Influence of Ag micro-particle additions on the microstructure, hardness and tensile properties of Sn–9Zn binary eutectic solder alloy

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ABSTRACT
In this study, an addition of Ag micro-particles (8–10 μm) with a content in the range between 0 and 1.5 wt.% to Sn–9Zn eutectic solder, were examined in order to understand the effect of Ag additions as the particulate reinforcement on the microstructural and mechanical properties as well as the thermal behavior of the newly developed composite solders. Here, an approach to prepare a micro-composite solder alloy by mixing Ag micro-particles with a molten Sn–Zn solder alloy was developed. The composite solder was prepared by mechanically mixing Ag micro-particles into the Sn–9Zn alloy melt to ensure a homogeneous distribution of the reinforcing particles. The distribution of the Ag micro-particles in the matrix was found to be fairly uniform. The Ag particles reacted with the Zn and formed AgZn3 intermetallic compounds (IMC) in the β-Sn matrix. It was found that the more Ag particles added to the Sn–9Zn solder, the more Ag–Zn compound formed. In the Sn–9Zn/Ag composite solder, the microstructure was composed of AgZn3 IMC and α-Zn phase in the β-Sn matrix. Interestingly, as the Ag particles in the composite solder increased, the α-Zn phase was found to be depleted from the matrix. The average tensile strength of the composite solders increased with the Ag micro-particles content up to a certain limit. Beyond this limit, the addition of Ag particles actually decreased the strength.

1. Introduction

The development of Pb-free solder has become an important issue for electronic interconnection materials because of the health and environmental safety concerning Pb usage. Owing to the realization of the harmful influence of Pb on the environment and human health, increasing efforts have been conducted to search for suitable Pb-free solders as replacement for the conventional Pb–Sn eutectic alloy [1–4]. Therefore, many research groups are concerned with the development of new lead-free solders and their composites. Many Sn-based Pb-free solder systems that have been disclosed in the literature include Sn–Ag, Sn–Au, Sn–Bi, Sn–Cd, Sn–Sb, Sn–Zn, Sn–Ag–Zn, Sn–Zn–In, Sn–Bi–Ag and Sn–Ag–Cu [5–8]. McCormack and Jin [9] have pointed to the 91Sn–9Zn alloy as a non-toxic binary Pb-free solder that has a melting temperature of 198 °C close to the eutectic temperature of Pb–Sn alloy. The Sn–Zn alloy has excellent mechanical properties but is susceptible to oxidation and corrosion.

In general, new lead-free solders must meet an expected level of mechanical and electrical performance, have a suitable melting temperature, be corrosion resistant, be relatively harmless to health and the environment and have a low material cost [10,11]. The reliability of a solder joint plays an important role in determining the lifetime of electronic devices. This reliability is mainly dependent on matching the coefficient of thermal expansion, having a high elastic modulus, hardness, yield strength and shear strength together with resistance to corrosion, fatigue and creep [12]. Studies have shown that a potentially viable and economically affordable approach to improve the mechanical properties of a solder is to add an appropriate second phase particles, of ceramic, metallic or intermetallic, to a solder matrix so as to form a composite. The formation, presence and growth of the second phase have been proposed as a potential mechanism that controls solderability [13]. Lin et al. studied the influence of reinforcing TiO2 and Cu particles on microstructural development and hardness of eutectic Sn–Pb solders, and the measured microhardness revealed that the addition of TiO2 and Cu particles enhanced the overall strength of the eutectic solder [14]. Mavoori and Jin [15] used TiO2 and Al2O3 particles as the reinforcement for a conventional 63Sn–37Pb solder and reported a significant enhancement in creep resistance and also in other mechanical properties. Mohan et al. [16] prepared Sn–Pb composite solders by the addition of single wall carbon nano-tubes (SWCNT) as the reinforcing agent and reported that the mechanical properties of theses composites such as hardness, yield strength and ultimate tensile strength were found to be superior to the unreinforced solder, while the melting point was not appreciably altered. Shen et al. [17] successfully
prepared a ZrO$_2$ reinforced composite solder by mechanically dispersing ZrO$_2$ particles into a eutectic Sn–3.5Ag solder paste, and the composite solders had a refined microstructure with an improved microhardness.

In the present study, different weight percentages of reinforcing Ag particles were mixed into an eutectic Sn–Zn solder melt to prepare Sn–Zn/XAg composite solders. The influence of a small amount of reinforcing Ag particles on the microstructural evolution, especially, the morphology and distribution of intermetallic compounds (IMCs) were investigated using metallographic analysis. In addition, the mechanical properties of these Sn–Zn/XAg composite alloys were measured depending on the content of the reinforcing Ag micro-particles.

2. Experimental procedure

The Pb-free solder alloys were prepared from the commercially available pure Sn and Zn. The constituent elements were melted in a furnace in a alumina crucible. The molten Sn–Zn alloys were homogenized at 350 °C. The composite solder was prepared by mechanically mixing Ag micro-particles into the Sn–9Zn alloy melt to ensure a homogeneous distribution of the reinforcing particles and then poured in a steel mold to prepare the chill cast ingot. The melting temperature of the composite solders was measured with a differential scanning calorimeter (DSC Q 10). For DSC analysis, a piece of about 10 mg of a composite solder was placed into an Al pan. For melting properties data, the sample was initially scanned from 25 °C to 150 °C at a rate of 25 K min$^{-1}$ and then at a rate of 5 K min$^{-1}$ up to 250 °C under nitrogen gas atmosphere.

The as-cast solders were sectioned and polished according to non-ferrous metallography with 0.5 μm Al$_2$O$_3$ particles in order to obtain the microstructure. After cleaning with acetone and alcohol, the samples were investigated by an optical microscope with digital camera (LEICA-MZFLIII) and followed by SEM. A Philips XL40 FEG scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) analysis system was used to inspect and to analyze the microstructures of the four different types of solders and to perform the semi quantitative analysis on those structures in order to approximate the phases. 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 microstructural study. EDX analysis

![Fig. 1. Schematic diagram of the tensile specimen.](image)

![Fig. 2. Optical micrographs of chill-cast samples of (a) Sn–9Zn, (b) Sn–9Zn–0.5Ag, (c) Sn–9Zn–1.0Ag, and (d) Sn–9Zn–1.5Ag alloys (all images taken at 400×).](image)
has been done to find out the phase identification of the structure. Grinding and polishing were necessary to obtain a polished, smooth and flat parallel surface before indentation testing. Thus, the polished samples were placed in a Brinell hardness tester to measure the macrohardness. The applied load was 1.0 kN for 30 s and at least 10 readings of different indentations were taken at room temperature to obtain the mean value.

The solder ingots were then mechanically machined into tensile specimens as shown in Fig. 1 with a gauge length marked 32.00 mm for each samples, the width and thickness of the samples were 6.00 mm and 5.00 mm respectively. Tensile tests were carried out with an Instron testing machine (Instron 3369 Universal Testing Machine) at a strain rate of 1.00 mm/min at 25 °C to obtain data on the stress–strain curves which contain information of elongation at fracture and the UTS. The fracture surfaces of these lead-free composite alloys were also investigated under SEM to find fracture mode.

3. Results and discussion

Fig. 2 shows optical micrographs of eutectic Sn–9Zn alloys depending on Ag content. In the binary Sn–Zn alloy, the acicular-shaped α-Zn phases were homogeneously distributed in the β-Sn matrix. It is known that the solid solubility of Sn in Zn is less than 0.05 wt.% and the maximum solid solubility of Zn in Sn is approximately 2 wt.% [18]. However, after the addition of Ag particles, a new dark phase was clearly observed as well as the fine α-Zn phase into the β-Sn matrix as shown in Fig. 2b–d. Another important thing is that as the Ag particle increases in the composite solder, the α-Zn phase is depleted from the matrix. With an increase in the Ag content, the α-Zn phases also become finer and the number of dark phase increases.

To clearly identify the microstructures of Sn–9Zn/XAg composites, the backscattered electron imaging mode of the SEM was used which is represented in Fig. 3. From the EDS profile and the elemental analysis, it is confirmed that the dark phase consisted of Ag and Zn. From the EDX analysis the percentage of Ag found here was about 35 wt.%. This observation implies that the dark phase may be the \( \varepsilon \)-AgZn\(_3\) compound. In Sn–Zn/XAg alloys, spherical-shaped AgZn\(_3\) intermetallic compounds as well as the acicular-shaped Zn-rich phases were observed in the β-Sn matrix. As already stated, the amount of AgZn\(_3\) IMCs increased as the Ag content increased. On the other hand, as the Ag content increased the acicular-shaped Zn-rich phases became finer and its amount decreased as shown in Fig. 3a–c. A plausible explanation here for the finer Zn-rich phase is that both the high melting Ag–Zn compounds and the Ag particles may act as the heterogeneous nucleation sites for the Zn-rich phase.

![Fig. 3. SEM micrographs of chill-cast samples of (a) Sn–9Zn, (b) Sn–9Zn–0.5Ag, (c) Sn–9Zn–1Ag, (d) Sn–9Zn–1.5Ag, alloys and (e) EDS profiles of the circular spot.](image-url)
From SEM images of Sn–9Zn/1.5Ag alloys, Zn phases are found to be broken enormously and the shape of the α-Zn phases are almost round rather than the regular acicular like shape. The AgZn$_3$ intermetallic compounds (IMCs) in the Sn–9Zn/1.5Ag alloy are arranged in a row of closely spaced small IMC island as a chain like dendritic arm structure than regular spherical like shape present in Sn–9Zn/1.0Ag alloy. In addition, some porosity also observed in the Sn–9Zn/1.5Ag alloy. From a reliability test, Jiang et al. [19] reported that after exposing Sn–Zn solder to 85 °C/43%RH (relative humidity) and 85 °C/85%RH atmospheres, the oxidation of Sn–Zn solder is attributed to the oxidation of Zn, which diffuses into the Sn grain boundaries and forms ZnO. These oxides are liable to give rise to cracks along the Sn grain boundaries. In our present study, the formation of AgZn$_3$ intermetallic compound possibly will improve the oxidation resistance of the Sn–Zn solder reinforced with Ag particles. During soldering, if these intermetallic compounds are formed uniformly through out the grain boundaries and later on are expected to block the penetration of the water vapor and oxygen which in turn are assumed to reduce the formation of ZnO along the grain boundaries. According to the microstructures, the 0.5% Ag and 1% Ag containing solders are expected to provide better oxidizing resistance with more uniform IMCs distribution than the 1.5% Ag containing solder. To confirm this expectation detail further study are needed.

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 working range for these composite solders. According to the microstructures, the 0.5% Ag and 1% Ag containing solders are expected to provide better oxidizing resistance with more uniform IMCs distribution than the 1.5% Ag containing solder. To confirm this expectation detail further study are needed.

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and 1.5% Ag containing solders was the result of the formation of this hypoeutectic β-Sn phase.

The hardness of a solder alloy depends on the motion of dislocations and also on the growth and configuration of grains. The processes are more sensitive to the microstructure of the solder than its chemical composition. So the mechanical property such as the hardness depends especially on the microstructure, processing temperature, and the composition. Fig. 5 shows hardness values of the Sn–9Zn alloys depending on Ag content. As shown in Fig. 5, the hardness of the alloys increased up to a certain amount of Ag content then decreased. For the case of Sn–9Zn/0.5Ag solders the value of the hardness is increased very slightly due to the presence of AgZn3 IMC. But in the Sn–9Zn/1.0Ag solders, the value of the hardness is increased considerably because of the presence of considerable amount of IMCs with the fine Zn-rich phases and both of these phenomena contribute in the dispersion-strengthening effect on the Sn–Zn matrix. Interestingly, for the case of Sn–9Zn/1.5Ag alloy the hardness value drops due to the lowest amount of α-Zn phases as well as chain like dendritic arm structure of AgZn3 intermetallic compounds. The presence of porosity in the microstructure may also another possible reason for decreasing BHN value for Sn–9Zn/1.5Ag composite solder alloy (Fig. 3d and e).

The ultimate tensile strength (UTS) is the maximum engineering stress, which a material can withstand in tension, on the engineering stress–strain curve [20]. The yield stress is the stress level at which plastic deformation begins. For solder alloys, the yield stress is commonly defined by the stress on the stress–strain curve at 0.2% strain offset. Thus, the effect of third alloying additives on mechanical properties can be seen from the strain–stress curves shown in Fig. 6. The ultimate tensile strength (UTS), hardness, and elongation values are listed in Table 1. The tensile strength of the Sn–9Zn, Sn–9Zn/0.5Ag, Sn–9Zn/1.0Ag and Sn–9Zn/1.5Ag alloys were 41, 41.3, 43.6 and 37 MPa, respectively. The elongation at failure of the Sn–9Zn, Sn–9Zn/0.5Ag, Sn–9Zn/1Ag and Sn–9Zn/1.5Ag were 43.4%, 37.1%, 19.4% and 20%, respectively. A significant improvement in the tensile strength is observed for 1.0% Ag addition, whereas strength is dropped for 1.5% Ag addition in Sn–9Zn binary eutectic alloy. The tensile strength of the composite alloys is increased up to a certain extent of Ag content then decreased. The elongation at failure of these alloys decreased with increasing Ag content.

Fig. 7 shows the tensile properties of Sn–9Zn alloy depending on the Ag particle content. The maximum proof strength is observed in Sn–Zn/1Ag alloy, which is about 42 MPa. An increase in 8.6% proof strength is observed for 1.0% Ag addition in Sn–9Zn alloy, while a 53% drop in elongation is observed for it. Fig. 8 shows the SEM fracture surfaces of Sn–Zn alloys depending on Ag content after tensile tests. Both Sn–Zn and Sn–Zn/0.5Ag solders displayed a typical ductile fracture mode. On the other hand, a mixed ductile and brittle fracture was observed for higher Ag containing solders. For 1.5% Ag containing alloy, brittle fracture mode was more prominent.

As per dispersion-strengthening theory the strength usually increases with the addition of a second phase particle in the matrix. For the case of 0.5% Ag and 1.0% Ag addition in Sn–9Zn the theory proved right, while for 1.5% Ag addition the theory contradicts with

<table>
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<tr>
<th>Alloys</th>
<th>Melting temperature (°C)</th>
<th>Hardness (BHN)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation (%)</th>
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</thead>
<tbody>
<tr>
<td>Sn–9Zn</td>
<td>199.50</td>
<td>13.6</td>
<td>41.0</td>
<td>43.4</td>
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<tr>
<td>Sn–9Zn–0.5Ag</td>
<td>201.21</td>
<td>14</td>
<td>41.3</td>
<td>37.1</td>
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<tr>
<td>Sn–9Zn–1.0Ag</td>
<td>201.54</td>
<td>16</td>
<td>43.6</td>
<td>19.4</td>
</tr>
<tr>
<td>Sn–9Zn–1.5Ag</td>
<td>201.96</td>
<td>14.5</td>
<td>37</td>
<td>20.0</td>
</tr>
</tbody>
</table>

Table 1 Melting temperature and mechanical properties of the alloys.
the results. These contradictory results can be explained from the microstructure and tensile fracture surface of the alloys very clearly. As discussed in microstructure region, the “chain” like IMCs observed in the microstructure of Sn–9Zn/1.5Ag composite solder. According to Dieter [21], the second phase element increases the tensile strength up to certain extent and after then the precipitate start to grow non-coherently results in a decrease of overall strength. In addition, with higher amount of Ag the stirring time was also higher for 1.5% Ag containing solder. As a result, the probability of addition of casting defects (e.g. air entrapment and dross inclusions) was also higher. On the other hand the percentage of elongation was decreased with increased Ag particles. The percentage of elongation of Sn–Zn alloy is about 41% while the percentage of elongation of Sn–Zn/1.5Ag alloy is about 20%.

It was reported that in the Sn–Zn–Ag system, both γ-Ag5Zn8 and ε-AgZn3 compound was observed in the microstructure of the cast product [22–25]. Interestingly, Saad et al. also found Ag5Sn and Ag–Zn IMCs in the microstructure of the Sn–8.8Zn–1.5Ag alloy [26]. Fascinatingly, from the XRD pattern of those studies, it is evident that with higher amount of Ag (for 3.5% Ag), the peaks of both Ag5Zn8 and AgZn3 compound was apparent. On the contrary the AgZn3 was more prominent in the XRD pattern with lower amount of Ag (1.5% and below)[22,24,25]. In our study, a single IMC phase was noticed as per the resolution of the SEM considered. The composition of the IMC phase (i.e. AgZn3) is confirmed with the EDX. The same trend was also reported in some other researches [27,28] also. From this analysis, it can be concluded that the formation of the ε-AgZn3 compound is more favorable in the Sn–Zn–Ag solder system with 1.5% or below of Ag.

In the earlier research, it was reported that the Ag micro-particles in the Sn–Zn paste reacts with the Zn surrounding to it and form dark ε-AgZn3 IMC compound on the surface of the micro-particle and the core of the Ag particle remains as pure Ag [28]. In that case, the reflow was carried out at 255 °C for 1 min. The actual time of contact between the molten solder and the Ag particles was less than 1 min. In this research, the stir mixing of Ag micro-particles in the Sn–Zn melt was carried out at 350 °C and the mixing time depended on the amount of Ag content. For 1.5% Ag, Sn–Zn solder consumed all of the Ag particles for three reasons – firstly the mixing temperature was higher, secondly the contact time of Ag particles with the Sn–Zn melt was higher and thirdly stir mixing also enhanced the reaction rate. As the stir mixing was done for less time, there were still some unreacted Ag cores observed in the microstructure of both 0.5% Ag and 1% Ag containing Sn–Zn solders (Fig. 9).

After the formation of AgZn3 IMC, the amount of Zn in the hypoeutectic Sn–Zn system can be determined from the equilibrium phase diagram as shown in Fig. 10 [29]. For simplicity, the Sn–Zn binary phase diagram was used for approximate calculation. For 1.5% Ag containing alloy, as all the Ag particles reacted with the Zn in the Sn–Zn alloy, around 2.7% Zn was calculated to be consumed by the Ag particles. From the equilibrium diagram, it was expected that the melting temperature of the hypoeutectic Sn–Zn system would be around 204.5 °C. On the contrary, the 2nd peak of the DSC curve was observed at around 210 °C for 1.5% Ag. As for non-equilibrium heating during DSC test, the liquidus line shifts to the higher temperature. Another important point is that
due to Ag additions, the eutectic melting temperature also shifts from 199°C to 201°C for the formation of near ternary eutectic Sn–Zn–Ag system. Lin et al. suggested the Sn–8.97Zn–0.3Ag system as a ternary eutectic system from the DSC analysis [30]. It is worthy to mention that as the reactivity of Zn is higher, during casting some Zn may loss by forming dross in the melt. As a result, the liquidus temperature of the Sn–Zn–Ag system was around 5.4°C higher than that of the calculated one in the equilibrium diagram.

4. Conclusions

It is found that the addition of a third element can promote the mechanical property of Sn–9Zn solder alloy without influencing the thermal property too much. The melting temperature of Sn–9Zn eutectic solder alloy increases very slightly after the addition of Ag; this is due to the formation of near ternary eutectic composition of Sn–Zn–Ag. The volume fraction of IMCs in ternary Sn–Zn–Ag alloys nucleates in contrast to that of the eutectic α-Zn phase, which decreased with increasing addition of Ag content. At the same time the eutectic α-Zn phase converts into fine structures rather than thick accicular-like lamella. After the addition of Ag micro-particles, the AgZn3 IMCs were clearly observed into the β-Sn matrix. However, the shape of the AgZn3 IMCs in the Sn–9Zn/1.5Ag alloy is dendritic arm like rather than regular spherical shape present in the Sn–9Zn/1.0Ag alloy.

As the mechanical properties are strongly depended on the microstructures, thus these properties improved up to a certain amount of Ag content then decreased for the eutectic Sn–9Zn/1.5Ag composite solder alloys. The tensile strength of the Sn–9Zn/1.5Ag solder alloy on the other hand elongation drops a little. Both Sn–Zn and Sn–Zn/0.5 Ag solders displayed a typical ductile fracture mode. On the other hand, a mixed ductile and brittle fracture was observed for higher Ag containing solders. In conclusion, as per the investigated area of this study Sn–9Zn/1.0Ag composite solder may be recommended as an alternative for conventional Sn–Pb solder in microelectronic packaging.

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