Influence of Nano-3%Al₂O₃ on the Properties of Low Temperature Sn-58Bi (SB) Lead-free Solder Alloy

S Amares¹, ⁴, M N Ervina Efzan², Rajkumar Durairaj³ and Aliasghar Niakan¹

¹Faculty of Engineering and Built Environment, SEGi University, No. 9, Jalan Teknologi, Taman Sains Selangor, Kota Damansara PJU 5, 47810 Petaling Jaya, Selangor, Malaysia.
²Faculty of Engineering and Technology, Multimedia University, 75450 Ayer Keroh, Melaka Malaysia.
³Lee Kong Chian Faculty of Engineering and Science, Universiti Tunku Abdul Rahman, Jalan Sungai Long, Bandar Sungai Long, 43000 Kajang, Selangor, Malaysia.

amaressinghgill@segi.edu.my

Abstract. This work studies the melting temperature, wettability, metallurgical and hardness properties of the Sn-58Bi (SB) lead-free solder alloy incorporated with nano-3%Al₂O₃. The melting temperature was observed at 143.44 °C upon the additions of the nano-3%Al₂O₃ with a low contact angle of 20.4°. A well-distributed microstructure with narrower lamellar structure and finer intermetallic compounds and Sn grains was detected for the nano-3%Al₂O₃ added SB solder alloy. Hardness evaluation based on the Vickers hardness value was as high as 17.1Hv. Overall, the Sn-58Bi + 3% Al₂O₃ solder alloy appears to harvest beneficial results for these properties and can be used as potential replacement in the current electronic packaging industry.

1. Introduction

Ultimately, efficiency of a solder alloy depends on the alloying process and examples such as Sn-Pb, Sn-Bi and Sn-Ag-Cu are a mixture of one or more elements producing a solder alloy. Alloying seems to boost the performance of a solder alloy by enhancing its property such as lowering the melting temperature (e.g. Sn-Pb, Sn-Bi), producing high hardness (e.g. Sn-Zn-Bi) and better wetting for better joint property [1]. Among many solder alloys, the Sn-Bi (SB) solder alloys are pointed out to be the potential candidate to be used in the electronic packaging industry. Studies by [2] and [3] agrees to this point. However, the SB solder alloys has drawback such as low mechanical properties and these properties are key to ensure the functional integrity of the electrical component [4]. Therefore, introductions of nanoparticle appears to overcome the concern [5]. Parallel to that, the melting, mechanical and metallurgical properties of the low melting temperature Sn-58Bi (SB) added with 3% Al₂O₃ nanoparticles solder alloy were studied in this research. The results were analysed and further discussed to provide information in this area of studies.
2. Experimental Setup
The Sn-58Bi (SB) + 3% Al₂O₃ solder alloy was prepared from 8.4g of tin (99.9%, Alfa Aesar), 11.6g of bismuth (99.9%, Alfa Aesar) and 3% of Al₂O₃ nanoparticles which then were mechanically mixed by melting in a furnace at 600°C for 1 hour to ensure a homogenous mixture. To enable a proper mixing of the nanoparticles, the solder alloy was re-melted using a hot plate at 300°C. Figure 1 confirms that the mechanical mixing method effectively incorporated the Al₂O₃ nanoparticles due to the presence of the aluminium (Al) and oxygen (O) as labelled. The Sn-58Bi (SB) + 3%Al₂O₃ solder alloy were then compressed into billets for the melting and hardness test. Prior to the test, the billets were polished and etched in Nital for 60 seconds and observed under the Optical Microscope for microstructural study. The wettability test was conducted by soldering the Sn-58Bi + 3% Al₂O₃ solder alloy on to the Copper (Cu) substrate and the contact angle was measured using the VIS Pro software. Melting temperature was studied by using the Differential Scanning Calorimetry (DSC) test. Hardness test meanwhile was conducted based on Vickers hardness with load of 1kN applied to the Sn-58Bi + 3% Al₂O₃ solder alloy.

Figure 1. Elemental analysis of 3% Al₂O₃ nanoparticles in SB solder alloy.

3. Melting Temperature
The DSC graphs for the Sn-58Bi + 3% Al₂O₃ solder alloy shows a sharp endothermic peak (figure 2) with the start of melting (solidus temperature, Tₛ) at 139.43°C, peak temperature which is the melting temperature, Tₘ at 143.44°C, and the liquidus temperature, Tₙ at 147.29°C indication of the point solder being fully melted. Comparing the bare Sn-Bi solder alloy (Tₘ=138°C) [6], a slight increment of 3% in the melting temperature was observed. Apparently, the Al₂O₃ nanoparticles retains its solubility limit in the molten solder alloy with no diffusion of the Al₂O₃ nanoparticles that could affect the melting temperature or in other words, the Al₂O₃ nanoparticles acts as discrete particles [24]. Hence, the slight increase in the melting temperature occurs due to minor local dissolution of the Al₂O₃ that has high melting temperature of 2072°C [7]. Similar observation noted by [8] upon adding zirconia, ZrO₂ as the ZrO₂ elevates the melting temperature of Sn-3.0Ag-0.5Cu solder system. Another reason is that the Al₂O₃ nanoparticles tends to gather at the surface of the molten solder alloy due to its high energy [9] and this increases the energy of the solder to melt and consequently making the melting temperature to increase [10]. Yet, such increase as detected is not a major concern as the increment is minimal and the melting range still falls under the low temperature solder alloys (< 150°C) [11]. In fact, the Sn-58Bi + 3% Al₂O₃ solder alloy has lower temperature compared to many other solders, Sn-Pb (Tₘ=183°C) [12], Sn-0.7Cu (Tₘ=227°C) [13], Sn-Ag-Cu (Tₘ=217°C) [14] and other solder alloys.

4. Wettability
The wettability is a crucial aspect that displays the integrity of the solder to the substrate and is studied based on the contact angle between the solder and substrate [15]. Lower contact angles are very much desired because it is known to avoid crack propagations [16]. The SB + 3 % of Al₂O₃ solder alloy was
soldered at temperature of 250°C, the soldering temperature in the electronic industry [17] and the contact angle was measured to be 20.4°, table 1. Compared to the traditional Sn-Pb solder alloy producing contact angle of 8° [18], the SB + 3% of Al2O3 solder alloy has 40% higher contact angle.

![DSC curve of SB + 3% Al2O3](image.png)

**Figure 2.** DSC curve of SB + 3% Al2O3

The presence Al2O3 nanoparticles will increase the melting temperature as pointed earlier [19] and disables a better spreading as a result in reduction in the fluidity for the solder alloy [7]. On top of that, the Al2O3 nanoparticles will increase the activation energy, leading to harder spreading of the molten SB solder alloy. The study of [20] noted similar reason. Additionally, typical characteristics of discrete nanoparticles are known to gather at the leading edge of the molten solder that then decreases the fluidity and increases the viscosity due to increase in surface tension [21]. Despite that, the SB + 3% Al2O3 solder alloy produces lower contact angle than most solder alloys, table 1. The contact angle of the SB + 3% Al2O3 solder alloy also falls within the desired range of contact angle (<30°) as verified by [22].

Table 1. Contact angle of solder alloys.

| Solder Alloy        | Average Contact Angle (°) | References |
|---------------------|---------------------------|------------|
| SB + 3%Al2O3        | 20.4                      | This Study |
| Sn-40Pb             | 8                         | [23]       |
| Sn–3.5Ag            | 38                        | [24]       |
| Sn–0.7Cu            | 35                        |            |
| Bi-40Sn-2In         | 31                        | [25]       |
| Sn-3.5Ag-0.7Cu      | 48                        | [26]       |

5. Microstructure Characteristics.
The additions of 3% Al2O3 nanoparticles in the SB solder alloy produces the microstructures as shown in figure 3. Result prevails there are light and dark phase identified as the bismuth precipitations and Sn-matrices respectively. The identification of the phases was similarly noted in the study of [27]. Upon additions of the nanoparticles, the grain sizes of the Sn-matrices were finely dispersed with the nearer gap.
between the alternating lamellar structures (black dotted region), figure 3. The existence of the Al$_2$O$_3$ nanoparticles will accumulate at the grain boundary of the solder and enables them to act as a site for nucleation for the primary Sn matrices and produce smaller and finer Sn matrices [28]. The theory of adsorption stated by [29] explains that the plane with the maximum surface tension grows fastest with an increasing adsorption element, the Al$_2$O$_3$ nanoparticles in this case for this study. However, with accommodation of many Al$_2$O$_3$ nanoparticles, the surface energy will be reduced together with the growth velocity [8], ensuring in finer microstructure as shown figure 3. The production of finer grain is also due to the heterogeneous nucleation site and impeded phase boundary due to the presence of the Al$_2$O$_3$ nanoparticles, an explanation likewise in the study of [15].

Figure 3. Microstructures of SB + 3% Al$_2$O$_3$ solder alloy, a) 50× and b) 100× magnification.

6. Hardness
The Vickers hardness for the SB + 3% of Al$_2$O$_3$ solder alloy was taken an average of 17.1Hv was noted based on five different indentations. Concerning the hardness, it is closely related to the well-defined microstructure and the presence of finer grains together with nanoparticles contributing to resisting deformations [30]. In this study, the reason behind the increase in hardness of the SB + 3% of Al$_2$O$_3$ solder alloy are due to the microstructure and the existence of the Al$_2$O$_3$ nanoparticles as well. The Al$_2$O$_3$ nanoparticles additions modifies the microstructure of the SB solder alloy and produces finer and nearer alternated lamellar structure together with a small grain production presented in figure 3. Consequently, these characteristics help the solder alloy to resist deformation by providing more stress needed to disrupt the microstructure configurations. Comparable explanation was confirmed by [4]. Apart from that, the Al$_2$O$_3$ nanoparticles contributes to increase in hardness by standing-in as hard particles accommodating in between the grain boundaries [31]. As when a loads are applied, these nanoparticles at the grain boundaries will be barrier for the dislocation to occur and directly increase the load needed to overcome the nanoparticles [31].

7. Conclusion
The objective of this study is to produce and analysis the characteristics of the Sn-58Bi + 3% Al$_2$O$_3$ solder alloy based key properties required in a solder allot. The Sn-58Bi + 3% Al$_2$O$_3$ solder alloy seems to have a low melting temperature of 143.44°C which is relatively lower than the Sn-Pb and the Sn-Ag-Cu solder alloy. At the same time, a lower contact angle portrays a good wettability characteristics of the solder. The solder alloy also produces a high hardness of averaged 17.1Hv which suggests that it offers resistance for deformation due to the well-defined microstructure together with the presence of 3% Al$_2$O$_3$ nanoparticles. Not many studies are conducted in incorporating nanoparticles to boost the properties, which is the objective of this research. Moreover, based on the study and results achieved, the Sn-58Bi + 3% Al$_2$O$_3$
nanoparticles solder alloy could be an alternative for the problem faced in the electronic packaging industry.

8. References
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