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Mechanical and Physical Properties of In-Zn-Ga Lead-Free Solder Alloy for Low Energy Consumption

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Abstract. Due to the demand in the use of electronics devices in industry, the usage of solder connections has increased. Concerning with the toxicity of lead in Sn-37Pb solder alloy, developing lead free solder alloy with low melting temperature is one of the most important issues in electronic industry. Previously, researchers found out that the most promising candidate of lead free solder alloy is Sn-3.0Ag-0.5Cu (SAC). However, the melting temperature of this solder alloy is 217°C, 34°C higher than Sn-37Pb. This can lead to high energy consumption in electronic industry. In this paper, In-Zn-Ga solder alloy was investigated as a potential candidate replacing SAC. This study covers on the physical and mechanical properties of the solder alloy. Differential Scanning Calorimetry (DSC) testing shows that this solder alloy gave low melting temperature as low as 141.31°C. The addition of Ga in In-Zn solder alloy lowered the melting temperature compared to SAC and Sn-37Pb. From coefficient of thermal expansion (CTE) analysis, the In-Zn-Ga solder alloy gives good expansion properties and able to avoid the mismatch between the solder and copper substrates. The density of In-Zn-Ga solder alloy is 6.801g/cm^3, lower than SAC and Sn-37Pb. For the strength, single lap shear testing was conducted on the In-Zn-Ga solder alloy and the results is near to the strength of SAC.

1. Introduction

Conventional soldering technology has become indispensable for the interconnection and packaging of virtually all electronic devices and circuits. The traditional tin-lead (Sn-Pb) solders have been widely employed as electrical interconnects in electronics industries (Zhang et. al, 2008). However, the toxic in Pb can cause harmful influence on the environment and health (Zhang et. al, 2008; Shen & Chan, 2009; Lin et. al, 2009; Islam et. al, 2005). The Europian Union directive on waste electrical and electronic equipment (WEEE) announced the prohibition of the use of Pb in the consumer electronics market after January 2006 (Tsao, 2011). Thus, it is urgent task to develop the lead-free solders with excellent properties.

Recently, a great amount of lead free solders have been reported and promising candidates such as Sn-Ag, Sn-Cu, Sn-Zn, Sn-Bi, Sn-Sb, Au-Sn, and Sn-Ag-Cu systems have been of interest (Goh et. al, 2013; Zhang et. al, 2008). Among the lead free candidates' solders, the Sn-Ag-Cu (SAC) family is believed to be the most promising (Tsao, 2011; Abtew and Selvaduray, 2000; Laurila et. al, 2005; Hung et. al, 2006; Yoon & Jung, 2008; Islam et. al, 2005). SAC alloys with melting temperature 217°C is extensively used as solder materials in the electronic industry (Alena et. al, 2010). It has been proposed as the most promising substitute for lead containing solders because of its relatively low melting temperature, its superior mechanical properties, and its relatively good wettability (Anderson, 2007; Glazer, 1994; Yoon et. al, 2009).

Despite this, its properties still not good enough for to be employed in temperature sensitive components, optoelectronics modules, step soldering processes and thin printed wiring boards that require a relatively low melting temperature (Ervina et. al, 2010). A higher melting point leads the increase in the peak reflow temperature required for assembly compared to that required for Sn-Pb eutectic solder (Whitney & Corbin, 2006). An increased temperature is detrimental to many microelectronic components, making assembly very difficult to be applied. In the other hand, high melting temperature may leads to high energy consumption in the industry.

A low processing temperature is desirable for preventing heat damage to electronic devices during soldering (Wong, 2006; Li et. el, 2006: Kim et. al, 2007). Low temperature soldering also reduce the risk of thermal shock induced by the thermal expansion mismatch among different materials in an electronic package (Ervina et. al, 2010). The alloying element employed to lower the melting temperature of solder alloys must be conform to the Restriction of Hazardous Substances (RoHS) directive, and possesses a low melting point, such as bismuth (Bi), gallium (Ga), and indium (In) (Kim & Suganuma, 2003; Fukuda et. al, 2003). Besides reducing the risk of thermal shock, step soldering is another application for low temperature solders. Step soldering is commonly used when soldering a device that requires more than one step. According to Mei et. al, (1996) step soldering is the availability of solders with lower melting points will make possible multiple reflow processes on a single board (Mei et. al, 1996). In this application, the solder used for subsequent steps should have a lower melting point than that used for preceding step (Ervina et. al, 2010).

The main elements of low temperature alloys are Sn, Pb, Bi, and In, (the Cd-bearing alloys are not considered because of their extreme toxicity) (Mei et. al, 1997; Mei et. al, 1996). Various compositions of these elements produce alloys that melt at any given temperatures between 50°C and 183°C (Mei et. al, 1997). Indium (In) is a kind of soft metallic element. Kanlayasari et. al, 2009) reported that In has the influence of reducing the solidus and liquidus temperatures. From the process point of view, Indium (In) has a lower melting point of 156°C compared to Sn, Pb and Bi (Liu et. al, 2003). Thus, it can reduce the soldering temperature. According to Kumar et. al the currently available low temperature solders with high indium-content have the requisite wetting properties, meet the desired reflow temperature requirements (Kumar et. al, 2008).

Nevertheless, the studies on the In-based lead free solder alloys are scarce. This paper discussed In-Zn-Ga as a good candidate for a low temperature lead free solder alloys. Since this solder alloy has low liquidus temperature, it may be used for low temperature soldering and lower the energy consumption in the production. The results of the investigation of the physical and mechanical properties of In-Zn-Ga will be reported in this paper.

2. Materials and Methods

In-Zn-Ga solder alloy was prepared from indium (99.9% pure, Alfa Aesar), zinc (99.9% pure, Alfa Aesar), and gallium (99.99% pure, Alfa Aesar) to obtain low melting temperature solder alloy. These elements were first weighed by digital electronic balance based on each nominal and then melted in a furnace by temperature of 450°C for 1 hour. In order to obtain a homogeneous composition, the ingot was re-melted for three times.

Then, the ingots were compressed to 1mm thickness by using Hydraulic Compression Machine and punched into the shape of billets by using puncher. The diameter of this billet is 5 mm with the thickness of 1 mm each as in Figure 1. The billets was ground with abrasive paper and polished with alumina powder into disk-like billets.

Figure 1. The diameter of the billets.

The billets were used for density testing. The density of In-Zn-Ga solder alloy was measured using an electronic densimeter machine for 3 billets to make sure the value was precise by calculate the average density. For thermal analysis, the melting temperature was analyzed using Differential Scanning Electron (DSC) from TA Instruments. The analysis was carried out at 10°C/min of heating rate with the temperature from 0 to 500°C under nitrogen atmosphere. The weight of the billets was approximately 10g. The coefficient of thermal expansion (CTE) of In-Zn-Ga was investigated using the L75 Platinum Series machine from Leiseis. The solder billet were prepared cylindrically with the diameter of 5mm and the height of 10mm. Shear testing were performed to test the joint strength. The maximum shear force was calculated with the crosshead speed of 0.01mm/s and then being converted to the shear strength using the Eq. 1. The soldered area on the substrate was 10×10mm and the substrate's dimension is 30×10×0.01mm.

$$\tau = F/A \ldots\ldots\ldots\ldots\ldots \text{(Eq. 1)}$$

Where τ = shear strength (MPa), F = shear force (N), and A = soldered area

3. Results and discussions

In order to serve as an alternative solder alloy, the solder should consume less mass and space as well as possess a density near to or lower than the Sn-37Pb solder (Humpston & Jacobson, 2004). In this investigation, the density value for In-Zn-Ga, SAC and Sn-37Pb are 6.801, 7.440 and 8.790 g/cm^3 respectively as tabulated in Table 3.1. The table also shows the density value of each elements used in In-Zn-Ga, SAC and Sn-37Pb.

Table 3.1. The density values for the compositions and elements.

Composition	Density (g/cm^3)	References
In-Zn-Ga	6.90	This research
SAC	7.44	Humpston & Jacobson, 2004
Sn-37Pb	8.36	Humpston & Jacobson, 2004
In	7.31	Callister & Rethwisch, 2010
Zn	7.14	Callister & Rethwisch, 2010

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Ag	10.49	Callister & Rethwisch, 2010
Sn	7.31	Callister & Rethwisch, 2010

The density of In-Zn-Ga is 8.59% lower than most promising lead free solder, SAC and 22.63% lower than the traditional Sn-37Pb solder. This is due to the density value of the elements in the composition of solder alloys. According to Chandra et. al, the density property of a solder is directly related to the atomic structure and the volume of the elements mixed (Chandra et. al, 2010). An addition of element with lower density value tends to lower the overall density of the solder alloys. This is due to the atomic structure of the lower density material has more space than the higher density material and will affect the density as the mass and volume of the composition also affected. According to (El-Daly et. al, 2014), the solder alloys should consume lower density value as the size of the pitch interconnections is becoming smaller. This requirement will be able to satisfy the need of miniaturization in the electronic packaging industry nowadays. A solder alloys should be lighter and less dense compared to lead solder (Sn-Pb) that is 8.79g/cm3 to accommodate the small space in the devices as the electronic devices are getting smaller.

The melting temperature is a critical solder characteristic because it determines the maximum operating temperature of the system and the minimum processing temperature that components must survive (El-Daly et. al, 2008). The melting curves of differential heat flow against temperature are shown in Figure 3.1. The melting point of In-Zn-Ga was determined from the single sharp endothermic peak of DSC heating curve within the temperature of 0 to 500°C. Onset temperature is the temperature when the solder starts to melt and termed as solidus temperature, while end temperature is the temperature when the solder is fully solidifies and termed as liquidus temperature. Meanwhile, peak temperature is the melting temperature.

Table 3.2. The analysis value of the DCS curve.

Composition	Onset (T_{onset})	End (T_{end})	Peak temperature (T_m)	References
In-Zn-Ga	119.60°C	148.45°C	141.31°C	This research
SAC	212.8°C	217.1°C	216.9°C	Sung et. al, 2004

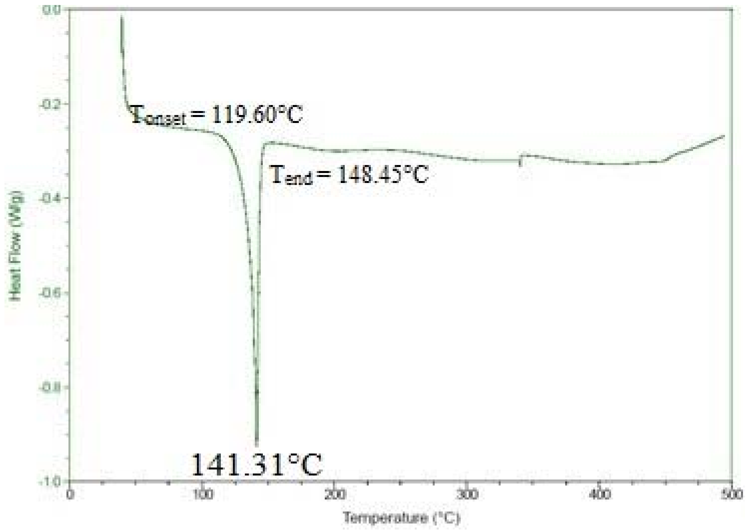

Figure 3.2. DSC curve showing the heating process of the In-Zn-Ga.

The DSC results in Figure 3.2 are summarized in Table 3.2. The melting temperature (T_m) of the In-Zn-Ga was measured as 148.45°C, 34.85% lower than the eutectic temperature of the SAC that is 217°C and 18.88% lower than the melting temperature of Sn-37Pb (T_m=183°C). Ga has the lowest melting point of all the metals, and it has been reported that Ga can enhance the flow ability of some lead-free solders (Zhang et. al, 2004; Chen et. al, 2010). Qiao et. al, 2008 investigated the effects of Ga alloying on melting behaviors. They founded that addition of Ga element on Sn-Ag-Cu solder can obviously decrease the melting point. Based on the experimental results and discussions, each percentage of Ga addition can decrease the melting point of the Sn–Ag–Cu eutectic solder alloy by about 4°C.

Global mismatch will predominate when dissimilar base materials are joined together. The coefficient of thermal expansion is an important parameter for solder alloys. If the thermal expansion coefficient of a solder alloy does not match with the base material, thermal stress will be formed at solder joints and affect the soldering quality.

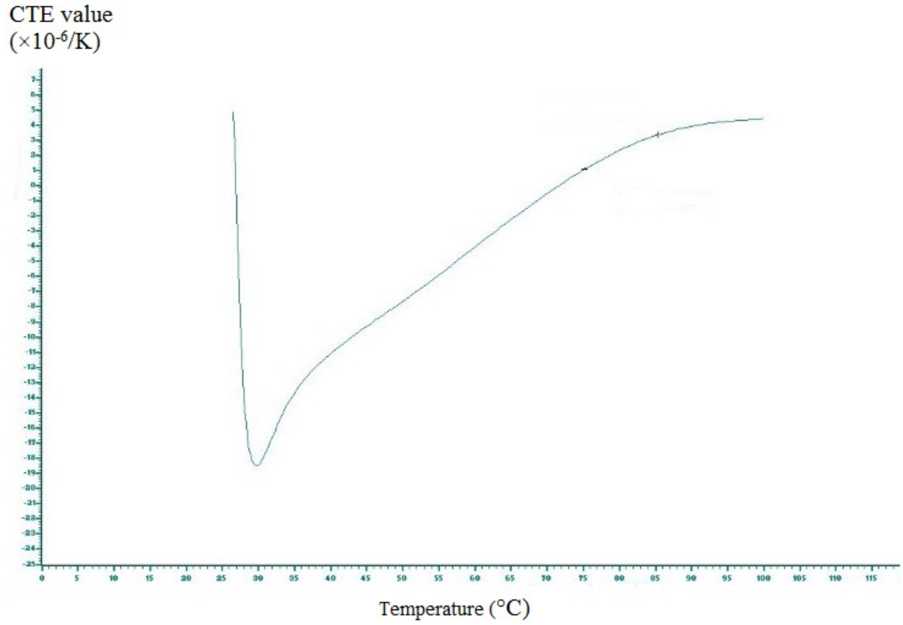

Figure 3.3. Thermal expansion for In-Zn-Ga.

From Figure 3.2, the result was decreasing from 0 to 30°C. This mean the shrinkage occur for the solder at the beginning. This shrink is happened because in the beginning, the atom have more energy to vibrate and the atom with smaller size have high energy to enter the space among the In-Zn-Ga solder alloy. However, it was increase at the temperature of 30 until 100°C. This showed that In-Zn-Ga solder alloy was expand when the temperature increase. When the temperature increase, the atom gain more energy and the vibration will lead to a big gap between the atom rather than fill the space among itself. It has been reported that the CTE value for Cu substrate is 17.0×10^{-6}/K while the CTE value for SAC is 40×10^{-6}/K. It is necessary to decrease the difference in the CTE value between the substrate and the solder alloy for a joint to be effective (Fallahi et.al, 2012). The CTE value of In-Zn-Ga is 1.1×10^{-6}/K. Hence, the difference of the Cu substrate and In-Zn-Ga is acceptable than the CTE value of SAC. If all of the components within the device have identical CTE value, then they will expand and contract at the same rate.

To investigate the shear strength of In-Zn-Ga, single lap shear test was conducted. The shear strength will acknowledge the quality of the solder alloy in terms of the strength in application when it endures shaking (Jeon et. al, 2008). Figure 3.4 show the stress versus train curve of In-Zn-Ga. The shear strength of this solder alloy is 190.188MPa and the shear strength of SAC and Sn-37Pb are 276 and 51.7MPa respectively. The shear strength is higher than Sn-37Pb but lower than SAC. According to Luo et. al (2012), the shear strength of a solder alloy joint depends on their microstructural. Hence, from this result the microstructure of In-Zn-Ga can be predict as less lamellar shape and nearer to each other as the strength is strong. In fact, In-Zn-Ga has an element with smaller atomic size. Hence, the smaller atomic size will fill up the blank space among the atoms making the atoms close to each other and higher the strength at once.

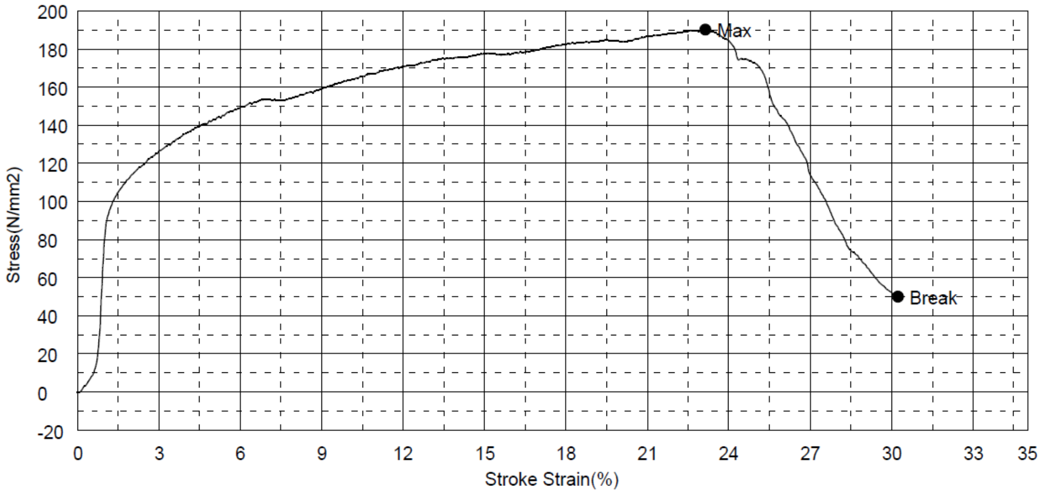

Figure 3.4. The stress strain curves for In-Zn-Ga.

4. Conclusions

The melting temperature of In-Zn-Ga is 148.45°C since the gallium have the capability to reduce the melting temperature effectively. The density of In-Zn-Ga is 6.90g/cm3 that is lower than SAC and Sn-63Pb. The CTE of In-Zn-Ga able to cover the mismatch between the solder and the Cu substrate. The CTE value is 1.1×10-6/K. As the shear strength of In-Zn-Ga is higher than Sn-37Pb, it is acceptable even though lower than SAC. The In-Zn-Ga is a new developed lead free solder alloy that able to replace the SAC. The low melting temperature of In-Zn-Ga can lower the energy consumption in the industry due to less heat need in soldering process.

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