The Wettability and Microstructure of Sn-Zn-RE Alloys

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Rare earth (RE) elements with concentrations of 0.05 wt.% and 0.1 wt.% of primarily Ce and La were added to the Sn-9Zn eutectic alloy to produce Sn-9Zn-RE alloys. A small amount of rodlike Zn-rich phases, which decreases in amount as the RE content increases, is distributed in the Sn matrix under slow cooling. The microstructure is refined with RE additions, and particulate-shaped Sn-RE compounds begin to appear when the RE content reaches 0.1 wt.%. There is no change in the liquidus temperature after RE additions. Of the rosin-activated (RA), rosin mildly activated (RMA), rosin-nonactivated (R), and volatile organic compounds (VOC)-free types of fluxes used for the wetting balance tests in ambient air at 245°C, 260°C, and 290°C, only the RA flux can provide wetting. The addition of RE elements or the increase in soldering temperature reduces the wetting angle and increases the wetting force. The microhardness of the Sn-Zn-RE alloy system was found to be higher than that of Sn-9Zn.

Key words: Lead-free solder, Sn-9Zn, rare earth, wetting force, wetting time, contact angle, microhardness

INTRODUCTION

The development of lead-free solders has been an essential and urgent task in the electronics packaging industry because of the restriction of lead use by legislations.[1] The eutectic Sn-Zn system has been one of the candidates for the replacement of Sn-Pb because its liquidus temperature (198°C) is very close to that of Sn-Pb eutectic alloy (183°C) so that existing production lines and electronic components do not require major modifications.[2] Apart from its favorable melting temperature, cost and mechanical properties have also been considered. The Sn-9Zn is the least expensive alloy when compared with Sn-Ag and Sn-In solders. Its mechanical properties, e.g., tensile strength, are better than that of the Sn-Pb. For example, the Sn-9Zn solder paste was found to provide a fairly high joint strength of about 50 MPa just after soldering.[3] High joint strength would be good for static load resistance but may not be a benefit for long-term reliability as high strength may translate into a shorter fatigue life of solder joints.

Poor wettability and oxidation resistance are the major drawbacks against the use of Sn-9Zn as a sol-

der alloy in the electronics industry. Because Zn is an active element in solder, the wetting and corrosion properties are impaired. For example, when wave soldering is conducted, this alloy tends to produce a lot of dross. To overcome the shortfall of Sn-9Zn, some authors have tried to add a third element, such as In, Bi, or Al, into the Sn-9Zn binary system. McCormack et al. added 5wt.%In into Sn-9Zn to reduce the melting temperature from 198°C to 188°C, which was very close to 183°C of Sn-37Pb.[4] The addition of Bi was also capable of lowering the melting temperature of the solder.[5] Kwang and Li studied the wetting behavior of adding Al into Sn-9Zn.[6] Furthermore, a flux specially designed for Sn-9Zn has been developed in Japan.[7] It is also possible that the incorporation of an inert environment, e.g., nitrogen flow in the furnaces, for the soldering process with an appropriate flux, will broaden the application for Sn-9Zn as the soldered products will be more reliable.

Recently, rare earth (RE) elements have been observed to possess many merits as doping elements in solders. In previous work, RE elements, primarily Ce and La, were added to Sn-0.7Cu and Sn-9Zn lead-free eutectic alloys to study the effects on the microstructure.[8,9] It was found that the addition of

RE elements could generally improve the microstructure by providing finer grain size so that the yield strength was improved. As the preceding aspects have suggested, the Sn-Zn-RE system has good potential as a lead-free solder alloy. This paper investigates the effects of its wetting properties. Four commercially available liquid fluxes, namely, the rosin-activated (RA), rosin mildly activated (RMA), rosin-nonactivated (R), and VOC-free types of fluxes were used to study the wettability of Sn-Zn-RE on Cu substrates at various soldering temperatures. The descriptions of these fluxes from their manufacturer can be found in Table I.

EXPERIMENTAL PROCEDURES

Solders and Coupons Preparation

The Sn-9Zn-xRE solders, where x (in wt.%) is 0, 0.05, and 0.1, were prepared from pure Sn (99.95%), pure Zn (99.999%), and RE elements, which are primarily Ce and La. These were melted in a vacuum furnace at 500°C for 5 h. Although RE elements melt at a relatively high temperature, they dissolved readily into the molten Sn-Zn bath. The molten solder in the crucible was slow cooled. The microstructure of Sn-Zn-RE systems was examined by scanning electron microscopy (SEM) with a voltage of 20 keV. Energy dispersive x-ray (EDX) microanalysis was used to identify the elemental compositions at selected areas. A differential scanning calorimeter (DSC) was used to determine the liquidus temperature of the Sn-Zn-RE systems with a heating rate of 10°C/min under the nitrogen atmosphere. Microhardness tests were conducted to investigate the effects of RE addition on microhardness. The wetting behavior of the Sn-Zn-RE solder alloys was investigated by the wetting-balance method using a pure Cu foil (99.9%) as the substrate coupon. The test coupons were cut into a size of 15 mm × 10 mm × 0.2 mm and were ground and polished. They were then degreased in a 1:1 solution of HCl and water for 1 min, ultrasonically cleaned in ethanol, and dried. These coupons were coated with alcohol-based or water-based liquid flux before they were tested in the wetting balance.

Solderability and Microhardness Measurements

In a spread test, a solder disc (e.g., 6-mm diameter and 1-mm thickness) is melted and allowed to solidify on a substrate (e.g., copper). This is a good simulation of the reflow soldering process because the solder disc in the spread test has a similar shape as the layer of solder paste by screen-printing or similar process. Also, the solder disc in the spread test and the solder paste in reflow soldering undergo the same method of heating, i.e., reflow at a temperature above the solder melting point, and are allowed to solidify. In a wetting-balance test, molten solder climbs up the coupon when it is dipped into the solder bath. This is similar to the situation in wave soldering, where a wave of molten solder is brought into contact with the substrate.

The quantitative measures of solderability for the wetting balance test are the contact angle, θ_c, and the wetting force, F_w. The contact angle formed on the surface of a Cu coupon is shown in Fig. 1. The equilibrium contact angle is determined by the interfacial surface tension, γ_{SF}, γ_{LF}, and γ_{SL} in the Young—Dupre equation.

$$\gamma_{SF} = \gamma_{SL} + \gamma_{LF} \cos \theta_c \qquad (1)$$

where $\cos \theta_c = \dfrac{\gamma_{SF} - \gamma_{SL}}{\gamma_{LF}}$, and γ_{SF}, γ_{LF}, and γ_{SL} refer to the surface tensions of the substrate/flux, liquid (solder)/flux, and substrate/liquid (solder) interfaces, respectively. When a good wetting occurs, the contact or wetting angle should be small, (i.e., with γ_{LF} small or ($\gamma_{SL} - \gamma_{SF}$) large).

The wetting force is a force exerted by the solder on the coupon and is directly proportional to the height of the solder that climbs up the coupon. When a coupon is partly immersed into a molten solder bath, it is subjected to a set of forces because of the buoyancy and the surface tensions. The measurement of the resultant force is representative of the meniscus and of the wetting angle and, consequently, of the solderability quality. The resultant force or wetting force, F_w, can be expressed as follows:

$$F_w = p\gamma_{LF} \cos \theta_c - \rho g V \qquad (2)$$

Table I. Details of the Four Types of Flux

| Flux (Alpha)	Type	Base	Surface Tension (mN/mm)	Description
A88	RA	Alcohol	370	No-clean foam flux with water-white rosin in organic solvents; not corrosive to solder or exposed copper.
A90-7	RMA	Alcohol	415	Similar to RA but mildly activated.
100-25	R	Alcohol	445	Similar to RA and RMA, except that it does not contain activators and meets the requirements of Type R of MIL-F-14256E.
NR330	VOC-free	Water	Not available	Bellcore compliant VOC-free, halide-free, rosin/resin-free, low solids no-clean flux, with proprietary mixture of organic activators.
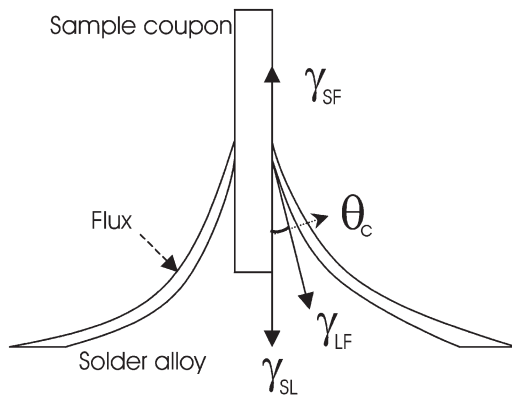
Fig. 1. The forces on the wetting test coupon.

where p is the perimeter of the coupon, γ_{LF} is the surface tension of the solder in contact with the flux, θ_c is the contact angle, ρ is the density of the solder, g is the acceleration caused by gravity, and V is an immersed volume. Hence, the wetting force and time of each solder system are revealed by the wetting-balance test.

A typical wetting curve is shown in Fig. 2, in which the wetting time, t_w, is the time at which the solder contact angle to the coupon is 90°, as shown at point B. Short wetting times are considered to be good. In the present tests, the immersion depth and time were 3 mm and 10 sec, respectively. The immersion rate was 15 mm/sec. The conditions used in the wetting-balance test were the same except for the temperature of the solder bath. The solder bath temperatures were 245°C, 260°C, and 290°C for the Sn-Zn-RE alloys and 235°C for Sn-37Pb. Five specimens were evaluated for the wetting force, and five more specimens were studied for the contact angle. The wetting tests for these solders were performed using four different fluxes, namely, the RA, RMA, R, and VOC-free in ambient air. The details of these fluxes are shown in Table I.

In the microhardness test, the load used was 50 g with the Vickers hardness scale. Ten measurements were conducted on the surface of each Sn-Zn-RE system.
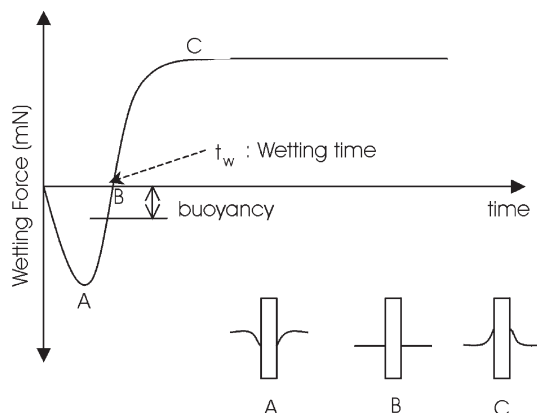

Fig. 2. The variation of wetting force with time.

RESULTS AND DISCUSSION

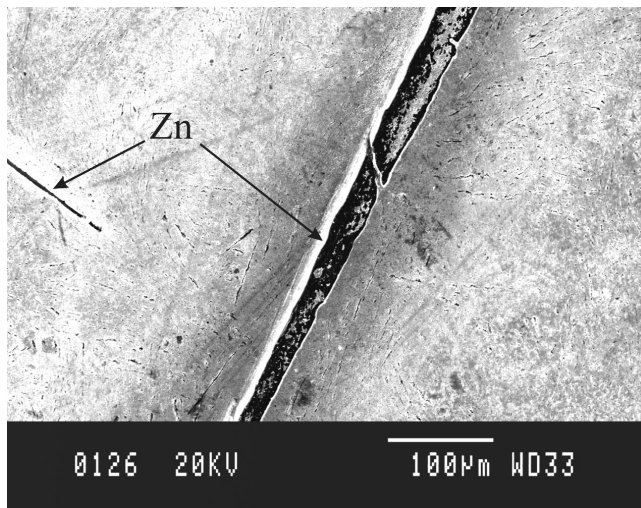### Microstructure and Liquidus Temperature

The Sn-9Zn eutectic alloy at 198°C consists of two phases, namely, the β-Sn and Zn-rich phases with less than 1% Sn.[9] Figure 3a—c show the microstructures of Sn-9Zn, Sn-9Zn-0.05RE, and Sn-9Zn-0.1RE alloys, respectively, under slow cooling. In this figure, the Zn was etched so that dark grooves were formed at the originally Zn-occupied sites. In particular, in the Sn-9Zn alloy, the long Zn-rich phase is a few millimeters long and about 30-μm wide. The rodlike Zn-rich phase is formed during solidification because of the conglomeration of small Zn-rich phases. With the addition of 0.1% RE, the number and size of these rodlike Zn-rich phases decrease, and a fine microstructure is obtained. In some soldering applications, such as those in electronics soldering, the cooling rate will be faster than that in the present situation, and so the rodlike Zn-rich phases will not be obtained.[9] Figure 4a and b shows the backscattered scanning electron micrographs of Sn-9Zn-0.05RE and Sn-9Zn-0.1RE, respectively. Although Sn and Zn can form an intermetallic compound with Ce and La individually, the reaction temperature for Sn-RE is under 300°C, while the temperature for Zn-RE is nearly 500°C. Hence, there is a tendency to form Sn-RE compounds under the slow cooling. In Fig. 4b, the particulate-shaped Sn-RE compounds with size of 5-10 μm can be observed in the Sn-rich matrix, but they cannot be found in the Sn-9Zn-0.05RE system. The amount of RE elements in Sn-9Zn-0.05RE is too small to be detected.

In the DSC analysis, the melting curves of differential heat flow against temperature are shown in Fig. 5a—c. There is no significant change of the liquidus temperature after the addition of RE into the Sn-9Zn system. The liquidus temperatures of Sn-9Zn, Sn-9Zn-0.05RE, and Sn-9Zn-0.1RE are 198.93°C, 198.70°C, and 198.96°C, respectively.

Effect of RE on Solderability

Figure 6 shows the wetting curves of the Sn-9Zn-0.05RE solder using the RA flux as well as that of Sn-37Pb using the RMA flux. The soldering temperatures were 245°C, 260°C, and 290°C for Sn-9Zn-0.05RE and 235°C for Sn-37Pb. The wetting force for Sn-37Pb is very large, but the force for Sn-9Zn is very small. The addition of 0.05% RE to Sn-9Zn has significantly improved the wetting force. Also, wetting at 290°C gives the largest wetting force among the three soldering temperatures. From Fig. 6, the wetting time can also be obtained. The wetting time of Sn-9Zn-0.05RE at 245°C, 260°C, and 290°C are 0.40, 0.26, and 0.22, respectively. These are all smaller than the value of 0.5 sec for Sn-37Pb. Figure 7 shows the change of wetting time with the amount of RE elements. It was found that 0.05 wt.% of RE addition gives the best wetting time.
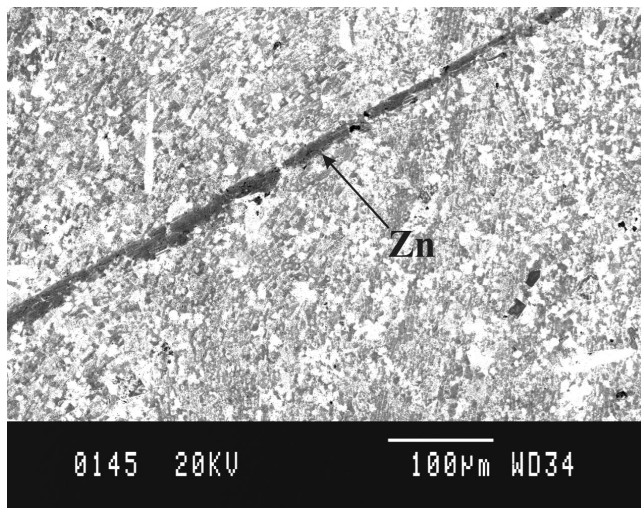
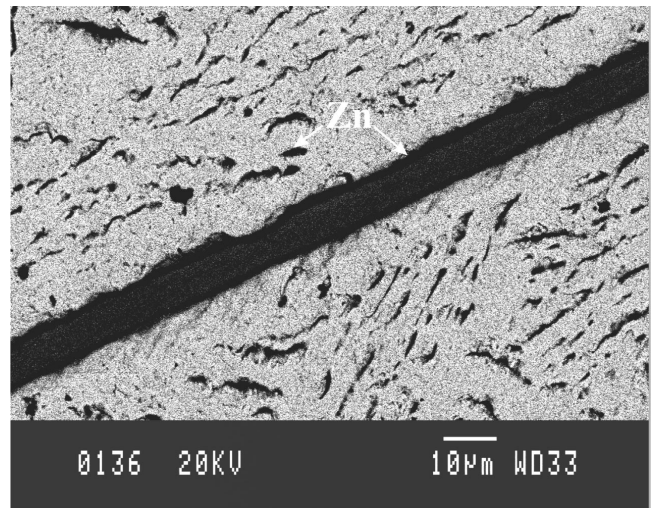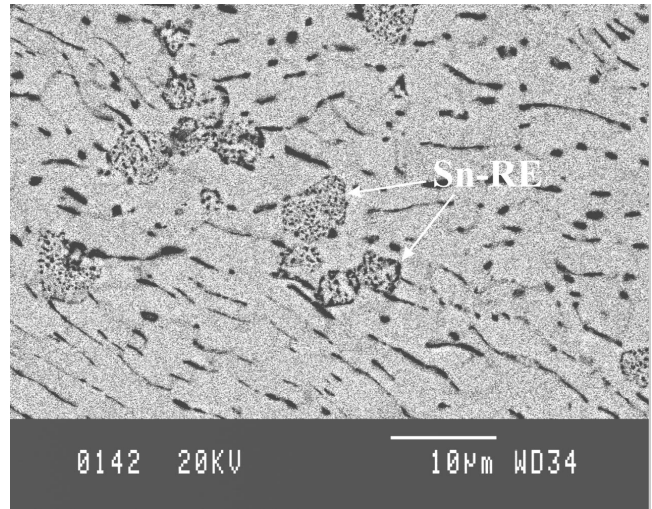The surface tension of Sn-9Zn is too large to provide a good wetting property. The enhancement ob-

a

a

b

b

Fig. 4. The backscattered scanning electron micrographs (a) Sn-9Zn-0.05RE and (b) Sn-9Zn-0.1RE.
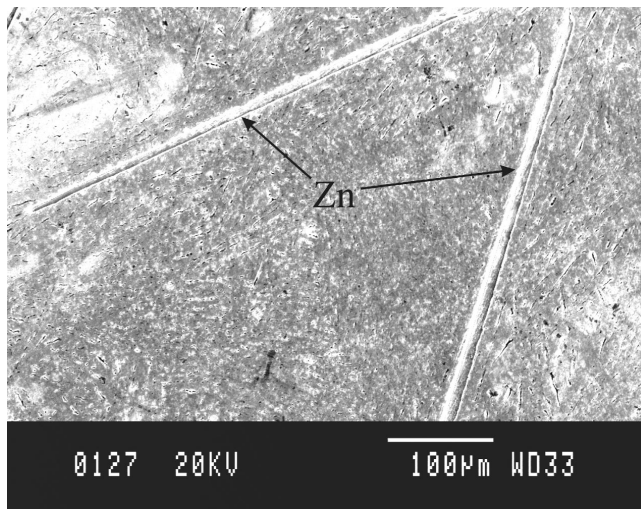
c

Fig. 3. The SEM SE micrographs of Sn-9Zn-RE systems under slow cooling: (a) Sn-9Zn, (b) Sn-9Zn-0.05RE, and (c) Sn-9Zn-0.1RE.

tained by adding a proper amount of RE can be analyzed through the effects of RE on the interfacial tensions, γ_{SF}, γ_{LF}, and γ_{SL}. According to the Ce-Cu phase diagram,[10] as shown in Fig. 8, below the soldering temperature of 300°C, interaction between Ce and Cu is very low. It is, therefore, impossible to reduce the γ_{SL} interfacial tension between the solder and the Cu substrate by the interaction of RE and Cu. On the other hand, as the same type of flux and substrate are used in each test, the interfacial tension between substrate and flux, γ_{SF}, is a constant. As RE is an active element, it is easier for them to accumulate at the solder/flux interface in molten state, and subsequently, the interfacial surface energy is decreased. Therefore, the γ_{LF} interfacial tension between solder and flux can be reduced.

Effect of RE Content, Soldering Temperature, and Flux Type
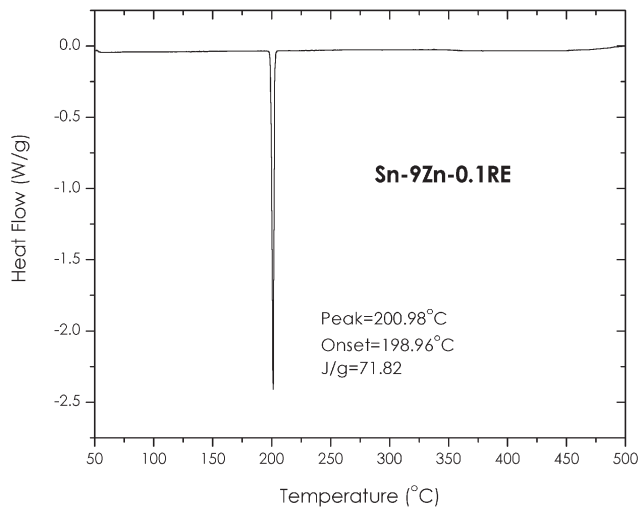
Figure 9a and b show the contact angle and wetting force, respectively, of the Sn-Zn-RE system
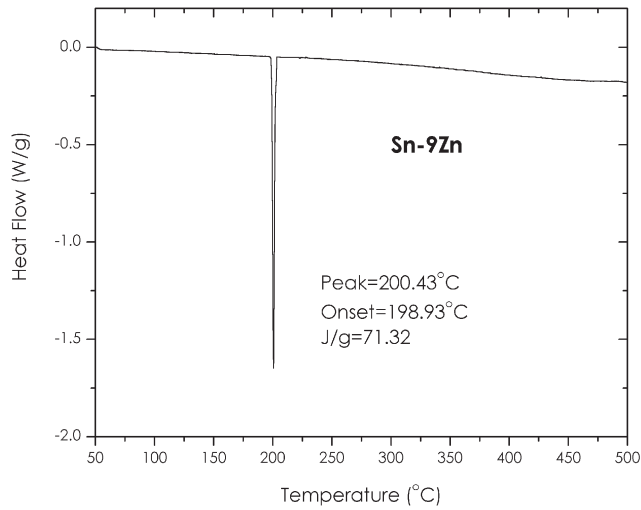
a
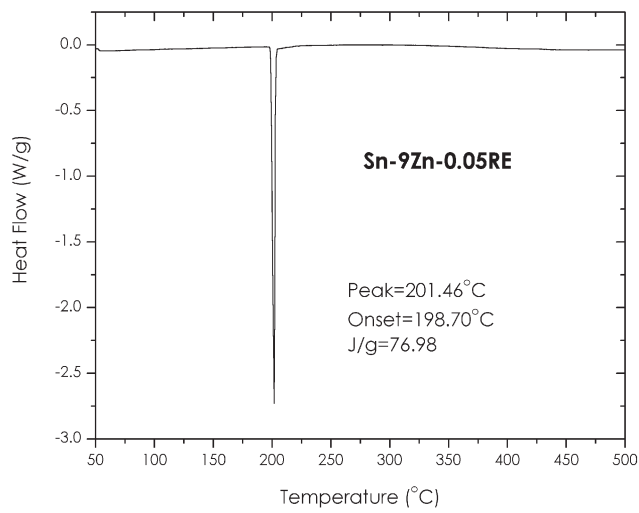
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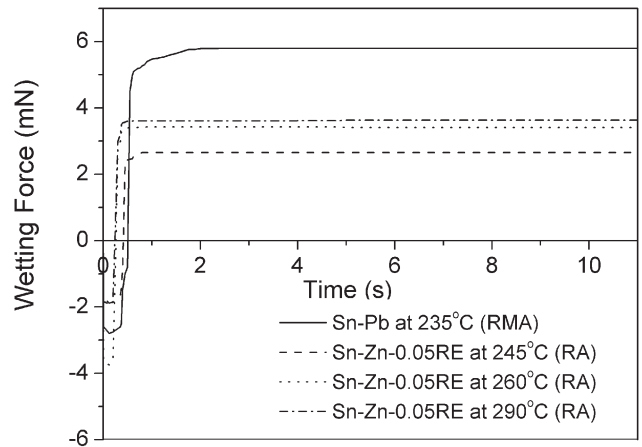Fig. 5. The DSC curves (a) Sn-9Zn, (b) Sn-9Zn-0.05RE, and (c) Sn-9Zn-0.1RE.

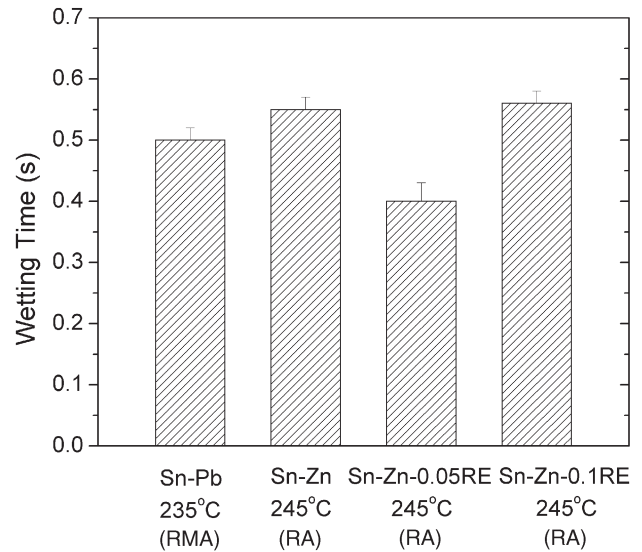Fig. 6. The wetting curves of Sn-Zn-RE solders compared with Sn-Pb.

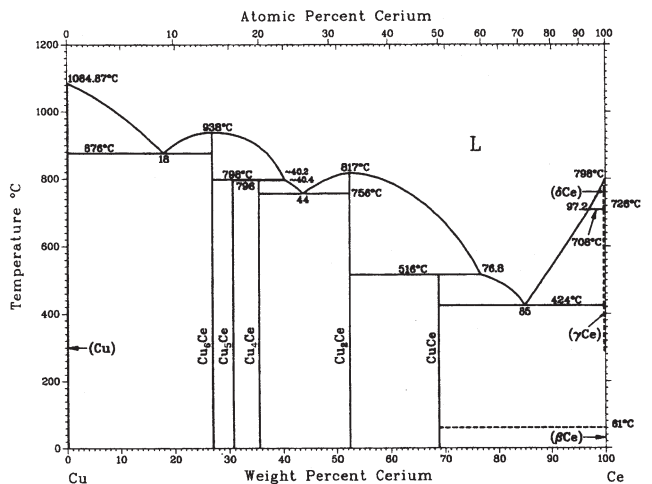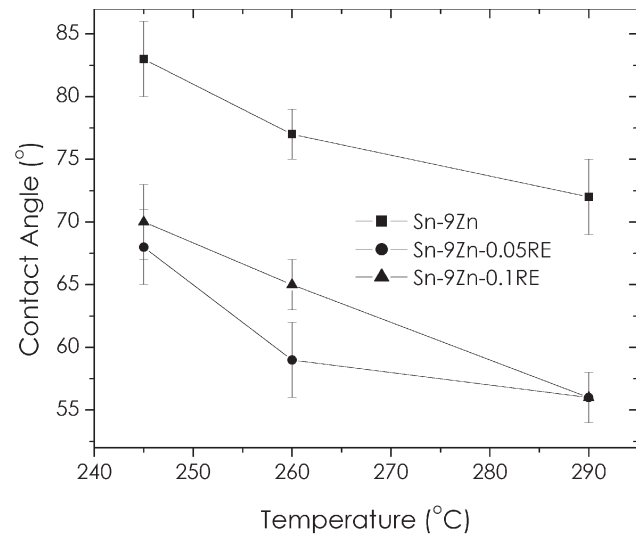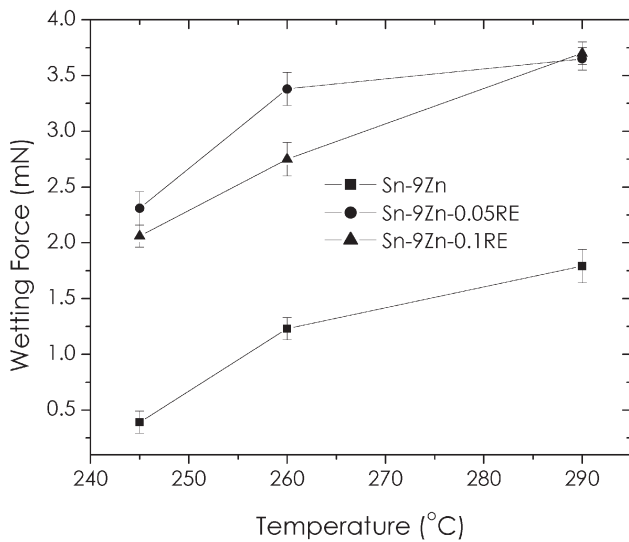Fig. 7. The variation of wetting time with amounts of RE elements at 245°C.

Fig. 8. The Ce-Cu binary phase diagram.

a

b

Fig. 9. The variation of (a) contact angle and (b) wetting force of Sn-Zn-RE systems with soldering temperature using RA flux.

against soldering temperature by using the RA flux. In Fig. 9a, the contact angle decreases with increasing soldering temperature. The wetting angle of Sn-9Zn-0.05RE is 68°, while that of Sn-9Zn is 83° at 245°C. The reason is that the higher temperature raised the ΔT, i.e., the range between soldering temperature and melting temperature. It is known that the wetting of the Sn-9Zn/Cu system is due to diffusion. At higher temperatures, the Sn and Zn atoms are more active. An increase in soldering temperature also decreases the value of γ_{SL} because of a large reactivity at this interface.[12] According to Eq. 1, lower γ_{SL} provides smaller contact angle and better wetting behavior.

By adding the RE elements, the reduction of γ_{LF} can provide a smaller contact angle, according to Eq. 1, and, consequently, better wetting quality can be obtained. However, adding more than 0.1wt.%RE into the solder appears to lower the wetting force when compared with 0.05wt.%RE alloy because of the increase in solder viscosity. Because both Zn and RE are easily oxidized during soldering, an increase in the amount of RE means an increase in the amount of oxides and inhibits the wetting behavior.

Figure 10a and b shows the contact angle and wetting force of the Sn-Zn-RE systems with the four different types of fluxes at 245°C in the wetting balance test. In these figures, the RA flux is shown to provide sufficient wetting, whereas the RMA, R, and VOC-free fluxes could not provide wetting. This is confirmed by the observation that the molten solder has partly coated the surface of the test coupons, with some areas of the coupons uncoated. As described in Table I, these three fluxes are either nonactivated, or have a lower degree of organic activation than the RA flux, and cannot provide an adequate wetting force and acceptable wetting angle for the Sn-Zn-RE alloy, even when the soldering is performed at high temperatures of 260°C and 290°C. These findings are similar to those obtained for the wetting tests for the Sn-9Zn-5In alloy, where an organically activated
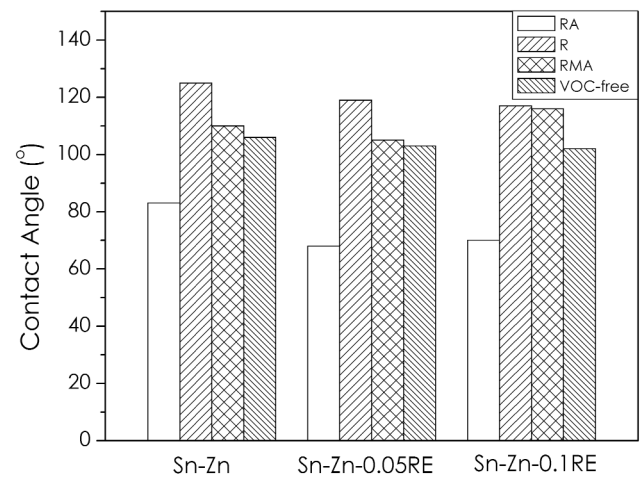
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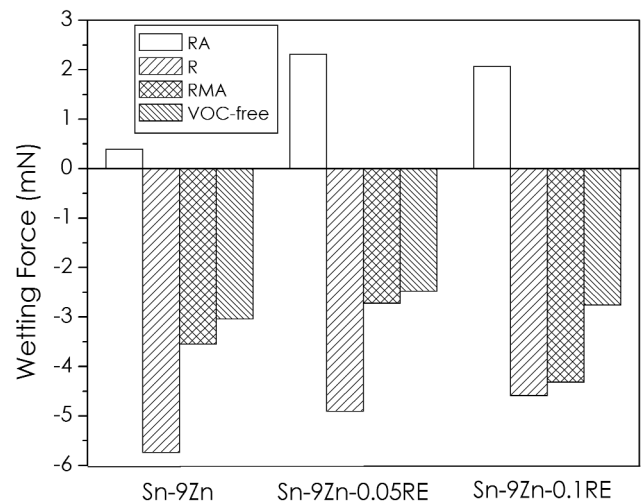
b

Fig. 10. (a) The contact angle and (b) wetting force of Sn-Zn-RE systems with four different types of flux at 245°C.

(OA) flux was capable of providing wetting.[4] These results indicate, as expected, that the choice of flux is important. For example, in Ref. 4, one of the nonactivated rosin flux was capable of providing a positive wetting force for the Sn-9Zn-5In alloy, although the force is less than that using the OA flux. It is worth noting that the RA flux used in the present study and the OA flux in Ref. 4 may have similar organic activators and may lead to long-term reliability problems if the flux can cause long-term material degradation of the components and the substrate. It is also noted that the OA flux used in Ref. 4 required cleaning and may be more active than the present RA flux, which does not require cleaning.

MICROHARDNESS

The mean hardness value is plotted against the RE content in Fig. 11. The mean value of each solder system is obtained from 10 hardness measurements with a 50-g load. The addition of 0.05% and 0.1% RE increased the microhardness by about 13% when compared with Sn-9Zn. It was noted earlier that after adding RE elements, a fine microstructure was obtained. In general, when the microstructure of an alloy is refined, its yield strength is increased. As hardness is an indication of the yield strength of an alloy, the refinement of the microstructure will increase the hardness. As mentioned previously, when using the solder material in a joint, high joint strength may not be a benefit for long-term reliability, as high strength may translate into shorter fatigue life of solder joints.

CONCLUSIONS

The Sn-9Zn-0.05RE and Sn-9Zn-0.1RE alloys were investigated for their wetting property, microstructure, and microhardness. These two alloys, as well as Sn-9Zn, have Sn-rich and Zn-rich phases and small amounts of rodlike Zn-rich phases distributed in the Sn matrix when they are slow cooled. The number and size of these rodlike Zn-rich phases decrease with the increase of RE content. A fine microstructure is obtained after RE addition because of the inhibition of grain growth, especially in Sn-9Zn-0.1RE. Particulate-shaped Sn-RE compounds begins to appear when the RE content reaches 0.1 wt.%. According to the DSC results, there is no change to the liquidus temperature after RE addition.

The wetting-balance tests were conducted in ambient air to reveal the wetting behavior. Four types of flux, i.e., RA, RMA, R, and VOC-free, were used to study the wetting properties of the Sn-9Zn-RE alloy systems at 245°C, 260°C, and 290°C. Only the RA flux can provide wetting. The addition of 0.05wt.%RE elements reduces the wetting angle and increases the wetting force because of the decrease of the interfacial tension between the solder alloy and the Cu substrate by the interaction of RE and Cu. However, further addition of RE to 0.1 wt.% provides less improvement to the wetting properties. The wetting properties are improved when the soldering temperature is increased.

The microhardness of the Sn-Zn-RE alloy systems was found to be higher than that of Sn-9Zn.

The preceding results show that RE elements as alloying elements have improved the wetting property of the Sn-9Zn alloy, making it more attractive to be used as electronic solder. Among the four fluxes tested, only the OA rosin (no-clean) flux can provide adequate wetting.
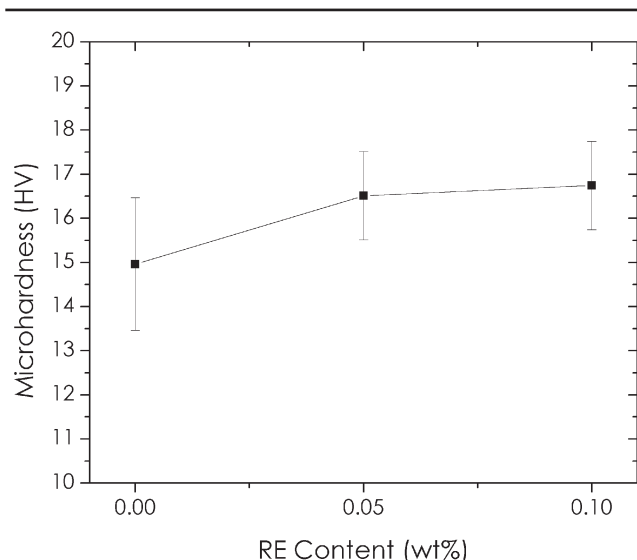
Fig. 11. The variation of microhardness with RE content.

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