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Effects of alloying elements on physical properties of tin-antimony based lead free solder alloys

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ABSTRACT

In order to prevent pollution of the environment with lead the use of tin/ antimony lead free solder alloy with some alloying elements is the best solder alloys for high temperature applications. Also a lower tin content in solder is very important issue because it results in slower intermetallic growth, thinner inter metallic layer, which is because tin reacts with the base metal form an alloy. In this study the effects of alloying elements on structure and some physical properties, such as resistivity, melting temperature, pasty range elastic modulus, hardness and internal friction of tin- antimony lead free solder alloy have been investigated using different experimental methods. $Sn_{93}Sb_5Bi_2$ alloy has lowest electrical resistivity value compared to the electrical resistivity ($34x10^{-8}$ Ω.m) of Sn-Pb commercial solder alloy. $Sn_{93}Sb_5Bi_1$ alloy has higher elastic modulus value.

KEYWORDS

Tin based lead free solder alloys;
Pasty rang;
Melting point;
Electrical and mechanical properties.

INTRODUCTION

Solders are generally described as fusible alloys with liquidus temperatures below 400 ºC. Due to the toxicity of Pb present in Sn/Pb solders, alternative solders need to be considered. As a general rule, most lead free solders melt at temperatures higher than those of tin-lead. The exceptions are alloys containing indium or bismuth, which tend to lower the melting point. Low melting point solders such as Sn/Zn and Sn/Bi alloys are expected to be used as a substitute for the Sn/Pb eutectic solder, because the melting temperatures of these solders are much closer to or less than of the Sn/ Pb eutectic solder compared to other Pb free solders. The soldering temperature can be raised above 160 ºC if the soldering time is shorted. These conditions provide high quality bonding and increase through put. Most Pb free solders are Sn-based alloys with additions of low melting metals such as Bi, Sb, and In or metals forming a eutectic reaction with Sn such as Ag and Cu. Some of these alloys have been used for component assembly with excellent results, however, their use in printed circuit board[1]. Also properties and soldering properties of lead free solders (e.g. Sn-Bi, Sn-In, Sn-Ag and Sn- Zn) are extensively studied[2-5]. Sn/Bi and Sn/Ag are cost effective (approximately the same cast as Sn/Pb alloys) and the alternative solder alloys used for electronics. Physical properties, such as electrical, thermal and mechanical, of Sn/Bi, Sn/In and Sn/Ag with other elements additions are extensively investigated in

Ref.[6-13]. The purpose of this study is to investigate the effects of adding bismuth or Zinc on structure and physical properties of tin-antimony alloy.

EXPERIMENTAL WORK

The $Sn_{95-x}Sb_5Bi_x$ (x=0 or x≤2) and $Sn_{95-x}Sb_5Zn_x$ (x=0 or x4) alloys were made, from high purity tin, antimony, bismuth and zinc as supplied by Prolabo Chemical Corporation (France), by conventional melting techniques. The resulting ingots were turned and re-melted at least four times to increase the homogeneity of the ingots. From these ingots long ribbons of a bout 4 mm width and ~ 70 μm thickness were prepared by a single roller method with surface velocity 31 m/s. The structure of these prepared alloys was examined by conventional X-ray diffraction and the electrical resistivity was measured by a conventional double bridge method. The melting endotherms were obtained using a Shimadzo thermal analyzer. Vickers hardness values were measured by a digital Vickers micro-hardness tester (Model-FM-7- Japan). The internal friction Q^{-1}, the thermal diffusivity, D_{th}, and the elastic constants were determined using the dynamic resonance method. The value of the dynamic Young's modulus, E, is determined from the following relationship[14-16].

$$\left(\frac{E}{\rho}\right)^{1/2} = \frac{2\pi L^2 f_0}{kz^2}$$

Where ρ is the density of the sample under test, *L* is the length of the vibrated part of the sample, k is the radius of gyration of cross section perpendicular to its plane of motion, f_0 is the resonance frequency and *z* is the constant depends on the mode of vibration and is equal to 1.8751. From the resonance frequency f_0 at which the peak damping occurs, the thermal diffusivity, D_{th}, can be obtained directly from the following equation:

$$D_{th} = \frac{2d^2 f_0}{\pi}$$

Where *d* is the thickness of the sample.

Plotting the amplitude of vibration against the frequency of vibration around the resonance f_0 gives the resonance curve, the internal friction, Q^{-1}, of the sample can be determined from the following relationship:

$$Q^{-1} = 0.5773\frac{\Delta f}{f_0}$$

RESULTS AND DISCUSSIONS

Low levels of Sb addition are known to improve the mechanical properties of Sn and to inhibit the allotropic transformation. The alloy with 5% Sb is being used for soldering plumbing fixtures. The physical properties of $SnSb_5$ rapidly solidified alloy, such as its electrical resistivity, melting point and its mechanical properties (elastic modulus, hardness, internal friction) are greatly affected by adding Bi or Zn to it.

X-ray diffraction patterns, Figure 1, of $Sn_{95-x}Sb_5Bi_x$ (x=0 or x≤2) and $Sn_{95-x}Sb_5Zn_x$ (x=0 or x4) alloys show that sharp lines of body-centered tetragonal Sn phase and dissolved Sb atoms in Sn matrix. Zinc atoms may be dissolved on grain boundary/or clustered in small cluster in the Sn- Sb matrix, which is appeared as small sphere in scanning electron micrographs by adding Zn to Sn- Sb alloy as shown in Figure 2. The analysis of x-ray diffraction patterns shows that adding Bi or Zn caused modification on the alloy's matrix structure such as changed in phases feature (intensity, position and brooding peaks). Also scanning electron micrographs confirmed the change in matrix structure.

Resistivity is one of the fundamental electrical prop-

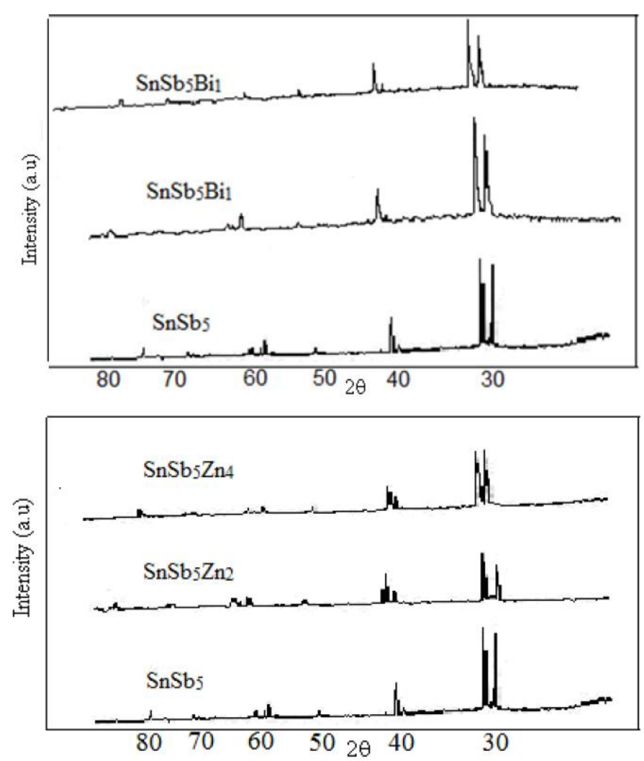

Figure 1 : X-ray diffraction patterns of $SnSb_5$, $SnSb_5Zn$ and $SnSb_5Bi$ alloys.

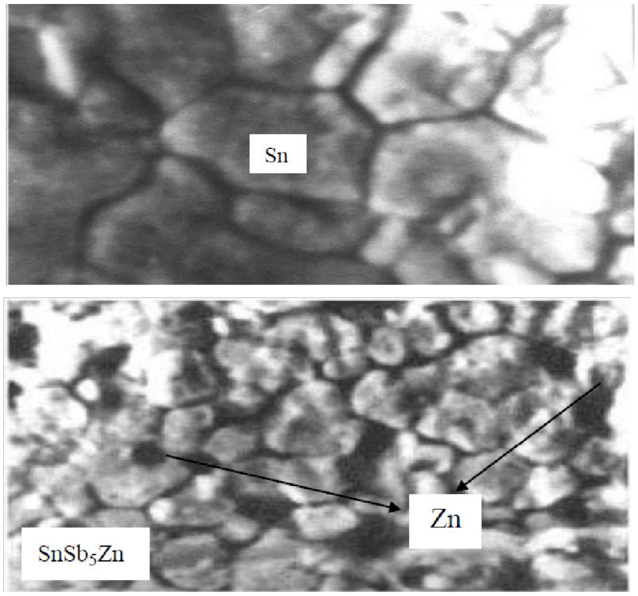

Figure 2 : Scanning electron micrographs of Sn, Sn-Sb and Sn-Zn.

erties of solder. For most electronics applications, the resistivity of solder is relatively low. The electrical resistivity of $SnSb_5$ alloy varied by adding Zn or Bi to it as shown in Figure 3. That is because Bi or Zn atoms dissolved in the matrix causing a change in the Sn- Sb matrix such as crystal size with dissolved Sb atoms in matrix or Zn atoms sticking in the grain boundary. $Sn_{93}Sb_5Bi_2$ alloy has lowest electrical resistivity value compared to the electrical resistivity ($34x10^{-8}$ Ω.m) of Sn-Pb commercial solder alloy. Temperature coefficient of resistivity (T. C. R) of $SnSb_5$ alloy varied by adding Zn or Bi to it as shown in Figure 4.

Thermal conductivity of $SnSb_5$ alloy varied by add-

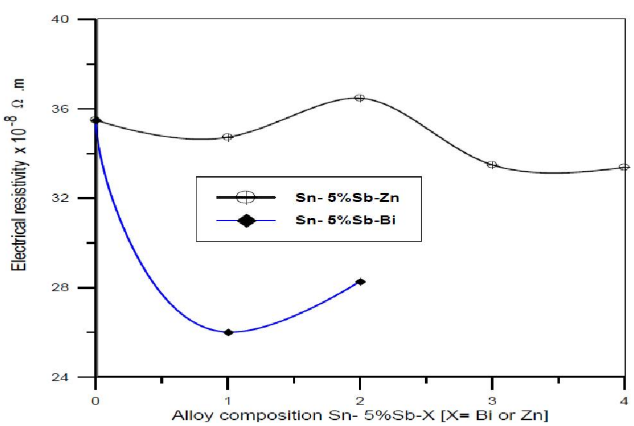

Figure 3 : Electrical resistivity of SnSb5X [X= Bi or Zn] alloys.

ing Zn or Bi to it as shown in Figure 5. $Sn_{93}Sb_5Bi_1$ alloy has highest thermal conductivity value.

An elastic modulus which is influenced consider-

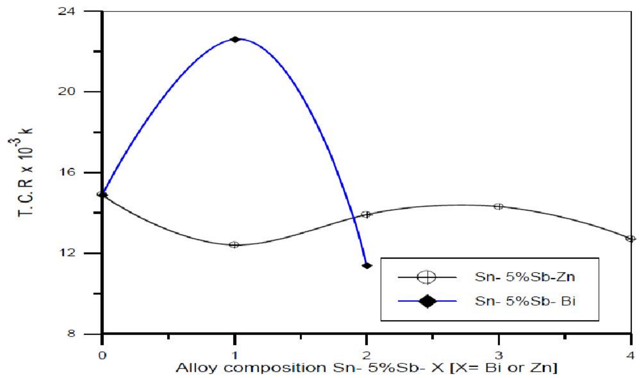

Figure 4 : T. C. R of SnSb5X [X= Bi or Zn] alloys.

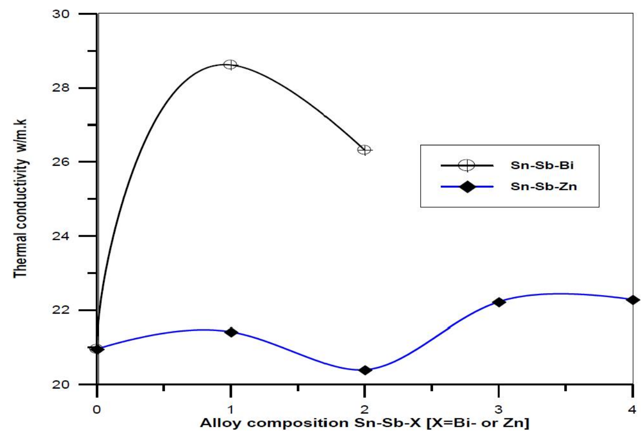

Figure 5 : Thermal conductivity of SnSb5X [X= Bi or Zn] alloys.

ably by microstructure is important as a basic physical constant also for solder. The elastic modulus of $SnSb_5$ alloy is varied by adding Zn or Bi to it as shown in Figure 6. That is because Bi or Zn dissolved in the matrix causing a change in the Sn- Sb matrix such as crystal size and Zn sticking in the grain boundary which affects on the matrix bond. $Sn_{93}Sb_5Bi_1$ alloy has higher elastic modulus value. Values of bulk modulus, B, shear modulus, μ, Fracture strain, σ_f and maximum tensile stress, μ_m, are tabulated in TABLE 1. It is also interesting to note that Ledbetter's theoretical value of μ/E is in good agreement with the experimental data[17].

Figure 7 : Shows the internal friction of $SnSb_5$ alloy which is varied by adding Zn or Bi to it. $SnSb_5Zn_4$ alloy has lower internal friction (lower lost energy through working) value.

Vickers hardness value of $SnSb_5$ alloy is varied by adding Zn or Bi to it as shown in Figure 8. $SnSb_5Zn_4$ alloy has higher Vickers hardness value.

The $SnSb_5X$ (X=Zn or Bi) alloys have higher melt-

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TABLE 1 : Bulk modules (B), shear modules (μ), fracture strain and maximum tensile stress of $SnSb_5X$ [X= Bi or Zn] alloys.

Alloy	σ_f (10^{-3})	μ_m (MPa)	B (GPa)	μ (GPa)	μ / E
$Sn_{95}Sb_5$	1.19	32.5	26.81	8.56	0.37
$Sn_{94}Sb_5Zn_1$	1.75	32.93	18.32	5.90	0.367
$Sn_{93}Sb_5Zn_2$	2.71	75.41	26.81	8.71	0.37
$Sn_{91}Sb_5Zn_4$	3.98	101.59	24.1	7.95	0.37
Alloy	**σ_f (10^{-3})**	**μ_m (MPa)**	**B (GPa)**	**μ (GPa)**	**μ / E**
$Sn_{94}Sb_5Bi_1$	1.74	47.74	37.49	12	0.37
$Sn_{93}Sb_5Bi_2$	1.17	32.58	30.25	6.48	0.37

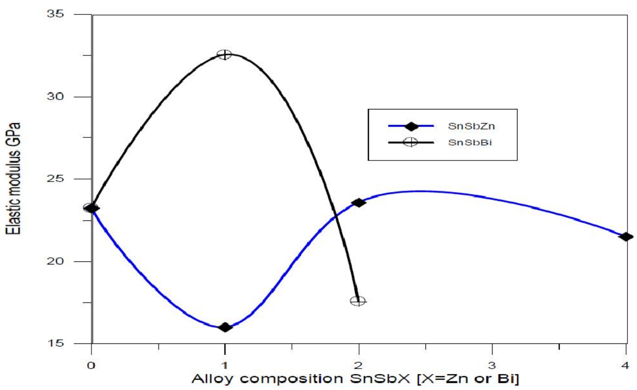

Figure 6 : Elastic modulus of $SnSb_5X$ [X= Bi or Zn] alloys.

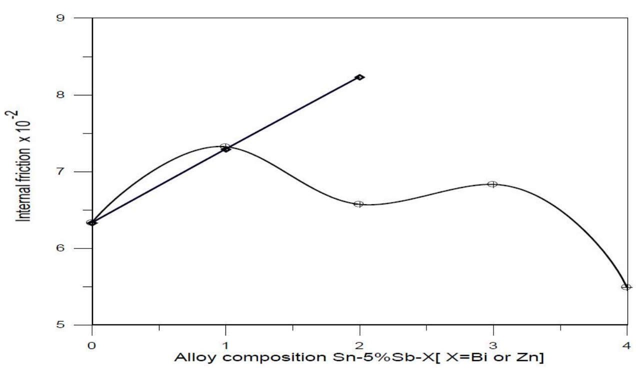

Figure 7 : Internal friction of $SnSb_5X$ [X= Bi or Zn] alloys.

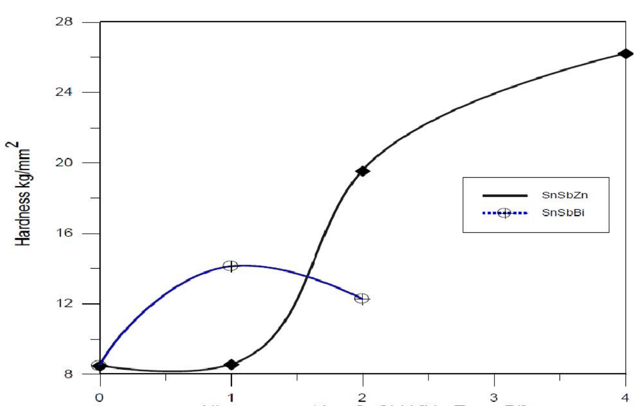

Figure 8 : Vickers hardness value of $SnSb_5X$ [X= Bi or Zn] alloys.

ing points with high pasty range compared to Sn-Pb alloy as shown in Figure 9. The pasty ranges (the difference between soldius and liqidius temperatures). The term pasty range is useful for these alloys give them chance to spread on the (wetting area increases) used substrate (copper). The melting point value of $SnSb_5$ alloy decreased but pasty range value increased by adding Zn or Bi to it as shown in Figure 9.

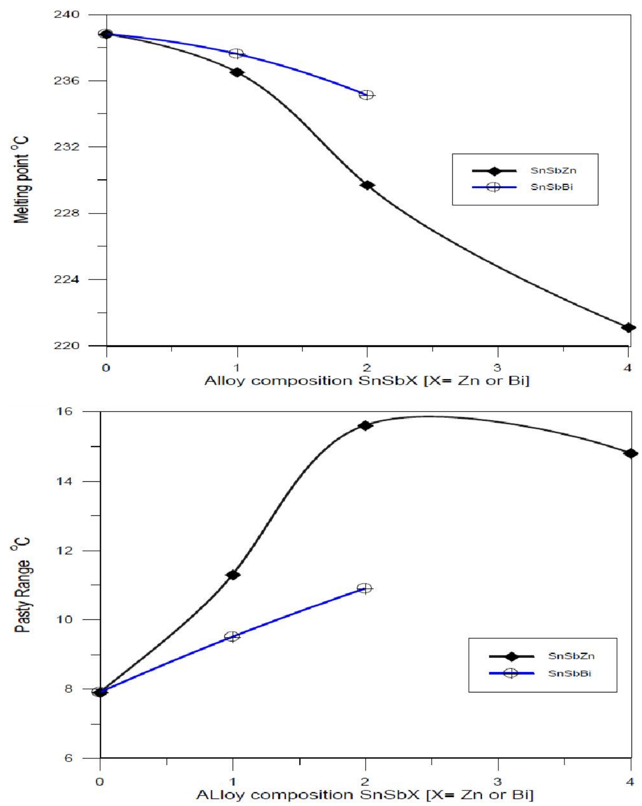

Figure 9 : Melting points and pasty range values of $SnSb_5X$ [X= Bi or Zn] alloys.

CONCLUSION

1. The physical properties (such as electrical resistivity, thermal conductivity, melting point elastic modulus, hardness, internal friction and pasty range) of $SnSb_5$ affected by adding Bi or Zn to it. That is because these elements caused a modification structure on Sn matrix.
2. The $SnSbZn_4$ alloy have a good properties for high temperature solders applications such as high values of electrical conductivity, elastic modulus, hardness and lower lost energy through working with low melting point.

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