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Microstructure, interfacial reaction and shearing property of Sn-58Bi solder joints reinforced by Zn particles during isothermal aging

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In this paper, micro-sized Zn particles were added into Sn-58Bi solder flux to form Sn-58Bi-xZn composite solder. The evolution of microstructure, interfacial IMCs and shearing properties during long-term aging were investigated. The wettability of Sn-58Bi-xZn solder decreased with the increase in Zn content. Adding the Zn element refined the microstructure of Sn-58Bi solder and mitigated the aggregation of Bi phases during aging. The interfacial IMCs changed from Cu₆Sn₅ to Cu₆(Sn,Zn)₅ with 0.5 wt% Zn addition. Further increasing the Zn content, Cu₅Zn₈ instead of Cu₆(Sn,Zn)₅ generated at the Sn-58Bi-2.0Zn/Cu interface. After long-term aging, Bi diffused into Cu₃Sn and formed an aggregation layer. With 0.5 wt% Zn addition the growth of interfacial Cu₆Sn₅ IMCs was suppressed. Shearing tests were conducted to evaluate the mechanical properties of Sn-58Bi-xZn joints before and after aging. Aging and excess Zn addition lead to a decrease in the shearing force of the joints. The fracture mode changed from solder fracture to interface fracture with excess Zn addition The Sn-58Bi-0.5Zn solder joints exhibited the optimal shearing properties during aging. The optimum amount of Zn addition to Sn-58Bi solder was 0.5 wt%.

KEYWORDS

Sn-58Bi, Zn addition, interfacial IMCs, shearing properties, aging

1 Introduction

Tin-lead solders have been widely used in the electronic packaging industry for decades. Due to the toxicity of lead and the increasing environmental concern, lead-containing solder has been banned since the ROSH Directive was enacted in 2006 (Zhang and Tu, 2014). Currently, several Pb-free solders such as Sn-Ag, Sn-Cu, Sn-Ag-Cu, Sn-Bi and Sn-Zn solder alloys have been extensively developed to replace the traditional Sn-Pb eutectic solder. Nevertheless, some application and reliability issues still need to be overcome (Abtew and Selvaduray, 2000). For example, the melting temperature of Sn-Ag, Sn-Cu and Sn-Ag-Cu solder alloys are too high to be compatible with printed circuit board (PCB) substrates during the soldering

process. Moreover, the excessive growth of Cu_6Sn_5 and Ag_3Sn intermetallic compounds (IMCs) in service will gradually reduce the reliability of solder joints (Berger et al., 2023; Mu et al., 2012; Zhang et al., 2024). The easy oxidation and poor wettability characteristics of Sn-Zn solder alloy hindered its application in the electronic industry (Liu et al., 2015; Xue et al., 2016).

Sn-Bi solder with its good solderability as the eutectic Sn-Pb solder, superior ultimate tensile strength and yield strength has drawn attention as an attractive candidate solder. However, the poor ductility and low reliability of Sn-Bi solder joints need to be improved (Zhang et al., 2022; Li et al., 2020). In recent years, reinforcement of solder alloys with micro or nanoparticles has been adopted to improve the performance of Sn-Bi alloy and is currently receiving great attention. The addition of micro Ni-particles significantly refined the microstructure of Sn-58Bi solder. Ni-Sn intermetallics obstructed the movement of Bi atom diffusion and improved the electromigration resistance of the Sn-58Bi composite solder joints (Xu et al., 2011). Li and Chan, (2015) have studied the mechanical properties and the growth of IMCs at the solder/Cu interface of Sn-58Bi solder with Ag nanoparticles addition. The results showed that the microhardness was increased by 12.2% and the shear strength was enhanced by 18.9% for the as-prepared solder. The dispersion strengthening theory was employed to elaborate the mechanical improvement mechanism. Some nanoparticles of non-metallic such as TiO₂ (Tsao et al., 2012), CNT (Shen et al., 2013; Sun et al., 2016; Sun et al., 2022), POSS (Zhang et al., 2010; Rashid et al., 2009), graphene (Yang et al., 2013; Ma et al., 2017; Peng and Deng, 2015), Al₂O₃ (Hu et al., 2015) have been added into Sn-Bi alloy. These particles can accelerate β -Sn heterogeneous nucleation during reflow and reduce the size of β-Sn significantly. The growth of interfacial IMCs was depressed with nano non-metallic particle addition. However, these particles could not have metallurgical bonding with Sn solder. The excessive nonmetallic particles will reduce the wettability due to the poor fluidity of composite solder (Yang et al., 2009).

Presently, most of the research is focused on the microstructure and mechanical properties of nanoparticle composite solder alloy itself, and few of them have studied the reliability of the micro joints using nanoparticle composite solder. Accordingly, this study aims to investigate the microstructure and mechanical properties of Sn-58Bi solder bearing micro-sized Zn-particles and prepare the ball grid array (BGA) solder joints using this composite solder alloy. The shearing test was conducted to evaluate the reliability of the solder joints. The effect of micro-sized Zn particles addition and solidstate aging on the reliability of Sn-58Bi micro-sized Zn particles composite solder joints was investigated.

2 Experimental procedures

2.1 Composite solder joints preparation

Commercial Sn-58Bi solder paste with 11.5 wt% flux was used as the base material. The Sn-58Bi-xZn micro particles composite solder paste was prepared by mechanically dispersing the microsized Zn-particles into the Sn-58Bi solder paste. The spherical pure Zn particles with about 2.0 μ m diameter were shown in Figure 1, and the content of Zn particles was set as 0, 0.5, 1.0, 1.5 and



FIGURE 1

Morphology of spherical pure Zn particles





2.0 wt% respectively. The mixed solder paste was stirred primarily under vacuum condition for at least 1 h to ensure the uniform distribution of Zn particles. Then, the composite solder paste was printed by a stainless steel stencil with a 1.2 mm diameter and 1 mm thickness. The printed circuit board (PCB) with a 0.8 mm diameter Cu pad was used as the substrate. Before soldering, Cu pads were cleaned by a 4.0 wt% HCl solution. The composite solder joints were heated on a heating platform at 180 °C for 40 s. After soldering, the joints were air-cooled and cleaned with alcohol as shown in Figure 2. The diameters of solder balls were about 1.0 mm.

2.2 Solid-state aging and shearing test

The as-soldered joints were solid-state aged by oil bath at 120°C for 10, 20, 30, 40 and 50 days. The average thickness of



FIGURE 4

Optical microstructure of the solder bumps aged for 0 days and 40 days. (a, b) Sn-58Bi, (c, d) Sn-58Bi-0.5Zn, (e, f) Sn-58Bi-2.0Zn.



Element mapping of the as-soldered Sn-58Bi-0.5Zn solder alloy. (a) Microstructure of the alloy (b) Sn element (c) Bi element and (d) Zn element.

interfacial IMCs was calculated by measuring the total area of the IMCs and dividing it by the total length of the images. The mechanical properties of Zn-particles composite solder joints were evaluated by a shearing tester. The shearing force was calculated as an average of 20 solder joints with a shearing speed of 0.01 mm/s.

2.3 Wettability test

The wettability of composite solder paste was evaluated according to the standard of JIS-Z3198-3. A certain quality of composite solder paste was printed on a polished Cu substrate as well as a stainless steel substrate by the stencil printing method. Then, the samples were heated at 180°C for 60 s. The height of solder balls wetted on stainless steel substrate and Cu substrate was measured by screw micrometer. The wettability of composite solder paste was evaluated by the spreading rate S, which can be expressed as Equation 1:

$$S = \frac{D - H}{D} \times 100\% \tag{1}$$

Where S is the spreading rate of composite solder paste, D is the height of composite solder paste wetted on a stainless steel substrate, and H is the height of composite solder paste wetted on a Cu substrate.

2.4 Microstructure characterization

To characterize the microstructure, the solder joints were mounted in resin and ground using different grit sizes of emery papers. Finally, the samples were polished with 3.0, 0.5 μ m diamond powder and 0.05 μ m silica suspension. The specimens were etched with a solution of 4 vol% HNO3 + 96 vol% C2H5OH. The microstructure of composite solder matrix, interfacial IMCs and fracture surfaces after the shearing test was observed using a scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometer (EDS).

3 Results and discussion

3.1 Wettability of the Sn-58Bi-xZn composite solder paste

The wettability is the primary condition for the usability of leadfree solder. Figure 3 presents the spreading rate of the Sn-58BixZn composite solder paste on Cu substrates. The Sn-58Bi solder paste showed satisfactory wettability and the spreading rate was 81.9%. The spreading rate of the composite solder paste decreased slightly when 0.5 wt% Zn particles were added into the Sn-58Bi solder paste. Moreover, the spreading rate decreased seriously with more Zn particles addition. Residual Zn particles can be observed around the solder caps after soldering. It is worth noting that the molten solder and the Cu are assumed to be fully covered by flux. The wettability of solder on Cu is reactive wettability. The wettability was affected by the formation of interfacial IMCs. Different from Sn-Bi-Zn ternary alloy, the Sn-58Bi solder flux needs time to absorb the Zn particles. Due to the high cooling rate, excess Zn particles were not yet absorbed by the molten Sn-58Bi solder and existed at the edge of the solder cap. The aggregation of Zn particles hindered the spreading of molten solder on Cu. Therefore, the wettability deteriorated with the increase of Zn particles content.



Cross-section and top-view microstructure of the initial IMCs at the interface. (a, b) Sn-58Bi/Cu, (c, e) Sn-58Bi-0.5Zn/Cu, (e, f) Sn-58Bi-2.0Zn/Cu.

3.2 Microstructure evolution of the Sn-58Bi-xZn solder bump during aging

Figure 4 shows the microstructure evolution of the as-soldered and aged composite solder bumps. The as-soldered Sn-58Bi solder bump shows a lamellar structure which mainly consists of Sn-rich phase and Bi-rich phase as shown in Figure 4a. With the addition of 0.5 wt% Zn particles, the microstructure of the composite Sn-58Bi-0.5Zn bump became finer with smaller Sn-rich phase and Bi-rich phase by comparing with the Sn-58Bi bump, as shown in Figure 4c. Fine Zn particles can be observed in the composite solder bump matrix.

Figure 5 shows the distribution of the Zn element in the assoldered Sn-58Bi-0.5Zn composite solder bump. It can be found that Zn particles were uniformly distributed in the Sn-rich phase. According to previous studies (Ma and Wu, 2016; Shen et al., 2014), no binary or ternary compounds will form in the Sn-Bi-Zn ternary system. The existence of Zn particles played the role of refining the composite alloy by heterogeneous nucleation. The microstructure of the Sn-58Bi bump was not further refined with more Zn particles addition, as shown in Figure 4e. When the Zn content increased to 2.0 wt%, needle-like Zn phases can be found in the bump. It is reported that the ultimate tensile strength of Sn-Bi alloy was improved by the existence of needle-like Zn phases. However, the elongation of Sn-Bi-Zn alloy deteriorated seriously due to the high aspect ratio Zn phases (Shen et al., 2014). The tensile strength and shearing strength of Sn-58Bi alloy is much higher than that of Sn-37 Pb alloy (Abtew and Selvaduray, 2000). It is the poor ductility of the Sn-58Bi alloy that limits its utilization. Many efforts have been made on this problem, but it has not been solved until now (Zhang et al., 2022; Li et al., 2020; Xu et al., 2011).

The microstructure of the Sn-58Bi bump became coarse after aging for 40 days, as shown in Figure 4b. The bulk Bi phases were separately distributed in the Sn matrix. Some Bi phases with small size were observed as illustrated by the red circles in Figure 4b. The Bi phase in the bumps with Zn addition slightly grew after aging, as shown in Figures 4d, f. The microstructure of the Sn-Bi-Zn bumps kept a lamellar structure after aging for 40 days. The addition of Zn mitigated the aggregation and growth of Bi phases. The solute atoms migration is significant during thermal aging in the binary system, such as Sn-Pb, Sn-Bi and Sn-Cu, etc (Philippe and Voorhees, 2013). Based on the Ostwald ripening, the smaller second phases will dissolve and the larger ones will grow due to the diffusion of the solute atoms. The radius of the second



FIGURE 7

Microstructure and composition of the IMCs aged for 40 days. (a) Sn-58Bi/Cu interface, (b) Sn-58Bi-0.5Zn/Cu interface, (c) Sn-58Bi-2.0Zn/Cu interface, (d) element compositions at position P1 and (e) element compositions at position P2.





Layered Bi aggregation in the IMCs at the interface after aging for 50 days. (a) Microstructure of Bi-rich layer, (b) Sn element, (c) Cu element and (d) Bi element. (c) Cu element and (d) Bi element. (c) Cu element and (d) Bi element.

phase can be expressed as Equation 2 (Kim and Voorhees, 2018; Lifshitz and Slyozov, 1961),

$$r^{3} = r_{0}^{3} + K_{0}t = r_{0}^{3} + \frac{8D\gamma C_{e}\Omega^{2}}{9RT}t$$
(2)

where r is the radius of the second phase, r_0 is the initial radius of the second phase at the initial stage, K_0 is the coarsening rate, t is the aging time, D is the diffusivity of solute atoms in the matrix, γ is the interface energy, Ce is the equilibrium concentration of solute atoms around the large second phase, Ω is the molar volume, R is the gas constant, T is the aging temperature.

According to the Sn-Zn binary alloy phase diagram, the solubility of Zn in Sn is approximately 0.7 at% at eutectic temperature (Wu et al., 2024). Due to the small volume and high undercooling of Sn-58Bi-xZn solder balls, zinc was not precipitated from Sn during the cooling process, resulting in the formation of supersaturated solid solutions. The solid solution atoms will hinder

the intragranular diffusion of Bi in Sn leading to the decrease of diffusivity of solute atoms (Delhaise et al., 2019). Therefore, the radius of the Bi phase in the Sn matrix with Zn addition decreased after thermal aging.

3.3 Microstructure evolution of interfacial IMCs during aging

The microstructure of the as-soldered solder/Cu interfaces is shown in Figure 6. The interfacial IMCs were observed from a cross-sectional view and top-view respectively. An extremely thin and scallop-shaped interfacial IMCs layer formed at the Sn-58Bi/Cu interface as shown in Figure 6a. According to the previous studies (Jeong et al., 2023; Chen et al., 2018; Hao et al., 2024), the composition of the IMCs was Cu₆Sn₅. The diameter of the IMCs was about 1.5 µm which can be observed from the top-view. Defects can



TABLE 1 Time exponent and diffusion coefficient of the interfacial IMCs at 120°C.

Solder/substrate	IMCs	n	<i>D</i> (m²/s)
Sn-58Bi/Cu	$Cu_6Sn_5 + Cu_3Sn$	0.45	$5.79 imes 10^{-20}$
Sn-58Bi-0.5Zn/Cu	Cu ₆ (Sn,Zn) ₅	0.29	3.66×10^{-20}
Sn-58Bi-1.0Zn/Cu	Cu ₅ Zn ₈	0.35	6.18×10^{-20}
Sn-58Bi-1.5Zn/Cu	Cu ₅ Zn ₈	0.37	$1.03 imes 10^{-19}$
Sn-58Bi-2.0Zn/Cu	Cu ₅ Zn ₈	0.34	1.42×10^{-19}



be found in the IMCs as illustrated with the red circle in Figure 6b. The as-soldered Sn-58Bi-0.5Zn/Cu was shown in Figures 6c, d. A flat layer of IMCs can be observed with the addition of 0.5 wt% Zn particles. The thickness of the IMCs layer slightly increased by comparison with the as-soldered Sn-58Bi/Cu interface. The EDS result indicated that some Sn atoms have been replaced with Zn atoms in the Cu₆Sn₅ IMCs. The composition of the IMCs changed from Cu₆Sn₅ to Cu₆(Sn,Zn)₅ with 0.5 wt% Zn addition. The topview morphology of Cu₆(Sn,Zn)₅ is shown in Figure 6d. It can be seen that the diameter and morphology of IMCs have not been changed by minor Zn addition. Significant changes in thickness and

morphology occurred when the content of Zn increased to 2.0 wt% in the Sn-58Bi solder as shown in Figures 6e, f. The thickness of IMCs at the as-soldered Sn-58Bi-2.0Zn/Cu increased with more Zn addition. It has been reported that adding about 1.7 wt% of Zn to Sn makes the γ -brass (Cu₅Zn₈) to be the first phase to form at the soldering temperature (Laurila et al., 2010). Another study found that the addition of 1 wt% Zn results in the formation of Cu₅Zn₈ IMC layer at the Sn-Bi-Zn/Cu interface (Li et al., 2006). Therefore, the composition of the IMCs in Figure 6e can be identified as Cu₅Zn₈ IMCs. The diameter of the Cu₅Zn₈ IMCs was lower than 1.0 µm which is much smaller than that of Cu₆Sn₅ and Cu₆(Sn,Zn)₅ IMCs. The IMCs particles changed from dense to sparse at the solder/Cu interface and may ultimately affect the mechanical properties of the solder joints as shown in Figure 6f.

Figure 7 shows the microstructure and composition of the interfacial IMCs at Sn-58Bi-xZn/Cu interface after aging at 120 °C for 40 days. Compared with the as-soldered IMCs shown in Figure 6, the thickness of the IMCs layer increased and IMCs became flattened after aging. A new interfacial IMCs layer formed at the Cu₆Sn₅/Cu interface as shown in Figure 7. According to the EDS results, the atomic percentage of Cu and Sn was approximately 3:1, indicating Cu₃Sn has formed after aging. Some voids can be found in the Cu₃Sn layer as shown in the magnified morphology in Figure 7. In the solid Sn/Cu diffusion couple, the dominant diffusion atoms are Sn and Cu in Cu₆Sn₅ and Cu₃Sn respectively (Yuan et al., 2016). The formation of Cu₃Sn can be contributed by two types of reaction. The interfacial Cu₆Sn₅ reacted with Cu to form Cu₃Sn IMCs. Meanwhile, Sn atoms diffused through the interfacial Cu₆Sn₅ IMCs and reacted with Cu to form Cu₃Sn IMCs. Due to the continuous diffusion of Cu in the Cu₃Sn, Kirkendall voids formed at the Cu₃Sn/Cu interface. Kirkendall voids are defects that will reduce the reliability of solder joints. Therefore, it is essential to inhibit the growth of Cu₃Sn IMCs.

The microstructure of the aged Sn-58Bi-0.5Zn/Cu interface is shown in Figure 7. The thickness of the IMCs is slightly lower than that of Cu_6Sn_5 IMCs at the Sn-58Bi/Cu interface. The elemental compositions of the IMCs at position P1 are shown in Figure 7d. The main components of the IMCs are Cu, Sn and contain a certain amount of Zn element. Based on the atomic percentage of element content, the IMCs can be determined as $Cu_6(Sn,Zn)_5$ compounds. It is worth noting that no compounds were generated







at the Cu₆(Sn,Zn)₅/Cu interface. This indicates that the addition of 0.5 wt% Zn in the Sn-58Bi solder delayed the growth of Cu₆Sn₅ IMCs and inhibited the generation of detrimental Cu₃Sn IMCs. With the increase of Zn content in the Sn-58Bi solder, a thick and flat IMCs layer formed at the Sn-58Bi-2.0Zn/Cu interface after aging as shown in Figure 7c. The thickness of the IMCs at the Sn-58Bi-2.0Zn/Cu interface was the thickest among the three types of solders. The elemental compositions of the IMCs at position P2 are listed in Figure 7e. The main components of the IMCs are Cu and Zn elements indicating Cu₅Zn₈ IMCs had formed after aging. By comparing the compositions of IMCs before and after aging, adding different amounts of Zn element did not change the composition of IMCs at the solder/Cu interface.

Further increasing the aging time to 50 days, the microstructure of the Sn-58Bi/Cu interface and the element mapping are shown in Figure 8. According to the distribution of Bi elements, Bi diffused through Cu_6Sn_5 and distributed in the Cu_3Sn layer. The physical properties of Bismuth are quite different from the Cu_6Sn_5 and Cu. The thermal expansion coefficient (CTE) of Bismuth decreases with the increase in temperature (Chen et al., 2024). However, the CTE of Cu_6Sn_5 and Cu increases with the increase in temperature. Therefore, the fatigue life of Sn-58Bi solder joints will reduce due to the Bi aggregation layer when bearing temperature cycling. The phenomenon occurred at the location where Cu_6Sn_5 came into contact with the Bi phase in the Sn-58Bi solder.

After aging for 50 days, the microstructure and elemental mapping of the IMCs at the Sn-58Bi-0.5Zn/Cu interface are shown in Figure 9. The IMCs near the Cu substrate showed a high content of Zn element, indicating $Cu_6(Sn,Zn)_5$ was first to generate. With the increase of aging time, the Zn near the solder/Cu interface has been consumed by the growth of IMCs. Therefore, the subsequently grown compounds at the interface were Cu_6Sn_5 IMCs. The Bi aggregation layer was not found at the interface. Meanwhile, $Cu_3(Sn,Zn)$ IMCs were hardly detected at the $Cu_6(Sn,Zn)_5$ /Cu interface indicating the formation of $Cu_6(Sn,Zn)_5$ hindered the diffusion of Sn and Cu. Therefore, adding minor Zn is beneficial for the long-term reliability of Sn-58Bi solder joints.

The thickness of the interfacial IMCs at the Sn-58Bi-xZn/Cu interface was measured and plotted in Figure 10a. The thickness of the IMCs increased with the aging time. Adding 0.5 wt% and 1.0 wt% Zn into the Sn-58Bi solder decreased the growth rate of IMCs. However, further increasing the Zn content (over 1.0 wt%) will accelerate the growth of IMCs. The growth of IMCs was examined as a function of aging time. The correlation between IMCs thickness and aging time can be expressed by Arrhenius Equation 3:

$$X = X_0 + Dt^n \tag{3}$$

Where X is the average thickness of interfacial IMCs after aging, X0 is the initial average thickness of interfacial IMCs. D is the diffusion coefficient at the aging temperature, t is the aging time, n is the time exponent. Accordingly, Equation 3 can be rewritten into Equation 4:

$$\log X = n \log t + \log D \tag{4}$$

The Previous studies indicated that the value of n was determined by the atomic diffusion mechanism (Zhang and Tu, 2014). When the time exponent n is close to 1, the growth of interfacial IMCs is controlled by interfacial reaction and follows the linear law, when n is close to 0.5, the growth of interfacial IMCs is controlled by volume diffusion and follows the parabolic law, when is close to 0.33, the growth of interfacial IMCs is controlled by grain boundary diffusion and follows the parabolic law.

Figure 10b shows the thickness of interfacial IMCs as a function of aging time in log-log format. The thickness was linearly related to aging time. According to the linear fitting results, the values of n were 0.45, 0.29, 0.35, 0.37 and 0.34, respectively. The values decrease with Zn addition. Moreover, the diffusion coefficient D was calculated in this study, as listed in Table 1. The time exponent n of the IMCs grown at Sn-58Bi/Cu interface is close to 0.5 indicating the growth of IMCs is controlled by volume diffusion. After Zn was added into Sn-58Bi solder, the time exponent n was close to 0.33. It indicated that the growth of the Cu₆(Sn,Zn)₅ and Cu₅Zn₈ were controlled by grain boundary diffusion. The addition of Zn into the Sn-58Bi changed the atomic diffusion mechanism at the solder/Cu interface. The diffusion coefficient of the IMCs at the aging temperature of 120°C was calculated by Arrhenius Equation 3. The diffusion coefficient of the IMCs at the Sn-58Bi/Cu interface was calculated to be 5.79 \times 10⁻²⁰ m²/s. The growth rate of the IMCs at the Sn-58Bi/Cu interface is much lower than that at the Sn-0.7Cu/Cu (Tian et al., 2017) and Sn-3.0Ag-0.5Cu/Cu (Tang et al., 2016) interface at 120 °C. The diffusion coefficient of Cu₆(Sn,Zn)₅ IMCs at the Sn-58Bi-0.5Zn/Cu interface decreased to $3.66 \times 10^{-20} \text{ m}^2/\text{s}$ indicating the addition of Zn inhibited the growth of IMCs. Adding more Zn into the Sn-58Bi solder changed the phase generation in the interfacial IMCs. The diffusion coefficient of Cu_5Zn_8 was slightly higher than that of Cu-Sn IMCs.

3.4 Shearing properties of Sn-58Bi-xZn solder joints

Figure 11 shows the influence of Zn content and aging time on the maximum shearing force of the composite Sn-58Bi-xZn solder joints. The Sn-58Bi joints exhibited a maximum shearing force of approximately 25.2 N before aging. The addition of Zn did not improve the shearing strength of the Sn-58Bi joints. With the increase of the Zn content, the shearing force decreases to 19.5 N when the Zn content is 2.0 wt%. The fracture surfaces of the as-solder Sn-58Bi-xZn solder joints are shown in Figure 12. Residual Sn-58Bi solder can be found on the fracture surface as shown in Figure 12a. Sn-58Bi solder has relatively low plasticity compared with Sn-Pb or other lead-free solders. The brittle fracture morphology is observed as exhibited in Figure 12b. The fracture surface of the Sn-58Bi-0.5Zn joint is shown in Figure 12c. Residual solder was observed on the fracture surface and the Cu pad was not exposed after shearing. The magnified fracture morphology of the Sn-58Bi-0.5Zn joint is shown in Figure 12d. Similar to the Sn-58Bi joint, the fracture mode was also a brittle fracture. It has been reported that the addition of Zn improved the ultimate tensile strength but decreased the ductility (Ma and Wu, 2015). In this study, the addition of 0.5 wt% Zn has a minor influence on the mechanical properties of Sn-58Bi solder joints. The fracture surface of the Sn-58Bi-2.0Zn joint is shown in Figure 12e. The fracture surface was further analyzed by EDS, the Cu elemental mapping indicating that the Cu pad was exposed after the shearing test. The fracture mode of the Sn-58Bi-2.0Zn joint is interface fracture. A plethora of voids can be observed on the surface as shown in Figure 12f. The abovementioned studies in Figure 3 indicate that the spreading rate decreases seriously when the Zn content is over 0.5 wt%. Due to the poor wettability, the soldering defects of voids were generated at the solder/Cu interface. Therefore, the shearing force decreased significantly with the excessive addition of Zn.

The shearing force of the solder joints decreased with the increase of aging time, as shown in Figure 11. After aging at 120 °C for 240 h, the shearing force of the Sn-58Bi joint decreased to 21.6 N. The shearing force of the Sn-58Bi joints ultimately stabilized at about 19.5 N after aging for 720 h. The fracture surface of the Sn-58Bi joint aged for 960 h is shown in Figures 13a, b. Interfacial IMCs of Cu₆Sn₅ and Cu₃Sn were exposed on the surface indicating the fracture mode changed from solder fracture to solder/interface mixed fracture. The shearing force of the as-soldered Sn-58Bi-0.5Zn joint decreased from 24.3N to 22.0 N after aging for 240 h. With the increase of aging time, the shearing force of the joints with 0.5 wt% Zn addition was higher than that of Sn-58Bi joints as plotted in Figure 11. The fracture surface of the Sn-58Bi-0.5Zn joint after aging for 960 h is shown in Figures 13c, d. Hardly any IMCs can be detected indicating Cu pad was not exposed on the surface. The fracture mode of the aged Sn-58Bi-0.5Zn joint was solder fracture. The location with high Cu element concentration in Figure 13c is magnified in Figure 13d. Rare amounts of Cu₆(Sn,Zn)₅ and Cu₃(Sn,Zn) IMCs were observed.

The Sn-58Bi solder with 0.5 wt% Zn addition exhibited outstanding mechanical properties than that of pure Sn-58Bi solder. With the increase of Zn content from 1.0 wt% to 2.0 wt%, the shearing force was 21.2 N, 20.2 N and 19.4 N, respectively. Further adding Zn in the solder, the initial shearing force of joints was lower than that of Sn-58Bi. The shearing force decreased with the increase of aging time. The shearing strength of the joints with Zn content beyond 1.0 wt% was lower than the pure Sn-58Bi and Sn-58Bi-0.5Zn joints. The fracture surface of Sn-58Bi-2.0Zn aged for 960 h is shown in Figure 13e. From the uniform distribution of Cu element, it is considered that the fracture mode of the joint was interface fracture. The magnified fracture surface is shown in Figure 13f. The sparse distributed Cu₅Zn₈ IMCs particles can be observed on the surface indicating poor mechanical properties of Sn-58Bi-2.0Zn joints. The above research indicates that 0.5 wt% Zn addition into the Sn-58Bi solder is beneficial to the long-term mechanical properties. Additive more Zn is detrimental to the reliability of Sn-58Bi joints.

4 Conclusion

In this paper, micro-sized Zn particles were added into Sn-58Bi solder flux to form Sn-58Bi-xZn composite solder. The evolution of microstructure, interfacial IMCs and shearing properties during long-term aging were investigated. The conclusions are drawn as follows:

- Minor Zn addition had little effect on the wettability of Sn-58Bi solder. When added with the content of Zn over 0.5 wt%, the wettability significantly decreased.
- (2) The addition of 0.5 wt% Zn refined the Sn-rich phase and Bi-rich phase in the Sn-58Bi solder. Neddle-like Zn phase occurred in the matrix of Sn-58Bi-2.0Zn. After aging at 120 °C for 40 days, Bi aggregated and formed bulk Bi phases due to the Ostwald ripening. The addition of Zn mitigated the aggregation and growth of Bi phases.
- (3) The composition of the IMCs at the as-soldered Sn-58Bi/Cu interface was Cu₆Sn₅. With 0.5 wt% Zn addition, Cu₆Sn₅ changed to Cu₆(Sn,Zn)₅. Further increasing the Zn content, Cu₅Zn₈ instead of Cu₆(Sn,Zn)₅ generated at the Sn-58Bi-2.0Zn/Cu interface.
- (4) After long-term aging, Cu₃Sn generated at the Cu₆Sn₅/Cu interface, Bi diffused into Cu₃Sn and form Bi aggregation layer. Minor Zn addition suppressed the growth of interfacial IMCs. When the Zn near the solder/Cu interface was consumed, the subsequently grown compounds at the interface were Cu₆Sn₅ IMCs. The Cu5Zn IMCs at Sn-58Bi-2.0Zn/Cu interface kept a high growth rate during aging.
- (5) The Sn-58Bi-0.5Zn solder joints exhibited optimal shearing properties during aging. The cracks propagated along the solder before and after aging. The fracture mode of pure Sn-58Bi joints changed from solder fracture to solder/interface fracture after aging. When the content of Zn increased to 2.0 wt%, voids were found on the fracture surface due to the poor wettability. The fracture of Sn-58Bi-2.0Zn joints was interface fracture. The optimum amount of Zn addition to Sn-58Bi solder was 0.5 wt%.

Data availability statement

The original contributions presented in the study are included in the article/supplementary material, further inquiries can be directed to the corresponding author.

Author contributions

XY: Data curation, Investigation, Methodology, Writing-original draft. ST: Funding acquisition, Resources, Supervision, Writing-review and editing. MZ: Conceptualization, Formal Analysis, Validation, Writing-original draft. HJ: Validation, Writing-review and editing. JW: Formal Analysis, Writing-review and editing. BW: Data curation, Writing-review and editing.

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Conflict of interest

Authors XY, ST, HJ, JW, and BW were employed by Wuxi Zhongwei High-tech Electronics Co., Ltd. Authors XY, ST, HJ, JW, and BW were employed by China Key System and Integrated Circuit Co., Ltd.

The remaining author declares that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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