

Microstructure, Solderability, and Growth of Intermetallic Compounds of Sn-Ag-Cu-RE Lead-Free Solder Alloys

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The near-eutectic Sn-3.5 wt.% Ag-0.7 wt.% Cu (Sn-3.5Ag-0.7Cu) alloy was doped with rare earth (RE) elements of primarily Ce and La of 0.05–0.25 wt.% to form Sn-3.5Ag-0.7Cu-xRE solder alloys. The aim of this research was to investigate the effect of the addition of RE elements on the microstructure and solderability of this alloy. Sn-3.5Ag-0.7Cu-xRE solders were soldered on copper coupons. The thickness of the intermetallic layer (IML) formed between the solder and Cu substrate just after soldering, as well as after thermal aging at 170°C up to 1000 h, was investigated. It was found that, due to the addition of the RE elements, the size of the Sn grains was reduced. In particular, the addition of 0.1wt.%RE to the Sn-3.5Ag-0.7Cu solder improved the wetting behavior. Besides, the IML growth during thermal aging was inhibited.

Key words: Lead-free solder, rare earth (RE) elements, solderability test, intermetallic layer

INTRODUCTION

The eutectic Sn-37Pb solder has been a dominant soldering material for electronic interconnection and packaging, due to its good material properties, low cost, and suitability for mass production. In terms of solder interconnection, physical bonding provides signal transmission and mechanical support, while chemical bonding provides an intimate connection due to the formation of a layer of intermetallic compound (IMC). During the last decade, the research on lead (Pb)-free alloys was intense, mainly due to the urgency in obtaining alternative environmentally friendly solders; Pb and Pb-containing compounds are believed to be toxic to humans. Although there also exist opinions that Pb-containing waste would not actually lead to contamination to landfills, as previously claimed, much legislation has already been introduced or is due to be introduced, and the industry is faced with the problem of choosing a reliable Pb-free solder alloy for manufacturing.

Most Pb-free solder alloys are Sn-containing binary or ternary alloys, with alloying elements of Bi, Cu, Ag, In, and Zn.¹ Among these Pb-free solders, the eutectic or near-eutectic Sn-Ag-Cu solder system

with melting range of 217–219°C is a popular substitute candidate for Sn-37Pb. Recently, the International Printed Circuit Association had indicated two choices for electronics manufacturers,² the Japanese-adopted tin-3.0wt.%silver-0.5wt.%copper (Sn-3.0Ag-0.5Cu) alloy and the North American Electronics Manufacturing Initiative Sn-3.9Ag-0.6Cu alloy, showing their support for the use of Sn-Ag-Cu alloys on a worldwide basis. Despite this effort, it is still believed that there is no strong consensus on a particular Sn-Ag-Cu composition.

Our recent work on binary Pb-free alloys doped with rare earth (RE) elements, primarily La and Ce, has indicated that the resulting alloys possess many merits as electronic solders. These merits include the enhanced thermal fatigue life and the reduction of the thickness of the interface intermetallic layer. Our recent research work^{3–6} has shown that only 0.05–0.5 wt.% of Ce and La was required to provide positive effects on the microstructure, wettability, creep resistance, and mechanical properties of Sn-3.5Ag, Sn-0.7Cu, and Sn-9Zn alloys.

In this work, the Sn-3.5Ag-0.7Cu-RE solders were first investigated for their solderability on Cu using a wetting balance. The effects of the addition of RE elements on the thickness of the IMC between the solder and the substrate under thermal aging were

also studied in this work. Thus, the soldered samples were heat treated at 170°C up to 1000 h. These heat-treated samples were cross sectioned to observe the IML growth.

EXPERIMENTAL PROCEDURES

Solders and Coupons Preparation

Cast ingots of Sn-3.5Ag-0.7Cu-xRE, (where $x = 0, 0.05, 0.1, \text{ and } 0.25 \text{ wt.}\%$), were used in this work. These alloys were prepared from pure Sn (99.95 wt.%), pure Ag (99.999 wt.%), and pure Cu (99.999 wt.%). The RE elements used were primarily Ce and La. The materials were melted in a vacuum furnace at 500°C for several hours. Although Cu and RE elements should melt at a relatively high temperature, they dissolved readily into the molten Sn bath. The molten alloys were chill cast into ingots in a copper mold. The chilled cast ingots were cut for microstructural investigation, on a polished cross section etched with a solution of 93vol.%CH₃OH, 5vol.%HNO₃, and 2vol.%HCl. A JEOL JSM-820 scanning electron microscope (SEM, Japan Electron Optics Ltd., Tokyo, Japan) equipped with an Oxford Instruments (High Wycombe, U.K.) energy-dispersive x-ray (EDX) was employed to examine and determine the elemental compositions at selected areas.

Solderability Test and Intermetallic Layer Growth

A wetting balance records the wetting force with time during a solderability test. This force-time relationship is known as the wetting curve, as schematically shown in Fig. 1. The factors affecting solderability are the contact angle, θ_c , the wetting force, F_w , and the wetting time, t_w . When a coupon is partially immersed into a molten solder bath, the wetting force is directly proportional to the height of the solder that climbed the coupon, as shown in Fig. 2. Under this condition, the coupon is subjected to a set of forces due to the buoyancy and to surface tensions, which are particularly high at the solder/flux interface. The measurement of the resultant force is

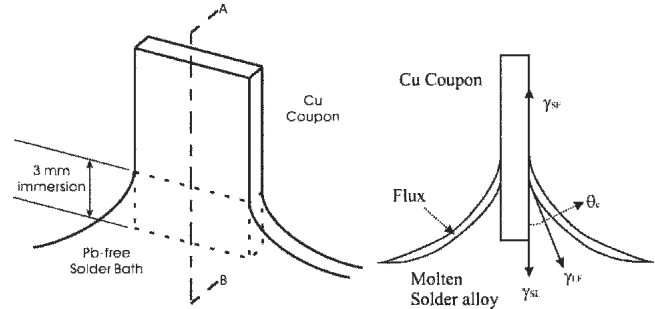


Fig. 2. Schematic diagram of the forces on the wetting test coupon.

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

$$F_w = p\gamma_{LF} \cos\theta_c - \rho gV \quad (1)$$

where

$\cos\theta_c = \frac{F_w + \rho Vg}{\gamma_{LF} p}$, 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 due to gravity, and V is the immersed volume.

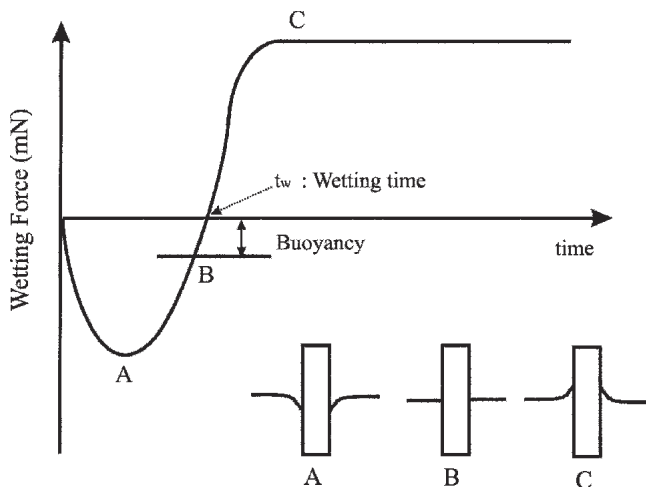
The chilled ingots were remelted in the solder bath of the wetting balance for the solderability test. The wetting behaviors of the Sn-3.5Ag-0.7Cu-RE alloys were investigated using a pure Cu foil (99.9% pure) as a substrate. The test coupons were cut to a size of 15 mm × 10 mm × 0.2 mm and were ground 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 an alcohol-based RMA-type flux before they were tested in the solderability tester in air. During the solderability test, the immersion depth and time were 3 mm and 10 sec, respectively. The immersion speed was 15 mm/sec. The soldering temperature of Sn-3.5Ag-0.7Cu-xRE alloys was 250°C.

After the solderability test, some soldered Cu coupons were kept for interfacial cross-sectional investigation, and the remaining ones were heat treated at 170°C in a furnace up to 1000 h. These heat-treated samples were cold mounted in epoxy, followed by mechanical grinding and polishing. The interfacial microstructure was also revealed by the same etching solution used for the ingot microstructure and examined by SEM and EDX.

RESULTS AND DISCUSSION

Microstructure of Sn-3.5Ag-0.7Cu-RE Solders

The microstructure of chill cast Sn-3.5Ag-0.7Cu, as shown in Fig. 3a, mainly consisted of phases of β -Sn, Cu₆Sn₅, and Ag₃Sn. Because of the fast cooling rate provided by the Cu mold, the β -Sn phases were distributed in the ternary eutectic region. The grain size of β -Sn phases was about 10–20 μm . In some regions, small Ag-Sn intermetallics coexisted with the β -Sn phases. The formation of the microstruc-



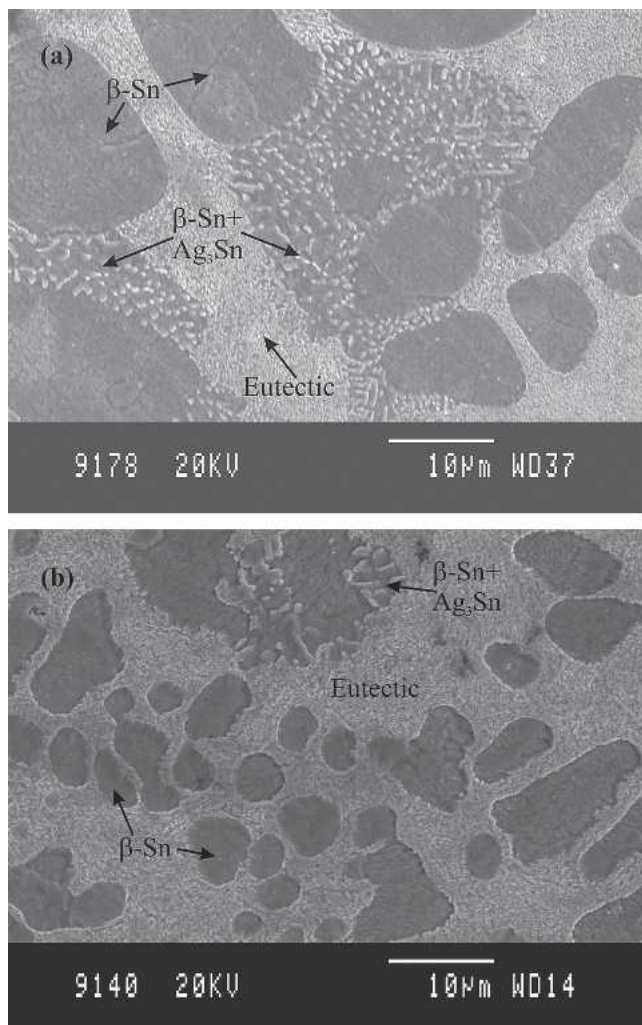


Fig. 3. SEM microstructure of (a) Sn-3.5Ag-0.7Cu, (b) Sn-3.5Ag-0.7Cu-0.25RE.

ture was due to the solidification sequence of the ternary alloys. The addition of RE decreased the original β -Sn grain size to 5–10 μ m, as shown in Fig. 3b. The RE-bearing phase could not be detected due to the small amount of RE addition and its fine dispersion.

Solderability of Sn-3.5Ag-0.7Cu-RE Solders

Figure 4 shows the wetting curves of the Sn-3.5Ag-0.7Cu-RE solders. Except for the Sn-3.5Ag-0.7Cu solder, the wetting time obtained from the Sn-3.5Ag-0.7Cu-xRE solders was reasonably short. The Sn-3.5Ag-0.7Cu-0.1RE solder achieved the largest wetting force. It can be seen that an excessive amount of RE addition had the effect of lowering the wetting force. The present result shows that Sn-3.5Ag-0.7Cu-0.25RE had the lowest wetting force among the Sn-3.5Ag-0.7Cu-xRE solders. Apart from this, the addition of RE elements could also lower the wetting angle, as shown in Fig. 5.

It is concluded that the wetting property of Sn-3.5Ag-0.7Cu is improved by adding 0.1 wt.% RE elements. An excessive amount of RE element addi-

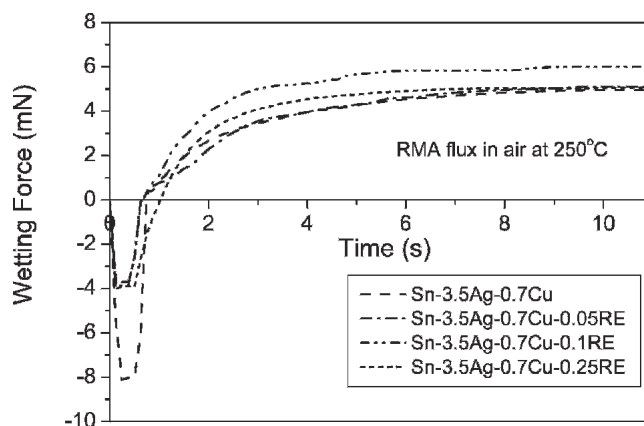


Fig. 4. Wetting curves of Sn-3.5Ag-0.7Cu-xRE.

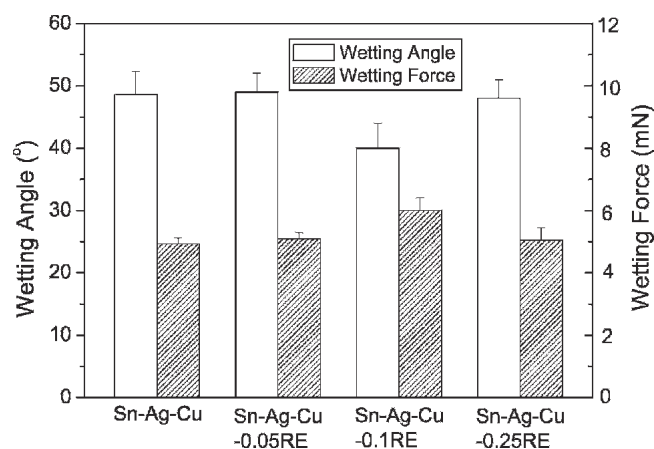


Fig. 5. Wetting angle and force of Sn-3.5Ag-0.7Cu-xRE.

tion will increase the solder viscosity during the solderability test. A similar phenomenon is observed in the Sn-Zn-RE system.⁶ Since Sn and RE are easily oxidized during soldering, these oxides will change the surface tension of the solder bath and inhibit the wetting behavior. An enhancement of the wetting behavior is attributable to the decrease of the solder/flux surface tension when a proper amount of RE elements is added to the solder.

Intermetallic Layer Growth of Sn-3.5Ag-0.7Cu-RE Solders upon Aging

The cross sections of as-reflowed Sn-3.5Ag-0.7Cu and Sn-3.5Ag-0.7Cu-0.25RE solders are shown in Fig. 6a and b, respectively. For these two solders, the Cu-Sn intermetallic layer in the shape of scallops was formed between the copper substrate and solder. This Cu-Sn intermetallic was identified to be Cu₆Sn₅ by EDX. The Ag₃Sn IMC was also detected in the solder matrix. By comparing Fig. 6a and b, the IML thickness of the Sn-3.5Ag-0.7Cu-0.25RE solder was found to be thinner than that of Sn-3.5Ag-0.7Cu.

Upon thermal aging at 170°C, the samples aged for 100 h, 200 h, 500 h, and 1000 h were also cross sectioned to investigate the IML thickness. After 100 h of aging, a layer of Cu₃Sn was found between the Cu₆Sn₅ layer and the Cu substrate. Many Kirk-

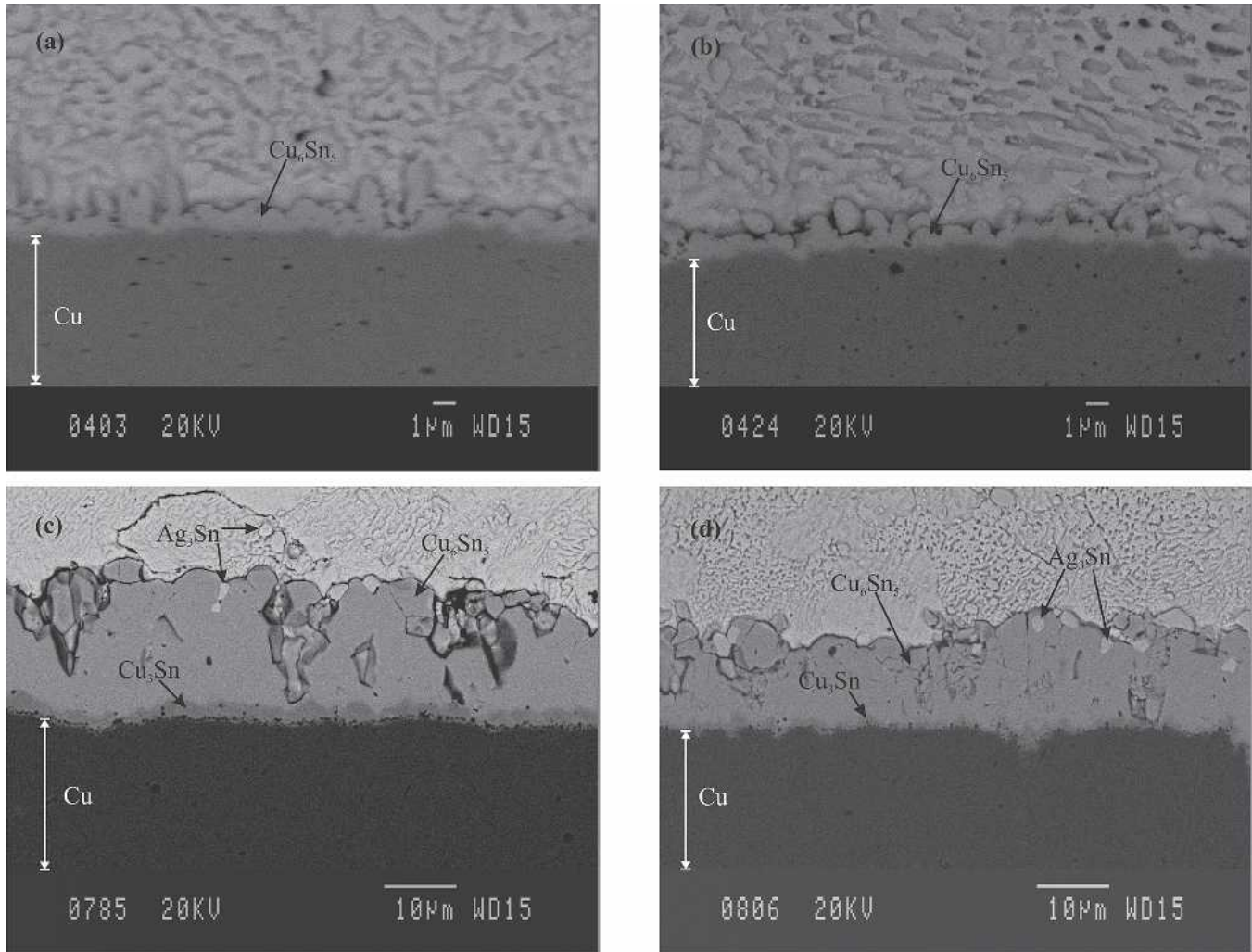


Fig. 6. BSE micrographs of as-soldered cross sections (a) Sn-3.5Ag-0.7Cu, (b) Sn-3.5Ag-0.7Cu-0.05RE, and of aged 1000 hr (c) Sn-3.5Ag-0.7Cu-0.1RE, and (d) Sn-3.5Ag-0.7Cu-0.25RE.

endall voids were found between the Cu_3Sn IMC layer and the Cu substrate. The formation of these voids was due to the different diffusion properties of Sn and Cu during the aging process. Also, the scallop-shaped Cu_6Sn_5 layer was changed into a layer with fairly constant thickness during aging. Upon further aging (for 200 h, 500 h, and 1000 h), both the Cu_6Sn_5 and Cu_3Sn intermetallic layers increased their thicknesses with the aging time. It was found that the coarsened Ag_3Sn IMC was embedded into the Cu_6Sn_5 layer. This observation is consistent with that of previous studies.^{7,8} Figure 6c and d are the cross sections of aged 1000 h Sn-3.5Ag-0.7Cu and Sn-3.5Ag-0.7Cu-0.25RE solders, respectively. Since the coarsened Cu_6Sn_5 IML was brittle, cracks were easily initiated during mechanical grinding. Figure 7 shows the variation of the total IML thickness (comprising Cu_3Sn and Cu_6Sn_5), with the square root of aging time. It can be seen that throughout the aging times considered in this paper, i.e., up to 1000 h, the IML growth was inhibited as a result of the addition of RE elements into the solder. The linear relationship observed from the aging

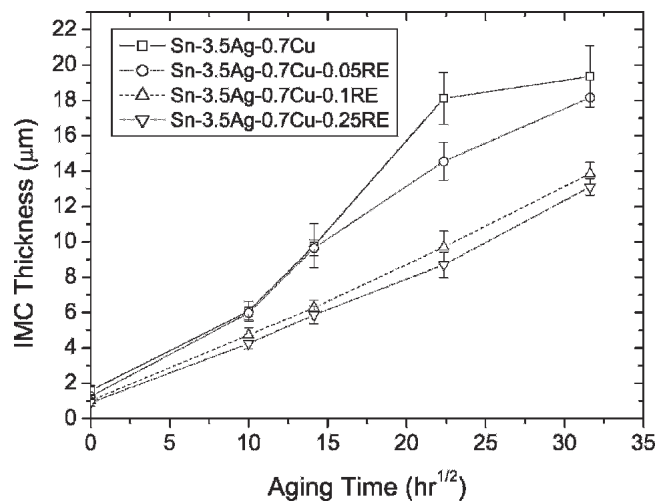


Fig. 7. Variation of Sn-3.5Ag-0.7Cu-xRE total IML thickness with aging time.

curves suggested that a thermally activated diffusion process had taken place for the IML growth in the Sn-3.5Ag-0.7Cu-RE system.

CONCLUSIONS

The addition of RE elements into the Sn-3.5Ag-0.7Cu solder was able to refine its microstructure. Its wetting behavior was improved by adding 0.1wt.%RE elements. The enhancement of wetting force was due to the decrease of the solder/flux surface tension. However, the addition of an excessive amount of RE elements would deteriorate the wetting property due to the solder surface viscosity increase during soldering.

During thermal aging at 170°C, the IML growth was a thermally activated diffusion process in the Sn-3.5Ag-0.7Cu-RE solders. A solder doped with RE elements always has the activity of Sn at the interface of the Cu₆Sn₅ IMC/solder lowered as a result of Sn-RE compound formation. Consequently, the IML growth was inhibited by adding RE into the solder.

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