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Effects of Composition and Processing on the Properties of Sn-3Zn-4Bi and Sn-Ag-Cu Solder Alloys for Electronic Packaging

Terence Soosai, Ervina Efzan Mhd Noor*, Mirza Farrukh Baig and Canan Akso

***Abstract* – The mechanical properties of lead-free solder alloys are critical for ensuring the reliability of electronic packaging, with shear strength and hardness being particularly important as electronic devices become smaller and interconnection densities increase. Thermal fluctuations and external mechanical impacts further intensify shear stresses on solder joints, raising concerns about long-term performance. In this study, the shear stress behavior of Sn-Ag-Cu and Sn-3Zn-4Bi solder joints was examined under different reflow temperatures. Sn-Ag-Cu, a widely researched lead-free solder, demonstrated strong resistance to high stress levels, reinforcing its suitability for high-reliability applications; however, its relatively high melting temperature (~221 °C) limits its use in low-temperature reflow processes. By comparison, Sn-3Zn-4Bi solder, with a melting temperature only ~12 °C higher than eutectic SnPb solder, showed potential for low-temperature soldering, while also exhibiting higher microhardness values than Sn-Ag-Cu, suggesting improved structural robustness. Despite these advantages, concerns remain regarding its compatibility with copper substrates, where interfacial reactions may affect joint integrity. Overall, the results suggest that Sn-Ag-Cu is preferable for applications requiring high strength and thermal resistance, whereas Sn-3Zn-4Bi offers notable benefits for low-temperature processing, provided substrate interactions are properly managed.**

Keywords—Solder, Lead-Free Solder, Intermetallic Compound, Sn-Pb, Sn-Zn-Bi, Electronic Packaging.

I. INTRODUCTION

Solder remains the most common interconnection material in electronic assembly processes [1]. Sn–Pb solder joints have been used for nearly two millennia [2]. Their widespread use in the electronics industry is attributed to a unique combination of low melting point, good solderability, high strength, low cost, favorable processing characteristics, and excellent mechanical properties [3], [4], [5], [6], [7]. However, due to the toxicity of Pb and the enforcement of RoHS regulations, Sn–Pb solders are being progressively replaced by lead-free alternatives [8], [9].

Currently, alloys such as Sn–Ag and Sn–Zn have demonstrated strong potential as replacements for conventional Sn–Pb solder [10]. Several lead-free solder compositions have been extensively studied, including Sn-25Ag-10Sb, Sn-9Zn-5In, Sn-1.0Ag-0.1Ce [11], Sn-0.7Cu [12], and Sn-4.7Ag-1.7Cu [13] and have demonstrated promising thermal and mechanical characteristics. More recent studies have further advanced this research; for example, the addition of Zn to eutectic Sn-Bi solder has been shown to improve electromigration resistance and mechanical performance on Cu substrates [14]. Other works have highlighted advances in Sn-based lead-free solder reliability, emphasizing the roles of interlayer materials,

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microstructure refinement, and process optimization [15]. Furthermore, previous studies have shown that incorporating nanoscale oxide films into Sn-based solders can significantly enhance corrosion resistance under harsh environmental conditions [16]. In parallel, detailed experimental investigations on multi-walled carbon nanotubes (MWCNTs)–epoxy nanocomposites have identified 0.2 wt% as the optimal concentration for improving mechanical properties, underscoring the potential of such materials for advanced robotic and automation applications[17].

Among lead-free systems, Sn–Zn alloys are particularly notable since their melting point is closest to that of Sn–Pb solder. The eutectic Sn-9Zn solder, with a melting temperature of ~198 °C, is comparable to eutectic Sn-37Pb. Nevertheless, its limited mechanical strength, poor wettability, and low corrosion resistance restrict practical applications [18]. As solder joints are required to ensure both electrical and mechanical reliability[9], [19], their strength and durability have become increasingly critical with technological advances, miniaturization, and the growing number of I/O pads [20], [21] . Despite improvements in Sn–Ag and Sn–Zn systems, challenges remain for temperature-sensitive components, optoelectronic modules, step soldering, and thin printed wiring boards, which require lower melting temperatures[22]. Moreover, Sn–Zn alloys suffer from oxidation susceptibility and poor wettability [9], [22]. Recent work, however, suggests that incorporating Bi can reduce the solidus and liquidus temperatures of these alloys, potentially overcoming these drawbacks[22].

Compared with other low-temperature solders such as Sn–Bi, Sn–In, and Sn–Ag-based alloys, Sn–Zn–Bi offers a more balanced combination of melting behavior, strength, and cost-effectiveness. Sn–Bi solders, while exhibiting excellent wettability and low melting points, tend to be brittle and unsuitable for thermally cycled environments, whereas Sn–Zn–Bi alloys maintain higher ductility and better mechanical stability under similar conditions[23].

Despite these advantages, existing studies on Sn–Zn–Bi solders have primarily focused on thermal properties and wettability, with limited emphasis on the influence of processing conditions; particularly reflow temperature; on mechanical reliability and intermetallic compound (IMC) evolution. The variation in reflow temperature can significantly affect joint morphology, IMC thickness, and void formation, which in turn determine shear strength and long-term performance.

To address this gap, the present study investigates the mechanical and thermal behavior of Sn–3Zn–4Bi solder and compares it with the industry-standard Sn–Ag–Cu alloy. By examining the influence of reflow temperature on shear strength, microhardness, IMC growth, and void formation, this work provides new insights into the processing–structure–property relationships of Sn–Zn–Bi solders and their suitability for next-generation, low-temperature, lead-free interconnection technologies.

II. Materials and Methods

Alloys of Sn-Ag-Cu and Sn-3Zn-4Bi were used in the present work. The Sn-Ag-Cu solder was prepared from high-purity tin (99.9%, Alfa Aesar), silver (99.9%, Alfa Aesar), and copper (99.9%, Alfa Aesar), while Sn-3Zn-4Bi solder was prepared from tin (99.9%, Alfa Aesar), zinc (99.9%, Alfa Aesar), and bismuth (99.9%, Alfa Aesar). Both solder compositions were produced by melting the raw elements in a furnace at 550 °C, followed by three cycles of re-melting to ensure homogeneity [24]. The molten alloys were cast into cylindrical steel molds to form billets of 0.5 in diameter and 0.25 cm thickness, which were mechanically cleaned with 800- and 1000-grit SiC abrasive papers and rinsed with ethanol.

For microstructural analysis, the billets were mounted in epoxy, polished with 0.05 µm alumina powder, degreased in water for 1 min, and cleaned with ethanol. Thermal properties were studied using differential scanning calorimetry (DSC) with a heating rate of 15 °C/min in the range of 50–300 °C under nitrogen to determine melting points [25], while hardness was measured using the Vickers method. Shear tests were performed on single-lap solder joints to simulate practical applications [26], [27], [28], using polished copper substrates (1 cm × 4 cm) [26], [29]. The solder billets were reflowed between two substrates separated by spacers to maintain constant joint height, producing hourglass-shaped joints. Reflow was conducted at 250, 270, and 290 °C for Sn-Ag-Cu, and 230, 250, and 270 °C for Sn-3Zn-4Bi, with a fixed reflow time of 10 s; flux was applied before reflow to improve wetting. Shear testing was performed using a Universal Testing Machine (Ag-1 Shimadzu) with a crosshead speed of 0.2 mm/s [20], [30], [31]. The fracture surfaces were examined using optical microscopy and scanning electron microscopy (SEM), and X-ray diffraction (XRD) was employed to confirm the microstructural observations.

III. Results and Discussions

A. *Melting Temperature*

In the DSC analysis, the results for Sn-Ag-Cu and Sn-3Zn-4Bi alloys are summarized in Table 1 within the studied temperature range of 50–300 °C. The Sn-Ag-Cu solder exhibited an onset melting temperature of approximately 221.13 °C. In DSC analysis, the onset point of the heating curve corresponds to the solidus temperature, while the peak point represents the liquidus temperature of the solder. For the Sn-3Zn-4Bi eutectic solder alloy, melting began at the solidus temperature (TS) and completed at the liquidus temperature (TL), with an onset temperature of approximately 194.92 °C. The onset temperature indicates the beginning of melting and is generally considered the solidus point, whereas the end temperature corresponds to complete melting of the sample, marking the liquidus temperature.

The Sn-Ag-Cu solder showed a single endothermic peak within the studied range, whereas the Sn-3Zn-4Bi alloy displayed two distinct peaks. These two peaks suggest the occurrence of multiple transformation processes during heating. Such transformations typically span a broad temperature range, which implies that Sn-3Zn-4Bi may remain partially liquid for an extended period upon solidification. This behavior can hinder the formation of reliable solder joints during processing [10].

From the DSC results, the melting temperature of the Sn-3Zn-4Bi alloy was 194.92 °C, lower than the 221.13 °C observed for Sn-Ag-Cu. Notably, the melting temperature of Sn-3Zn-4Bi is only ~12 °C higher than that of eutectic Sn-Pb solder (183 °C)[32]. From an operational perspective, this lower melting temperature makes Sn-3Zn-4Bi a promising candidate for low-temperature soldering applications.

TABLE 1. DSC results of Sn-Ag-Cu and Sn-3Zn-4Bi solder alloys.

Solder Alloy	Sample weight (mg)	Onset (°C)	Peak Temperature (°C)	Area (J/g)	Δ H (J/g)	± SD (ΔH)
Sn-Ag-Cu	9.69	217.36	221.3	69.439	69.438	±0.35
Sn-3Zn-4Bi	9.51	188.08	194.92	56.034	56.033	±0.41

B. Density and hardness

The density and hardness of solder alloys are of considerable interest since they are essential parameters for evaluating solderability [24]. The density of Sn-Ag-Cu and Sn-3Zn-4Bi solder alloys was found to be 6.638 g/cm³ and 7.136 g/cm³, respectively, with the Sn-3Zn-4Bi alloy exhibiting a slightly higher density, though the difference is not very significant. The average hardness, calculated from six points on the solder alloy surface, was 16.3 HV for Sn-Ag-Cu and 28.3 HV for Sn-3Zn-4Bi, indicating that Sn-3Zn-4Bi possesses significantly higher hardness. Hardness is often regarded as a measure of a material's resistance to wear and its durability [33], and microhardness provides insight into the hardness of grains and structural components of alloys [33]. Based on these results, it can be concluded that Sn-3Zn-4Bi solder alloy has a more reliable structure compared to Sn-Ag-Cu. This finding aligns with earlier reports suggesting that hardness observations provide an early indication that the bulk solder properties strongly influence the mechanical strength, particularly the shear strength, of the solder joint [34]. Therefore, Sn-3Zn-4Bi solder alloy can be expected to exhibit superior shear strength properties.

C. Shear Test

The shear stress test was performed to evaluate the effect of different reflow temperatures on the reliability of both solder joints, as shown in Figure 1. Each data point represents the average value obtained from three replicate samples, and the corresponding standard deviations (±SD) are included to indicate data reproducibility. The low variation among replicates confirms the consistency of the experimental procedure and strengthens confidence in the observed trends. The results reveal a notable difference between the Sn-3Zn-4Bi and Sn-Ag-Cu solder alloys. Although hardness test results suggested that Sn-3Zn-4Bi would exhibit superior shear strength, the shear stress test demonstrated the opposite trend, with Sn-Ag-Cu joints showing relatively higher shear stress than Sn-3Zn-4Bi joints. For Sn-Ag-Cu, the shear stress decreased slightly as the reflow temperature increased, indicating that reflow temperature had only a minor impact on joint strength. This observation is consistent with Chia et al. [34], who reported that Sn-Ag-Cu shear stress remains stable across varying temperatures and is generally higher than that of Sn-Pb solder, likely due to the alloy's stable surface tension. In contrast, the shear stress of Sn-3Zn-4Bi decreased at 250 °C but reached its highest value at 270 °C, suggesting that higher reflow temperatures enhance joint strength by promoting greater Bi saturation into Sn and Zn phases, thereby improving bond strength [31]. The addition of small amounts of Bi (≤4 wt%) has been reported to improve shear strength [10], [35], yet Zhou [10] also noted that Sn-3Zn-4Bi joints show lower shear strength compared to Sn-40Pb solder. Similarly, other studies have found Sn-Ag-Cu solder joints to exhibit higher shear strength than Sn-Pb solders [36], which aligns with the present findings showing Sn-Ag-Cu outperforming Sn-3Zn-4Bi. The lower shear strength of Sn-3Zn-4Bi observed in this study is likely due to oxidation, as Zn is an active element that promotes oxidation and reduces wetting ability during reflow [37]. While Bi improves wetting and tensile strength, the presence of Zn has been shown to increase oxidation and brittleness [37], thereby reducing the overall shear strength of Sn-3Zn-4Bi joints.

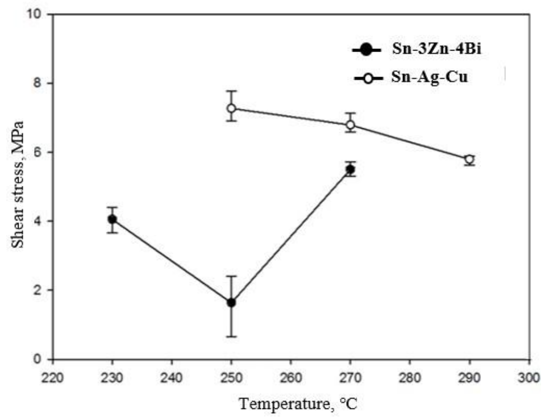


FIGURE 1. Shear stress variation with reflow temperature for Sn-3Zn-4Bi and Sn-Ag-Cu solder joints.

D. Microstructure shear analysis

The SEM observation of the fracture surface of the Sn-Ag-Cu solder joint is shown in Figure 2(d), where the fracture exhibits a ductile nature. The presence of dimples confirms ductile failure, consistent with reports that associate dimples with ductile fracture mechanisms [27], [28], [37]. Similarly, Figure 2(c) presents the SEM observation of the Sn-3Zn-4Bi solder joint, where the presence of large dimples also suggests a ductile fracture mode [38]. In addition, large voids are clearly visible in the fracture surface of Sn-3Zn-4Bi. Although both lead-free solders investigated in this study demonstrate ductile fracture behavior, the lower shear strength observed in Sn-3Zn-4Bi compared to Sn-Ag-Cu is primarily attributed to the presence of voids and the influence of intermetallic compound (IMC) layers.

1) Intermetallic compound layer

The formation and growth of the intermetallic compound (IMC) layer play a vital role in determining the shear strength and overall reliability of solder joints, as excessive IMC growth can cause brittleness and premature joint failure under low mechanical loads [39]. Table 2 summarizes the IMCs identified in the Sn-3Zn-4Bi and Sn-Ag-Cu solder joints. For the Sn-Ag-Cu solder joint, XRD analysis confirmed the presence of Cu_3Sn (ICDD: 03-065-4653), Cu_6Sn_5 (ICDD: 03-065-2303), and Ag_3Sn (ICDD: 01-070-5200). In contrast, the Sn-3Zn-4Bi solder joint exhibited CuSn (ICDD: 00-002-1436), Cu_5Zn_8 (ICDD: 00-025-1228), Cu_6Sn_5 (ICDD: 03-065-2303), and Cu_3Sn (ICDD: 03-065-4653), consistent with previously reported results [39]. Although quantitative IMC thickness measurements were not performed in this study, literature reports indicate that IMC layers within 1–3 µm generally maintain joint integrity, while excessive growth beyond 5 µm can lead to localized stress buildup and interfacial cracking [40].The morphology of the IMC layer is equally critical: uniform and continuous IMC layers, commonly observed in Sn-Ag-Cu systems, promote better bonding and load transfer, whereas coarse or irregular IMC structures, frequently found in Sn-Zn-Bi solders, serve as potential crack initiation sites under shear stress. Therefore, careful control of IMC thickness and morphology through optimized reflow temperature and duration is essential for enhancing the mechanical performance of lead-free solder joints. Although a complete phase diagram for the Sn-3Zn-4Bi alloy has not yet been published, its IMC phases can be analyzed by considering ternary subsystems that include the Sn-rich matrix, Ag_3Sn, Bi compounds, and Cu_3Sn [39]. Overall, prior studies confirm that the interfacial reactions leading to IMC formation between solder and substrate play a decisive role in mechanical behavior and long-term reliability of electronic assemblies [22].

TABLE 2. IMCs in Sn-Ag-Cu and Sn-3Zn-4Bi solder joints by XRD analysis.

Solder Alloy	
Sn-Ag-Cu	**Sn-3Zn-4Bi**
Cu_6Sn_5	CuSn
Cu_3Sn	Cu_5Zn_8
	Cu_6Sn_5
	Cu_3Sn

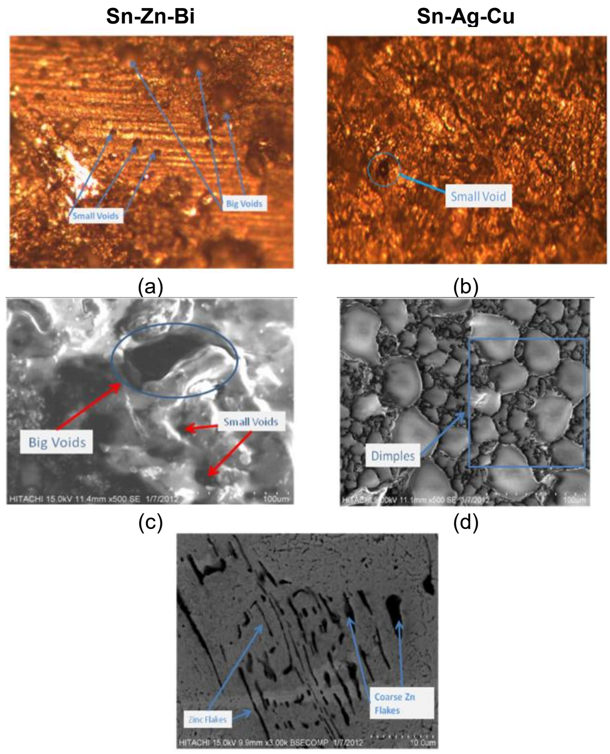
2) Void formations

Voids are one of the key factors that reduce the reliability of solder joints, as they form randomly and are difficult to control regardless of the alloy composition. In this study, voids were observed in the optical microscopy (OM) images of shear test samples for both solder types. Figure 2(a) shows that the Sn-3Zn-4Bi solder joint contains numerous large and small voids, while Figure 2(b) reveals only a few small voids in the Sn-Ag-Cu solder joint. The higher void density in Sn-3Zn-4Bi correlates with its relatively lower shear strength compared to Sn-Ag-Cu, as further supported by the shear stress versus temperature results in Figure 1.

Void formation can occur during the reflow process due to entrapped air from solder flux or surface reactions of the alloys [41]. During fluxing, metallization reactions can contribute to void nucleation, while IMC layers such as Cu_6Sn_5 and Cu_5Zn_8 further promote void formation, reducing joint reliability [35]. Although Cu_6Sn_5 also forms in Sn-Ag-Cu, the absence of Cu_5Zn_8 minimizes its voiding tendency. Another important mechanism is Kirkendall voiding, which occurs within the Cu_3Sn intermetallic layer beneath the Cu_6Sn_5. This phenomenon arises from unequal diffusivities of Cu and Sn [42], [43]. Since both solder alloys were reflowed on copper substrates and are Sn-based, the presence of Cu_3Sn IMC was expected and confirmed by XRD in Table 2.

To mitigate void formation and oxidation effects, process optimization during reflow is crucial. Conducting reflow soldering in a controlled or inert atmosphere, such as nitrogen, helps suppress oxidation on the molten solder surface; particularly important for Zn-containing alloys that readily oxidize. Additionally, adjusting the flux formulation, preheating stage, and reflow temperature profile can enhance wetting, reduce trapped gases, and minimize void nucleation. Maintaining a clean and oxygen-reduced reflow environment therefore plays a significant role in improving the interfacial bonding quality, reducing void density, and enhancing the shear strength and long-term reliability of Sn-3Zn-4Bi solder joints.

Cooling rate also influences void growth and morphology. Prabhu et al. reported that slower cooling encourages coarse Zn flake formation, which promotes void nucleation [38], while Hwang and Suganuma highlighted that cooling rate significantly affects the joint strength of Sn-Zn-Bi based solders [43]. Coarse Zn flakes hinder dislocation motion, leading to dislocation pile-up in Zn-rich regions and subsequent void formation. SEM analysis of bulk Sn-3Zn-4Bi (Figure 2(e)) in this study revealed coarse Zn flakes, consistent with air cooling, supporting the findings in [37].



(e)

FIGURE 2. Optical and SEM micrographs of solder joint fracture surfaces (a) Sn-3Zn-4Bi fracture surface under OM (20×) (b) Sn-Ag-Cu fracture surface under OM (20×) (c) SEM image of Sn-3Zn-4Bi fracture surface showing voids and microstructural features (d) SEM image of Sn-Ag-Cu fracture surface with smoother morphology (e) SEM micrograph of Sn-3Zn-4Bi bulk solder revealing grain structure and phase distribution.

Recent works have provided further insight into Kirkendall void evolution. Yang et al. demonstrated that voids at Sn/Cu solder joints appear only after an incubation period following Cu_3Sn formation, and under low-impurity conditions, they may even exhibit partial self-healing [44]. Baheti et al. showed that Cu impurities above ~0.1 wt% accelerate void nucleation and growth [45]. These findings suggest that void formation is controlled not only by cooling rate and microstructure but also by material purity and long-term aging, with higher cooling rates mitigating Zn coarsening and thereby reducing void density.

IV. Conclusion

In this study, Sn-Ag-Cu and Sn-3Zn-4Bi solder alloys demonstrated promising qualities as potential lead-free alternatives. The Sn-Ag-Cu alloy exhibited excellent shear strength with consistent performance across different reflow temperatures, confirming its suitability for high-reliability applications such as hand soldering and surface-mount technology, where durability and long-term stability are critical. In contrast, the Sn-3Zn-4Bi alloy showed comparatively higher hardness and acceptable shear strength, with performance improving at elevated reflow temperatures. Its melting point of ~195 °C, only about 12 °C higher than conventional Sn-Pb eutectic solder, enables integration into existing wave soldering processes with minimal modification to thermal profiles. However, issues such as void formation, oxidation due to Zn, and relatively lower shear strength compared to Sn-Ag-Cu must be carefully considered in terms of long-term reliability. Overall, Sn-Ag-Cu remains the stronger candidate for applications requiring stable shear performance, while Sn-3Zn-4Bi offers advantages in hardness and process compatibility for wave soldering, provided that strategies are developed to mitigate voiding, oxidation, and intermetallic compound growth. Future research should focus on alloying modifications, microstructural refinement, and process optimization to further improve the mechanical reliability, environmental compliance, and sustainability of these lead-free solder systems.

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Author contributions

Terence S.: Data Curation, Writing – Original Draft Preparation.

Ervina Efzan Mhd Noor: Conceptualization, Methodology, Validation, Project Administration, Supervision, Writing – Review & Editing;

Mirza Farrukh Baig: Validation, Writing – Review & Editing.

Canon Akso: Writing – Review & Editing.

Conflict of interests

No conflict of interests was disclosed.

Ethics statements

This study did not involve human participants, animal subjects, or the use of sensitive personal data; therefore, ethical approval was not required.

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