Solidification Behaviour of Sn-40Pb Lead Solder and Sn-0.7Cu Lead-free Solder

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Abstract. Lead-free solder, especially Sn-0.7Cu has been evolving due to the restriction of the lead solder usage which is environmental and health unfriendly. However, most of the lead solder properties show a better result compared to the lead-free solder. To further improve the properties of lead-free solder, the solidification state of Sn-40Pb and Sn-0.7Cu, which is one of the important behaviour in thermal analysis that affects the solder properties and performance, was investigated and compared in this study by natural cooling curve method. The result showed that Sn-40Pb has two nucleation phase while Sn-0.7Cu has only one during the solidification. The primary lead-rich phase was first nucleated in Sn-40Pb following by the secondary tin-rich phase when cooling; while the phase of Cu₆Sn₅ was nucleated in Sn-0.7Cu. In addition, it is found that the undercooling of Sn-40Pb is lower than Sn-0.7Cu in the cooling curve.

1. Introduction
Soldering has been an very important technique in industries to connect a material to another for different applications. Sn-Pb is the most common used solder as a medium during soldering process in few decades ago as a result of the rapid growth and development of various applications especially in electronic fields [1]. However, Sn-Pb is considered as a toxic material due to its existing of lead compounds that is harmful to the environment and causing the health issue in society. The strict legislation has been established by WEEE and RoHS directives for prohibiting the usage of lead-based solders [2-4]. Therefore, the development of lead-free solders has been triggered and become a trend in order to replace the lead-based solders. Anyhow, the properties of Sn-Pb are better than lead-free solders in terms of costing, solderability, low melting point and so on [5].

Sn-Cu based lead-free solder alloy has been studied and applied in present different applications. However, for further improving the properties of this Sn-Cu based solder for competing with lead-based solders, many researches have been on going. One of the factor that contributes to the different properties of solders is the solidification state during the soldering process. Thus, understanding of the solidification behaviour of the solder is crucial for controlling the microstructural that affects the solder properties [6-8]. The effect of different composition of copper in Sn-Cu solder on undercooling was researched since undercooling is one of the solidification parameter that plays a main role for solder
joint performance [9]. El-Daly et al. has carried out the researches on the change of solidification microstructure, tensile properties, thermal and creep behaviour of Sn-Bi based solders by rotating magnetic field [6, 10]. Furthermore, Mehreen has also studied the effect of nickel additions to the reaction and phase formation in Sn-10Cu during the alloy solidification [11].

There are different methods that can be used for thermal analysis in order to study the solidification behaviour, for example differential scanning calorimetry (DSC) as a common used for solders. On the other hand, there is another fundamental, simple and low cost method, which is the cooling curve method, used for understanding the solidification [12]. In this experiment, natural cooling curve method was performed on Sn-40Pb and Sn-0.7Cu to study the solidification of both solder alloys. Sn-0.7Cu solder alloy was selected for analysis since it is one of the widely used solder and can be a control in the research for lead-free based solders. The cooling curve of Sn-0.7Cu was then compared with the cooling curve of Sn-40Pb to understand the solidification differences between these two solders which might help in the further properties improvement for lead-free solders.

2. Experimental Procedure

Cooling curve method with natural cooling without controlling the cooling rate was performed in this study. The temperature change during the experiment was measured and recorded by Hioki LR8431-20 Memory Hilogger with the software of Hioki Logger Utility Revision 18 by connecting to the K-type thermocouple. The tip of the K-type thermocouple was covered by the stainless-steel tube for protection from direct contacting to the solder molten. On the top of that, the ceramic crucible was coated with a thin layer of boron nitride as the container for the solder molten before the experiment to avoid the impurities.

The pure metal ingots of Sn-40Pb and Sn-0.7Cu were supplied by Hasrat Bestari Sdn. Bhd. and Nihon Superior Co. Ltd., Japan respectively. The mass of each Sn-40Pb and Sn-0.7Cu solder alloys was weighted for approximately 60g. The solder alloy was then melted in the graphite crucible at 400 °C by using electric resistance furnace. As the solder molten was poured into the coated ceramic crucible, the K-type thermocouple was set up at the height as shown in figure 1. After that, the opening of coated ceramic crucible was covered and closed by 2 fire bricks to prevent the direct heat loss to the environment. The monitoring of the temperature change during the solidification for Sn-40Pb and Sn-0.7Cu was then carried out by the Hioki logger.

![Figure 1. The schematic experiment set up of natural cooling curve method for thermal analysis](image-url)
3. Results and Discussions

The cooling curve can be explained as the equilibrium between the heat evolution in solder molten and the heat flux released from the solder molten until the solder is solidified. The beginning of the solidification is then can be identified accordingly to the latent heat released during the transformation of liquid phase to solid phase. Derivative of the cooling curve is calculated for better detection on the difference of the temperature shifting during the solder solidification [13]. The cooling curves and its first derivative (dT/dt) for Sn-40Pb and Sn-0.7Cu solder alloys are illustrated in figure 2. The curve section before point a1 and a from figure 2a and 2b in the respective Sn-40Pb and Sn-0.7Cu dT/dt curves are the thermal stabilisation of thermocouple corresponding to the cooling of the solder molten [14].

![Cooling curves](image)

**Figure 2.** Cooling curve (T) and its first derivative (dT/dt) for: a) Sn-40Pb and b) Sn-0.7Cu solder alloys

The fluid flow that applied into the garlic peeling machine to peel off the garlic skin is pure air. The density of air is approximate to 1.225 kg/m³ and also has a viscosity of 1.983 x 10⁻⁵ Pa.s. The diameter of the air inlet of the new design garlic peeling machine is 50 mm and has a diameter of outlet with 50 mm. The design of peeling chamber has a diameter of 220 mm with height of 300 mm. The information of this new design parameter is then used into the simulation of fluid flow. The fluid flow simulation is able to show that how the streamline of the fluid flow formed in the peeling chamber and also how the air blows the garlic skin out from the peeling chamber.

Figure 6a) shows that the streamline of the air flow is formed in the spiral shape. The air comes from the bottom inlet and then goes out from the top of outlet. This result of streamline proves that the air flow is able to blow the garlic skin follows up with the spiral air flow and goes out through outlet. Once the air goes in, the velocity in yellow region with 2.022 m/s is considered in medium velocity. The yellow region getting reduces to green region of 1.348 m/s at bottom. While the air flow getting go up to the top, the air flow continues to slow down with only 0.6739 m/s in the region of light blue. After that, the air meets the outlet and ready to flow out, it becomes faster in red region and the velocity reaches 2.696 m/s. Figure 6b) shows the result of contour of the air flow formed in the design model. The blue region means that there is no contour produced at the area without velocity, 0 m/s. The surrounding of the model and the center are not involved due to there has the brushing rod is rotated at the center region. Besides that, there has only a little of velocity in the region of light green at the corner with 1.269 m/s. Hence, the major area that involved in the contour which is the light blue region with velocity of 0.7929 m/s.
Figure 3. Phase diagram for: a) Sn-Pb lead solder [17], b) Zoom in Sn-Pb lead solder, c) Sn-Cu lead-free solder [18], d) Zoom in Sn-Cu lead-free solder [19]

On the other hand, there are another two characteristic temperatures can be obtained from the cooling curve (T) besides the nucleation temperature from dT/dt curve based on the Tamminen method [12]. These two temperatures are the minimum temperature before the recalescence, TM; and the maximum reaction temperature after the recalescence which is the growth temperature, TG [21]. By using the TM and TG from the cooling curve, the nucleation undercooling, $\Delta T$ can be defined as:

$$\Delta T = TG - TM$$  \hspace{1cm} (1)

Where the nucleation undercooling is the temperature difference between the growth temperature and the minimum temperature before the recalescence [20]. Table 1 displays the temperatures of TM and TG, following with the nucleation undercooling, $\Delta T$. The results reveal that the undercooling of Sn-40Pb is lower than Sn-0.7Cu solder alloys. It is very important to study the undercooling parameter during solidification since it affects the development and evolution of microstructure in the solder alloys causing a various of properties. Cho et al. has demonstrated that the undercooling behaviours of different solder alloys influence the changes of microstructure and hardness property [22].

| Solder alloys | $T_M$ (°C) | $T_G$ (°C) | $\Delta T$ (°C) |
|---------------|------------|------------|----------------|
| Sn-40Pb       | 172.3      | 186.6      | 14.3           |
| Sn-0.7Cu      | 212.4      | 229.0      | 16.6           |

Table 1. The growth temperature (TG), the minimum temperature before recalescence (TM), and the nucleation undercooling (AT)
4. Conclusions
The dT/dt curve that derived from the cooling curve reveals the number of nucleation phase in the solder alloys during solidification and its nucleation temperature, TN can be obtained from the cooling curve. Two nucleation phases are found in Sn-40Pb which are the primary lead-rich phase and the secondary tin-rich phase; while Sn-0.7Cu only has one nucleation phase which is the phase of βSn+ Cu6Sn5. The phase transformation of Sn-0.7Cu in the experiment is same as the Sn-0.9Cu in phase diagram might due to the copper content difference is very small between both solder alloys. The undercooling, ΔT of solder alloy can be expressed by the growth temperature, TG and the minimum temperature before recalescence, TM, obtained from the cooling curve; showing that the undercooling of Sn-40Pb is lower than Sn-0.7Cu solder alloys.

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