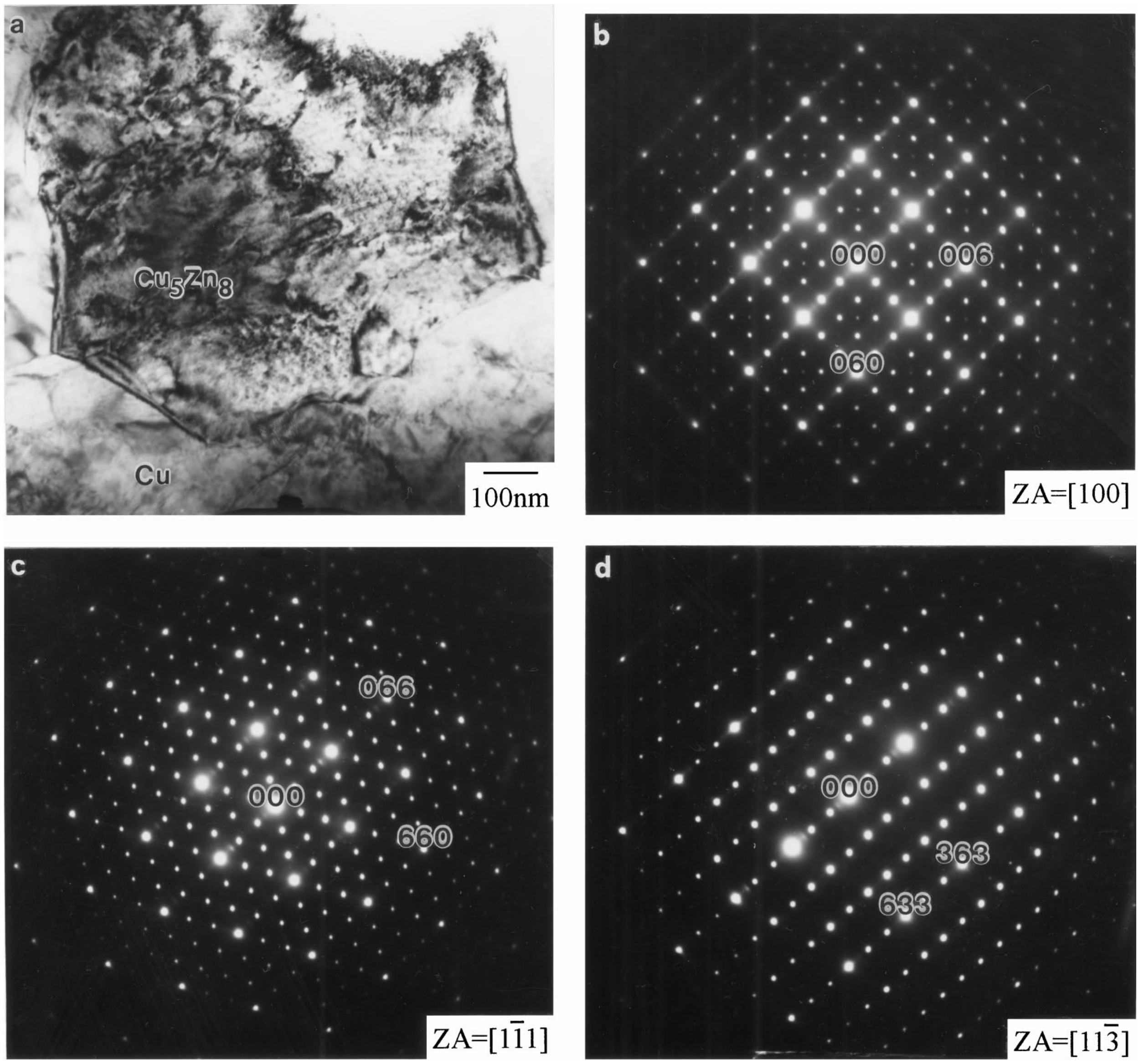


Figure 10 TEM photomicrograph and SAED patterns of the near-eutectic Sn-Zn-In solder as-dipped on Cu substrate at 250°C with 2.5 wt% DMAHCl flux, showing BF image and SAED patterns along various zone axes for (a) image of γ-Cu_5Zn_8 IMC, (b) [100], (c) $[1\bar{1}1]$ and (d) $[11\bar{3}]$.

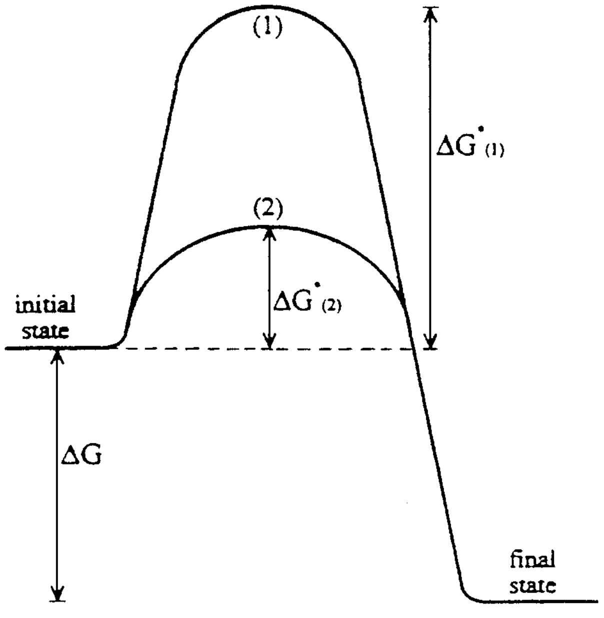


Figure 11 The free energy sketch of wetting reaction using different fluxes.

energies of the activated state for paths (1) and (2), respectively. $\Delta G^*_{(1)}$ is quite larger than $\Delta G^*_{(2)}$ indicating that DMAHCl or LA is more suitable than SA and OA as flux for the near-eutectic Sn-Zn-In/Cu system.

4. Conclusion

According to the wetting curves obtained by a wetting balance apparatus, the SA and OA are not the suitable flux for the near-eutectic Sn-Zn-In solder on Cu substrate. However, the LA and DMAHCl provide a good wetting for the soldering system. The lowest wetting time (0.27 s) was obtained with 3.5 wt% DMAHCl as flux at 300°C. When the dipping temperature increased from 250 to 300°C, the wetting time decreased from 0.6 to 0.4 s with LA and DMAHCl as flux. For the content of LA less than 5.0 vol% at 250°C and 2.5 vol% at 300°C, non-wetting or partial wetting was observed by wetting curves. In addition, for the content of DMAHCl less than 1.5 wt% at 250 and 300°C, non-wetting or partial wetting was also observed. Quite different from the most tin-based solders for Cu substrate, intermetallic compound γ-Cu_5Zn_8 was found by the X-ray diffraction (XRD) at the interface of solder and substrate after etching out the unreacted solder layer, and was examined by selected area electron diffraction (SAED) analysis. The Zn element was enriched at the interface between solder and Cu substrate as analyzed by line scanning.

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