

Precipitation of large Ag_3Sn intermetallic compounds in SnAg2.5 microbumps after multiple reflows in 3D-IC packaging

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ABSTRACT

Microbumps have been adopted as interconnects between Si chips in 3D integrated-circuit packaging. The solder volume of a microbump decreases dramatically due to fine-pitch requirement and it is approximately two orders smaller in magnitude than that of a traditional flip-chip solder joint. The metallurgical reactions in the microbumps may behave quite differently to those in flip-chip bumps. Liquid-state metallurgical reactions were examined in SnAg2.5 microbumps with Ni metallization. The results indicate that large particles of Ag_3Sn intermetallic compounds (IMCs) precipitate after a 10-min reflow on microbumps with 4.0- μm -thick solder, which does not occur with flip-chip solder bumps. It is proposed that the Ag concentration in the remaining solder may increase as Sn reacts with Ni. The increase in the Ag concentration is mainly responsible for the occurrence of the large Ag_3Sn precipitates. The formation of these Ag_3Sn IMCs would be detrimental to the mechanical properties of the microbumps.

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1. Introduction

Metallurgical reactions between Pb-free solders and the metallized pads on integrated-circuit (IC) chips have been the focus of much attention in recent years [1–7]. Pb-free SnAg alloys have been adopted as solder materials in flip-chip solder joints due to their excellent mechanical properties and their ability to be electroplated. Dispersed Ag_3Sn intermetallic compounds (IMCs) are used to enhance the mechanical properties of these SnAg alloys [8–10]. However, large, plate-like Ag_3Sn IMCs form inside the solder joints when the concentration of Ag is higher than 3.5 wt% [11], and cracks may initiate at the interface of these plate-like Ag_3Sn IMCs and the solder when the solder joints are subjected to stress [1]. Therefore, the IC packaging industry has adopted SnAg alloys with a low Ag concentration (~ 2.5 wt%) to avoid the formation of these Ag_3Sn IMCs.

Traditional flip-chip solder joints have greater solder volumes than do those with under-bump-metallurgy (UBM). A typical SnAg solder joint consists of an approximately 100- μm -thick layer of solder alloys and several microns to 20 μm of UBM materials [12]. Therefore, as the UBM materials (Cu or Ni) react with Sn to form micron-sized Cu–Sn or Ni–Sn IMCs during reflowing or solid-state aging, the composition of the solder alloys does not change much. However, as the packaging industry has moved to three-dimensional (3D) packaging, microbumps have been adopted as the

interconnects between chips [13–15]. The solder volumes here are dramatically decreased, and the thickness of the solder is reduced to a range between a few microns and 10 μm . The microbump volume is approximately two orders of magnitude less than in a traditional flip-chip solder joint. In contrast, the thickness of the UBM layers remains almost the same as that in flip-chip solder joints. Therefore, the solder composition may change significantly during multiple reflows, and the microstructures of the SnAg solder alloys may be different in microbumps. However, there have been no reported studies on this issue.

In this study, we investigated the metallurgical reactions in SnAg2.5 microbumps with Ni UBMs during reflows. We found that the Ag_3Sn IMCs precipitate to form large Ag_3Sn particles after 10-min reflows with 4- μm -thick SnAg2.5 microbumps. Theoretical calculations were performed to show that the Ag concentration increases as the Sn in SnAg alloys reacts with Ni, and it exceeds 3.5 wt% after a 10-min reflow. The increase in the Ag concentration may be responsible for the precipitation of the large Ag_3Sn IMCs.

2. Experimental

The microbumps used in this study consisted of 4.0- μm or 6.2- μm SnAg2.5 alloys sandwiched between 5- μm Cu/3- μm Ni UBMs on two Si chips, as illustrated in Fig. 1. The 6.2- μm microbump had more amount of SnAg2.5 solder than the 4.0- μm one. Here, the upper chip is denoted as the top chip, whereas the bottom one is denoted as the interposer chip. The solder volume is less than the total UBM volume. The diameter of the microbumps is 18 μm . The SnAg alloys and the UBM materials were electroplated and the

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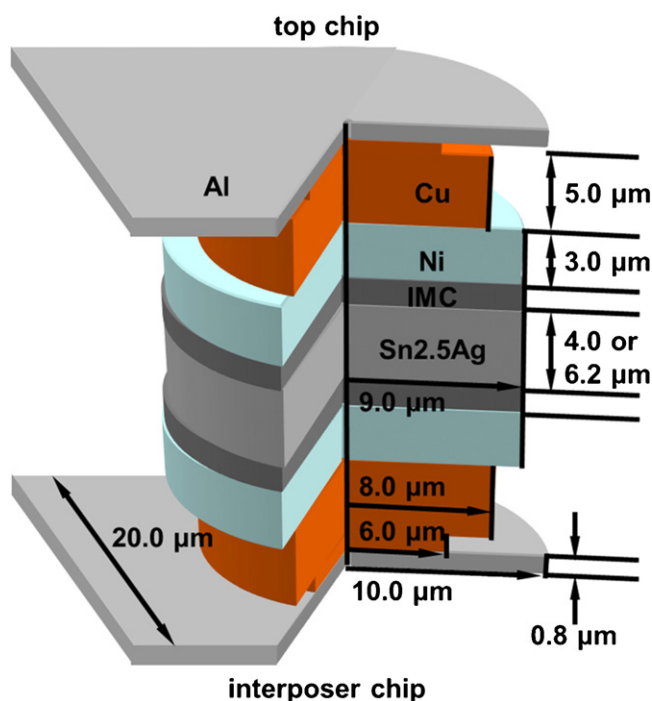


Fig. 1. Schematic diagram of the SnAg_{2.5} microbumps with Cu/Ni UBMs on both the top chip and the interposer chip.

microbumps were joined by thermo-compression at 285 °C for 25 s [16]. To study the metallurgical reactions in the liquid state, the samples were reflowed on a hot plate maintained at 260 °C for various time periods. The reflow times were 5, 10, and 30 min for the 4.0-μm-thick microbumps and 0, 5, 10, 40, and 90 min for the 6.2-μm microbumps. After the allotted reflow time, the samples were removed from the hot plate and cooled in air. The microstructures of the microbumps were examined with a JSM-6500F scanning electron microscope (SEM). Composition analysis was performed using energy dispersive spectroscopy (EDS) and an electron probe microanalyzer (EPMA, JXA-800M, JEOL).

3. Results and discussion

In the 4.0-μm sample, finely dispersed Ag₃Sn IMCs agglomerated into a few large precipitates after reflowing for 10 min. For the as-fabricated sample shown in Fig. 2(a), the Ag₃Sn IMCs were randomly distributed within the Sn matrix in the form of tiny particles. The sample showed a necking near the center of the solder joint, which is caused by a low compressive force during the bonding process. The solder volume was estimated from the cross-sectional SEM image, and the equivalent bump height was calculated to be approximately 4.0 μm. Fig. 2(b) shows back-scattered SEM images for another sample reflowed for 5 min. The Sn in the SnAg_{2.5} solder reacted with the Ni layers to form Ni₃Sn₄ IMCs on the both sides, resulting in the thickening of the Ni₃Sn₄ layers. The Ag₃Sn IMCs were still finely dispersed in the remaining solder. However, large Ag₃Sn particles were sometimes observed after reflowing for 10 min, as indicated by the arrows in Fig. 2(c). There was a large Ag₃Sn IMC precipitates emerging from the remaining solder layer. When the reflow time was increased to 30 min, the precipitation of large Ag₃Sn IMCs became more obvious. Fig. 2(d) illustrates the microstructure after reflow for 30 min. Here, the solder layer was almost completely transformed into Ni₃Sn₄ IMCs. It is interesting that large Ag₃Sn IMCs were frequently found inside the Ni₃Sn₄ IMCs. The large Ag₃Sn IMCs may be detrimental to the mechanical properties of the microbumps.

It is intriguing that precipitation of the large Ag₃Sn IMCs did not happen within 40 min of reflow with the microbumps with a 6.2-μm-thick solder layer. Fig. 3(a) is an SEM image showing the microstructure of the as-fabricated 6.2-μm-solder microbumps. Similarly to the results in Fig. 2(a), the Ag₃Sn IMCs were scattered throughout the Sn matrix. After 5-min and 40-min reflows, the interfacial Ni₃Sn₄ IMCs grew thicker, as depicted in Fig. 3(b) and (c), but no large Ag₃Sn IMCs were observed. However, when the reflow time was increased to 90 min, large Ag₃Sn IMCs started to emerge. Fig. 3(d) shows an SEM image of a 6.2-μm microbump after a 90-min reflow. A large Ag₃Sn inclusion appeared in the right-hand side of the joint, as indicated by the arrow in the figure. All the solder had reacted with Ni to form Ni₃Sn₄ IMCs at this stage.

At least 50 microbumps were inspected for each condition to ensure that the observed cross-sectional microstructures were representative of each condition. Herein, a large Ag₃Sn IMC is defined

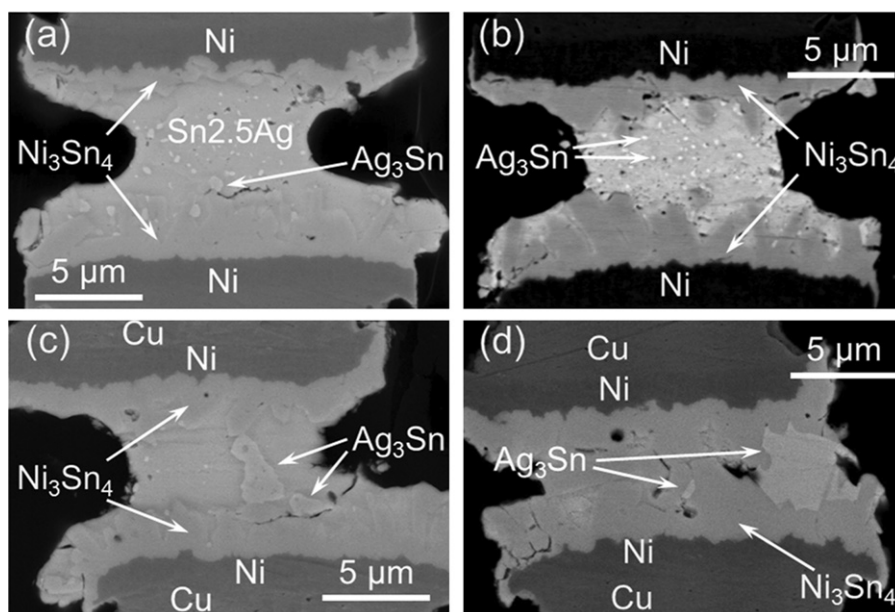


Fig. 2. Cross-sectional back-scattered SEM images of 4.0-μm-thick SnAg_{2.5} microbumps after reflowing for (a) 0 min, (b) 5 min, (c) 10 min, and (d) 30 min at 260 °C.

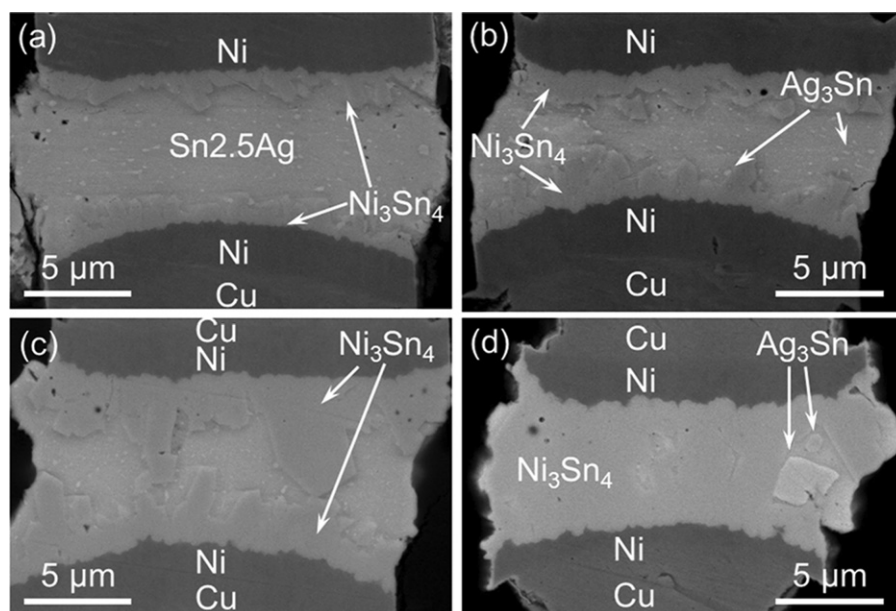


Fig. 3. Cross-sectional back-scattered SEM images of 6.2- μm -thick SnAg2.5 microbumps after reflowing for (a) 0 min, (b) 5 min, (c) 40 min, and (d) 90 min at 260 °C.

Table 1

Probability of observing Ag_3Sn IMCs larger than 2 μm for each specimen in the study.

Reflow time (min)	4.0- μm microbumps		6.2- μm microbumps	
	Sample amount	Probability (%)	Sample amount	Probability (%)
0	74	6.8	50	0
5	77	7.8	–	–
10	95	35.8	53	0
30	90	40.0	–	–
40	–	–	50	0
90	–	–	58	31

as one longer than 2 μm . The probability of observing a large Ag_3Sn IMC is listed in Table 1. The probability was also plotted against reflowing time, as depicted in Fig. 4. There was an approximately 7% chance of finding a large Ag_3Sn IMC in the as-fabricated and 5-min-reflowed 4.0- μm samples. However, the probability increased significantly for the 10-min-reflowed samples, to approximately 36%, and further increased to 40% after a 40-min reflow. In contrast, none of the 6.2- μm samples had large Ag_3Sn IMCs when the

reflow time was less than 40 min; however, the probability rose to 31% after reflowing for 90 min.

The increase in Ag concentration may have caused the precipitation of the large Ag_3Sn IMCs at extended reflow times. As the Sn reacted with the Ni metallization layer, the amounts of Sn in the SnAg solder decreased. Conversely, Ag does not form inter-metallic compounds with Ni, and there are no ternary compounds for the Sn–Ni–Ag system [8]. Therefore, the Ag concentration in the solder would be expected to increase with increasing reflow time. It has been reported that large Ag_3Sn plates form in SnAg solder at Ag concentrations over 3.5% [1,11]. Thus, large Ag_3Sn IMCs were observed in SnAg2.5 microbumps at extended reflow times. For flip-chip solder joints, the solder volume is approximately 100 times greater than that of the microbumps. Therefore, the Ag concentration remains unchanged after metallurgical reaction; there have been no reports of the increase in Ag concentration after metallurgical reactions in conventional flip-chip packaging. However, this issue will be critical for microbumps in 3D IC packaging.

To verify whether the Ag concentration is greater than 3.5 wt% after a specific reflow time, the following calculation was performed to examine the evolution of Ag concentration in the remaining solder. It is noteworthy that there may not be a critical Ag concentration, above which the precipitation of Ag_3Sn would occur. This is because the precipitation also depends on the cooling rate. We will discuss this point later. Yet, in this paper, we choose the eutectic concentration as the critical concentration, since the Ag_3Sn precipitation was found in Sn3.5Ag and Sn3.8Ag0.7Cu solders [1,11]. Because Ag does not react with Ni, all the Ag atoms should remain in the SnAg solder, as revealed in Figs. 2 and 3. The Ag there reacts with Sn to form Ag_3Sn IMCs when the specimens are

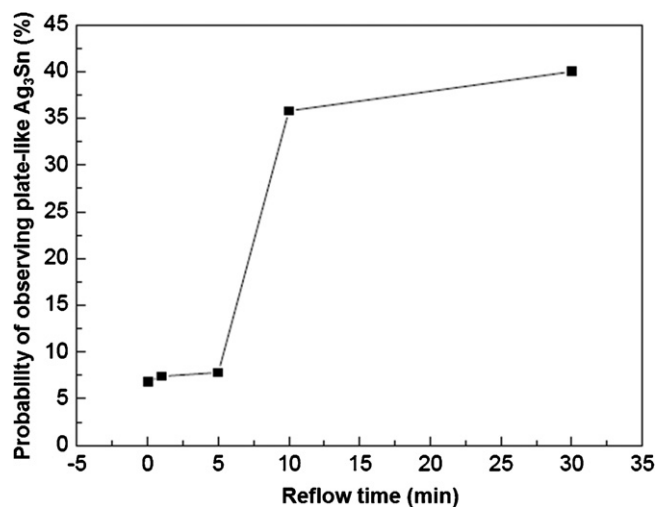


Fig. 4. The curve for the probability against reflowing time for the 4.0- μm samples. There is an abrupt increase around 10-min reflowing time.

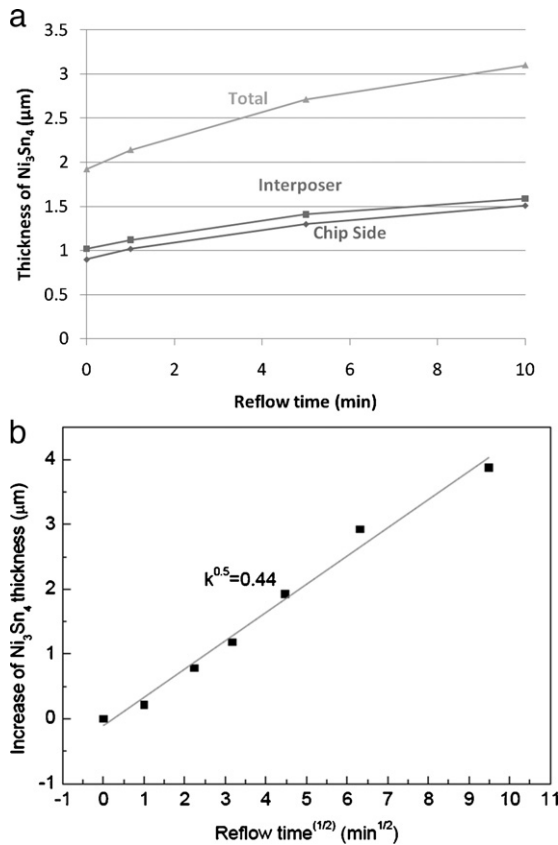


Fig. 5. The measured thickness of Ni₃Sn₄ IMCs against reflowing time for the chip side, the interposer side and the sum of the both sides.

cooled. However, according to Sn–Ag phase diagram [8], all the Ag atoms should dissolve in the molten SnAg solder at 260 °C. From a mass balance of Ag atoms, the Ag concentration C in the remaining solder can be expressed as:

$$C = \frac{V_s \rho_s I}{V_s \rho_s - V_i \rho_i f} \quad (1)$$

where I is the original Ag concentration in the SnAg2.5 solder, V_s is the original volume of the solder, ρ_s is the density of the SnAg2.5 solder (7.34 g cm⁻³), ρ_i is the density of the Ni₃Sn₄ IMCs (8.64 g cm⁻³ [9]), V_i is the volume increase of the Ni₃Sn₄ IMCs, and f is the weight fraction of Sn in the Ni₃Sn₄ IMCs (here 72.93%). The shapes of both solder and the Ni₃Sn₄ layers are nearly cylindrical, as shown in Fig. 3. Because the diameters of the Ni₃Sn₄ IMC and solder layers are roughly the same, Eq. (1) may be reduced to:

$$C = \frac{h_s \rho_s I}{h_s \rho_s - h_i \rho_i f} \quad (2)$$

where h_s is the original thickness of the SnAg solder, and h_i is the increase in thickness of the Ni₃Sn₄ layer on both top and bottom sides. In addition, the time-dependent thickness of the Ni₃Sn₄ layer can be expressed as:

$$h_t - h_0 = (kt)^{1/2} \quad (3)$$

where h_0 is the original thickness, h_t is the thickness after reflow for t min, t is reflow time in minutes, and k is the growth-rate constant.

Fig. 5(a) shows the measured Ni₃Sn₄ thickness as function of reflow time on the top and interposer sides for the 6.0-μm samples. The thickness of the Ni₃Sn₄ IMCs on the interposer side is thicker than that on the chip side. The exact reason for causing this difference is not clear. It may be related to the bonding process. The total thickness represents the sum of the thickness on the both sides.

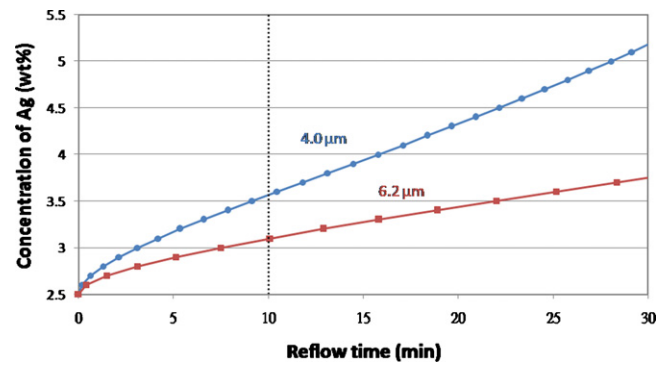


Fig. 6. The evolution of Ag concentration in the remaining solder after various reflow times for both the 4.0-μm and 6.2-μm microbumps. The Ag concentration exceeded 3.5 wt% after 13.0 min with the 4.0-μm-thick microbumps, whereas it took 25.0 min to do so with the 6.2-μm-thick microbumps.

Therefore, we can plot the increase in the Ni₃Sn₄ thickness against the square root of reflow time and the results are shown in Fig. 5(b). With the fitting curve, the rate constant was calculated to be 0.44. Combining Eqs. (2) and (3), the time-dependent Ag concentration can be expressed as:

$$C = \frac{I}{1 - ((kt)^{0.5} \rho_i f / h_s \rho_s)} \quad (4)$$

Fig. 6 shows the calculated Ag concentration in the remaining solder as a function of reflow time for the 4.0-μm and 6.2-μm microbumps using the rate constant from Fig. 4. With the 4.0-μm-thick microbumps, the Ag concentration increases to above 3.5 wt% after a reflow of approximately 9.0 min, whereas it takes approximately 22.0 min for the Ag concentration to exceed 3.5 wt% with the 6.2-μm-thick solder. This is because the 4.0-μm-thick microbump simply has less solder. Therefore, the consumption of Sn has a more obvious effect on the Ag concentration.

The calculated data fit the experimental results quite well. As shown in Fig. 4, the probability for observing large Ag₃Sn IMCs increased significantly after a 10-min reflow for the 4.0-μm-thick microbumps. The calculated data indicate that the Ag concentration was over 3.5 wt% after an 13.0-min reflow. Approximately 28.5 wt% of the Sn in the solder was consumed to form Ni₃Sn₄ IMCs, resulting in the Ag concentration exceeding 3.5 wt% in the remaining solder. Additionally, the experimental results showed that no large Ag₃Sn IMCs were found after a 40-min reflow with the 6.2-μm-thick microbumps, but the probability rose abruptly after a 90-min reflow. Note that here the calculated values show that the Ag concentration should exceed 3.5 wt% after a 25.0-min reflow. This difference may be attributed to the assumption of a constant reaction rate in the calculation. In reality, the reaction rate slows as the reflow time is increased. This may be responsible for the discrepancy between the experimental and theoretical results for the 6.2-μm-thick microbumps.

Fig. 7 shows the calculated concentration of Ag in the remaining solder as a function of solder thickness after 10-min reflow time when Sn2.5Ag, SnAg2.0, and SnAg1.5 Ag solders were adopted. The reason we choose 10 min is that solder bumps needs to pass reliability tests after approximately 10-min reflow. The results indicate that the thinner the solder, the more rapid in the concentration increase of Ag in the remaining solder. For example, when the solder thickness is 14.0-μm thick, the concentration of Ag only increases from 2.5 wt% to approximately 2.75 wt% after 10-min reflow. However, when the solder thickness decrease to 4.0-μm thick, the Ag concentration would increase over 3.5 wt% after 10-min reflow. The calculated critical solder thickness is 4.2 μm for the SnAg2.5 solder, below which the concentration of the Ag in the remaining solder would exceed 3.5 wt% after 10 min reflow.

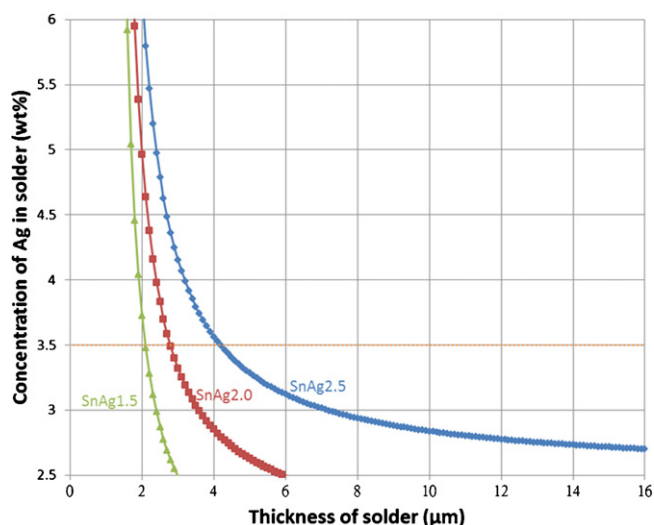


Fig. 7. The calculated Ag concentration in the remaining solder against thickness of solder after 10-min reflow for SnAg2.5, SnAg2.0 and SnAg1.5 solders.

The above results also suggest that reducing the Ag concentration in SnAg solder will ease the precipitation of the large Ag_3Sn IMCs. Fig. 7 also shows the calculated concentration of Ag in the remaining solder as a function of solder thickness after 10-min reflow time for SnAg2.0, and SnAg1.5 Ag solders. The critical solder thickness is 2.8 and 2.1 μm for the SnAg2.0 and SnAg1.5 solders, respectively. That is, when SnAg2.0 solder is used, the precipitation of Ag_3Sn may occur after 10 min reflow when the solder thickness is less than 2.8 μm .

Shen et al. studied the growth mechanism of Ag_3Sn precipitation in SnAg solder [17]. They proposed that the primary Ag_3Sn particles form before the onset of the eutectic reaction, more Ag_3Sn phase could nucleate adjacent to the primary Ag_3Sn precipitation, resulting in the formation of large Ag_3Sn IMCs. It is noteworthy that cooling rates may have a profound effect on the precipitation of Ag_3Sn IMCs [9–12,18]. Because Ag_3Sn IMCs are formed during the cooling process, a slow cooling rate facilitates the formation of large Ag_3Sn IMCs. In this study, the samples were cooled in air after reflow at a faster cooling rate than is typically used in the packaging industry. Therefore, the precipitation of large Ag_3Sn IMCs could be a critical reliability issue for microbumps if thin solder layers are adopted. In microbumps with few amount of solder, the solder reacts with Ni to form Ni_3Sn_4 IMCs after reflow and the entire solder layer may transform into IMCs, as shown in Figs. 2 and 3. The Ag_3Sn particles adhere to the Ni_3Sn_4 IMCs. Therefore, the $\text{Ag}_3\text{Sn}/\text{Ni}_3\text{Sn}_4$ interfaces will play a crucial role in the mechanical properties of microbumps. This deserves more future studies.

4. Conclusion

In summary, we investigated the liquid-state metallurgical reactions in microbumps with two solder thicknesses. Large Ag_3Sn precipitates emerged after a 10-min reflow with the 4.0- μm solder microbumps. When the solder thickness was increased to 6.2 μm , no large Ag_3Sn IMCs were found in the samples for reflow times below 40 min. Theoretical calculations indicated that the Ag concentration increases with reflow, because Sn reacts with the Ni UBM to form Ni_3Sn_4 IMCs, thus increasing the Ag concentration in the remaining solder with reflow time, which facilitates the formation of large Ag_3Sn precipitates during the cooling stage. These large Ag_3Sn inclusions may be detrimental to the mechanical properties of the microbumps; additional study is needed to investigate these effects.

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