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Study of the Effect of Aluminium Addition on Thermal and Electrical Properties of Tin-9Zinc Soldering Alloy

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Abstract**: *Sn-Zn based solder is a possible replacement of Pb solder because of its better mechanical properties. The alloys need to be studied and explored to get a usable solder alloy having better properties. In this work, eutectic Sn-9Zn and three Tin-Zinc-Aluminium ternary alloys were prepared and investigated their thermal and electrical properties. Thermo-mechanical Analysis and Differential Thermal Analysis were used to investigate thermal properties. Microstructural study is carried out with Scanning Electron Microscope. The alloys have single melting point. The co-efficient of thermal expansion and co-efficient of thermal contraction varies with alloy composition and temperature range. Electrical conductivity changes with Bi addition.***

Keywords: *Lead Free Solder Alloy, Eutectic Alloy, DTA, TMA, Conductivity.*

1. Introduction

From the point of environmental issue, lead is a very toxic metal and its compounds are poisonous. The use of these compounds will not only bring environmental pollution concerns, but also will affect the worker's health. The restriction of lead use in industry has been strongly promoted to protect the environment. Worldwide legislative moves to forbid the use of Pb in commercial electronics have spurred extensive searches for substitute materials for traditional Pb–Sn solder [1]. Extensive investigations have been on-going over the last few years to find an acceptable Pb-free solder for various electronic attachment applications [2-4]. Probable alternatives to the standard eutectic tin–lead solder investigated so far are based on tin alloys with a tin content significantly over 90 wt. % in combination with copper, silver, antimony, bismuth, or zinc. Recently, Sn-Zn solder is considering as a substitute for Sn-Pb eutectic solder [5-8]. Economically Sn-Zn is advantageous because Zn is a low cost metal. However, Sn-Zn eutectic solder is difficult to handle practically due to its highly active characteristics [9]. Because of oxidation and wetting problems eutectic Sn-9Zn solders has limited commercial validity [10]. Oxidation resistance and wetting behavior of eutectic Sn-9Zn solder alloy can be improved effectively by adding a proper alloying element. To improve the properties of eutectic alloy additional elements such as Bi, Cu, In and Zn are added. These additional elements lower the liquidus temperature and improve the tensile strength [11]. Al is very effective to enhance the atmospheric corrosion and oxidation resistance. The Al may form

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solid solutions with Zn and Sn [12] and improves the mechanical properties. It has been reported that the Al-Zn-Sn solders have good wettability on Al [13]. Besides mechanical properties melting temperature, thermal expansion and electrical conductivity etc. are very important issues for selecting a solder alloy. Optimization of the temperature of soldering process and solder microstructure is important not only from the economic reasons but also from the technological point of view, as a higher temperature means a higher risk for the electronic components and boards. Melting point of eutectic Sn-Zn alloy is 199°C which is very near to Sn-Pb alloy and this is another reason to consider it as a probable replacement of Pb solder [14,15]. Though Sn-Zn eutectic alloy is considered as a good candidate for the replacement of traditional Pb-containing solder alloy but available information in literature about the evolution and properties of Sn-Zn solder alloy is not enough. In this study eutectic Sn-Zn alloy and four Sn-Zn-Al ternary alloys containing 0.5%, 1%, 2% and 3% Al were developed and their thermal and electrical properties were measured. Melting temperature was studied with differential thermal analyzer (DTA). Thermo-mechanical analysis (TMA) was carried to study thermal expansion. Electrical conductivity was measured with Eddy current method.

2. Experimental Work

Sn-Zn-Al solder alloys were prepared by using Tin, Zinc and Al with 99.9% purity. Four alloys compositions were prepared and studied here. Proper amount of Sn and Zn were melted in a muffle furnace using a clay-graphite crucible at 450oC temperature for 30 minutes. Then Al was added and the mixture again kept in furnace at 700C for 30 minutes and then the liquid alloy poured in a cast iron mold having dimensions 300 mm × 10 mm × 10 mm and mold thickness was 10 mm. The Pouring temperature of the liquid solder alloys and the preheating temperature of the metal mold are 550oC and 350oC, respectively. The as-cast alloys were sectioned using hacksaw. Then they were polished with emery paper and finally wet polished. Polished samples were then cleaned and etched by ethanol with 5% HNO3 to observe microstructure. Prepared samples were investigated for optical microscope (NMM 800TRF, MTI Corporation, USA). Scanning micrograph was observed with JOEL JSM-7600F scanning electron microscope. Polishing was also necessary to get smooth and parallel surface for hardness study. Hardness of the samples was measured by HMV-2T, Shimadzu Co., Japan, Vickers Microhardness tester. The applied load was 100 gm for 6 seconds and five readings were taken at room temperature to get average value of microhardness. Tensile properties of the samples were measured with the Hounsfield 10KS Universal Testing Machine. In this paper alloys are referred as Sn-9Zn, Sn-8Zn-1Al, Sn-7Zn-2Al and Sn-6Zn-3Al according to table 1.

Table 1: Composition of the alloy.

Alloy	Sn (wt%)	Zn (wt%)	Al (wt%)
Sn-Zn	91	9.0	0.0
Sn-8Zn-0.5Al	91	8.5	0.5
Sn-8Zn-1Al	91	8.0	1.0
Sn-7Zn-2Al	91	6.0	2.0
Sn-6Zn-3Al	91	6.0	3.0

3. RESULTS AND DISCUSSION

3.1 Differential Thermal Analysis

Melting temperature is the main characteristic of a solder alloy while it determines the maximum operating temperature of the system and the minimum processing temperature its components must survive [16].

High melting temperature of the solder alloy increases the reflowing temperature in the electronic packaging process and causes thermal damage to the polymer substrate. Figure 1 shows the superimposed Differential Thermal Analysis (DTA) curves of Sn-Zn-Al alloys. Melting temperature, solidification temperature and pasty range of the alloys are presented in table 2. They are extracted from the DTA curves. Melting temperature of Sn-9Zn alloy is 199.4°C which is a good agreement with the literature value [17, 18]. The melting temperature of the Sn-Zn alloy with 0.5% Al addition reduces to 198.7°C. Sn forms a eutectic composition with 0.5% Al and this is why the melting temperature of this alloy reduces [19]. Another author reported similar result [20]. The melting temperature of eutectic Sn-Zn alloy increases with further addition of Al.

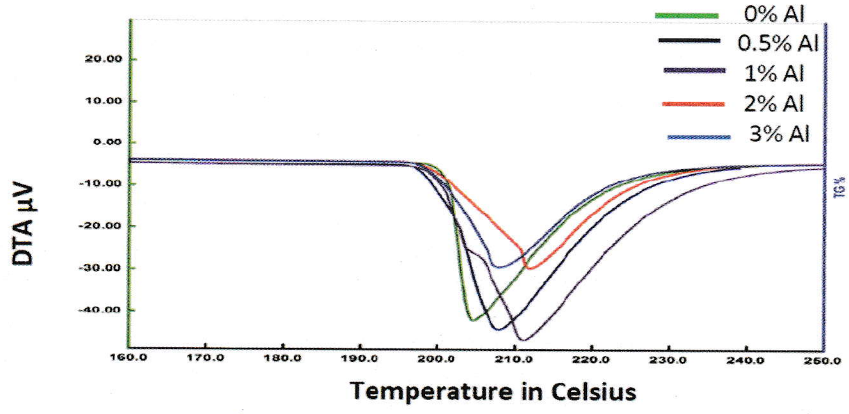


Figure 1: DTA curves of Sn-Zn-Al alloys

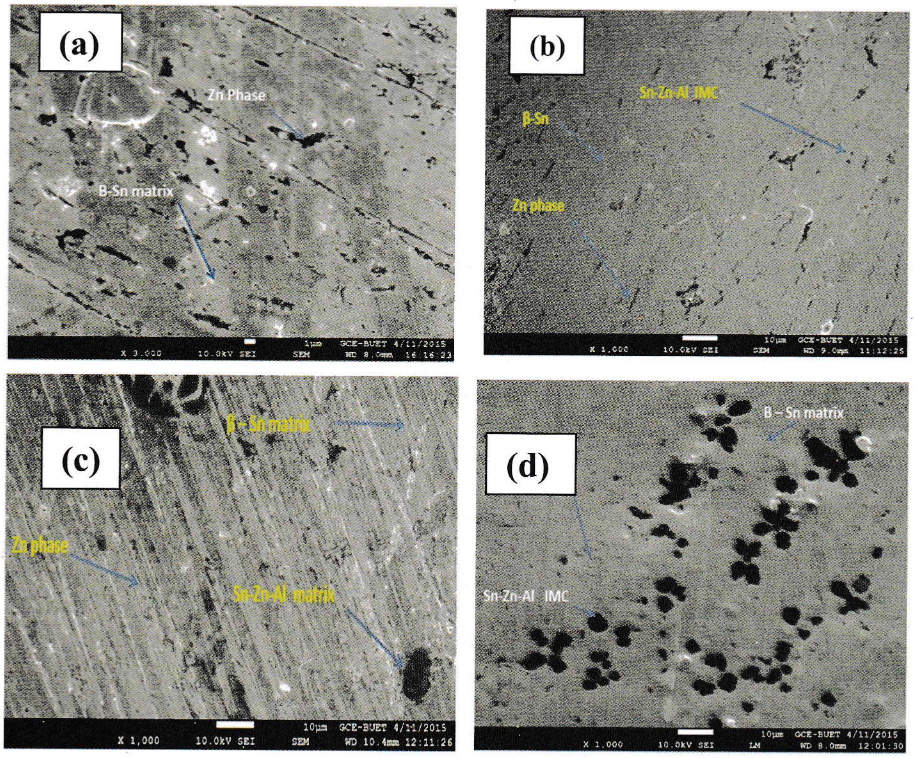
Table 2: Liquidus and Solidus points of Sn-(9-x)Zn-xAl alloys

Alloy	**Solidus Point (°C)**	**Liquidus point (°C)**	**Pasty Range (°C)**	**Endothemic peak (°C)**
Sn-9Zn	199.4	224	24.6	204.1
Sn-8.5Zn-0.5Al	198.7	224.8	26.1	206.6
Sn-8Zn-1Al	199.6	231.8	31.9	215.2
Sn-7Zn-2Al	201.3	233.8	32.5	214.1
Sn-6Zn-3Al	201.9	234.7	32.8	211

From figure 1 it is shown that all the alloys show single melting point while Sn-6Zn-3Al shows an extra phase during solidification. During heating cycle this extra peak may not visible due to fast heating. Low Zn content may cause this extra peak. Katsuaki Suganuma and Koichi Niihara observed same criteria with Sn-6Zn alloy [21]. Al forms solid solutions with Sn and Zn [12]. Figure 2 shows the SEM micrograph of the alloys. From the micrographs it is seen that Al addition decreases the eutectic phase and produces an Al rich phase. With the increase of the amount of Al the size of the globular shaped inter metallic compound (IMC) increases. This Al rich phase and IMC cause the increase in melting temperature. Same criteria were reported by another author [17, 22, 23].

3.2 Thermomechanical Analysis

The coefficient of thermal expansion and coefficient of thermal contraction of Sn-(9-x)Zn-xAl alloy obtained from the TMA curve are shown in figure 3. Thermal expansion changes with temperature and Coefficient of Thermal Expansion (CTE) is calculated for different temperature range while the Coefficient of Thermal Contraction (CTC) calculated average value for whole range. The coefficient of thermal expansion of Sn-9Zn alloy is $23.39 \times 10^{-6}/^{o}C$ which is a good agreement with the literature value [24]. Rate of thermal expansion and contraction increases with 0.5% Al addition but decreases with further addition of Al. Thermal expansion depends on bonding energy which also affects the melting point of the solid. High melting point materials likely to have lower thermal expansion [25]. Al increases the melting temperature of Sn-9Zn alloy. Again Al creates IMCs in Sn-Zn alloy which may cause the increase of CTE and CTC.



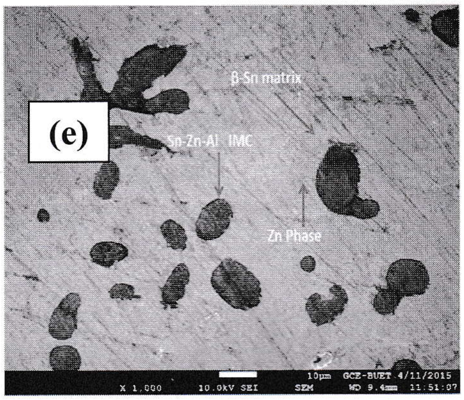


Figure 2: SEM micrograph of (a) Sn-9Zn (b) Sn-8.5Zn-0.5Al (c) Sn-8Zn-1Zn (d) Sn-7Zn-2Al alloy and (e) Sn-6Zn-3Al

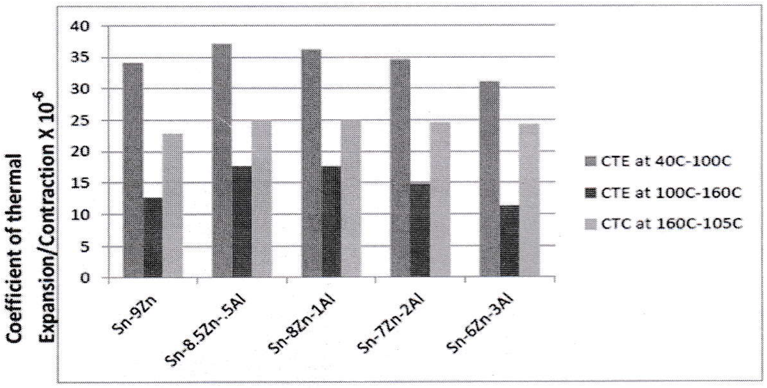


Figure 3: CTC/CTE of Sn-(9-x)Zn-xAl alloy

3.3 Electrical Conductivity

Conductivity of an alloy is affected by impurities and alloying elements. Conductivity decreases with alloying elements [26]. Then the conductivity of alloy decreases during alloying. Conductivity of pure Tin and pure Zinc also presented in the table 3. Electrical conductivity of Sn-9Zn alloy is obtained 15.6 %IACS which is similar with the value reported by another author [24]. Figure 4 shows the electrical conductivity of Sn-(9-x)Zn-xAl. From the microstructure image of Sn-Zn-Al alloy it is seen that some Sn-Zn-Al IMCs are formed. Any new phase in an alloy changes the grain size and electron distribution. Scattering of electron is affected by impurities and grain boundaries [24, 26]. This causes the decrease in conductivity of Sn-(9-x)Zn-xAl alloy.

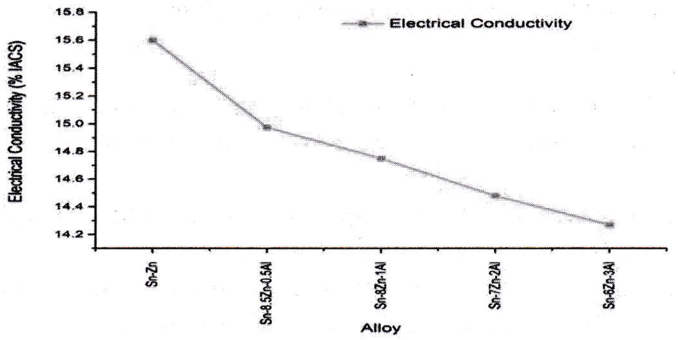


Table 3: Electrical conductivity of Sn-Zn-Al alloys alloys

Alloy	Electrical conductivity %IACS
Sn	15.000
Zn	28.000
Sn-Zn	15.600
Sn-8.5Zn-0.5Al	14.875
Sn-8Zn-1Al	15.050
Sn-7Zn-2Al	15.200
Sn-6Zn-3Al	15.400

4. Conclusion

Eutectic Sn-Zn alloy and four Sn-Zn-Al ternary alloys were cast. Melting behaviour, thermal expansion and contraction and electrical conductivity were investigated. Thermal properties of Sn-Zn alloy changes with Al addition. Melting point decreases with 0.5%Al addition and increases with further addition of Al. Coefficient of thermal expansion and coefficient of thermal contraction increase with 0.5%Al addition decreases with further addition of Al. Electrical conductivity decreases with Al addition.

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