Effect of Ag micro-particles content on the mechanical strength of the interface formed between Sn–Zn binary solder and Au/Ni/Cu bond pads


A Composite approach has been recently developed in lead-free soldering technology in the near future. The current leading Pb-free solder alloys are the ternary near-eutectic Sn–Ag–Cu alloys. The Sn–Zn binary eutectic system is the basis of one of the most promising group of lead-free solders with the advantages of low melting point (198 °C), excellent mechanical properties and acceptable costs. However, Sn–Zn alloys suffer from easy oxidation and relatively poor wettability. To improve the oxidation resistance and wetting behavior of Sn–Zn solder, the Sn–Zn–Ag alloys have been developed. Additions of Ag are also capable of increasing the ductility of Sn–Zn base solders, and a larger Ag alloy content resulting in the presence of Ag–Zn precipitates is not accompanied by an increase in strength.

1. Introduction

The electronics industry will make substantial progress toward a full transition to Pb-free soldering technology in the near future. The current leading Pb-free solder alloys are the ternary near-eutectic Sn–Ag–Cu alloys. The Sn–Zn binary eutectic system is the basis of one of the most promising group of lead-free solders with advantages of low melting point (198 °C), excellent mechanical properties and acceptable costs. However, Sn–Zn alloys suffer from easy oxidation and relatively poor wettability. To improve the oxidation resistance and wetting behavior of Sn–Zn solder, the Sn–Zn–Ag alloys have been developed. Additions of Ag are also capable of increasing the ductility and improving vibrational fatigue life of Sn–Zn based solders. The new Sn–Zn based alloys are still under development. Considering the improvement in wetting ability by Ag doping, McCormack and Jin also reported that small additions of Ag can improve the ductility of Sn–Zn base solders, and a larger Ag alloy content resulting in the presence of Ag–Zn precipitates is not accompanied by an increase in strength.

A Composite approach has been recently developed in lead-free solder research in an effort to improve the mechanical properties of solders, especially their creep and thermo-mechanical fatigue. The compositions of the composite solder alloys were Sn–9Zn with 0–4 wt.% Ag micro-particles. A commercially-available eutectic Sn–Zn solder paste was mixed with the Ag micro-particles. The average size of the Ag particles were about 8–10 µm. Then the mixed paste was screen printed on a polished alumina plate. The...
alumina plate with the printed solder paste on it was then reflowed at a temperature of 240 °C in a convection reflow oven (BTU VIP-70N) to prepare the composite solder balls. The thermal analysis of the alloys was carried out using a differential scanning calorimeter (2190-MDSC) in the temperature range from room temperature to 230 °C in a nitrogen gas flow of 50 ml/min. The heating rate was 25 K min⁻¹ up to 150 °C which was then equilibrated there for 1 min, finally 10 K min⁻¹ up to 230 °C.

A solder mask-defined copper bond pad on a BGA package was used as a base for electro-deposition of Ni and Au. The solder mask opening diameter was 0.6 mm with 7-µm-thick Ni on the ball pad. The average thickness of the Au layer was 0.5 µm. The lead-free composite solder balls with an average diameter of 0.70 mm were placed on the pre-fluxed Au/Ni/Cu bond pads of the substrates and reflowed at a temperature of 250 °C for 1 min to examine the interfacial reactions between the solder and the thin-film under-bump metallurgy (UBM). The flux used in this study was a commercial rosin activated flux (A88, Alpha Metals Ltd., HK).

Shear tests were performed for the as-reflowed samples using a Dage (Dage Holdings Ltd., Aylesbury, UK) Series 4000 Bond Tester. The shear tool height and the test speed of the shear test in this study were about 20 µm and 550 µm/s, respectively. The test load for shear was 5000 g for every test. About 40 randomly chosen solder balls were sheared to obtain the average and the extent of deviation for each composition.

Another set of composite solder balls were placed on a highly polished pure copper sheet and reflowed at 250 °C to find the wetting behavior. Finally, the spread of different solder balls was measured under an optical microscope with digital camera (LEICA-MZFLIII) to find the effect of the Ag particles on the spreading behavior.

The fracture surfaces after the ball shear tests were investigated thoroughly using a Philips scanning electron microscope (Eindhoven, The Netherlands) XL 40 FEG (SEM) in the secondary and backscattered electron mode as well as by energy dispersive X-ray spectroscopy (EDX). To investigate the microstructures and intermetallic layers at the interface, the as-reflowed samples were mounted in resin, cured at room temperature, mechanically ground, and then polished in order to obtain the cross sections of the solder/UBM interfaces. The chemical and microstructural analyses of the gold-coated cross-sectioned samples were obtained using the SEM equipped with an EDX spectrometer. The accuracy of the compositional measurement was about ±5%. To determine the formula composition of the intermetallic compounds (IMCs), the chemical analyses of the EDX spectra were corrected by standard ZAF software. The backscattered electron imaging mode of the SEM was used for the interfacial study.

3. Results and discussion

DSC analyses were carried out in order to investigate the fundamental thermal reactions on heating of the composite solder alloys and also to find the sustainable range for these composite solders. Fig. 1 shows typical DSC curves obtained for Sn–9Zn based Ag particulate composites on heating. On heating, the prominent endothermic peak for all composite solders appeared at around 201 °C, which corresponds to the eutectic temperature of the Sn–Zn binary system, Sn–Zn was 199 °C. An addition of Ag particles shifted the endothermic peak from 199 °C to this slight higher temperature. It has already been proven that the liquidus line of the Sn–Zn eutectic alloy rises with an increase in the Ag content [14]. It is noteworthy that the height of the first peak decreases with an increase in the Ag content. It is also interesting that a shoulder was observed at around 210 °C for 3% and 4% Ag containing solders.

The distribution of Ag rich-particles in the Sn–Zn matrix was found to be reasonably homogeneous in the composite solders prepared from the Sn–Zn paste and the Ag particles (Fig. 2). The Ag micro-particles in the bulk solder reacts with the Zn surrounding and then form dark ε-AgZn₃ “flower” like IMC compound particles on the surface of the Ag micro-particle as shown in Fig. 2. The core of the compound particle remains as pure Ag (lighter gray contrast – see Fig. 2d). As a result; the bulk solder matrix becomes depleted in Zn-rich phase with an increasing in the Ag micro-particle content in the Sn–Zn eutectic solder as shown in Fig. 3. The addition of larger amount of Ag into the solders resulted in the formation of larger amount of AgZn₃ compound. This reaction reduced the Zn content of the eutectic Sn–Zn composition which formed a hypoeutectic β-Sn structure [15]. Thus, the endothermic peak of the solders investigated resulted from two transformations. One was the melting of the eutectic Sn–Zn and the other was the melting of the hypoeutectic β-Sn. In the DSC curves in Fig. 1, the appearance of the shoulder for 3% and 4% Ag containing solders was the result of the formation of this hypoeutectic β-Sn.

Detailed cross-sectional studies were carried out to investigate the interfacial morphologies of the solders with the Au/electrolytic Ni/Cu pads. All interfaces, to a greater or lesser extent, reveal similar features—solidified solder, reaction zone, original electrolytic
Ni layer, and Cu pad. Most interestingly, a layer-type spalling at the interface was clearly observed in the Sn–Zn solder system from the initial reflow (Fig. 4a). EDX analysis of this spalled IMC layer revealed that the IMC was composed of Au and Zn and the Au percentage of this layer was about 25 at.%. This observation implies that the spalled IMC layer is made up of the AuZn$_3$ compound. A very thin layer of IMC was also noticed at the interface of the Sn–Zn solder system. The active nature of the Zn confirmed an instant reaction zone at the interface to maintain the bonding between the solder and the substrate.

![Fig. 2](image2.png)

**Fig. 2.** Matrices of composite solder alloys with uniformly distributed “flower” like AgZn$_3$ IMCs (a) Sn–9Zn + 4 wt.% Ag, (b) Sn–9Zn + 3 wt.% Ag, (c) Sn–9Zn + 2 wt.% Ag, and (d) enlarged view of a “flower” like IMC particle inside the bulk solder matrix of composition 3 wt.% Ag.

![Fig. 3](image3.png)

**Fig. 3.** Matrices of composite solder alloys at higher magnification showing depletion of α-Zn phases (which is the phase in darker gray contrast) (a) Sn–9Zn + 4 wt.% Ag, (b) Sn–9Zn + 3 wt.% Ag, and (c) Sn–9Zn.
With the addition of 1% Ag, no severe spalling of the initial IMC from the pad surface was noticed at the interface of the Sn–Zn composite solder/Ni system. On the other hand, there were places along the interface with no spalling. But some spalling of the IMCs was confirmed at some other places along the interface (Fig. 4b). A two-layered IMC structure was observed on the electrolytic Ni layer (Fig. 4c). The white thick layer was composed of Au, Zn and Ni. The upper gray layer was composed of Ag and Zn with a small amount of Au. It is also worth mentioning that the Ag particle distribution is fairly good even in the solder joint (Fig. 4b).

With 2–4% Ag, no spalling of the initial IMCs was observed at the interface. On the other hand, three distinct IMC layers were formed at the BGA bond pad and composite solder interface. These three different IMC layers were also different in chemical composition. Another important thing is that the Au does not dissolve into the Sn–Zn based solders. Instead, Au formed an IMC layer at the interface. The EDX analysis of the three IMC layers revealed that in the lower two IMC layers Au reacted with Sn and Zn to form different compounds which form different compounds.

The intermediate white IMC layers in Fig. 5 are made of Au and Zn. From the EDX analysis the percentage of Au found here is about 25 at.%. The thickness of these white layers remains almost the same for all the compositions at around 1.5 μm. Finally the third light dark IMC layer in Fig. 5 which is adjacent to the Au/Ni/Cu bond pad contains Zn, Au, Sn and a small amount of Ni. From the EDX analysis the average composition of the interfacial IMC layer near the substrate side was determined to be 55–63Zn, 14–23Au, 17–19Sn, and 3–9Ni (at.%).

The interfacial reactions between the Pb-free solders and the electrolytically deposited Au/Ni/Cu bond pads were conducted by holding at 250 °C for 1 min. The mechanical strength of the interface was measured for each different solder composition. The change of the average shear loads and their standard deviations are shown in Fig. 6. It may be noted that the average shear strength of joints increased with the Ag micro-particle content up to a certain limit. Beyond this limit, the addition of Ag particles actually decreased the joint strength. Overall the composite solders showed a higher shear strength than the eutectic Sn–Zn solder. The average shear loads of the solder joints were around 1.53, 1.51, 1.63, 1.56 and 1.48 kgf for 4, 3, 2, 1 and 0 wt.% Ag content in the Sn–Zn eutectic solder, respectively. For the 2 wt.% Ag particle content in the Sn–Zn eutectic solder, the shear load was higher than the rest of the compositions in the as-bonded condition on the electrolytic Au/Ni surface finish. With more than 2% addition of Ag, the joint strength decreased again.

The fractured surfaces of the pads and sheared balls were immediately studied by SEM. The results reported here (from fracture surface and cross-sectional studies) are based on the highest number of similar occurrences from each readout point of shear strength data. In most cases ductile fracture occurred within the solder for the reflowed samples. For 1% and 2% Ag containing com-
posite solder alloys, the fracture occurred at a location near but lower than the shearing height (20 μm), leaving a thick layer of solder on the pad. This indicates that the solder/pad bond is stronger than the bulk solder. Fig. 7 shows a fracture surface of the interface formed between a 2% Ag containing composite Sn–Zn solder alloy and an electrolytic Au/Ni/Cu bond pad after reflow at 250 °C for 1 min. The EDX analysis from these surfaces proved that fracture occurred through the solder alloys. From the EDX analysis (Fig. 7d) it is also confirmed that the dark spots shown in Fig. 7c are actually AgZn₃ IMCs and the bright irregular surfaces are mostly a Sn-rich phase. In the case of Sn–Zn eutectic solder the fracture morphology was also similar, but from the EDX analysis of the fracture surface it was clear that here the Zn content was higher compared to the other composite solders. For composite solders containing more than 2% Ag, the fractures were mainly ductile with few occurrences of a mixed mode of both ductile and brittle fracture as shown in Fig. 8.

It was confirmed that the Au–Zn IMC layer began to spall off from the interface of the Sn–Zn eutectic solder and Au/electrolytic Ni/Cu system after the initial reflow [16–18]. During soldering, Zn atoms start immediately to react with Au atoms at the interface [19]. The high surface tension of the Au–Zn compounds with the electrolytic Ni layer in the Sn–Zn solder may cause the Au–Zn layer to spall off from the interface in the molten state. The Ag particles in this experiment reacted with the molten solder (more precisely with the Zn therein) twice (firstly during ball preparation and secondly during the reflow soldering with the Au/Ni pad). During these reactions, a Ag–Zn IMC formed on the outermost surface of the Ag particles which tends to dissolve away from the surface of the Ag particles (Fig. 2d). For different Sn-based solders other than Sn–Zn, Au layer on the Ni UBM is used to react with the Sn atoms and form Au–Sn IMCs throughout the solder matrix. In the case of Sn–Zn solder during reflow, the Zn atoms react instantaneously with Au layer to form the Au–Zn layer. The high surface tension of the Au–Zn compounds with the electrolytic Ni layer in the Sn–Zn solder may cause the Au–Zn layer to spall off from the interface in the molten state. With the Ag addition, Zn also reacts with Ag particles to form Ag–Zn IMCs which tends to depart away from the original Ag particles. With the Ag reinforcement also the whole reaction chemistry was changed with the Au/Ni substrate. The Au–Zn layer may act as a favorable site for nucleation and growth of the dissolved Ag–Zn IMCs. These Ag–Zn IMCs ultimately redeposited over the Au–Zn compound layer. Simultaneously a new IMC layer of Au–Ni–Sn–Zn was formed beneath the Au–Zn IMC layer which made a bridge between the Ni substrate and Au–Zn IMC
to prevent the whole IMC layer lifting-off during reflow. With a 1% Ag addition, the formation and the redeposition of the Ag–Zn IMCs were insufficient to fully prevent the Au–Zn IMC layer spalling.

The wetting/spreading behavior is also a very important issue for a solder. Thus, a comparative study spreading was carried out for the different solders. From Fig. 9 it is clear that the spreading of Sn–Zn eutectic solder decreases slightly with an increase in the addition of Ag micro-particles.

The addition of Ag particles in the Sn–Zn solder gave two major consequences. With the increase in Ag content, the uniformly distributed AgZn3 coated Ag particles act as a reinforcing agent in the Sn–Zn matrix. The dissolved Ag–Zn IMC particles may also play some part in the composite structure. As a result the addition of Ag particles in the Sn–Zn alloy increased the shear strength of solder joints. On the other hand, with grater Zn consumption in the formation of Ag–Zn compounds, the bulk solder matrix became depleted in the eutectic α-Zn-rich phase and resulting in more Sn-rich phase in the bulk solder. Thus the addition of Ag particles beyond a certain limit in the Sn–Zn system actually decreased the strength of the solder joint. From the above considerations, the
Sn–Zn eutectic alloy with additions of 2% Ag particles can be recommended as a possible replacement of the conventional Sn–Pb alloy for soldering in microelectronic applications.

4. Conclusions

Several conclusions can be made about the effect of the reinforcement with Ag particle additions in Sn–9Zn eutectic composite solder alloys.

- The shearing strength can be increased by the addition of Ag particle into Sn–9Zn eutectic solder up to 2 wt.%. When more than 2 wt.% Ag particles were added to the Sn–9Zn eutectic solder, the shearing strength decreased significantly but was still higher than that of the pure Sn–9Zn eutectic solder.
- Three distinct IMC layers were formed with the BGA substrate for additions of 2–4 wt.% Ag particles addition, whereas two distinct IMC layers were found for a 1 wt.% Ag addition.
- For all the composite solders the fracture mechanism is mainly ductile, while for the higher (3–4 wt.%) Ag additions, a fracture of a mixed mode with both ductile and brittle areas was also observed.
- As the Ag particle in the composite solder increased, the α-Zn phase was depleted from the matrix.
- For 3 and 4 wt.% Ag particle additions the heating curves of the composite solders show a shoulder at around 210 °C, which is due to the hypoeutectic β-Sn phase.

Finally, it can be concluded that the shear strength of the Sn–9Zn eutectic alloy can be enhanced by the addition of Ag particles, but only up to a certain level. The Sn–9Zn eutectic reinforced with 2 wt.% Ag particles alloy may be recommended as a possible replacement of the conventional Sn–Pb alloy.

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