Effect of Zinc Additions on Sn-0.7Cu-0.05Ni Lead-Free Solder Alloy

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Abstract. This study focuses on the effect of zinc additions on Sn-0.7Cu-0.05Ni lead free solder alloy. Micro-alloying with additions of 0.5, 1.0 and 1.5 wt.% of zinc (Zn) was developed by using conventional casting method. Samples were analyzed using optical microscope (OM), scanning electron microscope (SEM), X-ray diffraction (XRD), differential scanning calorimetry (DSC) and vickers hardness testing. Analysis were carried out to investigate the microstructure, thickness of intermetallic compounds (IMCs), wettability, phase formation, thermal properties and hardness of Sn-0.7Cu-0.05Ni solder alloys with additions of different Zn percentage. From this study, it is found that different composition of Zn affected the physical and mechanical properties of Sn-0.7Cu-0.05Ni solder alloys. Results shows that increasing Zn could increase the wettability, reduce the melting point and slightly reduce the ultimate tensile strength of the solder alloy.

1. Introduction
In this digital-age era, solder plays an important role in electronic packaging industries. Most electronic devices uses solder as interconnects material connecting one component to another. As interconnects material, solder provides electrical and mechanical support to the electronic device. Solder alloy usually consist of two or more addition of microalloying where soldering process is a method used to join the component with a filler metal by melting two or more of metal below their melting point. Nowadays, lead free solders has been a major demand in the electronic industries due to the health and safety concern where lead solder has been banned.

Due to environmental and health concern, the consumption of lead is forbidden in electronic packaging industry [1, 2]. One of the most popular lead-free solder alloy used in wave soldering process is Sn-0.7Cu-0.05Ni. The excellent property of Sn-0.7Cu-0.05Ni solder alloy is it has good fluidity which may result in good uniformity to the solder thickness on copper substrate after wave soldering. It is also less erosive to printed circuit board (PCB) compared to Sn-Ag-Cu solder alloys [3]. However, Sn-0.7Cu-0.05Ni has limitation of high melting point and mechanical properties [4, 5].

Thus, a way in improving the alloy, additions of Zn will be carried out. It is predicted that additions of Zn in Sn-0.7Cu-0.05Ni will improve the microstructure, mechanical properties and wettability [6, 7]. Literatures indicates that additions of Zn may reduce the melting point of solders [6]. It is also good for improvement of wettability which enhance the ability of molten solder to spread over the substrate (copper) [6]. In addition, Zn is considered cheap compared to other microalloying elements.

Different compositions of Zn may also result in different effects to intermetallic compounds (IMCs) phases, thermal properties and mechanical properties. In this study, different wt. % of Zn
additions to Sn-0.7Cu-0.05Ni will be investigated. The microstructure, thermal and mechanical properties of the Zn microalloyed solder will be discussed.

2. Experimental Procedure
Solder alloy of Sn-0.7Cu-0.05Ni was used as a base material. The solder alloy samples were fabricated with additions of different composition (wt. %) of Zn by using conventional casting technique. The solder alloys were mixed with three different compositions (0.5, 1.0 and 1.5 wt. % of Zn). Base solder alloys were firstly heated above their melting point and maintained for one hour. Then, the temperature was increased to superheat temperature at 600 °C for Zn additions. Every ten minutes of constant temperature for 30 minutes, the mixing material was stirred for homogeneity and solidified to room temperature.

For microstructural analysis, samples were divided into (i) bulk sample and (ii) sample soldered on substrate microstructure analysis. For bulk sample microstructure analysis, cross-sections were done after casting. While for sample soldered on substrate microstructure analysis, cross-sections were done after solder alloy samples were solder reflowed on a Cu substrate in a F4N reflow oven. Some activated rosin flux was applied during reflow soldering to act as a cleaning agent to remove and prevent the formation of oxides. All samples were mounted with epoxy resin, grinded and polished for microstructure observations. The microstructure observations were carried out by optical microscopy (OM) and scanning electron microscope (SEM). In this microstructure analysis, intermetallic compound thickness and wettability of solder alloys (as shown in Figure 1) were measured.

![Figure 1](image1.png)

**Figure 1.** Wettability measurement by measuring the contact angle of the solder alloy soldered on Cu substrate.

For thermal analysis samples, differential scanning calorimeter (DSC) was used in investigating the thermal properties of the solder during soldering. Samples were in solder balls shape (600 µm diameter) and sample experiment setup were prepared as in figure 2. Samples were heated from room temperature to 250°C at a heating and cooling rate of 10 °C/min.

![Figure 2](image2.png)

**Figure 2.** Sample preparation for differential scanning calorimeter (DSC) experiments.

For mechanical and phase analysis, analysis was conducted on bulk samples after casting. Vickers hardness indenter was used to measure the hardness of sample by using an indentation load of 1kgf at 10 s dwell time and 15 indentation for each sample was measured. For phase identification analysis, x-ray diffraction (XRD) was conducted with 0.1° step size at 25°-80° range.
3. Results and Discussion

3.1. Bulk Microstructural Analysis

Figure 3 shows the optical micrograph of Sn-0.7Cu-0.05Ni solder alloy that containing 0, 0.5, 1.0 and 1.5 wt. % addition of Zn. One of the important solder material properties depends on their microstructure and based on studied by G. Zeng et al. [8], grain structure of the solidified alloy is depending on the solder composition.

![Figure 3](image)

Figure 3. Optical micrograph of Sn-0.7Cu-0.05Ni solder alloy (a) Pure, (b) containing 0.5 wt.% Zn, (c) containing 1.0 wt.% Zn and (d) containing 1.5 wt.% Zn.

The typical microstructure Sn-0.7Cu-0.05Ni solder alloy that forms usually consist of primary β-Sn dendrites that surrounded by eutectic which is combination of β-Sn and intermetallic Cu$_6$Sn$_5$ [9]. W.Ng et al. [10] stated that Zn addition by itself did not make to a eutectic microstructure while Ni addition make the way it closer to eutectic microstructure. With the combination of Ni and Zn, its can refinement to near completely eutectic microstructure of the solder alloys [10-12]. As seen in Figure 3 (a), the pure Sn-0.7Cu-0.05Ni solder alloy consists a large number of primary β-Sn cells with small intermetallic compound Cu$_6$Sn$_5$. It also has uniform eutectic structure phase microstructure. On the other hand with 0.5 wt.% addition of Zn as shown in Figure 3 (b), the microstructure of β-Sn was refined and has smaller number of intermetallic compound Cu$_6$Sn$_5$.

Interestingly, with a small addition of the Zn make the β-Sn cell become more refined compared to pure Sn-0.7Cu-0.05Ni solder alloy. The crystals forms can be considered to improve the reliability of solder joint. By the addition of Zn into the solder alloys, the primary β-Sn dendrites are still present in the microstructure but the eutectic been modified with the incorporation of Zn into the Cu$_6$Sn$_5$ crystal [10]. With the addition of 1.0 wt.% Zn into the Sn-0.7Cu-0.05Ni solder alloy as shown in Figure 3 (c), the microstructure become non-uniform because consist of very large β-Sn cells with larger number of intermetallic compound Cu$_6$Sn$_5$. The microstructure phase by addition of 1.5 wt. % of Zn also make a large β-Sn cell and smaller number of intermetallic compound Cu$_6$Sn$_5$ with primary intermetallic. This
is because of the higher amount of Zn involves did not completely homogeneously dissolved in Sn-0.7Cu-0.05Ni solder alloy.

3.2. Interfacial Intermetallic Compounds (IMCs)

Figure 4 (a) show the average thickness of (Cu,Ni)6Sn5 intermetallic compounds (IMCs) are 10.7 µm higher than others. The addition of 0.5 wt% Zn in the solder system make the average thickness become 7.6 µm where was inadequate to suppress the intermetallic compounds (IMCs) formation. However, when 1.0 and 1.5 wt% Zn were added into the solder alloys, the graph show an increasing to IMC layer average thickness of the (Cu,Ni)6Sn5 intermetallic growth. Both of the composition only have smaller different average thickness value of layer which is 8.6 µm and 8.9 µm respectively. This is shows that with only small addition of the Zn was effective to suppress the IMCs thickness of the solder alloys.

In previous reviewed, G.Zeng et al. [8] stated that the performance of the interfacial IMCs layers can be improve by added minor alloying into solder. Based on I.Yahya et al. [13], Cu6Sn5 intermetallic is the first phase that formed on the copper substrate for all solder system with scallop structure. There has another formation of thin IMC layer that located between Cu6Sn5 intermetallic compounds (IMCs) and copper substrate. The Cu6Sn5 in the intermetallic is an unstable layer then it make Cu3Sn intermetallic compounds (IMCs) to form [13]. Figure 4 shows SEM images for as-soldered solders. Figure 4 (a) show the pure Sn-0.7Cu-0.05Ni solder alloy only contain (Cu,Ni)6Sn5 intermetallic compounds without any addition of Zn and have a balance scallop structure than others. In J. Yoon et al. [14] investigation, the form of (Cu,Ni)6Sn5 layer are form with of 4.3 at.% Ni [14].

Q.S.Zhu et al [15] observed that small addition of Zn in lead-free solders can depress the growth of intermetallic compounds (IMCs) which make the growth of Cu3Sn and the formation of Kirkendall voids can be restrain [13, 15]. For figure 4 (b), (c) and (d), the un-balance scallop structure forms and the addition of Zn make the Cu3Sn become thinner. However, the different composition of Zn in the Sn-0.7Cu-0.05Ni solder alloy make (Cu,Ni)6Sn5 intermetallic compounds (IMCs) layer have different thickness. It has been confirmed by H.Wang et al. [16] that Zn would alloy interfacial Cu6Sn5 during interfacial reaction between the solder and substrate. In addition, the stabilizing effect by addition of Ni and Zn also can minimize the thermal expansion mismatch between the interfacial Cu6Sn5 and substrate [16].
3.3. Wettability

Wettability of solder alloys are depends on surface properties and also solder alloys proportion [17]. By minimize the value of the contact angle, the wettability can be optimized that corresponds to lower surface-interfacial energy. Based on the bar graph in figure 5, the contact angle for pure Sn-0.7Cu-0.05Ni solder alloy sample is 23.61° which is higher than 0.5 wt.% Zn but lower than 1.0 and 1.5 wt% addition of Zn. Y.Wang et al [18] explain that the addition of Ni into a solder alloys can improve the reliability and wetting properties of many Sn based solder alloys are well known [18, 19]. The addition of 0.5 wt% Zn in the solder system make the contact angle become 17.32° where much lower than others composition. J.Shen et al. [20] discovered that the addition of 0.01 and 0.03 wt.% Ni can decrease the wetting force and the wetting time of Sn-Cu solder cannot be effected [20]. This is show that the Ni and Zn have exactly same properties to lowered the wetting angle by addition of small amount of element.

Figure 4. SEM images of Sn-0.7Cu-0.05Ni solder alloy (a) Pure, (b) containing 0.5 wt.% Zn, (c) containing 1.0 wt.% Zn and (d) containing 1.5 wt.% Zn.
However, when 1.0 and 1.5 wt.% Zn was added into the solder alloys, the contact angle slightly increase into 26.78° and 28.48° respectively. L. Zang et al. [21] shared that improvement of the wettability on the Cu substrate with molten solder alloy are related with the formation of intermetallic [21]. By the formation of intermetallic that have been investigate for the addition of 1.0 and 1.5 wt.% of Zn, the higher thickness have been occurred and formed a higher wetting angle. In addition, alloying of Zn element into the Sn-based solder is concerned because Zn is very active and may deteriorate wetting performance of lead-free solder at molten state [16].

3.4. Phases Analysis

Figure 6 revealed the additional of another element in Sn-0.7Cu-0.05Ni solder alloys. For figure 6(a), only β-Sn and Cu₆Sn₅ phases are detected by XRD and there are no new addition of another element in the solder system. The crystal system occurred in this Sn-07Cu-0.05Ni solder alloy are tetragonal (Sn) and hexagonal (Cu₆Sn₅).

Figure 6. Peak of Sn-0.7Cu-0.05Ni solder alloys (a) Pure, (b) containing 0.5 wt.% Zn, (c) containing 1.0 wt.% Zn and (d) containing 1.5 wt.% Zn.

Figure 6 (b), (c) and (d) show that there is new peak are involved which is known as NiZn when different amount of Zn is added. The NiZn presence in the Sn-0.7Cu-0.05Ni solder alloy in cubic
shape. According to G.Zeng et al.[11], the addition of Ni and Zn can effect over the polymorphic phase transformation of powdered Cu₆Sn₅ [11]. However, with the addition of different amount of Zn, the intensity β-Sn and Cu₆Sn₅ phase change are not fixed. It also believed that the addition of Zn can change the phase in solder system.

3.5. Phases Analysis

Melting temperature is a critical characterization for solder alloys because it determines the operating system temperature. Figure 7 shows the melting point of the Sn-0.7Cu-0.05Ni solder alloy with the addition of 0.5, 1.0 and 1.5 watts. % Zn. The Sn-0.7Cu-0.05Ni solder alloy with the addition of 0.5 wt.% have highest melting temperature with 230.93°C while the addition of 1.0 wt.% Zn have the lowest melting temperature which is 227.63 °C. This process is known as endothermic process because the process towards to heating process. T.T.Bao et al. [22] found interesting behavior in the phase diagram by using simple regular model which is claims when the positive interaction of solid and negative liquid occur, all the solidus and liquidous with the eutectic point move at the lower melting point component [22]. In addition, Y.Liu et al. [23] explain that the higher addition of Bi in the solder alloys could increase the melting range and can lead to the initiation of solidification crack of the solder joints [23].

![Figure 7](image-url)

**Figure 7.** Melting point of Sn-0.7Cu-0.05Ni solder alloy with addition of 0.5, 1.0 and 1.5 wt. % Zn.

DSC result obtained the undercooling temperature has shown in the figure 8. Undercooling range temperature refer to solder alloys transfer from liquid to solid. The undercooling value can be calculated by minus the onset heating point with onset cooling point. Bar graph shows the higher temperature is on pure Sn-0.7Cu-0.05Ni solder alloy with 63.84°C compare to addition of 0.5 wt. % of Zn which have very low undercooling temperature. This is show that the optimum value for undercooling temperature is 0.5 wt. % addition of Zn because have low temperature different to change from liquid to solid.

For thermal analysis, it can be concluded that the low melting point achieved when 1.5 wt. % Zn are added. However, there are no slightly different value of melting point temperature for all samples. The melting point temperature are still around with eutectic or near-eutectic composition. For undercooling temperature, it shows that the addition of 0.5 wt. % of Zn has a short time to transfer from liquid to solid.
3.6. Mechanical Properties

Figure 9 shows the average of vickers hardness value for pure Sn-0.7Cu-0.05Ni solder alloy sample are 9.82 HV which is lower than addition of 0.5, 1.0 and 1.5 wt. % Zn. The addition of 0.5 wt. % Zn in the solder system make the higher value of hardness become 12.38 Hv. However, when 1.0 and 1.5 wt. % Zn was added into the solder alloys, the hardness slightly decreasing from 10.48 Hv to 9.87 Hv respectively. In fact, the motion of dislocation and growth and configuration of grains effected the micro-hardness of a solder alloys [24]. H.Wang et al. [17] concluded that the addition of Zn would induce the formation of CuZn and Cu6Sn5 which resulting to prevent plastic deformation and increase the hardness of Cu6Sn5 [17].

Figure 10 shows the average ultimate tensile strength for pure Sn-0.7Cu-0.05Ni sample which is lower than addition of 0.5, 1.0 and 1.5 wt. % Zn. The addition of 0.5 wt. % Zn in the solder system make the higher value which is become 97.53 MPa. However, when 1.0 and 1.5 wt. % Zn was added into the solder alloys, the value of ultimate tensile strength slightly decrease into 92.58 MPa and 91.6 MPa respectively. The micro-hardness results of all the solder alloys system showed an improvement for certain amount of Zn.

The microstructural observation reveals that the distribution of Zn element through the refining of microstructure for each sample which can be considered as the main reason for the improvement in micro-hardness values of Sn-0.7Cu-0.05Ni solder alloy. It was concluded that Sn-0.7Cu-0.05Ni solder alloy with 0.5 wt.% Zn had the highest value of mechanical value among the four samples. It has also...
been observed that the mechanical value decreases with the increasing in the percentage of Zn content. However, when 1.0 and 1.5 wt% Zn was added into the solder alloy, the value of hardness slightly increase. Both of the composition only have small different value in the mechanical value. Mohd Salleh et al. [25] reported that the mechanical properties are affected by the grain size of the solder which the finer grains of microstructure have higher mechanical values [25]. In other studies, W. Ng et al. [10] claims that the addition of Zn can increase the mechanical properties of solder but when the Zn addition is combined with Ni, it can refine the eutectic microstructure which give beneficial effect [10].

Figure 10. Average ultimate tensile strength of Sn-0.7Cu-0.05Ni solder alloy with addition of 0.5, 1.0 and 1.5 wt. % Zn.

4. Conclusion
The effect of Zn additions on Sn-0.7Cu-0.05Ni lead free solder alloy was examined through this study. The solder alloys were mixed with three different compositions (0.5, 1.0 and 1.5 wt.% of Zn) by using casting technique. The conclusions which can be drawn from this study are:

i. Large primary β-Sn dendrites with smaller number of the primary Cu₆Sn₅ were observed. Therefore, by additions of Zn, Cu₆Sn₅ could be refined and become smaller.

ii. By additions of Zn in Sn-0.7Cu-0.05Ni solder alloy, the thickness of interfacial (Cu, Ni)₆Sn₅ can be reduce.

iii. Mechanical properties increases with small wt.% of Zn content in Sn-0.7Cu-0.05Ni solder alloy.

iv. For thermal analysis, there are changes in the melting point and undercooling temperature of solder alloys after addition of 1.5 wt. % Zn.

v. Overall, Sn-0.7Cu-0.05Ni solder alloy with addition of 0.5 wt.% Zn were observed to be the most preferred composition compared to other Zn percentage.

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