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Variable eutectic temperature caused by inhomogeneous solute distribution in Sn–Zn system

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Abstract

The microstructure and thermal properties of Sn–Zn–(Bi, In, Ga) solder alloys were examined in this study. Results show that the addition of those alloying elements gave rise to a reduced melting point, more broadened melting range and a less uniform microstructure comprising alternate normal–irregular eutectic cells. It was also found that the formation of an abnormal eutectic structure and a unique phenomenon, namely, continuously varying eutectic temperature and thus an enlarged solidus–liquidus temperature range, are due to the inhomogeneous dissolution feature of the solute elements.

Keywords: Pb-free solders; Sn–Zn; Eutectic structure

1. Introduction

The Sn–Zn eutectic system, which is basically classified as an anomalous eutectic alloy, has a broken-lamellar type eutectic structure [1]. The faceting lamellas are Zn and the nonfaceting phase is the Sn matrix. Under rapid cooling conditions, the lamellar Zn becomes fibrous [1,2].

Since the Sn–Zn eutectic alloy exhibits a melting point (198 °C) approximately the same as that of conventional Sn–Pb eutectic solder (183 °C), it has recently been considered as a candidate for a lead-free solder material [3,4]. However, modification by alloying is still needed to reduce its melting point. Several low melting point elements such as Bi (271.3 °C) [5], In (156.6 °C) [6] and Ga (29.8 °C) [7] have been tried and can successfully lower the melting temperature of eutectic Sn–Zn.

McCormack and Jin [6] reported that an In addition of 5 wt.% results in a lower melting temperature of about 188 °C and, notably, the formation of a much coarser and less uniform microstructure. A study regarding the effect of Bi on the Sn–Zn eutectic alloy [8] also showed that with an increase in the Bi content both the solidus and liquidus temperatures decrease and the pasty range, the temperature difference between them, slightly increases. Moreover, our study demonstrates that Ga is also able to reduce the melting temperature of eutectic Sn–Zn alloy without affecting the latent heat.

This present study aimed to find out the common features among these Sn–Zn alloys with low melting point solute elements, Bi, In or Ga with respect to microstructure and thermal behavior. The formation of a non-uniform eutectic structure and expanded melting range are the main concerns.

2. Experimental procedures

Master alloys of near-eutectic binary Sn–Zn alloy and those with alloying additions, Sn–Zn–Bi, Sn–Zn–In and Sn–Zn–Ga, were prepared by melting pure metals in a high frequency induction furnace. The chemical compositions of the solder alloys investigated are listed in Table 1 where the samples are designated according to their compositions. These prepared alloy ingots were re-melted and cast into

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Table 1
Chemical compositions of the specimens (wt.%)

	Sn	Zn	Bi	In	Ga
Sn–8.6Zn	Bal.	8.6	–	–	–
Sn–8Zn–3Bi	Bal.	8.0	3.0	–	–
Sn–8Zn–3In	Bal.	7.9	–	3.0	–
Sn–8.5Zn–0.5Ga	Bal.	8.5	–	–	0.5
Sn–8.5Zn–1.0Ga	Bal.	8.5	–	–	1.0
Sn–8.4Zn–1.8Ga	Bal.	8.4	–	–	1.8

a cylindrical metal mold with a diameter of 30 mm. The cooling rate for the specimens, which is measured as the average value from 300 °C to 200 °C, was 1 °C/s.

The thermal behavior of the solders was investigated using differential scanning calorimetry (DSC) and cooling curves. DSC analysis was conducted at a constant heating rate of 0.5 °C /min from 25 °C to 300 °C. Cooling curves were obtained by inserting a thermocouple into 200 g of molten solder placed in a MgO crucible. The initial temperature of the molten solder was above 600 °C. The microstructures of the solders were investigated with a scanning electron microscope (SEM) and electron probe microanalysis (EPMA).

3. Results and discussion

3.1. Microstructural characteristics

Fig. 1 shows the microstructure of the Sn–Zn alloys investigated. The Sn–8.6Zn specimen, Fig. 1(a), displays a typical rapidly-solidified Sn–Zn eutectic structure. Each eutectic cell possessed aligned acicular Zn-rich particles. The microstructures of Sn–8Zn–3Bi (Fig. 1(b)), Sn–8Zn–3In (Fig. 1(c)) and Sn–8.5Zn–1.0Ga (Fig. 1(d)) show an identical structural feature, that is, irregular regions with misaligned coarse Zn particles and normal eutectic cells formed alternately.

Magnification of the eutectic structure and EPMA elemental analysis of Sn, Zn and Bi of the Sn–8Zn–3Bi specimen, Fig. 2(a), also revealed that broad irregular regions and normal eutectic structure formed alternately. The signal of Bi in the coarse eutectic cells is relatively brighter than that in the normal regions. Similarly, elemental mapping of the Sn–8Zn–3In samples illustrates that the coarse eutectic cells possessed a greater concentration of In, Fig. 2(b). This also indicates that the In content in the coarse eutectic cells did not remain constant. The In signal was stronger in the center than at the outer peripheral regions. Fig. 2(c) displays the microstructure in the vicinity of the boundary between a normal cell (lower right corner) and an adjacent irregular one (upper left corner) in the Sn–8.4Zn–1.8Ga specimen. We see that on the edge of the normal eutectic region the Zn particles were tending to become massive and the Ga concentration was increasing gradually toward an irregular structure. Worthy of notice is that Ga was detected in both the Sn matrix and Zn-rich particles.

3.2. Thermal properties

Fig. 3 shows the DSC endothermic peaks of the Sn–Zn–Bi and Sn–Zn–In samples upon heating. It reveals that the wedge-shaped peak for the Sn–Zn eutectic reaction became less sharp with the addition of Bi or In. The whole peak obviously shifted to a lower temperature, and the temperature range for absorbing heat of fusion was expanded. A little endothermic tail adjacent to the main peak for Sn–

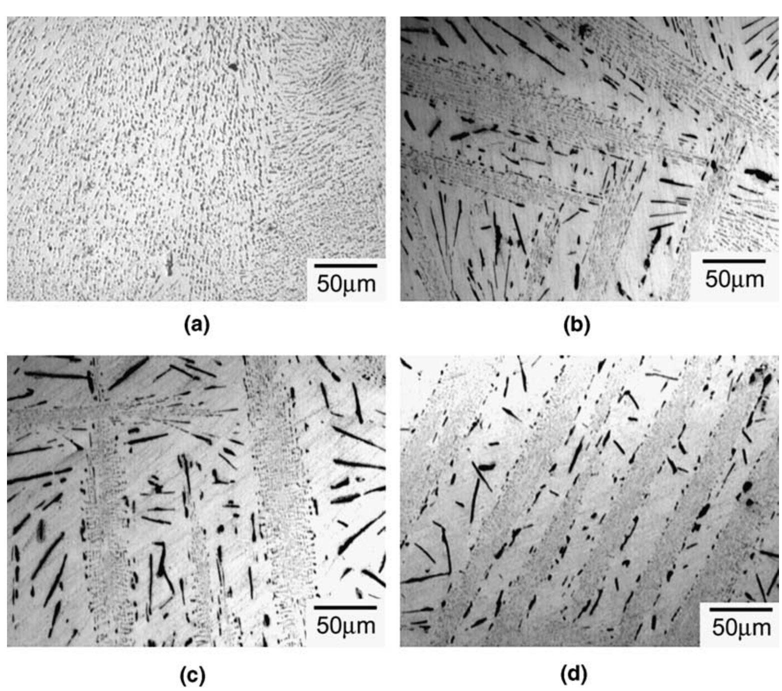

Fig. 1. Microstructure of the specimens: (a) Sn–8.6Zn; (b) Sn–8Zn–3Bi; (c) Sn–8Zn–3In; and (d) Sn–8.5Zn–1.0Ga.