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Structural morphology, electrochemical corrosion behavior, electrical, thermal and mechanical properties of quenched tin- bismuth alloys

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ABSTRACT

This study investigated structural morphology, electrochemical corrosion behavior, thermal, electrical and mechanical properties of quenched tin-bismuth alloys using different experimental techniques. The Bi-Sn phase is appeared after adding 50% Bi in tin- bismuth alloy. Corrosion rate of tin-bismuth alloy in different chemical solutions (0.5 M HNO₃, 0.5 M H₂SO₄, 0.5 M HCl) is increased by increasing the bismuth amounts in it. Elastic modulus and melting point values of tin- bismuth alloy is decreased by increased the bismuth amounts in it but electrical resistivity value is highly increased by increased the bismuth amounts in it. Internal friction and thermal diffusivity values of tin- bismuth alloy are varied with increasing the bismuth amounts in it. Enthalpy, Solidus and Liquidus points are calculated from DTA thermograph. Our results show that, SnBi₃₀ is the best solder alloy for electronic industrial application compared to commercial Pb- Sn solder alloy. © 2009 Trade Science Inc. - INDIA

KEYWORDS

Structural morphology;
Corrosion;
Elastic modulus;
Enthalpy;
Alloy.

INTRODUCTION

Fusible alloys are low melting temperature compositions containing bismuth, lead, tin, cadmium or indium. There is increasing technological interest in low melting point alloys suitable for use in soldering with lead free materials. Low-melting alloys are found in heat-treatment bath for tempering tools, chain links, or special steel strip for springs and razor blades. They can be used, with little or no loss and their applications are only limited by man's ability to find solutions to the most complex applications. Moreover, there are many other end-uses, i.e. solders, conventional, or with melting points low enough to eliminate heat damage to sensitive

microelectronics, fabrics, plastics and foods. They also make permanent seals for multi-glazed insulating panes. Not to forget safety devices melting at predetermined temperatures: fuses, water, sprinklers, and safety valves. Straumanis and Brakss^[1,2] used x-ray techniques to examine the crystallographic relationship between the phases in selected areas of bulk specimens of the Cd-Zn eutectic alloy and studied the orientation characteristics of Bi-Cd, Cd-Sn, Sn-Zn and Al-Si eutectic alloys. Many researches were done to evaluate and discuss structure and physical properties of bismuth- lead and bismuth-tin eutectic alloys, bismuth- lead- tin, bismuth- lead- tin- cadmium, tin- antimony and these alloys with other elements additions^[5-15]. Therefore, the

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scope of the present work is to explore structural morphology, electrochemical corrosion behavior, thermal, electrical and mechanical properties of tin- bismuth fusible alloys.

EXPERIMENTAL WORK

Bismuth and tin alloys were made from high purity bismuth (99.99%) and tin (99.99%) by conventional melting techniques. The resulting ingots were turned and re-melted more times to increase the homogeneity. From these ingots, long ribbons of about 4 mm width and ~50 μm thickness were prepared by a single roller method in air (melt spinning technique). The surface velocity of the roller was 31.4 m/s giving a cooling rate of $\sim 3.7 \times 10^5$ K/s. The samples then cut into convenient shape for the measurements using double knife cutter. The structure of the used alloys was examined by conventional x-ray diffraction and scanning electron microscopy. The electrical resistivity was measured by a conventional double bridge method at various temperatures. The melting endotherms were obtained using a Shimadzo thermal analyzer. Corrosion rate measurements were done in Corrosion laboratory at Faculty of Science, Mansoura University. 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 modulus E is determined by the following relationship^[16-18]:

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

Where ρ the density of the sample under test, L the length of the vibrated part of the sample, k the radius of gyration of cross section perpendicular to its plane of motion, f_0 the resonance frequency and z 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:

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

Where Δf the half width of the resonance curve

RESULTS

X-ray diffraction patterns of tin- bismuth alloys, Figure 1, show sharp lines of tin phase, bismuth phase and Bi- Sn intermediate phase. Bi- Sn intermediate phase is appeared at 60% bismuth. It obvious that adding more bismuth amounts to Sn due change in its Sn-Bi matrix such as forming Bi phase, solid solution of Bi-Sn phase with forming Bi- Sn intermediate phase.

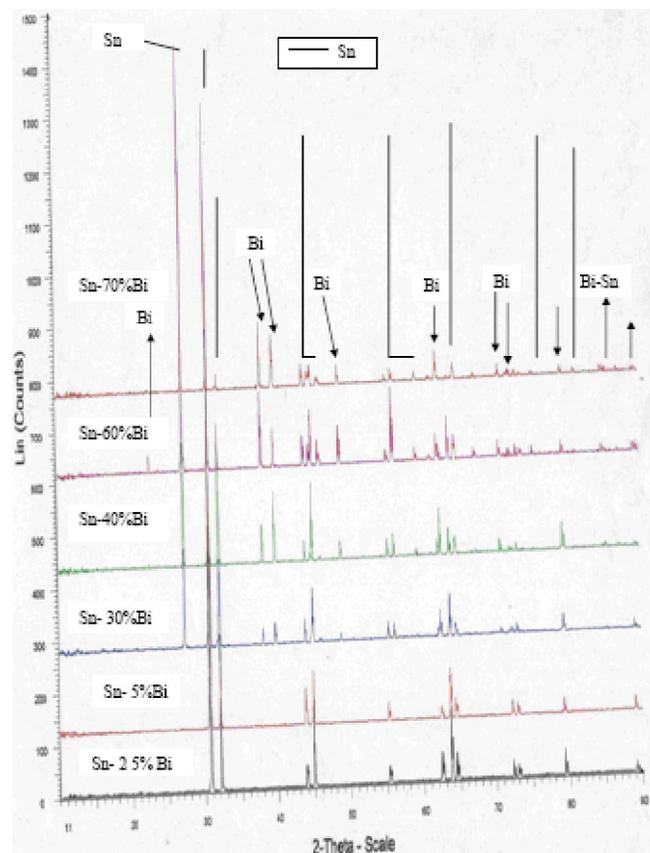


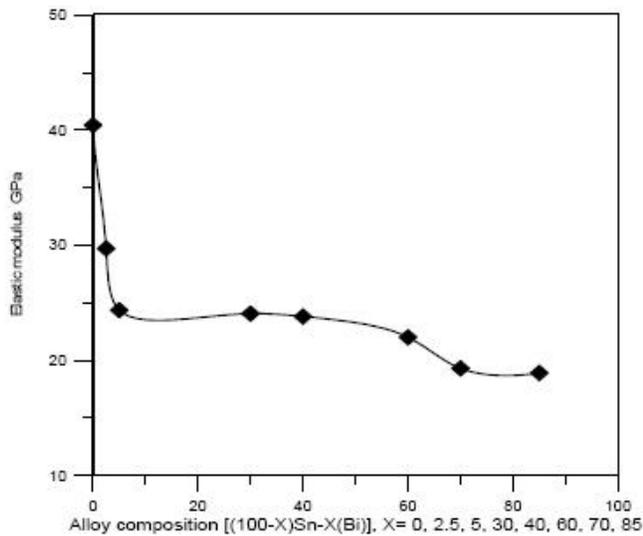
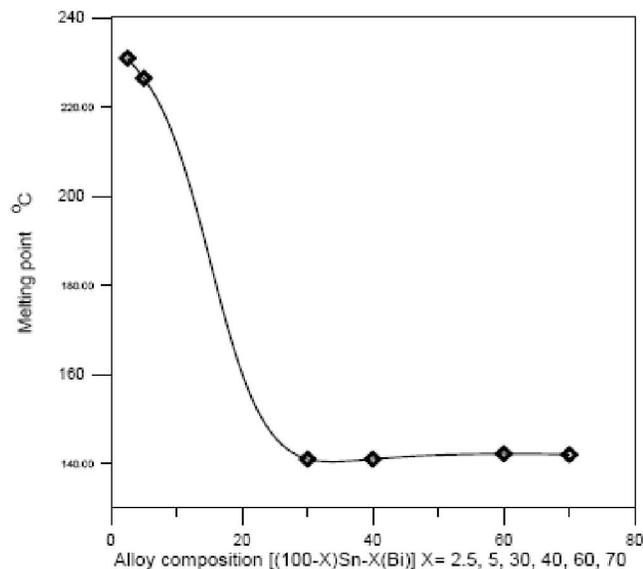
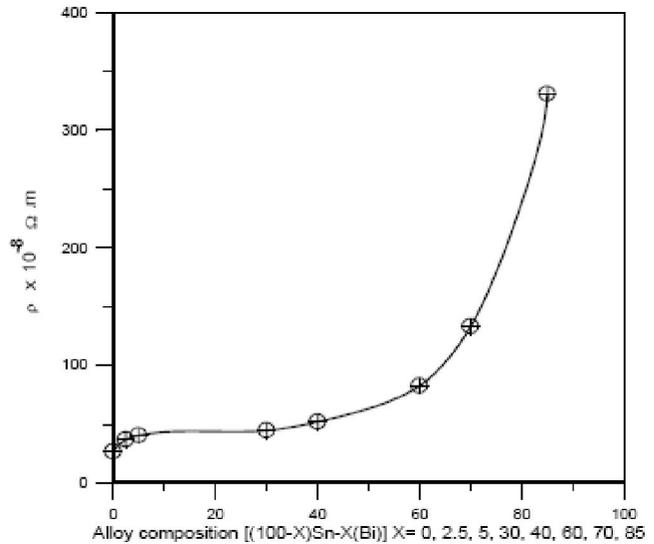
Figure 1 : X-ray diffraction patterns of Sn- Bi alloys

Corrosion rate of tin- bismuth alloy in different chemical solutions (0.5 M HNO_3 , 0.5 M H_2SO_4 , 0.5 M HCl) is increased by increasing bismuth amounts in it as seen in TABLE 1. That is because adding bismuth formed more phases as seen in Figure 1 and increase its segregation phase in Bi- Sn matrix which increase its corrosion rate value.

TABLE 1 : Corrosion rate of Sn –Bi alloys in different chemical solutions

Alloy Solution	Sn-2.5% Bi	Sn-5% Bi	Sn-15% Bi	Sn-30% Bi	Sn-40% Bi
HNO ₃ 0.5M	1.897	2.90	3.682	4.79	5.035
H ₂ SO ₄ 0.5M	1.426	1.678	2.971	3.869	4.782
HCl 0.5m	0.987	1.273	1.402	1.571	2.484

Adding bismuth to tin decreased its elastic modulus and melting point as shown in Figures 2 and 3 but increased its electrical resistivity as shown in Figure 4.

**Figure 2 : Elastic modulus of Sn- Bi alloys****Figure 3 : Melting points of Sn- Bi alloys****Figure 4 : Electrical resistivity of Sn- Bi alloys**

That is because adding bismuth due change in Sn- Bi matrix, (such as dissolved Bi atoms, forming Bi phase and Bi- Sn intermediate phase), which affects on scattering center for conduction electrons (increasing its electrical resistivity) and decreasing its matrix bond strength (decreasing its elastic modulus and melting point).

Temperature coefficient of resistivity is calculated as seen in TABLE 2 and its value is varied by increasing bismuth amounts. From these results it's obvious that temperature coefficient of resistivity is decreased by adding Bi to Sn.

TABLE 2 : Temperature coefficient of resistivity of Sn- Bi alloys

Alloy	T.C.R x10 ⁻³ (k ⁻¹)
Sn	10.04
Sn-2.5% Bi	2.10
Sn-5% Bi	2.53
Sn-30% Bi	2.43
Sn-40% Bi	4.02
Sn-60% Bi	3.74
Sn-70% Bi	3.97
Sn-85% Bi	2.37

Thermal conductivity and thermal diffusivity are essential properties since transfer of heat is involved in many industrial applications and processes. Thermal conductivity is the intrinsic property of a substance describing its ability to conduct heat, where thermal diffusivity indicates how fast the heat is conducted. Thermal conductivity value of Sn- Bi alloy is decreased by

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increased Bi amount as shown in Figure 5 but thermal diffusivity value is increased as seen in TABLE 3.

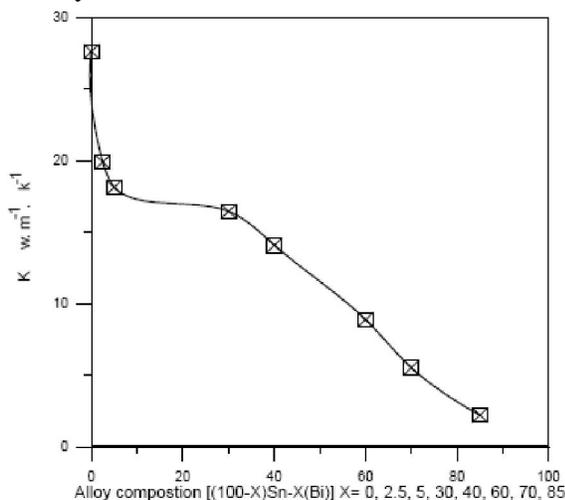


Figure 5 : Thermal conductivity of Sn- Bi alloys

TABLE 3 : Thermal diffusivity of Sn- Bi alloys

Alloy	D _{th} x 10 ⁻⁴ (cm ² . Sec ⁻¹)
Sn-2.5% Bi	2.8
Sn-5% Bi	6.81
Sn-30% Bi	5.73
Sn-40% Bi	4.61
Sn-60% Bi	2.03
Sn-70% Bi	4.53
Sn-85% Bi	10.83

Enthalpy is the heat (gain or loss) in a constant pressure process. Enthalpy is occasionally referred to as the heat content. Enthalpy is known from DTA thermographs as shown in Figure 6 but specific heat is determined from equation:

$$D = K/\rho \times C_p$$

Where D= thermal diffusivity (m². s⁻¹) ρ =density (kg.m⁻³) and

C_p = Specific heat (j. kg⁻¹.k⁻¹)

Internal friction, specific heat and enthalpy values are varied by adding bismuth content to tin- bismuth alloy.

TABLE 4 : Internal friction, specific heat and enthalpy values of Sn- Bi alloys

Alloy	Q ⁻¹	Specific heat (j.kg ⁻¹ .k ⁻¹)	Enthalpy (μv.s/mg)
Sn-2.5% Bi	0.0215	96.66	14.1555
Sn-5% Bi	0.026	35.89	10.1553
Sn-30% Bi	0.034	35.71	2.0697
Sn-40% Bi	0.034	36.88	5.7517
Sn-60% Bi	0.030	49.77	11.1365
Sn-70% Bi	0.033	13.49	7.2619

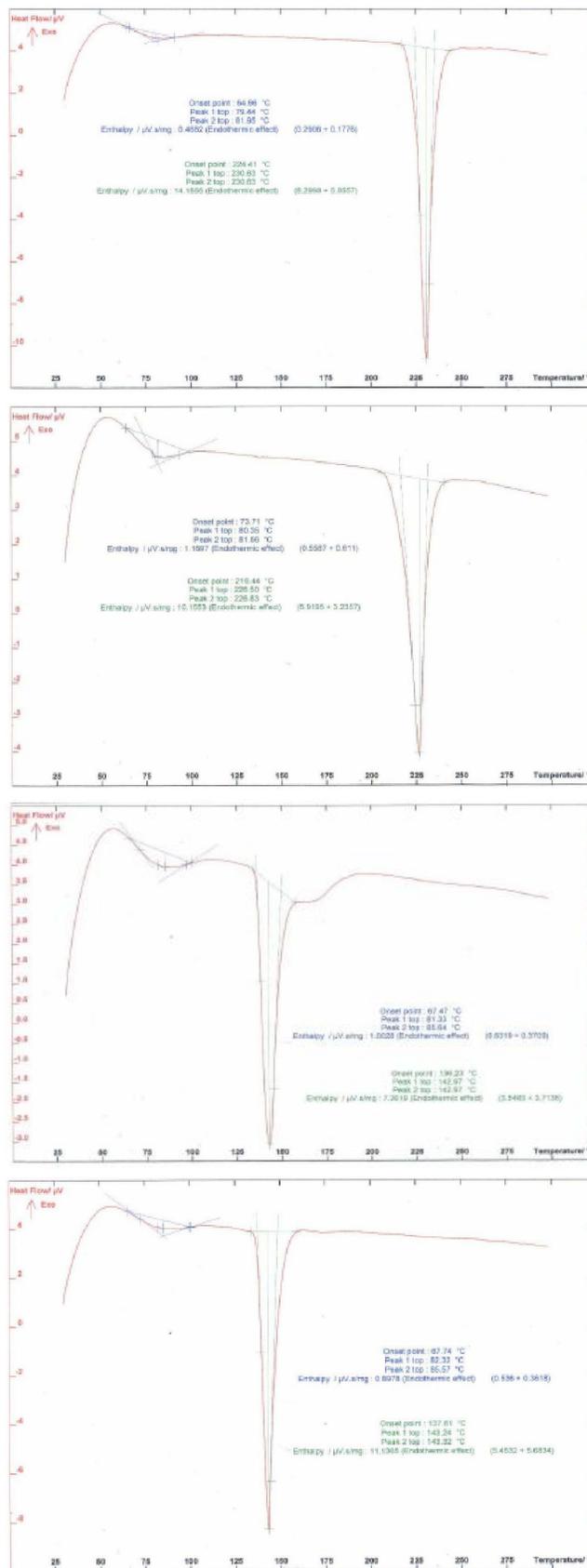


Figure 6 : Thermographs of Sn- Bi alloys

The term pasty range is useful for these alloys give them chance to spread on the (wetting area increases) used substrate (copper). Or those alloys would exist as part liquid for a long time on solidification. This character of the alloys disables themselves from forming reliable joints in the process of welding. From DTA thermograph, the pasty range, (difference between solidus and liquidus temperatures), of rapidly solidified SnSb₃ alloy is increased by adding Bi content as shown in Figure 7.

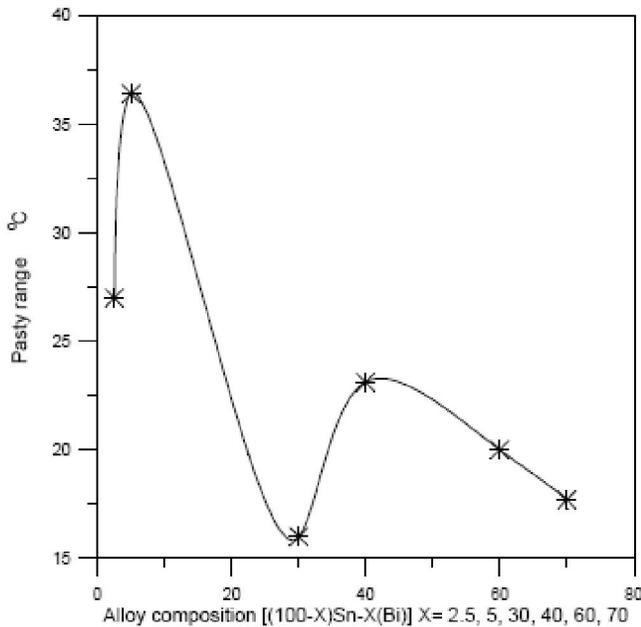


Figure 7 : Pasty range of Sn- Bi alloys

From melting point measurements (DTA thermograph), it possible to know some knowledge about the cohesive energy of used alloy using equation^[20]:

$$T_M = 0.0328 \Delta E/k_B$$

Where T is melting temperature, ΔE is cohesive energy, k_B the Boltzmann's constant

The cohesive energy of Sn- Bi alloy is decreased by increasing Bi amount in it. That is because adding Bi decreasing melting point.

CONCLUSION

- 1- Adding bismuth to tin- bismuth alloy decreases its elastic modulus, thermal conductivity, temperature coefficient of resistivity, specific heat, enthalpy and melting point.
- 2- Adding bismuth to tin- bismuth alloy increases its

electrical resistivity, internal friction and thermal diffusivity.

- 3- Tin- 30 % bismuth alloy has best properties (low values of pasty range, melting point, temperature coefficient of resistivity, enthalpy and adequate values of elastic modulus and electrical resistivity) for low industrial applications such as lead free solder for microelectronic equipments and other applications.
- 4- Corrosion rate of tin- bismuth alloy in different chemical solutions (0.5 M HNO₃, 0.5 M H₂SO₄, 0.5 M HCl) is increased by increasing the bismuth amounts in it

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