Effect Additions Zn on Sn-0.7Cu Lead-Free Solder: A Short Brief

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Abstract: Sn-0.7Cu lead-free solder is an alternative solder material that suitable to replace Sn-Pb solder in electronic manufacturing. However, it has a weakness of high melting temperature and lower mechanical strength. In this study, the change in microstructure, elements, the structural and melting point of Sn-0.7Cu after the addition of different compositions of Zn element was discussed. The result shows that after adding a small amount of Zn, a refinement microstructure of Sn-0.7Cu-xZn solder alloy was obtained, and the melting point of the solder decreased from 227.7 ºC to 225.7 ºC. Besides, the formation new phase of was investigated by scanning electron microscope (SEM) followed by energy-dispersive x-ray spectroscopy (EDX) and x-ray diffraction (XRD). Besides, the behaviour of Sn-0.7Cu-xZn solder alloy can be further studied via open circuit potential (OCP) to determine the corrosion potential.

1. Introduction

Nowadays, soldering technology is important especially in electronic packaging. The manufacturing of electronic components such as capacitors, resistors, light-emitting diode (LED) and transistors get high demand nowadays. To produce different kind of electronic device such as computers, gaming devise, mobile phones, iPads and cameras it is needed to join the component of electronic together by soldering method.

Soldering is a metallurgical joining technique using a filler material which is solder with melting point below of 425 ºC [1]. The melting point of filler metal must lower than the metal to be joined. Typically, solder is an alloy that contain 0.75% of copper and 99.25% of tin. Tin will be a major component in solder because it has a lower melting temperature which is 232 ºC.

Lead-free solder usually contains less than 0.2 % of Pb [2]. Lead-free solder is environmentally friendly and have a better property than Sn-Pb alloys. Besides, Sn-Cu also interesting than SAC solder alloy due to lower cost because of the absence of expensive Ag. Sn-0.7Cu solder alloy also has good thermo mechanical fatigue resistance [3].
On other hand, in the Sn-Cu phase diagram at Sn-rich side Sn-0.7Cu is a hypoeutectic composition while β-Sn and Cu₆Sn₅ are the main phases at room temperature [4]. Micro-alloying is an improvement process of an alloys through addition of small quantity of element via solidification. Micro-alloying will influence the equilibrium states of binary alloy system although only a small quantity of alloying element is used [5]. Hence, micro-alloying will modify the alloy system and it usually will be described by refinement of microstructure and improvement in physical or functional properties.

However, an excessively thick Cu-Sn IMC layer will develop at the interface of Sn-0.7Cu solder joint during the reflowing process and can affect the reliability of the solder [3]. The formation of Cu₆Sn₅ intermetallic could help to improve the mechanical strength due to the fine intermetallic particles that will strengthen the solder materials [5]. However, Cu₆Sn₅ will dramatically grow during in service condition or annealing process and it is a faceted phase. Hence, it will cause defect and brittle intermetallic that will cause the cracks and degradation of solder joint [6].

To enhance the properties of the Sn-Cu solder the addition of third elements are require such as Cu, Al, Zn, Ag, Ga, In, Sb and rare earth. According to previous study by [5] addition of Zn element is very good to improve the microstructure, mechanical strength and it also may reduce the melting point of solder alloys and it is also cheaper than other micro-alloying elements. Zn also excellent for improvement of wettability th at it will enhance the ability of the molten solder to spread over the substrate. Thus, higher concentration of Zn will lead to form Sn-Zn IMC which stable and difficult to spall-off on the surface of substrate [7].

2. Soldering Process

Soldering is a process which two or more metal are jointed together by melting and then flowing a filler metal into the joint. The properties of the filler metal are it has low melting point and soldering is used to form a permanent connection between electronic components [8]. The metals to be joined determine the solder, flux, and heating methods to be used. Usually base metals have specific properties such as electrical conductivity, weight, and corrosion resistance.

There are several basic steps of soldering process which is there are two types of cleaning step. Firstly, through mechanical way which is using emery cloth and Scotch Brite pad. Secondly, through chemical way which is cleaning using acids such as hydrochloric and sulphuric to remove the rust, sulphide and scale. Next, flux must promote wetting of the surface by the solder and should able to be removing oxides on heating and stop it from reforming. Besides, wetting the metal surfaces then filling the gap between the wetted surfaces with solder. Cooling the joint as soon as possible after soldering the joint using air blast or water spray this is because slow cooling can cause excessive alloying and cause a brittle joint. Lastly, remove the corrosive flux residues that fluxes containing zinc chloride to prevent corrosion.

3. Solder Materials

There are different types of alloys are uses in solder applications. Usually, eutectic alloy of 60% of Sn and 40% of Pb are used in electric joining applications. The absences of a plastics phase in eutectic formulation quickly enable time for solder cool and quicker wetting out as the solder heats up. Besides, eutectic formulation has lowest melting point that help minimizes stress on component during the soldering process. When the differential movement are occurred during the plastic phase it will cause crack and unreliable joint on the solder. Having good and quality solder joint are very importance in manufacturing and application of electronic packaging. Solder joints give structural support and electrical connection in the micro-electromechanical systems and electronic industry.
3.1 Lead-Solder
Solder also define as lower melting eutectic alloy. The eutectic alloy has a single melting point and the melting point are not only lower than the two components in the eutectic system. When the temperature has reached its eutectic point the entire joint will melt and the interfaces are joined at the same time.
63Sn-37Pb alloys was widely used in electronic packaging before the lead-free solder was developed [1]. Benefit of low melting temperature of Sn-Pb alloy is it will minimize the risk during handling the operation and low temperature of soldering help to prevent any microstructure change in surrounding area of the solder.

However, Pb also plays an important role in the process of soldering and the properties of Pb are contributes to increases in wettability by reducing the surface tension of Sn. The Tin/Pb solders available with tin concentration between 5% and 70% by weight. The greater the tin concentration, the greater tensile strength and shear strength of the solder [9-10]. In fact, Pb has lower cost than another alloy and easily to get. Mechanical properties of Sn such as ductility will improve with the presence of Pb.

Even though Sn-Pb lead solder have widely used in electronic packaging industry with excellent properties that suitable use for soldering but it is also having the weakness. However, is toxicity and poisoning that can affect human health and environment. Lead is a natural component with unique properties such as softness, ductility, low melting point and high malleability.

Several studied state that lead potent environmental toxin with non-biodegradable nature and its toxic [11]. In India higher amount of lead cause the increasing of environmental health problem [12]. It also harmful and potent poison to living organisms. Due to lead exposure it can cause digestive, respiratory, cardiovascular and urinary diseases [11]. Lead can enter human body through uptake of food (65%), water (20%) and air (15%). It also can cause kidney damage, brain damage, miscarriage, and subtle abortion.

3.2. Lead-Free Solder
Due to the lead driven to produce toxins to human health and the environment there are several lead-free solder alloys available to replace traditional Sn-Pb alloys such as Sn-Zn, Sn-Bi, Sn-Ag, Sn-Cu, Sn-Au, Sn-In, Sn-Sb and Sn-Pd. Lead-free solder was develop to replace eutectic or near eutectic Sn-Pb solders that melt at 183 °C [13].

Besides, there are a few necessities needed by lead-free solder alloy exchange in term of melting temperature, wettability, thermal fatigue resistance and low cost. The addition of third or fourth elements in solder alloy will improve the thermal, physical, mechanical and corrosion resistance properties of the solder [14].

4. Binary system Lead-Free Solder
Binary system is a metallic solid that composed of a mixture of two metal. The microstructure of alloys is develop from the phase transformation change that occur when the temperature is altered usually upon cooling. The purpose of this system is to increase the specific characteristic or properties of the component. The examples of binary system lead-free solder are Sn-Zn, Sn-Bi and Sn-Cu.

4.1. Sn-Zn
Pure zinc has excellent thermal shock resistance between 40 °C and 300 °C and low cost. Commonly Pb are used as high temperature solder but due to issues that Pb is dangerous that can affect human health and environment this lead-solder will replace with high-temperature lead-free solder. Zn-10Sn alloy contains 88% solid state of Zn phase in the Zn-Sn binary phase diagram and the other is liquid state of Sn phase at 523 K so with high Zn content in Zn-Sn alloy it is suitable used in high temperature electronic packaging.

Sn-Zn is more ductile compared to other alloys because there is no intermetallic compound in these alloys. This alloys also have proper melting range, good electrical conductivity and good thermal conductivity [15]. Besides, Sn-Zn has lowest melting temperature in compare with Sn-Ag-Cu which
gives the different is 18 °C and eutectic temperature for Sn-Zn is 198 °C [2]. Certain Sn-Zn composition can act as a sacrificed anode with a good anticorrosive property for the ferrous base metal. The shear strength of Cu/solder/Cu joint with the Sn-Zn is higher than Sn-Pb solder.

4.2. Sn-Bi
The eutectic point of the Sn-Bi is 139 °C. The properties of the Sn-Bi such as wettability, melting behaviour and mechanical properties can be improves by adding the alloying element. Bi is used as alloying element in the binary Sn-Bi system to provide suitable substitutes for Sn-Pb solder alloys.

Sn-Bi solder alloy has low temperature range. The advantage from this low temperature range in soldering applications are the solder joints of temperature-sensitive and the outer layers of classification packaging can reduce the influence of soldering temperature on the inner layer of classification packaging [16]. However, Sn-Bi solders also have the limitation which is poor ductility and frangibility.

4.3. Sn-Cu
One of the alternative lead-free solder is a Sn-Cu. Based on the study, the eutectic Sn-0.7Cu alloys have good fluidity, low tendency of hot cracking, narrow crystallization temperature range and segregation [18]. Even though, Sn-Cu have excellent properties it is also have the limitation which is lower mechanical strength and high melting temperature than Sn-Pb so to increases the performances of the solder and to overcome this limitation of Sn-Cu the addition of micro-alloying element such as zinc, titanium, bismuth, nickel and aluminium are used [14].

The growth of intermetallic compound (IMCs) between two metal which is the interface of solder alloy and copper substrate can determine through the phase diagram in specific temperature. Cu$_5$Sn and Cu$_6$Sn$_5$ IMC are the main reactants at the interface between the liquid solder and the metal substrate. There are two crystal structures of Cu$_5$Sn$_5$ in the solid state where the allotropic transformation occurring at 186 °C. At lower temperature from monoclinic where $\gamma'\text{-Cu}_5\text{Sn}_5$ is transform to hexagonal $\eta\text{-Cu}_5\text{Sn}_5$ at higher temperatures [19]. The formation of IMC will reduce the strength of solder joint due to brittle nature of these compound. However, the cost of other lead-free solder alloys is two times and three times greater than Sn-Pb meanwhile the cost of Sn-Cu is 1.3 times greater than Sn-Pb [20].

5. Conclusion
The result for morphology of Sn-0.7Cu-xZn was proved that the refinement of the microstructure was occur when 0.25, 0.50, 0.75 and 1.00 wt% of Zn was added to the solder alloys. The XRD patterns indicate that the crystal structure of IMC for Sn-0.7Cu-xZn is Cu$_6$Sn$_5$ and Cu$_5$Zn$_8$. DSC result has been confirmed that the melting point of the Sn-0.7Cu-xZn was decreases due to higher amount of Zn addition.

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