Impact of 3% Molybdenum(Mo) nanoparticles on the interfacial and shear properties of lead-free Sn58Bi/Cu solder joint.

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Abstract. The research investigates the impact of 3 % molybdenum (Mo) nanoparticles on the interfacial properties and shear stress of the leadfree Sn58Bi (SB) solder joint. The research aims to provide a resemblance between the interfacial and shear properties with the additions of Mo nanoparticles. The interfacial between Mo added to the solder joint comprises of the common intermetallic (IMC) layer of Cu₆Sn₅ and additional IMCs of MoSn₂ that acted as further strengthening mechanism for the joint. Therefore, the shear strength of Mo reinforced solder joint was 32% higher compared to the pristine solder. The introduction of Mo into the SB solder resulted in an advantageous outcome.

1. Introduction

Inoculations of nanoparticles into the Sn-based solder alloys are predicted to provide better interconnection between the components and the printed circuit board (PCB) [1, 2, 3]. Nanoparticles like argentum (Ag) [4], zirconium oxide(ZrO₂) [5], cobalt (Co) [6], molybdenum (Mo) [7], aluminium oxide Al₂O₃ [8] and titanium dioxide (TiO₂) [9] are among the common nanoparticles added to the solder alloys. High melting temperature solders mainly the SnAgCu and SnAg solder system are vastly investigated in terms of its properties, and further studied by adding nanoparticles to the solders. Inclusion of nanoparticles did not affect the melting temperature because the atomic configuration of the elements in the solder alloy is not disturbed [10, 11]. This is important to preserve low temperature soldering. Improving the mechanical properties of low temperature solder alloys such as the SnBi solders will be useful for low temperature soldering. The study conducted by [12] shows an increase in the shear strength by 14.9 % upon additions of 0.5 % TiO₂ compared to that of the non-reinforced Sn1.0Ag0.5Cu. In another work, the overall IMC layer thicknesses of the Sn3.8Ag0.7Cu solder joint was thinner after adding Mo nanoparticles. The relationship between the IMC layer and shear properties werecorrelated [13]. The Cu₆Sn₅ and Cu₇Sn IMC layers were present at the interfacial region of the titanium carbide (TiC) added SnAgCu solder joint. However, the growth rate of the layers was lower [14]. Thicknesses of IMC layers ranging between 1-5µm known to enhance the solder joint’ reliablility. Few studies have concluded the inability of nanoparticles to react with Sn and Cu and its presence as discrete particles obstructs the formation of thick IMC layers [14, 15, 16]. Aided
with the presence of the nanoparticles at the interfacial layer, the effects of maintaining a thinner IMC layer are more certain [17, 18].

As reported by many studies, minimal amount of the weight percentages of nanoparticles additions improves the properties of a solder alloy, while higher weight percentages of additions shows deterioration in the properties [19, 20]. A recent study on the SnBi solder alloy reinforced with 0.25 wt. % Mo nanoparticles showed improvement in the shear and tensile strength of the solder joint [21]. The presence of Mo nanoparticles as the load-bearing effect was noted to be the factor for the increment.[22] added 2 wt. % Al₂O₃ into the Sn58Bi solder and witnessed a hike of 6.7 % to the hardness value. However, up to now, not many comparisons have been used with different types of nanoparticles, especially involving the additions to low temperature solder alloys. Plenty of work have been done on high melting solders with minimal attention given to the low melting solders [23,24]. Nevertheless, low melting solders promotes soldering at much lower temperature and can provide protection to other electronic parts [3]. Studies involving nanoparticles addition to the SnBi solder alloy are limited. This study focuses on the relation between the interfacial properties and shear strength of a low melting (139°C) SnBi solder added with 3% Mo nanoparticles.

![Figure 1. Phase diagram of Sn-Bi alloy [25].](image1)

2. Materials and experimental procedure
The Sn (Alfa Aesar-99.9%) and Bi (Alfa Aesar-99.9%) were weighed to the eutectic percentage as in figure 1, where the total weight of the Sn was 8.4 g and 11.6 g for the Bi respectively. These elements were mixed and melted at 600°C in a heat treatment furnace for 1 hour. The solder alloy was then let to solidify in the furnace. The Mo (Alfa Aesar-99.9%) nanoparticles were weighed according to 3 % from the total 20 g of the Sn58Bi. The high magnification image of Mo nanoparticles under scanning electron microscope (SEM) is shown in figure 2.

![Figure 2. Mo nanoparticles at × 50 000 magnification.](image2)
The average size of the particles was measured to be 42 nm. The Mo nanoparticles were then added to the Sn58Bi solder alloy to the mixture. The Mo added solder is labelled as SB + 1 % Mo while the non-reinforced is termed as SB solder alloy onwards in this paper. Re-melting using the hot plate at 350°C for 15 minutes with stirring was done to enable the nanoparticles to disperse well on the solder. This process allows a proper dispersion of Mo nanoparticles. After solidifying, the solders were cut into 50 mm × 10 mm billets. The Cu substrates were cut into 40 mm × 5 mm × 10 mm following the ASTMD1002 standard to be used for the shear test. Soldering of the SB and SB + 3 % Mo solder billets on to the Cu substrates was done at 230°C for 1 minute. The single shear lap test method was used to perform the shear test on the solder joints.

\[40 \text{ mm} \quad \text{10 mm}\]

\[\text{Soldered area/joint}\]

\[\text{Grip area = 25 mm}\]

\[\text{Shear direction}\]

**Figure 3.** (a) Single shear lap specimen before soldering, (b) arrangement of samples prior soldering, (c) shear lap specimen after soldering (d) shear lap specimen cleaning with ultrasonic machine, (e) shear lap specimen prior testing and (f) shear test using universal tensile machine.
The specimens were then cleaned using ethanol and water. The cross sections of the solder joints were reviewed using the SEM (S3400N HITACHI) machine equipped with energy dispersive x-ray (EDX) which is used to detect and analyse the element at the interface.

Universal tensile machine (Instron 5582Q4970) is used to perform the shear test and the shearing of the joint was done with a crosshead speed of 1.3mm/min. The shear stress was calculated and the data were analysed in relation to the interfacial properties. The shear test setup and machines are shown in figure 3. The overall flow chart of the methodology is shown in figure 4.

![Figure 4. Flow chart of the methodology](image)

3. Results and discussion

3.1 Interfacial properties of SB/Cu and SB + 3 % Mo/Cu joints

On the solder side, Bi (white phase) and the Sn (dark phase) were observed in a lamellar manner for the SB solder. Meanwhile, well-dispersed Mo nanoparticles were detected via EDX together with the Sn and Bi in the SB + 3 % Mo solder.

The regions at the interfacial layer analysed by SEM and EDX are shown in figure 4. The reinforced solder joint shows also showed well dispersed Mo nanoparticles distribution. This was clarified with the EDX analyses. In a Sn-based solder joint, the common reaction between the Sn and the substrate forms a typical IMC layer of Cu$_6$Sn$_5$[26]. This layer would grow thicker with more presence of Sn and in many circumstances would react with Sn to produce another layer of Cu$_3$Sn$_7$[27]. These thicker Cu$_6$Sn$_5$ and Cu$_3$Sn contributes to the weakening of the joint [28].

Cross section images of Cu$_6$Sn$_5$ IMC layer in the bare SB/Cu joint are shown in figure 5 (a). In this system, Bi element plays the role of the non-reacting element and acts as a barrier for the diffusion between Sn and Cu. However, the Cu and Sn are more reactive with higher temperatures, the diffusion gets rapid and production of the Cu$_6$Sn$_5$ could not be restricted [16]. In fact, the presence of Cu$_6$Sn$_5$ layer was found in the SB/Cu joint below the Cu$_6$Sn$_5$ layer, with a thicker and non-uniformed layer. Such condition of the IMC layer would be the weakening point for a solder joint [17,28]. These are few of many problems that needs to be sorted. Interestingly, with the reinforcement of the Mo nanoparticles, the Cu$_6$Sn$_5$ IMC layer was seen to be flatter and uniform as shown in figures 5(b).

Nevertheless, the presence of Mo nanoparticles allowed the Cu$_6$Sn$_5$ to form stably and blocked the formation of the Cu$_3$Sn IMC layer. Other IMC’s, such as MoSn$_2$ and Cu$_{10}$Sn$_3$, were also produced upon
further XRD analyses. The Mo nanoparticles presence was not visible from the SEM imaging but the EDX and XRD analyses confirmed the existence of the nanoparticles.

The IMC layer thicknesses of the SB/Cu and SB + 3 % Mo/Cu measures 1.2682 µm and 0.8739 µm, respectively, as shown in figure 6. The reinforced solder joint produced a thinner IMC layer that would be more reliable towards shearing. The thickness measurement of less than 1 µm classifies this as a thin layer [29]. Additionally, with existence of Mo$_2$Sn IMC, growth of the Cu$_3$Sn layer is reduced as Mo reacted with Sn and blocked the diffusion between Sn and Cu. The production of a thin IMC layer for the reinforced solder joint is attributed due to the blocking of the vast diffusion between Sn and Cu by the Mo nanoparticles that were found to be presented at the top side of the IMC layer. The Mo nanoparticles were not visible from the SEM image due to their nano-scaled size but with the EDX and XRD analyses, Mo nanoparticles was detected there. So, with these analyses, an illustration based on the real SEM image of the blocking process is shown in figure 7.

![SEM image and EDX of (a) SB/Cu and (b) SB + 3 % Mo/Cu solder joints.](image)

| Element | Wt% | At% |
|---------|-----|-----|
| Cu      | 63.00 | 77.70 |
| Bi      | 07.45 | 02.79 |
| Sn      | 29.54 | 19.51 |
| Cu      | 44.25 | 64.21 |
| Bi      | 22.41 | 09.89 |
| Sn      | 33.34 | 25.90 |
| Cu      | 02.02 | 05.98 |
| Bi      | 89.25 | 80.21 |
| Sn      | 08.73 | 13.81 |
| Mo      | 03.63 | 04.90 |
| Bi      | 54.08 | 33.54 |
| Sn      | 26.08 | 28.48 |
| Cu      | 16.21 | 33.07 |
| Mo      | 03.56 | 03.88 |
| Bi      | 22.53 | 11.28 |
| Sn      | 48.15 | 42.44 |
| Cu      | 25.76 | 42.41 |
| Mo      | 03.42 | 03.68 |
| Bi      | 31.58 | 15.58 |
| Sn      | 32.83 | 28.53 |
| Cu      | 32.17 | 52.21 |

**Figure 5.** SEM image and EDX of (a) SB/Cu and (b) SB + 3 % Mo/Cu solder joints.
3.2 Shear properties of SB/Cu and SB + 3 % Mo/Cu joints

The single shear lap joint for the SB/Cu and SB + 3 % Mo/Cu was subjected to the shear test with the average maximum load and average maximum shear stress taken as the shear properties to be evaluated. The results for the SB/Cu and SB + 3 % Mo/Cu are shown in figures 8 (a) and (b). The average maximum load and average maximum shear stress of the SB + 3 % Mo/Cu joint were higher by 34 % than the non-reinforced solder joint. The increment is linked to the presence of the Mo nanoparticles, IMC layer and IMC compounds present at the interfacial layer as discussed in section 3.1.

As discrete and evenly dispersed particles, the Mo nanoparticles presented as a second phase strengthening mechanism at the solder joint. This simply means that the particles will be an added strengthening factor upon shearing. Hence, the shearing will not occur with ease and the resistance toward deformation increases, resulting in higher shear stress. These particles are presented at the interfacial due to the high energy area at the region that attracts the active nanoparticles [30, 31]. This resistance from shearing is not found for the SB/Cu solder joint. Furthermore, Mo being hard unbreakable particles, the shear load will be absorbed by these particles that increase the shear stress to break the joint. This strengthening effect is termed as a load-bearing effect [24,32].

Presence of the Mo$_2$Sn IMCs along the interfacial at the solder joint acts as precipitation strengthening to the solder joint. Precipitation strengthening occurs when particles obstruct the dislocation of motion upon shearing [33]. The existence of more Mo$_2$Sn IMC at the interfacial layer
creates more dislocation loops, which then increases the dislocation density. Hence, the shear stress for Mo reinforced solder joint increases as a result of the high dislocation densities. Contrariwise, the presence of Bi alone as the precipitation strengthening produced a lesser strengthening effect for the bare SB/Cu solder joints. Another reason for the increase in the average maximum load and average maximum shear stress is the thin IMC layer of Mo reinforced solder joints. Thinner IMC layers are less prone to crack initiation that resembles a stronger joint. This hypothesis is supported by many others too [24, 25, 32].

![Figure 8.](attachment:image.png)

**Figure 8.** (a) Average maximum load and (b) Average maximum stress of SB/Cu and SB + 3 % Mo/Cu solder joints.

### 4. Conclusion

The impact of Mo nanoparticles on the SB solder alloy was studied in this work by investigating the interfacial and shear properties. The common Cu₆Sn₅ IMC layer was observed at both solder joints while the Cu₃Sn layer was only observed for the unreinforced solder joints. The presence of Mo as discrete particles together with the Mo₂Sn IMCs was found throughout the SB + 3 % Mo/Cu solder joints. Precipitation strengthening (Mo₂Sn), thin IMC layer and load bearing effect (Mo nanoparticles) influenced the increase in the shear properties of Mo reinforced solder joint. Reduction by 31 % in the IMC layer thickness observed upon addition of Mo nanoparticle. Increase in average maximum shear load and average maximum shear stress by 34 % was found for the reinforced solder joints. Certainly, the data of the shear properties correlated to the findings of the interfacial properties, showing the relevancy of this research with the hypothesis from other studies. These two properties are key in judging the credibility of a solder alloy in order to be implemented as the medium of interconnection between electronic components and printed circuit board of an electronic component at lower soldering temperature. Based on the primary results from this work, the SB + 3 % Mo had the potentiality.

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