

Modification Structure of Tin-Based Alloys and Effects on their Properties for Electronic Industrial

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Abstract

The aim of research is to design alloy with superior solder properties as a solder in industrial applications. To do that, different experimental techniques were used to study the structure and physical properties of tin (Sn) based alloy with added antimony (Sb)- bismuth (Bi)- zinc (Zn). Choosing different ratio from these alloying elements to improve soldering properties. X-ray analysis and scanning electron micrographs for $\text{Sn}_{93-x}\text{Sb}_7\text{Bi}_x$ ($x=0, 8, 18$ and 28) and $\text{SnSb}_7\text{Bi}_{18}\text{Zn}_3$ alloys show tetragonal β - Sn, rhombohedral Bi phase, Sb-Sn and Sn-Bi intermetallic phases with dissolved atoms as a solid solution. Adding bismuth to $\text{Sn}_{93}\text{Sb}_7$ alloy decreased crystal size and melting temperature with increasing hardness. $\text{SnSb}_7\text{Bi}_{18}\text{Zn}_3$ alloy has superior solder properties as melting temperature and wettability for electronic industrial application.

Key words: tin-based solder alloys, wettability, microstructure, hardness

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1. Introduction

Soldering is defined as the joining of two base materials through a third filler metal a melting temperature below the substrates. Generally, solders based on tin containing binary and ternary alloys, and several elements selected alloying elements added as zinc or bismuth or copper or silver or antimony [1- 3]. Solders divided into eutectic and non-eutectic alloys. Non-eutectic solder alloys have a solidus and liquidus region, eutectic solder alloys have definite melting temperature. Some ^{researches} show that, adding different alloying elements as bismuth or bismuth-indium to $\text{Sn}_{96.5}\text{Ag}_{3.5}$, $\text{Sn}_{99.3}\text{Cu}_{0.7}$, $\text{Sn}_{91}\text{Zn}_9$, $\text{Sn}_{96}\text{Zn}_4$ and $\text{Sn}_{96}\text{Zn}_4$ alloys led to a change in microstructure, elastic modulus, thermal behavior, internal friction and contact angle [4- 8]. Tin- zinc eutectic solder alloy has poor wettability, reliability, strength, easy oxidation and micro-void formation, to avoid disadvantages or improve properties added small amount of Bi or Cu or In or Ag or Al or Ga or Sb or Cr or Ni or Ge elements for consisting ternary and quaternary alloys [9- 12]. Tin- zinc eutectic alloy has low melting point, excellent mechanical properties and low cost for solder applications [13-15]. El-Bediwi et al studied structure, thermal parameters, internal friction, wettability and electrochemical corrosion behavior of $\text{Bi}_{30}\text{Sn}_{50}\text{Sb}_{10}\text{Al}_5\text{Zn}_3\text{Cu}_2$, $\text{Bi}_{25}\text{Sn}_{61}\text{Sb}_5\text{Zn}_4\text{Al}_3\text{Ag}_2$, and $\text{Bi}_{20}\text{Sn}_{60}\text{Sb}_7\text{Al}_5\text{Zn}_3\text{Cd}_3\text{Cu}_2$, alloys using different experimental techniques, the results show, some properties of $\text{Bi}_{60}\text{Sn}_{40}$ alloy improved after adding Sb-Zn or Sb-Ag elements [16-19]. The aim of this work is to design new solder alloy from tin based alloy by

adding different alloying elements {bismuth and antimony to improve melting point and strength and zinc to improve corrosion resistance}.

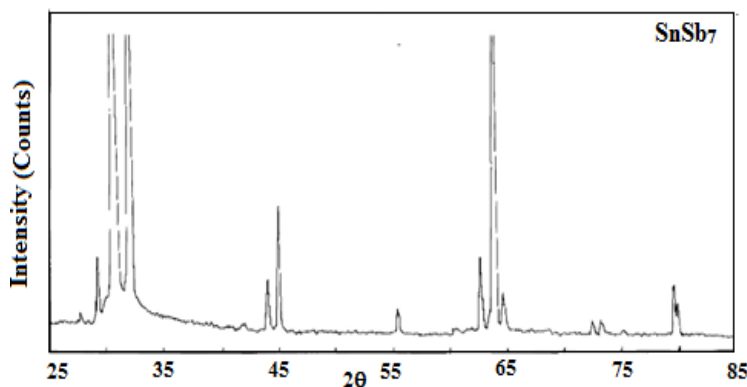
2. Materials and methods

Tin, bismuth, antimony and zinc metals with purity more than 99.9 % were used to prepare $\text{Sn}_{93-x}\text{Sb}_7\text{Bi}_x$ ($x=0, 8, 18$ and 28) and $\text{SnSb}_7\text{Bi}_{18}\text{Zn}_3$ alloys. These mixed metals weight percentage melted and normal 2casted on substrate and prepared in convenient shape for all tests {structure, thermal parameters and hardness}. Structure of alloys studied using Shimadzu X-ray Diffractometer {(Dx-30, Japan), Cu-K α radiation with $\lambda=1.54056 \text{ \AA}$ at 45 kV and 35 mA and Ni-filter, in the angular range 2θ ranging from 0 to 100° in continuous mode with a scan speed 5 deg/min} and scanning electron microscope (JEOL JSM-6510LV, Japan). The DSC thermographs obtained by Universal V4. 5A TA Instrument with heating rate 10 k/min in the temperature range 0-400 °C. The Vickers hardness value of used alloys was measured by a digital Vickers microhardness tester (Model-FM-7, Japan) at indentation load 10 gf and indentation time 5 sec.

3. Results and discussion

Microstructure

X-ray diffraction patterns of $\text{Sn}_{93-x}\text{Sb}_7\text{Bi}_x$ ($x=0, 8, 18$ and 28) and $\text{SnSb}_7\text{Bi}_{18}\text{Zn}_3$ alloys, Figure 1, have sharp lines of tetragonal β - Sn, rhombohedral Bi phase, Sb-Sn and Sn-Bi intermetallic phases with dissolved atoms forming a solid solution. The details of x-ray analysis of used alloys which comes from device (2θ , Int. %, $d \text{ \AA}$, FWHM and area) and cards (phase and Miller indices) are listed in Table 1. The peak intensity, peak broadness, peak position, miller indices and area under peaks of $\text{Sn}_{93}\text{Sb}_7$ alloy changed after adding different ratio of bismuth or zinc as shown in Table 1. Lattice parameters (a and c), volume of unit cell (V) and crystal size (τ) of β - Sn phase in $\text{Sn}_{93-x}\text{Sb}_7\text{Bi}_x$ ($x=0, 8, 18$ and 28) and $\text{SnSb}_7\text{Bi}_{18}\text{Zn}_3$ alloys are determined and listed in Table 2. A little variation in lattice parameters and unit volume cell of β - Sn phase with a major variation in crystal size after adding different ratio from bismuth. Adding bismuth to $\text{Sn}_{93}\text{Sb}_7$ alloy decreased crystal size with increasing volume of unit cell. From the relation between full width half maximum (β) and $4\tan\theta$, the induced internal lattice micro-strain of $\text{Sn}_{93-x}\text{Sb}_7\text{Bi}_x$ ($x=0, 8, 18$ and 28) and $\text{SnSb}_7\text{Bi}_{18}\text{Zn}_3$ alloys calculated then listed in Table 3. The lattice strain of $\text{Sn}_{93}\text{Sb}_7$ alloy is increased after adding bismuth and zinc for it.



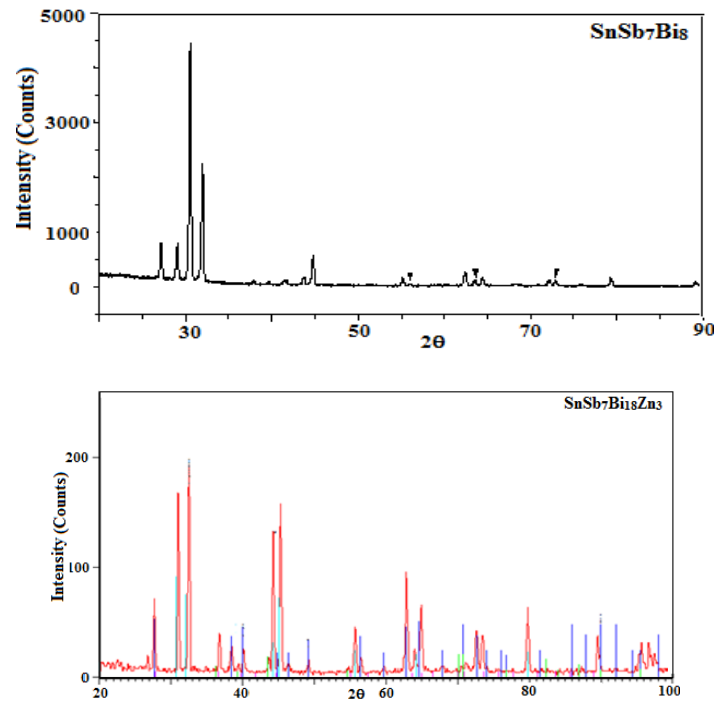


Figure 1: X-ray diffraction patterns of used alloys

Table 1: X-ray diffraction analysis of used alloys

X- ray analysis of Sn ₉₃ Sb ₇ alloy				
2θ	d Å	hkl	Phase	Int.%
27.7	3.22	012	Sb	17
29.3	3.05	202	Sn-Sb	30
31	2.88	200	Sn	100
32.2	2.78	101	Sn	100
42	2.15	110	Sb	9
44	2.06	220	Sn	23
45	2.01	211	Sn	46
54.4	1.69	301	Sn	14
62.7	1.48	112	Sn	30
64	1.45	400	Sn	100
64.6	1.44	321	Sn	18.5
72.4	1.30	420	Sn	9.5
73.2	1.29	411	Sn	10
79.6	1.20	312	Sn	21.5
79.8	1.20	312	Sn	15

X- ray analysis of SnSb ₇ Bi ₁₈ alloy				
2θ	d Å	hkl	Phase	Int.%
27.7	3.22	012	Sb	17.16
31.13	2.88	101	Sn	57.74
32.48	2.76	101	Sn	100
38.43	2.34	104	Bi	9.83
40.12	2.25	110	Bi	7.81
44.24	2.05	220	Sn	22.19
45.3	2.02	211	Sn	66.53
49.2	1.85	202	Bi	6.04
55.69	1.65	301	Sn	17.09
62.84	1.48	112	Sn	22.52
64.1	1.45	400	Sn	5.66
64.87	1.44	321	Sn	18.33
72.69	1.30	321	Sn	6.48
73.38	1.29	411	Sn	10.83
79.73	1.20	312	Sn	20.74
89.57	1.09	306	Bi	6.33
95.74	1.04	431	Sn	5.62

X- ray analysis of SnSb ₇ Bi ₁₈ Zn ₃ alloy				
2θ	d Å	Phase	hkl	Int. %
27.70	3.22	Sb	012	17.16
31.13	2.87	Sn	101	57.74
32.48	2.76	Sn	101	100
38.43	2.34	Bi	104	9.83
40.11	2.25	Bi	110	7.81
44.24	2.05	Bi	015	22.19
45.3	2.00	Sn	211	66.53
49.20	1.85	Bi	202	6.04
55.69	1.65	Sn	301	17.09
62.84	1.48	Sn	112	22.52
64.10	1.45	Sn	400	5.66
64.87	1.44	Sn	321	18.33
72.69	1.30	Sn	321	6.48
73.38	1.29	Sn	411	10.83
79.73	1.20	Sn	312	20.74
89.57	1.09	Bi	306	6.33
95.74	1.04	Sn	431	5.62

Table 2: Lattice parameters, crystal size and volume of unit cell of used alloys

Alloys	τ Å	a Å	c Å	V (a ² .c) (Å ³)
Sn ₉₃ Sb ₇	462.62	5.859	3.14	108.14
Sn ₈₅ Sb ₇ Bi ₈	330.27	5.869	3.21	110.2
Sn ₇₅ Sb ₇ Bi ₁₈	279.86	5.859	3.19	109.47
Sn ₆₅ Sb ₇ Bi ₂₈	317.62	5.898	3.17	110.27
SnSb ₇ Bi ₁₈ Zn ₃	295.4	5.823	3.174	107.628

Table 3: Lattice micro-strain of used alloys

Alloys	ϵ
Sn ₉₃ Sb ₇	0.018
Sn ₈₅ Sb ₇ Bi ₈	0.022
Sn ₇₅ Sb ₇ Bi ₁₈	0.028
Sn ₆₅ Sb ₇ Bi ₂₈	0.042
SnSb ₇ Bi ₁₈ Zn ₃	0.031

Scanning electron microscope analysis (SEM)

Figure 2 shows the scanning electron micrographs of Sn_{93-x}Sb₇Bi_x (x=0, 8, 18 and 28) and SnSb₇Bi₁₈Zn₃ alloys. Sn₉₃Sb₇ micrograph has dendrite structure for antimony or antimony-tin phase (white color) and homogenous structure for the matrix tin phase (black color). Sn_{93-x}Sb₇Bi_x micrographs have lamellar structure (tin phase is a gray color; bismuth phase is a black color)

contained white color (which is may be zinc or bismuth-tin or cluster from dissolved atoms) with different shape and size. $\text{SnSb}_7\text{Bi}_{18}\text{Zn}_3$ alloy have a symmetric lamellar structure. From SEM graphs analysis, it obvious that, these alloys have heterogeneous structure.

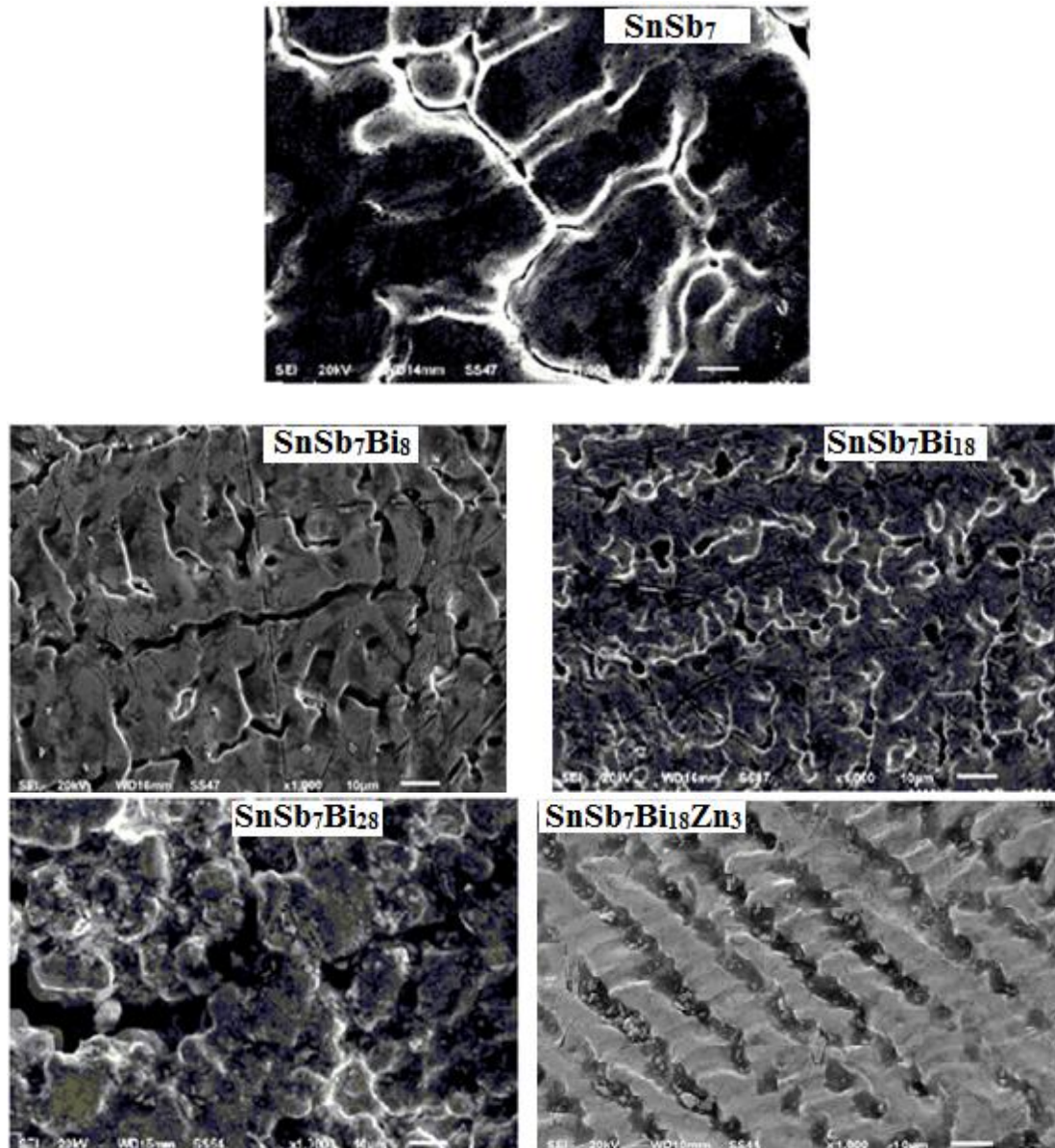


Figure 2: scanning electron micrographs of used alloys

Melting temperature

Thermal analysis depends on the nature of solid phase and temperature, used to study solid state transformations, solid liquid reactions. The melting temperature determined from DSC thermographs, obtained heating rate $10\text{ }^{\circ}\text{C}/\text{min}$ in the temperature range $0\text{--}400\text{ }^{\circ}\text{C}$. The melting temperature of $\text{Sn}_{93-x}\text{Sb}_7\text{Bi}_x$ ($x=0, 8, 18$ and 28) and $\text{SnSb}_7\text{Bi}_{18}\text{Zn}_3$ alloys, listed in Table 4, depend

on alloys composition and less than the eutectic alloys formed from these elements which decreased after adding bismuth and zinc.

Table 4: melting temperature of used alloys

Alloys	Melting temperature °C
Sn ₉₃ Sb ₇	243
SnSb ₇ Bi ₈	229
SnSb ₇ Bi ₁₈	210
SnSb ₇ Bi ₂₈	192
SnSb ₇ Bi ₁₈ Zn ₃	190

Wetting behavior

Wettability quantitatively assessed by the contact angle from the solder substrate's flux triple point. The spreading of Sn_{93-x}Sb₇Bi_x (x=0, 8, 18 and 28) and SnSb₇Bi₁₈Zn₃ alloys on pure Cu substrate in air is shown in Figure 3. Table 5 shows the contact angles of Sn_{93-x}Sb₇Bi_x (x=0, 8, 18 and 28) and SnSb₇Bi₁₈Zn₃ alloys on pure Cu substrate in air. The contact angle (spreading on Cu substrate) of Sn₉₃Sb₇ alloy varied after adding bismuth or zinc. Contact angle dependent on alloy composition (cohesive force and adhesive force) as shown in Figure 3. Also, Sn_{93-x}Sb₇Bi_x (x=0, 8, 18 and 28) and SnSb₇Bi₁₈Zn₃ alloys have good wetting process because the contact angles of them less than 50 °C.

Table 5: contact angle of used alloys

Alloys	Contact angle
Sn ₉₃ Sb ₇	27
SnSb ₇ Bi ₈	28
SnSb ₇ Bi ₁₈	30
SnSb ₇ Bi ₂₈	33
SnSb ₇ Bi ₁₈ Zn ₃	25





Figure 3: spreading of used alloys on pure Cu substrate in air

Hardness measurements and maximum shear stress

The measured Vickers hardness value, H_v , for the $\text{Sn}_{93-x}\text{Sb}_7\text{Bi}_x$ ($x=0, 8, 18$ and 28) and $\text{SnSb}_7\text{Bi}_{18}\text{Zn}_3$ alloys is listed in Table 6. There is an increase in the hardness value of $\text{Sn}_{93}\text{Sb}_7$ alloy after added different ratio of bismuth and zinc contents, attributed to the solution hardening, the substitutional bismuth and zinc atoms cause local elastic strain in the Sn- Sb matrix, this local strain hinders the motion of dislocations and increase the hardness. Also, the hardening, the presence of a dispersion of δ (Sn-Sb) intermetallic compound hard phase increases the hardness.

The maximum shear stress (τ_m) value for $\text{Sn}_{93-x}\text{Sb}_7\text{Bi}_x$ ($x=0, 8, 18$ and 28) and $\text{SnSb}_7\text{Bi}_{18}\text{Zn}_3$ alloys is calculated using the equation [20], where ν is Poisson's ratio of the elements in the alloy and then listed in Table 4.

$$\tau_m = \frac{1}{2} H_v \left\{ \frac{1}{2} (1 - 2\nu) + \frac{2}{9} (1 + \nu) [2(1 + \nu)]^{\frac{1}{2}} \right\}$$

The maximum shear stress (τ_m) for $\text{Sn}_{93-x}\text{Sb}_7\text{Bi}_x$ ($x=0, 8, 18$ and 28) and $\text{SnSb}_7\text{Bi}_{18}\text{Zn}_3$ alloys increased with increasing bismuth content due to dissolved bismuth and zinc atoms in matrix formed hard inclusion as solid solution/or some atoms accumulated to form non-detected traces of phases.

Table 6: Vickers hardness and maximum shear stress for used alloys

Alloys	H _v kg/mm ²	(τ _m) kg/mm ²
Sn ₉₃ Sb ₇	21.05±1.8	6.3
Sn ₈₅ Sb ₇ Bi ₈	29.12±2.1	8.7
Sn ₇₅ Sb ₇ Bi ₁₈	30±2	9
Sn ₆₅ Sb ₇ Bi ₂₈	23±1.9	6.9
Sn ₆₂ Sb ₇ Bi ₁₈ Zn ₃	26±2	7.8

Conclusions

Adding bismuth to Sn₉₃Sb₇ alloy decreased its crystal size and melting temperature with increasing hardness. Also, SnSb₇Bi₁₈Zn₃ alloy has superior solder properties as melting temperature and wettability for electronic industrial application.

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