Kirkendall voids formation in the reaction between Ni-doped SnAg lead-free solders and different Cu substrates

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1. Introduction

At temperatures greater than 50–60 °C, the solid-state reactions between Cu and many Sn-based solders produce two reaction products, Cu6Sn5, and Cu3Sn [1]. The growth of Cu3Sn tends to induce the formation of Kirkendall voids, while the growth of Cu6Sn5 does not [1–4]. Zeng et al. [4] reported that a large number of Kirkendall voids formed when electroplated Cu was reacted with the eutectic PbSn solder at 100–150 °C. These voids located not only at the Cu/Cu3Sn interface but also within the Cu3Sn layer. The formation of Kirkendall voids is not limited to the eutectic PbSn solder. Kirkendall voids were also reported to form when electroplated Cu was reacted with SnAgCu solders [5], or pure Sn [1]. The relatively rapid diffusion of Cu out of the Cu3Sn layer could be the major contributing factor for the formation of these voids. It was indeed shown that although both Cu and Sn were mobile within Cu3Sn, the Cu flux was somewhat greater than that of the Sn flux (three times greater at 200 °C) [6–8].

The formation of Kirkendall voids accompanying the Cu3Sn growth raises serious reliability concerns because excessive void formation increases the potential for brittle interfacial fracture [2,4,5,9,10]. Since the formation of Kirkendall voids is associated with the growth of Cu3Sn, it is reasonable to assume that the amount of Kirkendall voids can be reduced by reducing the Cu3Sn thickness. Recently, it was shown that Ni addition to Sn3.5Ag (3.5 wt.% Ag, balance Sn) in amounts as minute as 0.1 wt.% could substantially retarding the Cu3Sn growth [11–13], raising the hope that Ni addition can alleviate the problems caused by Kirkendall voids.

In addition to the effect of Ni addition, it was further pointed out that the type of Cu substrate used also had a marked effect on the Kirkendall voids formation [1]. It was reported that Kirkendall voids formed when electroplated Cu was used, while no such void was detected when OFHC (oxygen-free high conductivity) Cu substrate was used [1]. The objective of this study was to investigate the effect of Cu substrate and the effect of Ni additions on the formation of Kirkendall voids within the Cu3Sn phase. Specifically, the reactions between Sn2.5Ag solder doped with different levels of Ni (0–0.1 wt.%) and two different types of Cu substrate, the electroplated Cu and the OFHC Cu substrates, were studied.

2. Experimental

Solder balls with four different compositions, Sn2.5Ag, Sn2.5Ag0.01Ni, Sn2.5Ag0.03Ni, and Sn2.5Ag0.1Ni were prepared from 99.999% purity elements. The solder ball compositions were verified by using ICP-AES (inductively coupled plasma atomic emission spectroscopy), and it was estimated that the reported compositions had a maximum 0.005 wt.% uncertainty. For a given solder ball composition, there was no measurable ball-to-ball variation in composition. Each solder ball had a mass of 10 mg.

The solder balls were placed on Cu substrates with 600 μm diameter wettable openings. The solder could not wet the Cu substrate outside this opening, and the solder as a result formed a
sphere only over this wettable opening. Two types of Cu substrates were used, electroplated Cu and OFHC Cu. The Cu plating solution was CuSO₄-based and did not contain the C₆H₁₂O₆S₄Na₂ additive. The reflow temperature profile had a peak temperature of 235 °C and 90 s duration during which the solder was molten. The nominal ramp rate and cooling rate were both 1.5 °C/s. After reflow, the samples were subjected to solid-state aging at 160 °C for 500, 1000 or 2000 h.

The samples were then mounted in epoxy, sectioned by using a low-speed diamond saw, and metallurgically polished in preparation for characterization. The reaction zone for each sample was examined using an optical microscope and a scanning electron microscope (SEM). The compositions of the reaction products were determined using an electron microprobe, operated at 15 keV. In microprobe analysis, the concentration of each element was measured independently, and the total weight percentage of all elements was within 100 ± 1% in each case. For every data point, at least four measurements were made and the average value was reported.

3. Results

Fig. 1a1–a4 shows the backscattered electron micrographs for the samples using the electroplated Cu substrate with different Ni additions that were reflowed for one time. The corresponding micrographs for the OFHC substrates are shown in Fig. 2a1–a4. For both types of Cu substrates, the Cu₆Sn₅ phase is clearly visible. At this stage, the Cu₆Sn₅ phase was the only phase observed at the interface, and Cu₃Sn was not observed. Comparing Fig. 1a1–a4 to their counterparts in Fig. 2a1–a4, one concludes that these two different substrates produced essentially the same microstructure. In other words, the substrate effect was not important in the as-reflow condition.

Figs. 1a1–a4 and 2a1–a4 also shows that the additions of Ni to Sn₂.⁵Ag made the amount of Cu₆Sn₅ at the interface increase substantially. For Sn₂.⁵Ag without any Ni addition, the Cu₆Sn₅ layer was thin, continuous, and void-free, consistent with the classical scallop microstructure reported in the literature [14–16]. With the addition of 0.01 wt.% Ni, Cu₆Sn₅ still retained the scallop microstructure. Nevertheless, with the addition of 0.03 wt.% Ni, Cu₆Sn₅ became thicker, and had many voids between these Cu₆Sn₅ grains. As had been pointed out in our previous study [11,12], these voids were originally occupied by trapped solder. During sample preparation, the trapped solder in these voids was etched away. When the Ni addition increased even more, the amount of Cu₆Sn₅ near the interface increased correspondingly. The above observation showed that Cu₆Sn₅ formed at the interface without regard to the Ni additions. The alloy additions, however, did change the amount of Cu₆Sn₅ and its microstructures at the interface.

Fig. 1a1–a4 shows the backscattered electron micrographs for Sn₂.⁵Ag alloys with different Ni additions that were reflowed once over the electroplated Cu substrates and then aged at 160 °C for 0, 500, 1000, or 2000 h. The symbol SA denotes the Sn₂.⁵Ag alloy, and SA0.01Ni denotes Sn₂.⁵Ag0.01Ni, etc.

Figs. 1 and 2 show that, for all combinations of Ni additions and Cu substrates, both Cu₆Sn₅ and Cu₃Sn thickened with aging. During aging, the most striking feature is that the additions of Ni substantially reduced the Cu₃Sn to Cu₆Sn₅ thickness ratio. For samples with the same aging, the Ni additions had different effects on the growth of Cu₆Sn₅ and Cu₃Sn. Ni additions to Sn₂.⁵Ag increased the Cu₆Sn₅ thickness substantially, as shown in Fig. 3. The Ni additions, however, decreased the Cu₃Sn thickness substantially, as shown in Fig. 4. In short, the types of the Cu substrate did not seem to have a clear effect on the growths kinetics of Cu₆Sn₅ and Cu₃Sn.
In addition, both types of Cu substrates produced Cu₆Sn₅ and Cu₃Sn with very similar microstructures.

Although different Cu substrates produced the same intermetallic compounds at the interface with very similar microstructure and growth kinetics. One key difference is the existence of the Kirkendall voids within the Cu₃Sn phase when the electroplated Cu was used, as shown in Fig. 1. Zoom-in micrographs for Fig. 1d1–d4 showing the details of Kirkendall voids are presented in Fig. 5. For all the solder compositions used, the Kirkendall voids started to appear at an aging time between 500–1000 h. In contrast, there was no such void observed when the OFHC Cu was used even after aging for 2000 h, as shown in Fig. 2. With the electroplated Cu substrate, the amount of the Kirkendall voids increased with the aging time. For Sn2.5Ag without any Ni addition, 2000 h of aging at 160 °C produced a nearly continuous series of Kirkendall voids near the Cu/Cu₃Sn interface, shown in Fig. 5a. Such a pronounced degree of void formation without question posted a serious reliability concern for solder joints. With Ni additions, the Cu₃Sn layer became thinner, and the amount of Kirkendall voids decreased correspondingly, as shown in Fig. 5. In other words, Ni addition did have its effectiveness in reducing the amount of the Kirkendall voids.

4. Discussion

This study showed that the reaction products were always Cu₆Sn₅ during reflow, and Cu₆Sn₅+Cu₃Sn during aging at 160 °C.

Fig. 2. Backscattered electron micrographs for Sn2.5Ag alloys with different Ni additions that were reflowed once over the OFHC Cu substrates and then aged at 160 °C for 0, 500, 1000, or 2000 h. The symbol SA denotes the Sn2.5Ag alloy, and SA0.01Ni denotes Sn2.5Ag0.01Ni, etc.

Fig. 3. Total thickness of Cu₆Sn₅ formed near the interface versus the aging time at 160 °C.

Fig. 4. Thickness of Cu₃Sn formed near the interface versus the aging time at 160 °C.
was helpful in reducing the amount of voids within Cu3Sn, because the formation of these voids was directly related to the growth of the Cu3Sn layer.

This study shows that the types of Cu substrate used have a prominent effect on the observation of Kirkendall voids within the Cu3Sn layer. The reason why the Cu substrate had such a strong effect deserves further discussion. Other than the Kirkendall voids, the two different substrates, electroplated and OFHC, behaved very similarly, in term of the intermetallic growth kinetics and microstructure. Since the growth kinetics and microstructure were controlled to a large degree by the interdiffusion of the elements, it seems reasonable to assume that as far as diffusion-related phenomena were concerned the two types of substrate behaved the same. In short, the Cu substrates simply served as the end-members of the diffusion couples, and maintained a constant Cu thermodynamic activity at the Cu/Cu3Sn interface.

Although the compound formation did not change with the Ni addition, the amount of compound at the interface did increase substantially with Ni additions, as shown in Figs. 1 and 2. Our recent preliminary data show that for a given Ni addition, different cooling rates produced different amounts Cu6Sn5 near the interface, with slower cooling rate producing thicker Cu6Sn5. This observation seems to suggest that a major part of the Cu6Sn5 actually formed during the solidification of the solder. A faster cooling rate corresponded to less time for Cu diffusion, and as a result the dissolved Cu atoms precipitated out as Cu6Sn5 evenly throughout the entire joint. Consequently, less Cu6Sn5 located near the interface. Conversely, a slower cooling rate corresponded to more time for Cu diffusion, and as a result the dissolved Cu atoms could diffuse back to the interface to precipitate out as Cu6Sn5, and more Cu6Sn5 located near the interface. Similar cooling rate effect had also been reported in a very recent study on the reaction between Sn and CuNi alloy substrates with various compositions [17].

An interesting observation was that additions Ni was able to reduce the Cu3Sn thickness substantially. It was effective even after aging at 160 °C for 2000 h, which surpassed the typical industrial high temperature storage requirement of 150 °C for 1000 h. The reason why Ni addition was effective in reducing the Cu3Sn thickness is unclear at this moment. Several theories have been proposed, including thermodynamic arguments [18] and kinetic arguments [12,19]. More studies are needed to elucidate this point. The reduced Cu3Sn thickness with the Ni addition

5. Summary

(1) Kirkendall voids formed only when electroplated Cu was used. No such void was observed when OFHC Cu was used.

(2) Apart from the Kirkendall voids, the two different Cu substrates behaved very similarly, in term of intermetallic thickness and microstructure.
(3) In the case of electroplate Cu substrate, Kirkendall voids formed after aging at 160 °C for more than 500 h. The amount of voids increased with the aging time.

(4) The additions Ni was helpful in retarding the Cu3Sn growth, thus reducing the amount of Kirkendall voids when the electroplated Cu was used.

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References


