Behavior of Sn$_{0.7}$Cu$_x$Zn lead free solder on physical properties and microstructure

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Abstract. The issues to substitute Tin-Lead Solders is concerning the health and environmental hazards that is caused by lead, and also legislative actions around the world regarding lead toxicity, which has prompted the research community to attempt to replace solder alloys for the traditional Sn-Pb alloys lead which has been used by industrial worker throughout history because it is easily extracted and refined at a relatively low energy cost and also has a range of useful properties. Traditional industry lead has been used in soldering materials for electronic applications because it has low melting point and a soft, malleable nature, when combined with tin at the eutectic composition which causes the alloy to flow easily in the liquid state and solidifies over a very small range of temperature. One of the potential candidate to replace tin-lead solder is Sn-Cu-Zn eutectic alloy as it has a lower melting temperature. Consequently, it is of interest to determine what reactions can occur in ternary systems derived from the Sn-Cu-Zn eutectic. One such system is Sn$_{0.7}$Cu$_x$Zn. The specimen was elaborated on physical properties. The chemical content was analyzed by using Shimadzu XRD and melting point was analyzed by using Differential Scanning Calorimeter (DSC). The results has shown that the highest addition of Zinc content (15%Zn) will decrease the melting temperaturer to 189°C compared to Sn-Pb at 183°C. Increasing the amount of Zn on Sn$_{0.7}$Cu$_x$Zn alloys will decrease Cu$_2$Sn intermetallic compound.

I. INTRODUCTION

Lead Free Solder has been developed in recent years to substitute lead-tin soldering alloys widely used in Microelectronics. The substitution of Lead-Tin solder has been triggered rapidly by European Union’s (EU) proposal to reduce waste from electrical and electronic equipment (WEEE) and RoHS regulation$^{1,2,3,4}$. The research was elaborated to substitute Lead as a toxic material$^{5,6,7}$. Several candidates has been identified as a possible substitute for Lead-Tin as it requires a close melting point value as Lead-Tin which is at 183°C $^{1,8,9,10}$. These candidates of Lead Free Solder have a typical melting temperature between 198°C and 227°C $^{11,12,13,14}$. These candidates had been selected to obtain Lead Free Solder which has similar behavior to Lead-Tin Solder $^{6,7,12,14}$ A System containing Zn, Cu, Ag, Bi, In and other elements have been the subjects of experimental investigation, but many of them has not yet been explored$^{15,16,17}$.

There are some characteristics which are considere for lead-free solders as substitute of tin lead solders used in electronic soldering, which are a lower melting temperature of solder, good wetting properties, adequate strength, good thermal conductivity, low cost and also the most important characteristic is its effects on the environment such as its toxicity $^{8,10,12}$. 

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The environmental effect is a major consideration to design Lead Free Solders for interconnects in electronic applications to replace Lead-Tin solders. Basically all the research which have been focused in the development of Lead Free Solders to replace eutectic or near eutectic Lead-Tin solders that melts at 183°C, have not resulted in a development of a satisfactory solder substitute\cite{18,19,20}. Currently, Lead Free Solders such as Sn-Ag, Sn-Ag-Cu eutectic solders with the melting temperature of 221, 227 and 217 °C respectively are being used\cite{6,8,12}. One candidate which can very likely be used in the long term is Sn-Zn based solders which are found extensively in the applications of Lead Free Solders electronic components\cite{8,10}. Sn-Zn base solders are much less costly than SnAg-Cu solders and they melt at 189°C. Furthermore it is possible to design Zn –containing lead-free solders with melting or solidification characteristics similar to near eutectic Sn-Pb solders. This can help the existing manufacturing infrastructure in device fabrication to find suitable interconnect material for the chip to chip carrier application. One of the important mechanical behaviour of Sn-Zn is that it has a superior isothermal fatigue compared to Sn-Pb eutectic solder\cite{10,11}. This is another reason why Sn-Zn eutectic solder is of interest to the electronics industry. These Sn-Zn also has a lower melting point and improves wetting behaviours \cite{12,13,14}. In this research Lead Free Solder Sn-Cu-Zn was designed by melting Sn-0.7Cu with Zn. The present paper focuses on the structure and melting temperature of Sn-0.7Cu-xZn cold rolling alloy. This alloy is one of the important alternative alloys recommended to substitute Tin-lead solders. This recommendation is due to its close lower melting point compared to tin lead solders at 183°C eutectic alloy. Moreover Sn-0.7Cu-xZn alloy is advantageous from the economic point of view, because Zn is a low cost metal and is abundant in the world.

II. Method and Materials
The Sn0.7Cu alloy which has a purities value of 99.8% and Zn which has a variety percentage of weight were obtained from the industrial market and were weighted by a liquid metallurgy route. The alloys were casted then solidified in cast-iron in the form of 8 mm diameter x 2 mm thick. The casting was done in a graphite mould at a temperature of 600°C and thermally agitated to perform the homogenization. The resulting alloys were then cold rolling into long sheets of about 3 mm in width and 1 mm in thickness. The alloy samples are illustrated in Table 1. X-Ray diffraction analysis was performed on the flat surface of all alloys by using an X-ray diffractometer (Dx- 30, Shimadzu, Japan) of Cu-Kα radiation and Ni-filter in the range from 20° to 100° of 2θ value (λ = 0.154056 nm, 4.5kV and 35mA). The samples were made to weigh 2.500 mg in the nitrogen atmosphere with 30[ml/min] flow rate.

Melting temperature is a critical solder characteristic because it determines the maximum operating temperature of the system and the minimum processing temperature in which the components can survive. DSC analysis was carried out in order to investigate the fundamental thermal reactions on heating of the solder alloy. Fig. 3.2 shows the thermographs relation between heat flow (V) and temperature (°C)) of the used alloys.

Sn0.7CuZn solders were mechanically polished with 1 μm diamond paste. The etching solution contained 93% methanol, 5% nitric acid, and 2% hydrochloric acid. The microstructure of these solders were examined by Shimadzu optical microscope (OM). The Optical Microscope was utilized to analyse the spatial distribution of chemical species for identification of intermetallics SnZn and CuSn.
III. Results and Discussion

3.1. Structure of Sn$_{0.7}$Cu$_x$Zn Alloy Samples

Table 1. Chemical analysis of the Sn-Cu alloy Containing Zn

| Sample | Chem. Form | Zn  | Sn   | Code   |
|--------|------------|-----|------|--------|
| 1      | Sn-0.7Cu   | 11% | Balance | SnCuZn$_1$ |
| 2      | Sn-0.7Cu   | 12% | Balance | SnCuZn$_2$ |
| 3      | Sn-0.7Cu   | 14% | Balance | SnCuZn$_3$ |
| 4      | Sn-0.7Cu   | 15% | Balance | SnCuZn$_4$ |

Figure 3.1 a. XRD patterns of (a) SnCuZn$_1$, (b) SnCuZn$_2$, (c) CuZn$_3$ and (d) SnCuZn$_4$ alloys.
X-ray diffraction method was used to determine the phases of the four solder alloys by using D\textsubscript{x}-30, Shimadzu, Japan, see Fig.3.1 (a-d). The pattern in Fig.3.1(a-d) indicates the formation of both phases of Sn and Zn. However, Fig.3.1 (a-d) shows that Sn and Zn phases are the main constituents. From Fig. 1 (a-d), it is clear that Cu is absent which means a complete solubility of Cu in Sn matrix. The addition of wt. % Zn leads to the formation of the intermetallic compounds SnZn\textsubscript{2} and SnZn\textsubscript{3} respectively.

3.2 Melting Temperatures

![Figure 3.2 DSC pattern on variety Of Zn containing of lead-free solders.](image)

Fig 3.2 shows the melting temperatures of the investigated SnCuZn\textsubscript{1}, SnCuZn\textsubscript{2}, SnCuZn\textsubscript{3} and SnCuZn\textsubscript{4} alloys. With the addition %wt of Zn element, the melting temperature slightly decreased to 189°C as compared to 217 °C of SnCu eutectic alloy which will improve the soldering properties in electronic packaging. The amount of wt.% of Zn addition lowers the
melting temperature of the solder significantly. The melting temperature was decreased from 217°C of SnCu as compared to 15%Zn at 189°C for SnCuZn alloys respectively.

3.3 Microstructures

![Figure 3.3. Sample of SnCuZn1](image1)

![Figure 3.4. Sample of SnCuZn2](image2)

![Figure 3.5. Sample of SnCuZn3](image3)

![Figure 3.6. Sample of SnCuZn4](image4)

In this case, during the soldering operation, Cu is dissolved into liquid from the substrate, forming in the Sn$_{0.7}$CuXZn alloy system and thereby introducing the possibility of ternary phase reactions. The intermetallic Cu$_6$Sn$_5$ is important due to the large number of tin-lead and lead-free solder joints formed directly to copper. This intermetallic compound forms in an interfacial layer and can be found in the bulk microstructure of tin-lead solder joints where excessive time and temperature are involved during the soldering process. In addition, the Cu$_6$Sn$_5$ intermetallic is a primary feature in the microstructure of lead-free solder joints such as SAC 305 alloy (96.5Sn-3Ag-0.5Cu)\[20,21\].

The intermetallic Cu$_3$Sn is important as it forms an interfacial layer between the copper and Cu$_6$Sn$_5$ IMC layer in tin-lead and lead-free solder joints formed directly to copper. The combination of the Cu$_3$Sn & Cu$_6$Sn$_5$ layers seems to result in a very strong bond between the solder and the copper\[22,23,24,25\].

Based on the microstructures of lead-free solders as above the apparent increase of Zn in Sn$_{0.7}$CuXZn has a decreasing effect on the intermetallic compound of Cu$_3$Sn. It will decrease its Hardness number. Also with a solubility of Zn in solid SnCu about 15 wt% Zn will result in a eutectic temperature, 189°C. The spalling phenomenon has been reported to occur also when Sn-Zn solders are used on a copper substrate.

IV. Conclusion

In this paper, the increase of Zinc %wt to Sn$_{0.7}$CuXZn lead-free solder has proved to be an effective way to improve the microstructure and physical properties of Sn$_{0.7}$CuXZn. Melting temperature results shows an improvement with a higher amount of Zint in the solder Sn$_{0.7}$CuXZn, and optimal melting temperature was observed with the content of 15wt.% Zinc. The influence of Zinc content on Sn-Cu alloys lead-free solder at 15 wt % has showed a lowered melting temperature when compared to SAC led-free solder by approximately 28 °C. It appears that melting temperature of Sn$_{0.7}$CuXZn lead free solder is closer to SnPb eutectic.
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