Microstructures, Thermal and Tensile Properties of Sn-Zn-Ga Alloys

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The effects of Ga content on the microstructure, thermal behavior and mechanical properties of Sn-Zn eutectic alloy were examined in this study. Results show that Ga was dissolved in both Sn and Zn phases. This gave rise to irregular eutectic structure with misaligned, less distributed massive Zn-rich phase, relatively low melting point, and solid solution strengthening effect. Due to the inhomogeneous dissolution feature of Ga in Sn matrix, Sn-Zn-Ga alloys exhibit a broad melting range and an alternate normal-irregular eutectic structure. Notably, the addition of Ga into the Sn-Zn alloy will improve the tensile strength without reducing the ductility when the Ga content ranges from 0.05 to 1 mass%.

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1. Introduction

It is desirable that a Pb-free solder has approximately the same melting temperature or solidus/liquidus range as that of conventional Sn-Pb solder. Sn-Zn eutectic alloy has recently been considered as a candidate for lead-free solder material because of its low melting point (198°C), excellent mechanical properties and low cost.¹⁻³⁾ However, the Sn-Zn eutectic alloy exhibits problems of poor wetting, easy oxidation, and dross formation.^{4,5)} It should be of interest to develop a new Sn-Zn based alloy that addresses these problems.

Alloying elements of In,⁶⁾ Bi,⁷⁾ Al,⁸⁾ Ag⁹⁾ and rare earths (RE, mainly La and Ce)^{10,11)} were chosen to lower the melting temperature or improve the wettability. As for the effect of the alloying additions on melting point, previous investigations indicated that Bi and In effectively decrease the melting temperature of Sn-Zn alloy, while there is no significant change in the melting point with small additions of Ag, Al and RE. Among these, when the Ag content exceeds 0.5 mass%, it will result in an off-eutectic structure and thus an endothermic tail on DSC curve representing the fusion of primary Sn phase found at temperatures slightly higher than eutectic point.¹²⁾

The addition of Bi, In, Al and RE into the Sn-Zn system significantly increases the tensile strength and reduces elongation. In contrast, a recent report¹³⁾ demonstrated that Ag addition leads to a higher ductility, reduced tensile strength and lower elastic modulus. In addition, dendritic Ag-Zn intermetallics,¹⁴⁾ Al-Zn-Sn¹⁵⁾ and Sn-RE compounds¹¹⁾ can be observed in Sn-Zn-Ag, Sn-Zn-Al and Sn-Zn-Re solders respectively. Bi precipitates are finely dispersed and In might form solid solution with Sn. In-rich phase can also be found in Sn-Zn-In alloys.⁶⁾

Ga, of which melting point is 29.78°C, has been applied to increase the strength, enhance fatigue life and lower the melting temperature of solders.^{14,16,17)} Worthy of notice is that, Ga is capable of suppressing dross formation when the molten solder is exposed to air.¹⁶⁾ To develop an appropriate replacement for Sn-Pb alloy, Ga seems to be a potential alloying element in alloy design for Sn-Zn solders. This

Table 1 Chemical composition of the specimens investigated (mass%).

Sample	Ga	Zn	Sn
0 Ga	0	8.6	Bal.
0.05 Ga	0.05	8.6	Bal.
0.1 Ga	0.1	8.6	Bal.
0.25 Ga	0.25	8.6	Bal.
0.5 Ga	0.5	8.5	Bal.
1.0 Ga	1.0	8.5	Bal.
1.8 Ga	1.8	8.4	Bal.

present study aimed to investigate the properties of Sn-Zn-Ga alloys, including microstructural, thermal and tensile properties.

2. Experimental Procedures

Master alloys of near-eutectic Sn-Zn solder alloy and those with a Ga content of 0.05~1.8 mass% were prepared by melting pure tin, pure zinc and pure gallium 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 a Y-shaped graphite mold with a constant thickness of 2.4 mm.

The thermal behavior of the solders was investigated with differential scanning calorimetry (DSC) and cooling curve. DSC analysis was conducted at a constant heating rate of 0.5°C/min from 25 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.

Phase identification of the various solders was performed by an X-ray diffractometer operated at 30 kV and Cu-K α radiation was used, with a scanning speed of 1°/min. The microstructures of the solders were investigated with a scanning electron microscope (SEM) and electron probe microanalysis (EPMA).

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Fig. 1 Microstructure of Sn-Zn-Ga alloys with various Ga contents: (a) 0 mass%, (b) 0.05 mass%, (c) 0.25 mass%, (d) 0.5 mass%, (e) 1 mass%, (f) 1.8 mass%.

3. Results

3.1 Microstructural features

Figure 1 shows the microstructure of the Sn-Zn alloys investigated. The 0 Ga specimen, Fig. 1(a), displays a typical microstructure of rapidly-solidified Sn-Zn eutectic structure. Each eutectic cell possessed aligned acicular Zn-rich particles. With a small addition of Ga (Figs. 1(b) and (c)), a few coarse Zn particles, indicated by the arrows, were observed in the vicinity of eutectic cell boundaries. These irregular Zn particles existing in-between eutectic cells are no longer aligned. When the Ga content reached 0.5 mass% and above, it was found that broad irregular regions and normal eutectic structure form alternately (Figs. 1(d)–(f)).

This morphological transition of the Zn-rich particles takes place gradually as seen in Fig. 2(a). The magnified structure of the high-Ga specimen (1.8 Ga), Fig 2(a), shows that on the edge of the normal eutectic region the Zn particles were tending to become massive toward the irregular structure. The Ga content, Fig. 2(b), of the matrix Sn phase also increased gradually. The backscattering electron image, Fig. 3(a), of the near cell boundary area between a normal eutectic structure (lower right corner) and an irregular region (upper left corner) also illustrates that the Zn needles became coarser from the normal cell to irregular region. Worthy of notice is that Ga was detected in both the Sn matrix and Zn-rich particles. It also shows that the Ga content in Sn phase between these two regions also changed gradually, as indicated by the variation in brightness of Ga signals. The quantitative analysis results, Fig. 3(b), evidence that the Sn phase within the irregular structure possesses a relatively

higher Ga content than the normal structure. These results indicate that there might exist a critical Ga content of about 1.6 mass% for the microstructural transition. The normal Sn-Zn eutectics become coarse and disoriented at above 1.6 mass% for Ga content.

The XRD patterns, Fig. 4, of the samples with varying Ga content, indicate that no other phase than the β -Sn and Zn-rich phases could be identified. However, an increase in Ga content resulted in a slight shift of the Sn (220) and Sn (211) peaks toward a higher angle, while the diffraction peaks of Zn phase move to a lower angle.

3.2 Thermal properties

Figure 5 shows the DSC endothermic peaks of the samples used upon heating. It reveals that the wedge-shaped peak for the Sn-Zn eutectic reaction became less sharp with a higher Ga content. The whole peak obviously shifts to a lower temperature when the Ga content exceeds 0.1 mass%. The transition points for each specimen, including the temperatures of the solidus, liquidus, peak and onset, are shown in Fig. 6(a). The onset temperature, regarded as the melting point, is determined by first identifying the steepest portion of the low temperature side of the heat absorption, defining the slope at that point, and extrapolating this slope line to the temperature axis of zero differential heat flow.¹⁸⁾ All the transition temperatures of the Sn-Zn solders decreased with a higher Ga content, especially the solidus temperature. The solidus temperature, the starting temperature of the endothermic peak, is as low as 167.5°C for the 1.8 Ga specimen. Ga addition also significantly expands the solidus/liquidus range. By computing the peak area of the DSC curves, the

Fig. 2 (a) Magnified structure of the region in-between normal and irregular structures of the 1.8 Ga sample; (b) Ga content of the marked areas in (a) (analyzed by EDS).

enthalpy of fusion (latent heat) of these specimens was determined. Figure 6(b) indicates that the addition of Ga did not significantly affect the latent heat in spite of the change in the shape of the endothermic peak. In addition, the Sn-Zn alloys examined in this study exhibited a higher enthalpy of fusion in comparing with eutectic Sn-Pb and Sn-Ag solders.¹⁹⁾

The cooling curves of the specimens, Fig. 7, indicate that all the samples show a eutectic feature and no inflection point above the eutectic temperature. However, there existed some differences between the unalloyed and Ga-containing specimens. An increase in Ga addition lowers the temperature of the plateau after the supercooling signal and makes the plateau become a descending curve.

3.3 Tensile properties

An increase in Ga content increases the tensile strength of the specimens, as seen in Fig. 8. The total elongation, Fig. 9, remains almost constant, but drops drastically as the Ga content reaches 1.8 mass%. Notably, the uniform elongation rises with respect to the increasing Ga content at above 0.5 mass%.

Figure 10 illustrates the tensile fracture surface, and reveals that all the specimens show a ductile dimple pattern. Remarkably, there were some smooth facets, Fig 10(g), on the fracture surface of the 1.8 Ga specimen. These smooth appearances correspond to the surface of irregular massive Zn particles as seen in Fig. 10(h).

Fig. 3 (a) Backscattering electron image of the 1.8 Ga sample; (b) quantitative analysis results of Ga using WDS.

Fig. 4 (a) X ray diffraction patterns of the samples with different Ga contents; (b) magnified patterns ranging from 43° to 46° of (a).

4. Discussion

4.1 Formation of the normal-irregular structure of Sn-Zn-Ga alloys

The results of microstructural investigation and elemental analysis show that the irregular structure possesses a relatively higher Ga content. The Ga content increases continuously from normal structure to irregular structure. The addition of Ga causes the shift in the diffraction peaks of both Sn and Zn (Fig. 4). These phenomena can be ascribed to the dissolution of Ga in the Sn and Zn phases and the inhomogeneous distribution of Ga.

According to the Ga-Sn²⁰⁾ and Ga-Zn²¹⁾ binary phase diagrams, Ga may form solid solutions with Sn and Zn. The atomic radii of tin, zinc, and gallium are 0.158 nm, 0.133 nm, and 0.135 nm respectively.²²⁾ The reduced lattice parameter of Sn (the X-ray diffraction peaks shift to a higher angle) and enlarged lattice parameter of Zn (the diffraction peaks shift to a lower angle) demonstrate that Ga was dissolved in both Sn and Zn.

Fig. 5 DSC curves of the eutectic Sn-Zn alloy and (a) low Ga samples and (b) high Ga samples upon heating.

Previous reports have classified the structure of the eutectic Sn-Zn alloy with a broken-lamellar appearance as an anomalous non-faceted (N.F.)/faceted (F) eutectic system.²³⁾ The Zn-phase possesses a fibrous appearance in the case of high growth rate and lies generally along the growth axis.^{23,24)} Moreover, the entropy of solution (ΔS) for Zn-rich phase in the Sn-Zn eutectic²³⁾ was estimated to be $7.6 \text{ cal K}^{-1} \text{ mol}^{-1}$.

As mentioned above, adding Ga can cause changes in the lattice parameters of Sn and Zn, and subsequently an increase in entropy of solution, which may result in the morphological change of eutectic microstructure from broken lamellar to irregular flake.²⁵⁾

At a small addition of Ga (less than 0.25 mass%), Ga atoms tend to segregate at the cell boundary regions. The segregation of Ga breaks up the interface between the cells and

Fig. 6 (a) Transition points as a function of Ga; (b) latent heat of Sn-Zn-Ga alloys and several solder alloys.

Fig. 7 Cooling curves of the samples with different Ga contents, the highest temperature values within the plateaus are also indicated.

Fig. 8 Tensile strength with respect to the Ga content.

Fig. 9 Elongation of the specimens with respect to the Ga content: (a) total elongation and (b) uniform elongation.

Fig. 10 Tensile fracture surface of the samples: (a) 0 Ga, (b) 0.05 Ga, (c) 0.1 Ga, (d) 0.25 Ga, (e) 0.5 Ga, (f) 1 Ga, (g) 1.8 Ga (the arrows indicate the smooth facets) and (h) insert of (g).

transforms the microstructure into an irregular morphology. A further increase in Ga content converts the eutectic structure to a part-normal and part-irregular structure. This phenomenon is attributed to the composition variation of the solidification front. The initially solidified eutectic cells formed a normal morphology and then the residual liquid with a greater Ga content solidified to become the irregular eutectic structure at a lower temperature. Thus the alternate normal-irregular structure formed and the changed morphology and composition are gradual.

4.2 Characteristics of a normal-irregular mixed structure

The results of cooling curves and DSC analysis indicate that the whole specimen maintains eutectic behavior regardless of the extent of Ga additions in the present study. Ga additions significantly lower the eutectic point of the Sn-Zn eutectic, and the reduction of temperature depends on the Ga content of each eutectic cell. Due to the normal-irregular mixed structure and the nonuniform Ga distribution, the melting range of the Sn-Zn-Ga alloys, particularly high Ga specimens, is enlarged.

The dissolution of Ga in Sn matrix results in the

strengthening effect of Ga additions. In view of the fact that needle-like Zn phase is the preferred crack initiation site,¹³⁾ reducing the fraction and rounding the shape of the Zn particles by Ga additions may contribute to the high uniform elongation in the high Ga specimen. On the other hand, the decohesion between the unusual massive Zn particles, Figs. 10(g) and (h), and matrix within irregular regions were probably responsible for the deterioration in the total elongation when the Ga content reaches 1.8 mass%.

5. Conclusions

The addition of Ga significantly changes the microstructure characteristics, thermal properties and mechanical properties of the Sn-Zn eutectic alloy. The alloy maintains eutectic behavior when the Ga content up to 1.8 mass%. The dissolution of Ga in the Sn-Zn eutectic significantly lowers the melting temperature, however, the inhomogeneous distribution of Ga expands the melting range. It also can be found that the enthalpy of fusion of the Sn-Zn eutectic alloy is about 70 J/g regardless of Ga content. The eutectic structure in the vicinity of cell boundaries becomes irregular at less than 0.5 mass% Ga. The needle-like Zn phase becomes blunted, enlarged and less densely distributed. The irregular eutectic regions are extended and aligned alternately with normal structure at above 0.5 mass%Ga. The tensile strength of Sn-Zn solders increases drastically with increasing Ga content and the elongation remains almost constant at less than 1.0 mass%Ga. On the other hand, a Ga content of exceeding 1.0 mass% results in a sharp drop in the total elongation but the improved ability against necking.

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