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Thermal and Electrical Properties of Sn-Zn-Bi Ternary Soldering Alloys

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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-Bismuth 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

Tin-Lead solders have been widely used in electronic and optoelectronic packaging due to their low cost and low melting temperature and good soldering properties. But lead is an aggressive threat for human health and the environment due to its toxicity. Many countries banned using lead and lead alloys [1] [2] for their use in packaging. Waste Electronic and Electronic Equipment (WEEE) and Restriction of Hazardous Substances (RoHS) approved banning the use of lead in European Union countries effective July 2006. The USA, the EU and Japan forbade the use of Lead containing products [3] [4]. Because of the toxicity of lead, traditional Sn-Pb solders are now being replaced with Sn-base soldering alloys containing additions of other metals (Ag, Bi, In, etc.) [5]-[9]. Au-Sn is thought to be alternative but its mechanical properties are not sufficient [10] [11]. SAC

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solder also an alternative has eutectic point at 217˚C [12] and good wetting properties [13]. The search for a perfect Lead-free solder alloy with equivalent mechanical and thermal properties to Sn-Pb solder is an urgent task. Targeting the deadline (July 1, 2006), a large number of studies on Lead-free solders were being conducted worldwide to find an appropriate replacement. Nowadays, Sn-Ag base alloys containing one or more additional metal are being used as alternating soldering alloy [5] [6] [8] [14]. Soldering alloy is the prime material for electronic packaging. Melting temperature, mechanical properties, wetting properties, thermal expansion and electrical conductivity, etc. are very important issue for selecting a solder material. Recently Sn-Zn eutectic alloys have received particular attention due to its low melting temperature [15] [16]. Sn-Zn eutectic alloy is considered as a good candidate for the replacement of traditional Pb-containing solder alloy [17]-[19]. However, available information in literature about the evolution and properties of Sn-Zn solder alloy is not enough [20]. In this study eutectic Sn-Zn alloy and three Sn-Zn-Bi ternary alloys containing 1%, 2% and 3% Bi 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-Bi solder alloys were prepared by using Tin, Zinc and Bi with 99.9% purity. Four alloys having different compositions were prepared and studied here. Sn-Zn with desire composition was melted in an electrical furnace in a clay-graphite crucible at 450˚C temperature for 30 minutes. Then Bi was added and the mixture again kept in furnace for 20 minutes. Then the liquid alloy poured in a cast iron mould having dimensions 300 mm × 10 mm × 10 mm and 10 mm mould thickness. The as cast alloys were sectioned and polished with emery paper and then wet polished. Polished samples then cleaned and etched by ethanol with 5% HNO_3 to observe microstructure. Prepared samples were investigated by JOEL JSM-7600F scanning electron microscope. The co-efficient of thermal expansion was studied up to 170˚C with TMA/SS6300, SII Nanotechnology Inc; Japan at a heating rate of 10˚C/min. Melting behavior was studied with TG/DTA6300 SII nanotechnology, Japan at a heating rate of 20˚C/min in a nitrogen environment. In this paper four alloys are referred as Sn-9Zn, Sn-8Zn-1Bi, Sn-7Zn-2Bi and Sn-6Zn-3Bi. The pouring temperature of the liquid solder alloys and the preheating temperature of the metal mold are 450˚C and 220˚C, respectively.

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 [21]. **Figure 1** shows the superimposed Differential Thermal Analysis (DTA) curves of Sn-Zn-Bi alloys. Melting temperature, solidification temperature and pasty range of the alloys are presented in **Table 1**. They are extracted from the DTA curves. The melting temperature is one of the most important considerations for the development of the solder alloy because the high melting temperature of the solder alloy increases the reflowing temperature in the electronic packaging process and causes thermal damage to the polymer substrate. Melting temperature of Sn-9Zn alloy is 199.4˚C. It is seen that Bi addition decreases the melting temperature of Sn-9Zn alloy. From the SEM microstructure it is seen that Bi rich platelets are observed in Sn-6Zn-3Bi alloy (**Figure 2(d)**). Bi forms 43Sn-57Bi eutectic composition with the addition of Bi in Sn-9Zn alloy which has a relatively low melting temperature. This eutectic formation contributes in lowering the melting temperature of Sn-9Zn alloy. It is thought that some of high concentration Bi area might have formed 43Sn-57Bi eutectic. Similar criteria have also been reported by other authors [22] [23]. All the alloys show single melting temperature.

3.2. Thermo-Mechanical Analysis

Thermo-mechanical Analysis (TMA) data obtained for Sn(9-x)Zn-xBi alloys at different temperature range is shown in **Figure 3**. It is observed that co-efficient of thermal expansion (CTE) changes with temperature. This is why CTE presented for two temperature range. The coefficient of thermal expansion of Sn-9Zn alloy is 23.39867 × 10^{-6}/˚C which is a good agreement with the literature value [24]. At low temperature range CTE of Sn-9Zn alloy increases with Bi addition. At high temperature range nature of CTE is similar with low

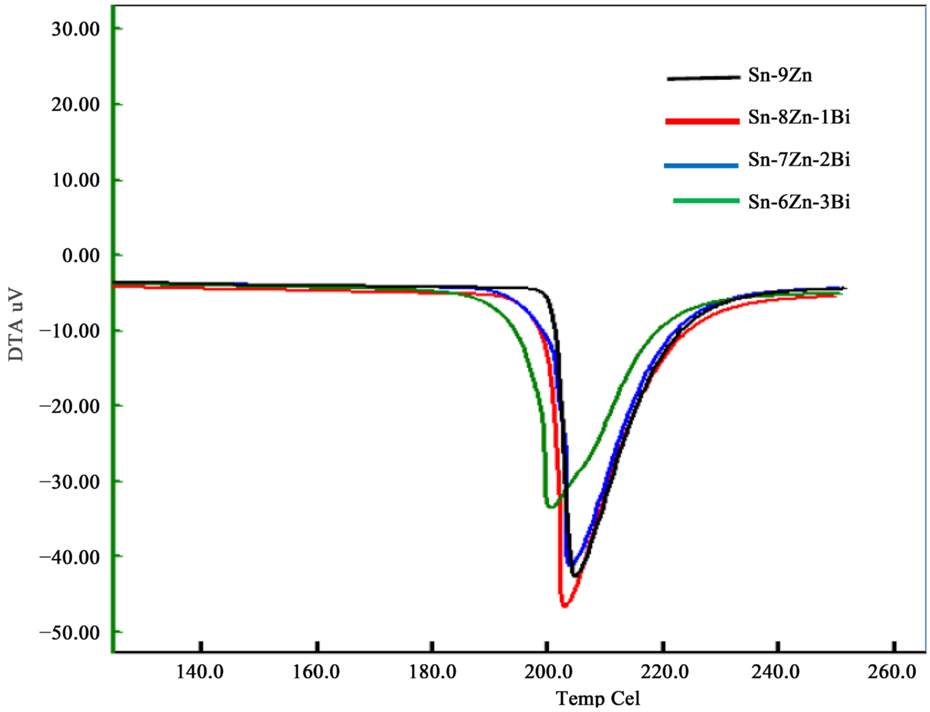
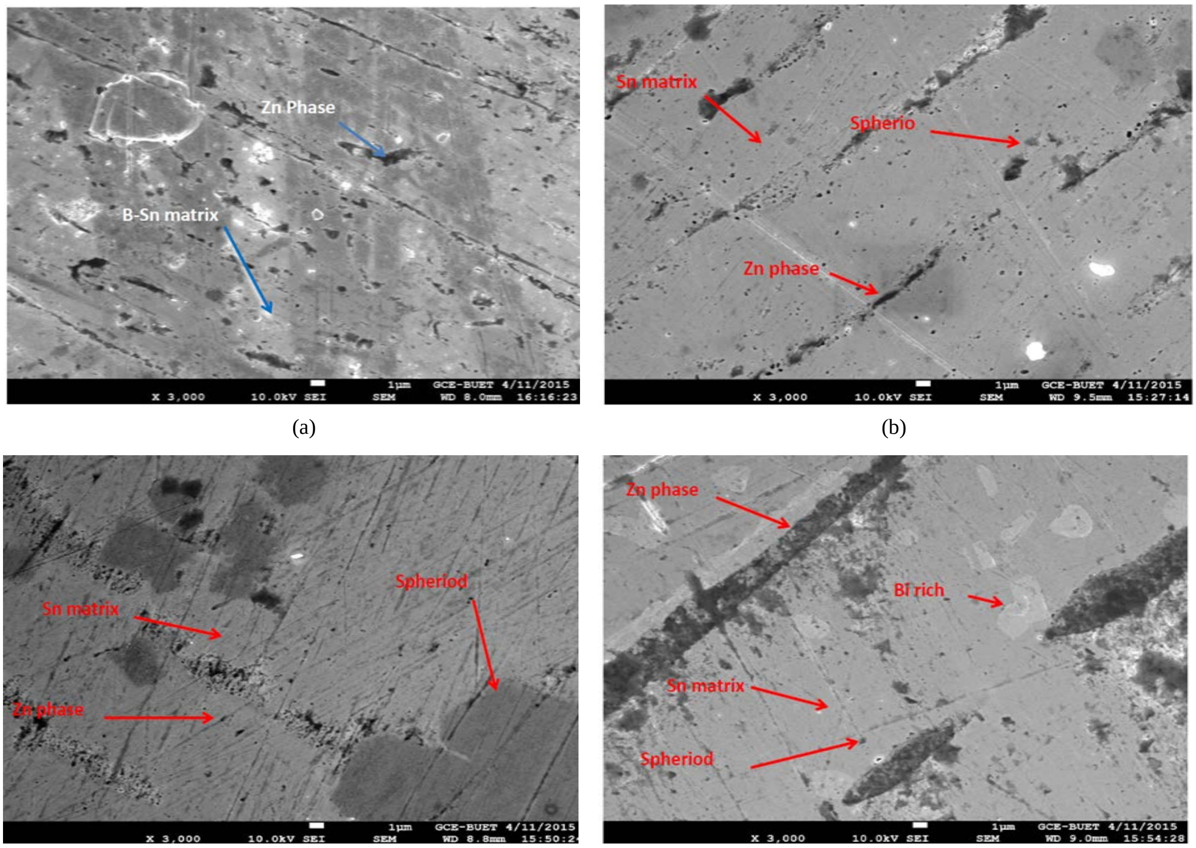


Figure 1. Endothermic peaks of the Sn-(9-x)Zn-xBi alloy.



(a)

(b)

(c)

(d)

Figure 2. SEM micrograph of (a) Sn-9Zn alloy, (b) Sn-8Zn-1Bi alloy, (c) Sn-7Zn-2Bi alloy and (d) Sn-6Zn-3Bi alloy.

Table 1. Liquidus and solidus point.

Alloy	Solidus Temperature ˚C	Liquids Temperature ˚C	Pasty Range ˚C	Endothermic Peak ˚C
Sn-9Zn	199.4	224	24.6	204.1
Sn-8Zn-1Bi	198.1	223.5	25.4	203.1
Sn-7Zn-2Bi	197.3	224.8	27.5	202.4
Sn-6Zn-3Bi	196.1	225.5	29.4	203.1

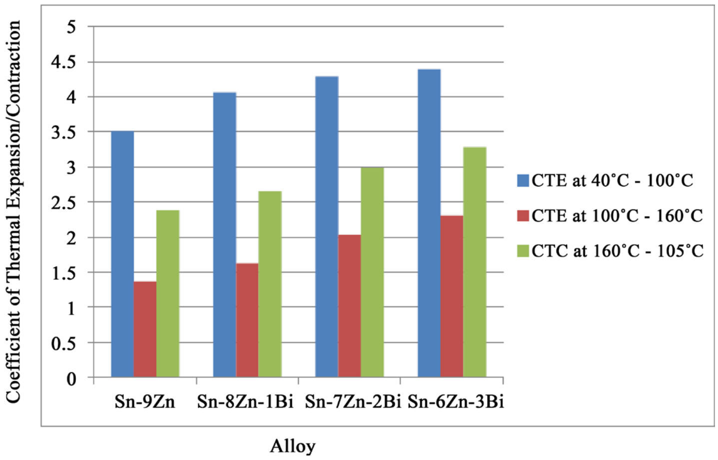


Figure 3. CTC/CTE of Sn-(9-x)Zn-xBi alloy.

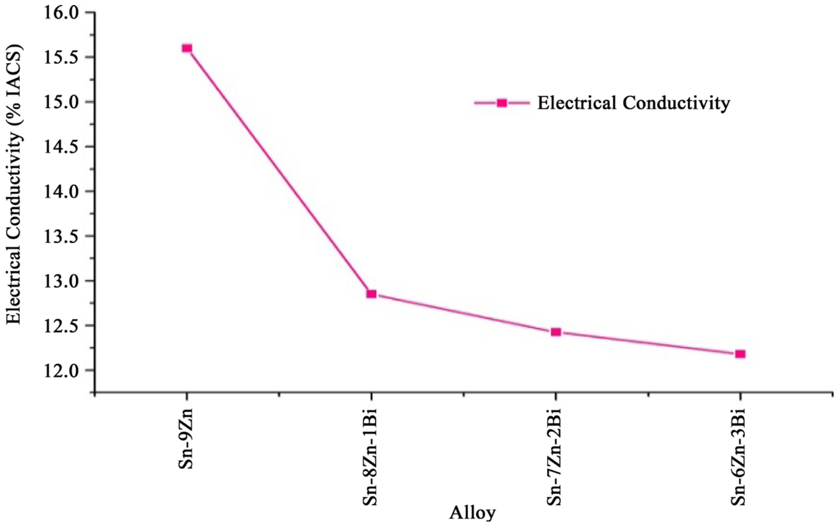


Figure 4. Electrical conductivity of Sn-Zn-Bi alloy.

temperature but the numerical value of CTE is less than that of the low temperature. Co-efficient of thermal contraction (CTC) of Sn-9Zn alloy increases with addition of Bi. 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]. From DTA it is observed that Bi decreases the melting temperature of Sn-9Zn alloy. Low melting points means low bonding energy which decreases the CTE.

3.3. Electrical Conductivity of Sn-(9-x)Zn-xBi

Figure 4 shows the electrical conductivity of Sn-(9-x) Zn-xBi alloy. It shows that the conductivity is continuously decreases with Bi addition. Bi is soluble in β-Sn and up to 3wt.% Bi can remain in solid solution. The implication of this would be to expect some contribution to hardening from solid solution [13] [22]. Bi rich platelets are observed in SEM microstructure of Sn-6Zn-3Bi alloy (**Figure 2(d)**).The continuous decrease of conductivity can be attributed to solid solution of high resistance Bi phase in solder matrix, which acts as scattering centers for conduction electrons in crystals [26]. Similar criteria were reported by other author [27].

4. Conclusion

Eutectic Sn-Zn alloy and three Sn-Zn-Bi ternary alloys were cast. Melting behavior, thermal expansion and contraction and electrical conductivity were investigated. Thermal properties of Sn-Zn alloy changes with Bi addition. Melting point decreases with Bi addition. Coefficient of thermal expansion and coefficient of thermal contraction increase with Bi addition. Electrical conductivity decreases with Bi addition.

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