Thin Film Characteristics of Sn–3.5Ag–(2.0Cu) Alloy

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Sn–Ag–Cu lead-free solders have recently been applied generally in electrical packaging, but a discoloring of the solders often occurs at the injection-ball or the reflow processes. This study investigates the solidification surface characteristics of both the Sn–3.5Ag alloy and the Sn–3.5Ag–2.0Cu alloy to discuss and clarify the differences in composition between the surface and the thin film of subsurface. The results indicate that the solidification surface films of the Sn–3.5Ag–(2.0Cu) are mostly composed of SnO phase and SnO₂ phase. The concentration of Sn⁴⁺ is higher than that of Sn²⁺ on the film. And the binding energy of O atoms increases at sites near the solidification surface. On the solidification surface thin film, the Ag content of the Sn–3.5Ag–2.0Cu specimen is higher than the Sn–3.5Ag specimen. In addition, there is few Cu on the solidification surface film of the Sn–3.5Ag–2.0Cu specimen, and adding Cu into Sn–3.5Ag alloy not only can repress the growth of the SnO_x phase but also reducing the degree of discoloring.

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1. Introduction

Sn–Ag–Cu alloy systems have been recognized as one of the best choices as a lead-free solder to replace conventional Sn–Pb eutectic.^{1–3)} Following the size decrease of electrical packaging elements, the dimensions of the solders have also decreased. This has also led to a gradual increase in the importance of the solidification surface characteristics of tin balls.^{4,5)} As of now, the discoloring phenomenon often occurs at the tin ball surface under solidification processes, and a surface film with high roughness has also been observed at the solders. These effects are closely related to the quality of the solder and the solder joint reliability.^{6–8)} However, the characteristics of the solidification surface film have still not been examined. In order to understand the possible reasons for the color change effect, the current study will discuss the structure of the surface thin film. This study uses the Sn–3.5Ag alloy and the Sn–3.5Ag–2.0Cu alloy to investigate the structural characteristics of the surface thin film under solidification, and a comparison is performed of the composition between the surface and the subsurface.

2. Experimental Procedure

Master alloys of the Sn–3.5Ag alloy and the Sn–3.5Ag–2.0Cu alloy were prepared by melting pure tin, pure silver and pure copper in a high-frequency induction furnace. The alloy ingots were then remelted and cast into a Y-shaped graphite mold. For the casting process, the tin alloy melting temperature was selected to be 310°C and the temperature for the graphite mold was 230°C, followed by cooling to room temperature. In order to collect the solidification film data, rectangular specimens (gauge length section: 10 mm × 10 mm × 2 mm) were also prepared to perform thin-film XRD and XPS analysis.

For surface analysis, the solidification surface of the specimens with no treatment will hereafter be referred to as “surface” (the surface of the specimens possessed a light yellow color). After polishing the solidification surface of the

specimens, a silver color was obtained and this will be referred to as “subsurface”. The microstructures of the alloys were determined using an image analyzer. In addition, both XPS and thin-film XRD were also used to obtain data of the surface and the subsurface. For thin-film XRD analysis, the Cu-K α standard ($\lambda = 1.5403$ nm) was selected for X-ray diffraction. The scanning angle was varied from 20° to 90° and the scanning velocity was 3°·min^{–1}. In order to compare the experimental results, the solidification film data of the pure tin specimen was also examined using the thin-film XRD analysis method.

3. Results and Discussion

Figure 1 shows the microstructures of the Sn–3.5Ag and the Sn–3.5Ag–2.0Cu alloy. A previous study of Sn–3.5Ag–xCu (x = 0–2.0 mass%) alloys revealed that the Cu₆Sn₅ compounds increased and the shape of β -Sn phase transformed from dendrite into dispersed with increasing the Cu content. In addition, dendritic β -Sn phase and eutectic phase were also observed in the Sn–3.5Ag alloy [see Fig. 1(a)]. In Fig. 1(b), precipitated Cu₆Sn₅ was produced in β -Sn phase. Ag₃Sn phase was not observed in either Figs. 1(a) or (b). In order to examine the difference in composition between the surface and the subsurface, thin-film XRD analysis of the Sn–3.5Ag and the Sn–3.5Ag–2.0Cu alloy were performed.

Figure 2 shows the thin-film X-ray diffractive patterns of the Sn–3.5Ag alloy. The evidence reveals that both β -Sn phase and Ag₃Sn phase existed at the surface and the subsurface. As for the relative composition, the content of Ag₃Sn phase had increased only very slightly from the surface to subsurface. To compare the data, thin-film XRD analysis of the Sn–3.5Ag–2Cu alloy was also performed (see Fig. 3). In addition to β -Sn phase, Ag₃Sn compounds and Cu₆Sn₅ compounds also formed, and the content of the latter two compounds also had a tendency to increase from the surface to the subsurface. The secondary ion mass spectrometry (SIMS) data of the Sn–3.5Ag–2Cu alloy also revealed that both the concentration of ⁶³Cu[–] and ¹⁰⁷Ag[–] were lower near the surface in relative composition (not given here). The solidification surface films of both the Sn–3.5Ag specimen

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Fig. 1 Microstructure of the alloy: (a) Sn–3.5Ag, (b) Sn–3.5Ag–2.0Cu.

and Sn–3.5Ag–2.0Cu specimen exhibited discoloring, but neither Figs. 2 nor 3 can explain the mechanism of the solidification surface film completely. In order to understand the solidification thin film characteristics, XPS was performed at the surface and the subsurface.

Figure 4 shows the full XPS spectra of both the Sn–3.5Ag specimen and the Sn–3.5Ag–2.0Cu specimen. Figure 4 reveals differences between the surface and the subsurface. In Fig. 4(a), comparing the surface with the subsurface, a large amount of Sn ($\text{Sn}3s^1$) or SnO_x ($\text{Sn}3p^3$) was found at the subsurface. For the Sn–3.5Ag–2.0Cu alloy [see Fig. 4(b)], the subsurface also contained a larger amount of Sn ($\text{Sn}3s^1$) or SnO_x ($\text{Sn}3p^3$) than the surface. According to the above findings, the full XPS spectra was unable to differentiate between Sn and SnO_x phase. Moreover, the concentration of every element in the experimental specimen was also analyzed by XPS to explain the thin film characteristics.

A comparison of the XPS–Sn analysis on the Sn–3.5Ag alloy and the Sn–3.5Ag–2.0Cu alloy is shown in Fig. 5. The surface peaks of both specimens are of the single-peak type, and their subsurface peaks are of the double-peak type. Thus it can be seen that there is an obvious difference between the chemical combination of Sn at the surface and the subsurface.

Fig. 2 Thin-film XRD patterns of the Sn–3.5Ag specimen: (a) surface, (b) subsurface.

Fig. 3 Thin-film XRD patterns of the Sn–3.5Ag–2.0Cu specimen: (a) surface, (b) subsurface.

XPS–Ag analysis on both the Sn–3.5Ag alloy and the Sn–3.5Ag–2.0Cu alloy (see Fig. 6) revealed that the Ag content at the surface was very low and the majority of Ag was found at the subsurface. Comparing the Ag content on the surface of the two specimens, the Ag content had a very slight tendency to increase as Cu was added. XPS–Cu analysis of the Sn–3.5Ag–2.0Cu specimen shows that there was no detectable

Fig. 4 Full-XPS spectra: (a) Sn-3.5Ag, (b) Sn-3.5Ag-2.0Cu.

Fig. 5 XPS-Sn analysis: (a) Sn-3.5Ag, (b) Sn-3.5Ag-2.0Cu.

Cu at the surface. Figure 7 shows a comparison of the XPS-O analysis on the Sn-3.5Ag alloy and the Sn-3.5Ag-2.0Cu alloy. It can be seen that the binding energy of O increased from the subsurface to the surface.

The curve-fitting data of XPS-Sn analysis on the Sn-3.5Ag alloy and the Sn-3.5Ag-2.0Cu alloy are shown in Figs. 8 and 9^{9,10)} (based on the single-peak spectrum curve and double-peak spectrum curve of Fig. 5). In Fig. 8 (Sn-3.5Ag specimen), the single-peak curves of the surface and the double-peak curves of the subsurface are composed of three curves, namely Sn^0 , Sn^{2+} and Sn^{4+} curves. As for relative composition, the Sn^0 content of the subsurface was higher than the surface, and both the Sn^{2+} and Sn^{4+} content

were lower at the subsurface. So, the content of both the Sn^{2+} and Sn^{4+} were closely related to the discoloring.

A similar phenomenon also occurred in the Sn-3.5Ag-2.0Cu specimen (see Fig. 9). Notably, the Sn^{2+} and Sn^{4+} spectra are still observed at the subsurface of Figs. 8 or 9. The evidence shows that tin alloys are highly susceptible to oxidation in air. In addition, the peak of the Sn^0 fitting-curve increased while the peak of the Sn^{2+} curve decreased from surface to subsurface, resulting in the spectrum curve of the real XPS-Sn transforming from double-peak type to the single-peak type. In other words, it can be inferred that oxidation occurred obviously at the surface. To understand the reaction mechanism of the Sn^{2+} , Sn^{4+} and O, XPS-O

(a)

(a)

(b)

(b)

Fig. 6 XPS-Ag analysis: (a) Sn-3.5Ag, (b) Sn-3.5Ag-2.0Cu.

analysis of the curve fitting of the Sn-3.5Ag-2.0Cu was performed (see Fig. 10). Ignoring the atmosphere, the results indicate that the solidification surface thin film and the subsurface film were mostly composed of SnO phase and SnO₂ phase. The roughness of the solidification surface film was greater than that of the subsurface, resulting in the atmosphere fitting-curve of Fig. 10(a) possessing higher intensity than Fig. 10(b). To sum up the data of Figs. 5 and 8–10, the solidification surface oxidative films of both the Sn-3.5Ag specimen and the Sn-3.5Ag-2.0Cu specimen were mostly composed of SnO and SnO₂. For the Sn-3.5Ag-2.0Cu specimen, a little Ag was able to exist (possibly as Ag₃Sn compounds) at the solidification surface oxidative films.

Fig. 7 XPS-O analysis: (a) Sn-3.5Ag, (b) Sn-3.5Ag-2.0Cu.

Meanwhile, the intensity of the Sn fitting curve of Figs. 8(a) and 9(a) also explains how Cu repressed the growth of SnO_x in the Sn-3.5Ag alloy. So, the possible copper-microsegregation is not the main reason for the discoloring phenomenon. The SnO and SnO₂ of the solidification surface affected the degree of discoloring.

The thin-film XRD results of both Figs. 2 and 3 cannot provide a complete profile of the solidification oxidative films. Therefore, this study avoided the influence of Ag and Cu, selecting a pure Sn specimen to perform thin-film XRD analysis (see Fig. 11, the conditions are the same as Figs. 2 and 3). Both SnO phase and SnO₂ phase were found on the solidification surface oxidative film. So it is safe to say that the Ag₃Sn compounds affected the thin-film XRD analysis of

Fig. 8 Sn-3.5Ag/XPS-Sn analysis: (a) surface, (b) subsurface.

Fig. 10 Sn-3.5Ag-2Cu/XPS-O analysis: (a) surface, (b) subsurface.

Fig. 9 Sn-3.5Ag-2Cu/XPS-Sn analysis: (a) surface, (b) subsurface.

Fig. 11 Thin-film XRD analysis of the pure Sn specimen.

the surface oxidative film in this system (the diffractive peak of both the Ag_3Sn phase and the SnO phase are confused easily, $2\theta = 30^\circ\text{--}40^\circ$). For this reason, the analytic methods of the surface oxidative film of tin alloys must be chosen very carefully. Additionally, according to the Gibbs free energy¹¹⁾ of Sn, Ag, Cu and O, most of the O atoms and the Sn atoms in both the Sn–3.5Ag alloy and the Sn–3.5Ag–2.0Cu alloy react to form the oxidative film of SnO_x . This explains how the O reacted with Sn melt to produce the oxidative film of SnO_x during the solidification process. Meanwhile, no AgO phase or Cu_xO phase was found at the solidification surface thin films.

4. Conclusion

- (1) Adding 2.0 mass%Cu into the Sn–3.5Ag alloy, precipitated Cu_6Sn_5 was produced in the β -Sn phase. The two kinds of solidification surface oxidative films of the Sn–3.5Ag specimen and the Sn–3.5Ag–2.0Cu specimen were mostly composed of SnO and SnO_2 . Cu can repress the growth of SnO_x phase in the Sn–3.5Ag alloy. The SnO and SnO_2 of the solidification surface affected the degree of discoloring.
- (2) On the solidification surface films, the Ag content of the Sn–3.5Ag–2.0Cu specimen was higher than the Sn–3.5Ag specimen. There was almost no Cu on the solidification surface of the Sn–3.5Ag–2.0Cu specimen. As for the Sn–3.5Ag–(2.0Cu) films, the Sn^{4+} concentration was higher than that of the Sn^{2+} . The binding

energy of O increases when the site is near the solidification surface.

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