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Structural, electrical, mechanical and thermal properties of melt spun bismuth based fusible alloys

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ABSTRACT

The aim of this research was to improve physical properties of bismuth based fusible alloys for different industrial applications. For this reason, two groups of fusible alloys, binary and ternary bismuth based fusible alloys, were prepared using melt spinning technique. Structure, electrical, mechanical and thermal properties of binary and ternary bismuth based fusible alloys were investigated to understand physical properties changing and thermal behavior of binary and ternary bismuth based fusible alloys for improving their required properties for industrial applications. Thermal behavior and physical properties of bismuth based fusible alloys changed correlated to the formation of hexagonal Pb_7Bi_3 intermetallic compound and solid solution after rapid solidification. The $Bi_{62.5}Pb_{25}Cd_{12.5}$ alloy has the lowest melting point, 94 °C. © 2014 Trade Science Inc. - INDIA

KEYWORDS

Structure;
Electrical resistivity;
Elastic modulus;
Melting point;
Hardness;
Melt spun;
Fusible alloy.

INTRODUCTION

Fusible alloys are one such category of materials, which have attracted the attention of scientists and technologists all over the world. Fusible alloys are usually eutectic mixtures of bismuth, lead, tin and cadmium. Because fusible alloys expand and push into mould detail when they solidify, they are excellent for duplication and reproduction processes. This characteristic of expansion and/or non-shrinkage, combined with low melting temperature and ease of handling, are the major reasons for their extensive use. Also rapid solidification has become an important industrial process because of its ability to produce materials with novel properties. It can be used to refine the microstructure, extend the solute solubility, suppress the micro segregation and form metastable phases in the solidified solid[1]. Microstructure electrical resistivity, hardness, creep indentation, mechanical and thermal properties of Bi-Sn-Cd-Pb and Bi-Pb-Sn-Cd-Sb fusible alloys have been studied and analyzed[2-7]. The results gave an indicator for the most prominent alloys for various applications such as solder, bearing and shielding blocks which used in radio therapy. Also the measured properties are greatly affected by rapid quenching preparation. Structure, wettability, melting point, electrical and mechanical properties of Sn-Zn-Bi-Cu-In, Sn-In, Sn-In-Ag, Sn-Zn-Ag-In, Sn-Zn-In, Bi- Sn, Sn-Bi- In and Sn-Ag lead free solder alloys have been investigated[8-13]. The results show that, these alloys have required properties for solder applications. The Sn-3.5%Ag-1%Zn with superior mechanical properties[14] and Sn-Zn-In based alloys with lower melting that are sufficiently similar as to serve as a drop-in replacement for the eutectic Pb-Sn solder[15]. The aim of present work is to understand physical properties changing and thermal behavior of binary and ternary bismuth based fusible alloys for improving their required properties for industrial applications.

EXPERIMENTAL WORK

In this work two groups of fusible alloys, binary and ternary bismuth based fusible alloys, were used as seen in TABLE 1. These groups' alloys were molten in the muffle furnace using high purity, more than 99.95%, bismuth, lead, tin, zinc and cadmium. The resulting ingots were turned and re-melted several times to increase the homogeneity of the ingots. From these ingots, long ribbons of about 3-5 mm width and ~ 70 μm thickness were prepared as the test samples by directing a stream of molten alloy onto the outer surface of rapidly revolving copper roller with surface velocity 31 m/s giving a cooling rate of 3.7×10^5 k/s. The samples then cut into convenient shape for the measurements using double knife cuter. Structure of used alloys was performed using an Shimadzu X–ray Diffractometer (Dx–30, Japan) of Cu–Kα radiation with λ=1.54056 Å 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. Electrical resistivity of used alloys was measured by a conventional double bridge method. The melting endotherms of used alloys were obtained using a SDT Q600 V20.9 Build 20 instrument. A digital Vickers micro-hardness tester, (Model-FM-7- Japan), was used to measure Vickers hardness values of used alloys. Internal friction Q^{-1} and the elastic constants of used alloys were determined using the dynamic resonance method[16-18]:-

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

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:

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

Where Δf is the half width of the resonance curve

TABLE 1 : Composition of melt spun alloys and weight percent of each element

	Composition	Bi wt%	Sn wt%	Pb wt%	Cd wt%
First group	$Bi_{75}Pb_{25}$	75	0	25	0
	$Bi_{87.5}Sn_{12.5}$	87.5	12.5	0	0
	$Bi_{87.5}Cd_{12.5}$	87.5	0	0	12.5
Second group	$Bi_{62.5}Pb_{25}Sn_{12.5}$	62.5	12.5	25	0
	$Bi_{75}Sn_{12.5}Cd_{12.5}$	75	12.5	0	12.5
	$Bi_{62.5}Pb_{25}Cd_{12.5}$	62.5	0	25	12.5

RESULTS AND DISCUSSION

X-ray diffraction analysis

X-ray diffraction patterns and its analysis, Figure 1a, of bismuth based binary melt spun alloys show that, The $Bi_{87.5}Sn_{12.5}$ alloy consisted of rhombohedral bismuth phase and little of tetragonal tin phase, $Bi_{87.5}Cd_{12.5}$ alloy consisted of rhombohedral bismuth phase and little hexagonal cadmium phase and $Bi_{75}Pb_{25}$ alloy consisted of rhombohedral bismuth phase and hexagonal Pb_7Bi_3 phase. Also x-ray diffraction patterns and its analysis, Figure 1b, of bismuth based ternary melt spun alloys show, that, $Bi_{62.5}Pb_{25}Sn_{12.5}$ alloy consisted of rhombohedral bismuth phase, little tetragonal tin phase and hexagonal Pb_7Bi_3 phase, $Bi_{75}Sn_{12.5}Cd_{12.5}$ alloy consisted of rhombohedral bismuth phase and little tetragonal tin phase and $Bi_{62.5}Pb_{25}Cd_{12.5}$ alloy consisted of rhombohedral bismuth phase and little hexagonal cadmium phase. The details of formed phases (intensity,

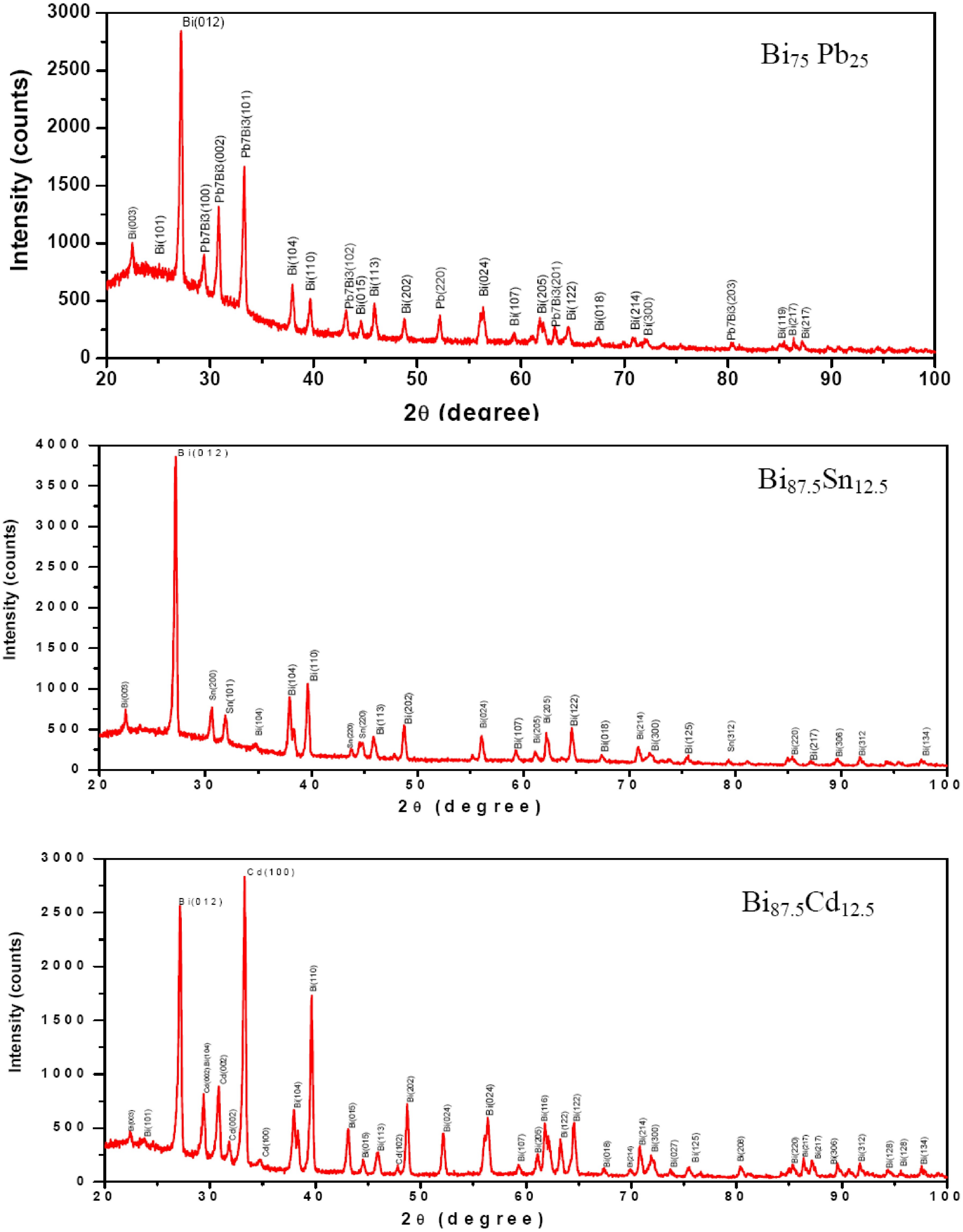

Figure 1a : X-ray diffraction patterns of binary bismuth based alloys

broadness, position and Miller indices) are shown in Figure 1(a and b).

TABLE 2 shows the calculated lattice parameters, (a and c), and the unit volume cell of rhombohedral bismuth phase[19] in binary and ternary bismuth based melt spun alloys. From these results, lattice parameters and unit cell volume of rhombohedral bismuth phase changed related to alloys structural, formed phases, after rapid cooling..

Electrical properties

In general, the plastic deformation raises the electrical resistivity as a result of the increased number of

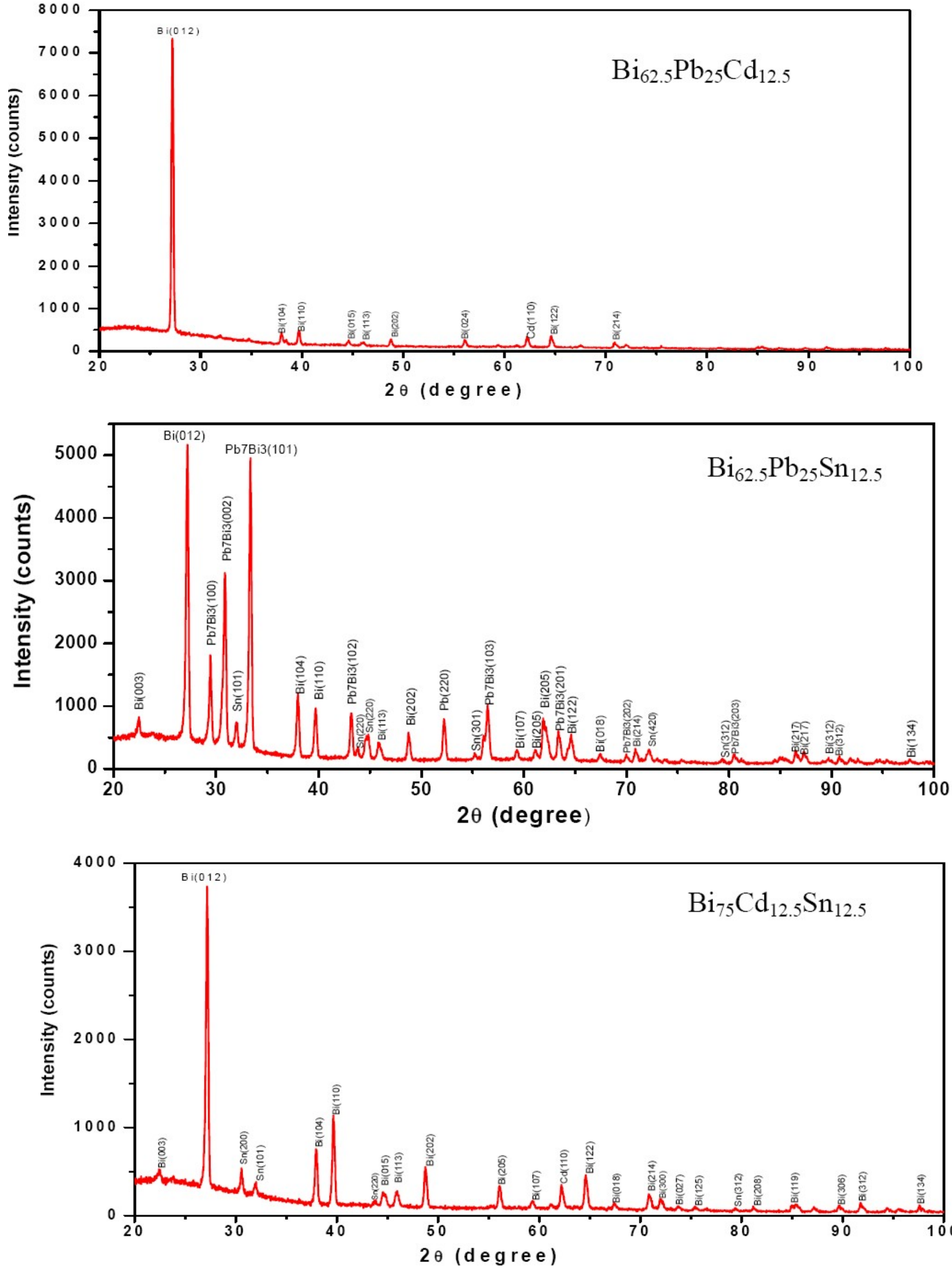

Figure 1b : X-ray diffraction patterns of ternary bismuth based alloys

electron scattering centers. Crystalline defects serve as scattering center for conduction electrons in metals, so the increase in their number raises the imperfection. This depends on temperature, composition and the degree of cold working of a metal specimen. The scattering of electrons may be caused by several types of lattice defects: by phonon scattering, by impurities and by mechanical deformation. For this reason, the rate of rise

TABLE 2 : Lattice parameters, (a and c), and the unit volume cell of rhombohedral bismuth phase in binary and ternary melt spun alloys

Alloys	a_{rho} Å	c Å	Unit cell volume Å ^{3}
$Bi_{75}Pb_{25}$	4.745	11.864	70.68
$Bi_{87.5}Sn_{12.5}$	4.75	11.875	70.89
$Bi_{87.5}Cd_{12.5}$	4.75	11.875	70.89
$Bi_{62.5}Pb_{25}Sn_{12.5}$	4.747	11.877	70.50
$Bi_{75}Sn_{12.5}Cd_{12.5}$	4.748	11.872	70.73
$Bi_{62.5}Pb_{25}Cd_{12.5}$	4.740	11.846	70.48

of electrical resistivity of a metal with temperature is depedent of the small amount of alloying present and of the state of deformation.

The measured electrical resistivity values of binary $Bi_{75}Pb_{25}$, $Bi_{87.5}Sn_{12.5}$, $Bi_{87.5}Cd_{12.5}$ and ternary $Bi_{62.5}Pb_{25}Sn_{12.5}$, $Bi_{75}Sn_{12.5}Cd_{12.5}$, $Bi_{62.5}Pb_{25}Cd_{12.5}$ melt spun alloys at room temperature are listed in TABLE 3. It is obvious that, electrical resistivity values of melt spun alloys are high than the same conventional alloys, that is because the rapid cooling, in fact, freezes the vacancies, which are plentiful at high temperature, because they are not allowed to have enough time to move about in the crystal and disappear at grain boundaries and dislocations. These vacancies act as scattering center for conduction electrons, increasing their number, increasing the resistivity value. Also resistivity value change from one alloy to other related to its structural change, formed phases, as seen in x-ray analysis.

The variation of electrical resistivity of binary $Bi_{75}Pb_{25}$, $Bi_{87.5}Sn_{12.5}$, $Bi_{87.5}Cd_{12.5}$ and ternary $Bi_{62.5}Pb_{25}Sn_{12.5}$, $Bi_{75}Sn_{12.5}Cd_{12.5}$, $Bi_{62.5}Pb_{25}Cd_{12.5}$ melt spun alloys with temperature is shown in Figure 2. It can be seen that the electrical resistivity increased with temperature. The increasing continues until the melting point is reached. Also temperature coefficient of resistivity values for melt spun alloys is listed in TABLE 3.

From the above results, the electrical resistivity and

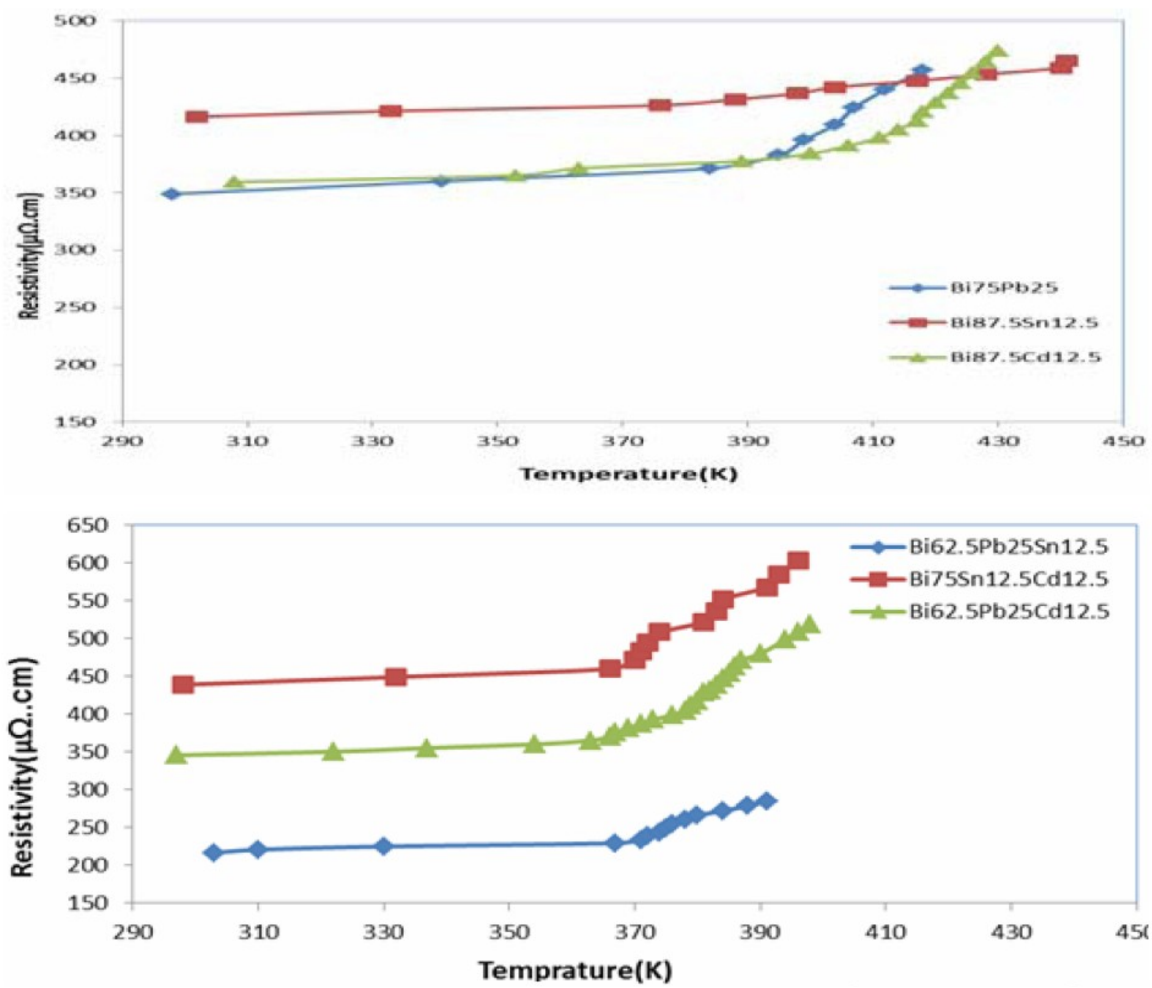

Figure 2 : Electrical resistivity of melt spun alloys versus temperature

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TABLE 3 : Electrical resistivity and temperature coefficient of resistivity of melt spun bismuth based alloys

Alloys	Resistivity x10^{-8} Ω.m	T.C.R x 10^{-3} K^{-1}
$Bi_{75}Pb_{25}$	1.7 ±349.412	2.213
$Bi_{87.5}Sn_{12.5}$	4.2 ±416.442	0.811
$Bi_{87.5}Cd_{12.5}$	1.57±359.45	2.448
$Bi_{62.5}Pb_{25}Sn_{12.5}$	216.51± 1.23	2.945
$Bi_{75}Sn_{12.5}Cd_{12.5}$	345.6± 2.38	5.159
$Bi_{62.5}Pb_{25}Cd_{12.5}$	438.94± 1.25	3.627

temperature coefficient of resistivity values of binary $Bi_{75}Pb_{25}$, $Bi_{87.5}Sn_{12.5}$, $Bi_{87.5}Cd_{12.5}$ and ternary $Bi_{62.5}Pb_{25}$ $Sn_{12.5}$, $Bi_{75}Sn_{12.5}Cd_{12.5}$, $Bi_{62.5}Pb_{25}Cd_{12.5}$ melt spun alloys are increased with increasing Bi content in it. That is because Bi is a semimetal. Also forming metastable phase affects on scattering center for conduction electrons changing electrical resistivity value.

Elastic modulus

The elastic constants of solid are important for both fundamental and practical reasons. The elastic constants are directly related to atomic bonding and structure. It is also related to the atomic density (atomic volume). From a practical view point, the elastic constants describe the linear response of a material to an applied stress.

Values of bulk modulus, B, and shear modulus, μ, of binary $Bi_{75}Pb_{25}$, $Bi_{87.5}Sn_{12.5}$, $Bi_{87.5}Cd_{12.5}$ and ternary $Bi_{62.5}Pb_{25}$ $Sn_{12.5}$, $Bi_{75}Sn_{12.5}Cd_{12.5}$, $Bi_{62.5}Pb_{25}Cd_{12.5}$ melt spun alloys are calculated using the standard equations:

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

Where ν is Poisson's ratio?

After calculating the Young's modulus, E, using the dynamic resonance method is shown in TABLE 4. Elastic modulus value of binary $Bi_{87.5}Cd_{12.5}$ and $Bi_{87.5}Sn_{12.5}$ is high compared than ternary $Bi_{62.5}Pb_{25}$ $Sn_{12.5}$, $Bi_{75}Sn_{12.5}Cd_{12.5}$ and $Bi_{62.5}Pb_{25}Cd_{12.5}$ melt spun. These elastic values changed related to alloys structural,

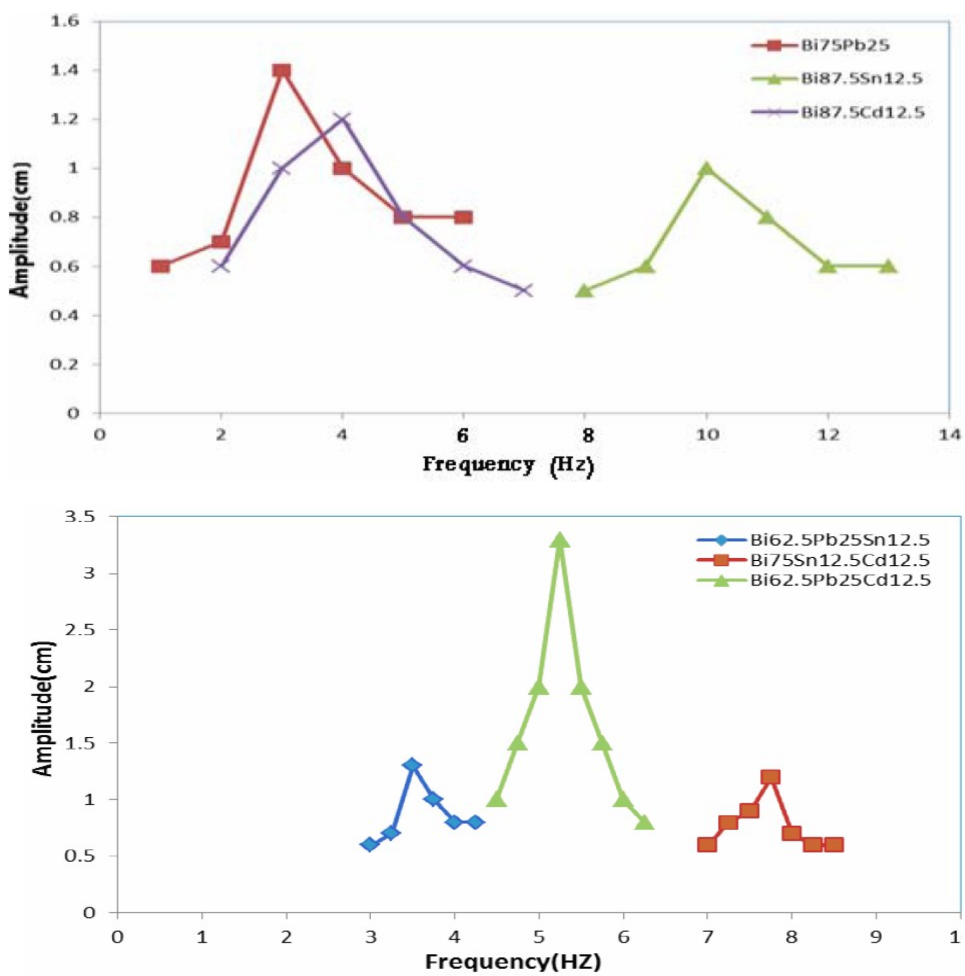
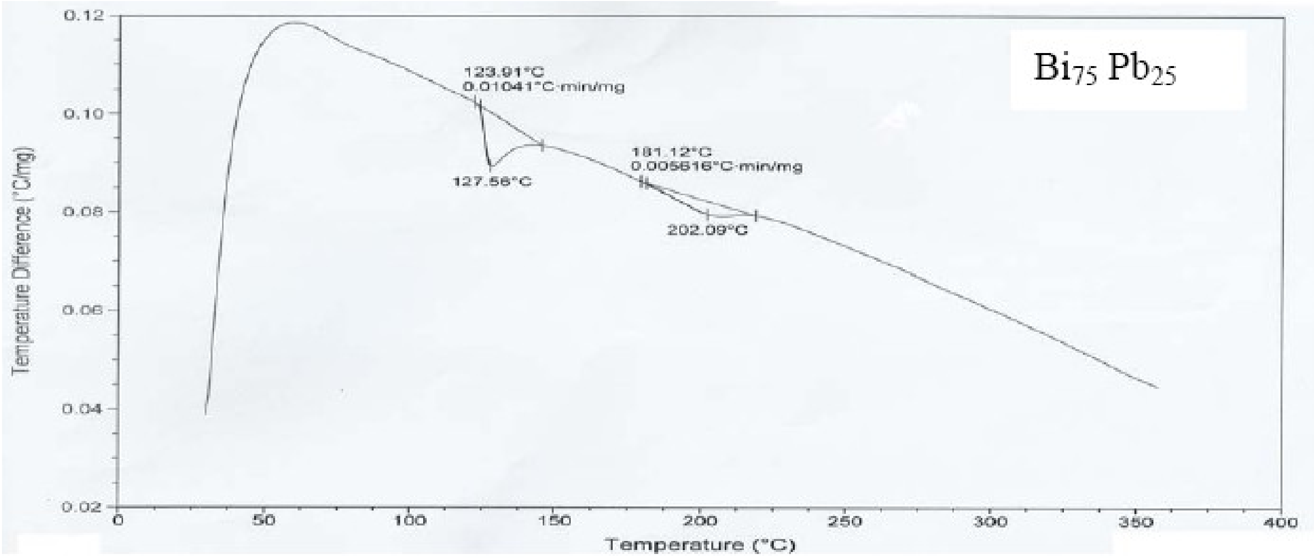
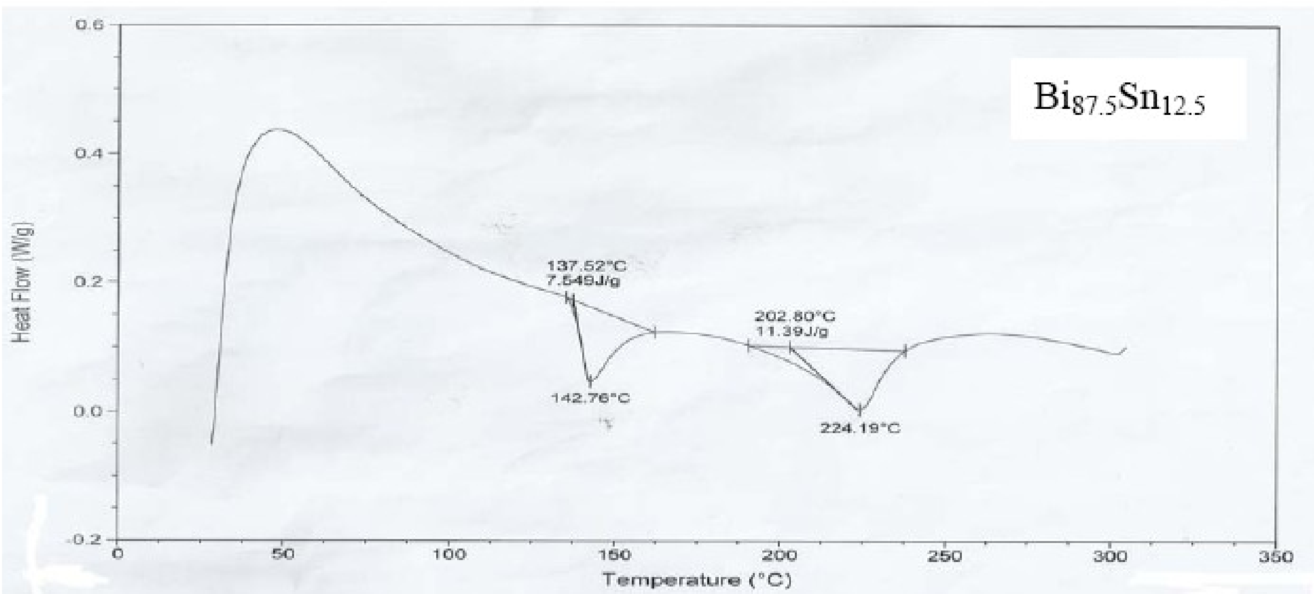
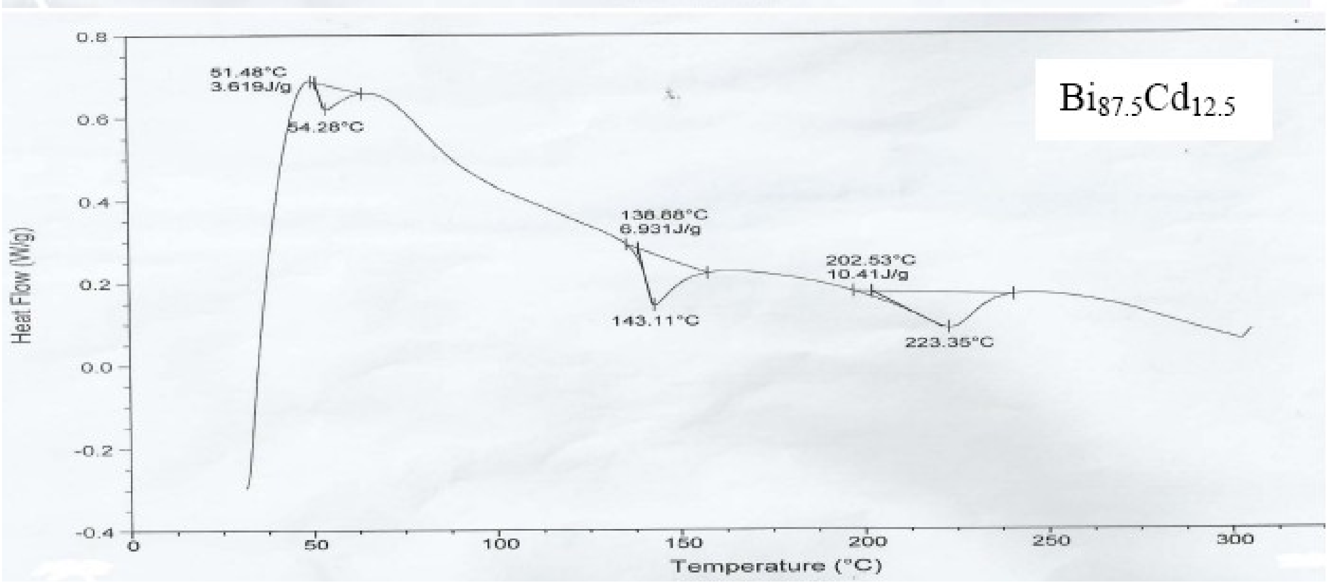


Figure 3 : Resonance curves of melt spun alloys


Bi75 Pb25
123.91°C
0.01041°C·min/mg
127.56°C
181.12°C
0.005616°C·min/mg
202.09°C
Temperature Difference (°C/mg)
Temperature (°C)


Bi87.5Sn12.5
137.52°C
7.549J/g
142.76°C
202.80°C
11.39J/g
224.19°C
Heat Flow (W/g)
Temperature (°C)


Bi87.5Cd12.5
51.48°C
3.619J/g
54.28°C
138.68°C
6.931J/g
143.11°C
202.53°C
10.41J/g
223.35°C
Heat Flow (W/g)
Temperature (°C)

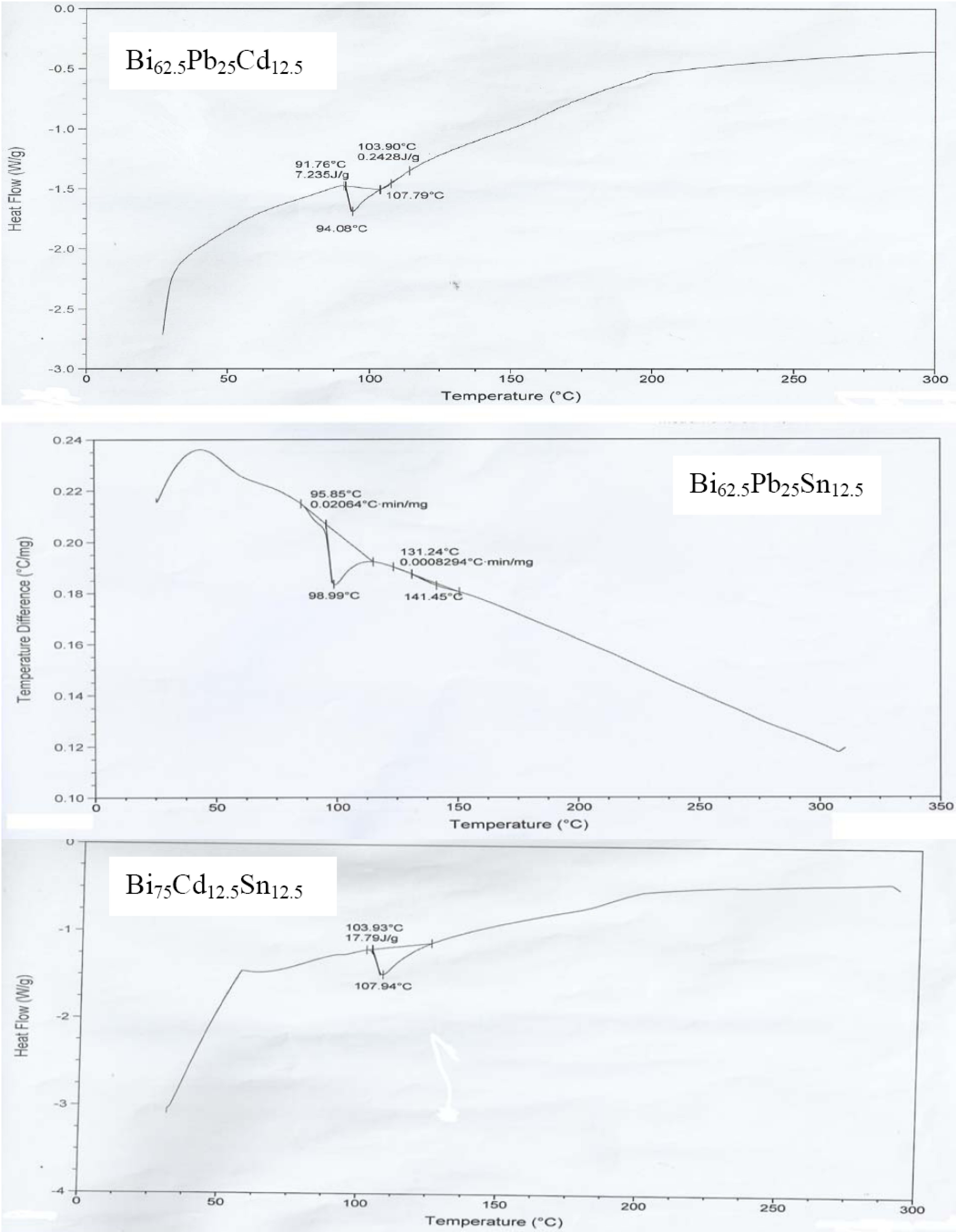


Figure 4 : DSC thermographs of binary and ternary bismuth based alloys

TABLE 4 : Elastic modului of binary and ternary bismuth based melt spun alloys

Alloys	E (GPa)	μ (GPa)	B (GPa)
$Bi_{75}Pb_{25}$	19.36±3	7.13	22.64
$Bi_{87.5}Sn_{12.5}$	35.73±2.57	13.4	35.87
$Bi_{87.5}Cd_{12.5}$	31.67±1.25	11.94	30.38
$Bi_{62.5}Pb_{25}Sn_{12.5}$	21±1.54	7.71	26.23
$Bi_{75}Sn_{12.5}Cd_{12.5}$	24.54±0.98	9.23	24.06
$Bi_{62.5}Pb_{25}Cd_{12.5}$	24.44±10.11	9.03	27.86

TABLE 5 : Internal friction and thermal diffusivity of melt spun alloys

Alloys	$(Q^{-1})\ 10^{-3}$	$D_{th}x10^{-8}$ (m^2/sec)
$Bi_{75}Pb_{25}$	0.42±58.05	3.7
$Bi_{87.5}Sn_{12.5}$	2.75±25.33	31.6
$Bi_{87.5}Cd_{12.5}$	5.73±81.03	3.8
$Bi_{62.5}Pb_{25}Sn_{12.5}$	4.13±73.8	2.09
$Bi_{75}Sn_{12.5}Cd_{12.5}$	2.1±36.52	27.68
$Bi_{62.5}Pb_{25}Cd_{12.5}$	4.15±73.9	4.4

formed phases, as seen in x-ray analysis.

Internal friction and thermal diffusivity

Internal friction is an energy loss or dissipation in a stressed material not due to external process. Internal friction is a useful tool for the study of the structural aspects of fusible alloys. Resonance curves of binary $Bi_{75}Pb_{25}$, $Bi_{87.5}Sn_{12.5}$, $Bi_{87.5}Cd_{12.5}$ and ternary $Bi_{62.5}Pb_{25}Sn_{12.5}$, $Bi_{75}Sn_{12.5}Cd_{12.5}$, $Bi_{62.5}Pb_{25}Cd_{12.5}$ melt spun alloys are shown in Figure 3 and the calculated internal friction values are presented in TABLE 5. From resonance frequency at which the peak damping occur using the dynamic resonance method the thermal diffusivity value calculated and then listed in TABLE 5.

Vickers microhardness and minimum shear stress

The hardness is the property of material, which gives it the ability to resist being permanently deformed when a load is applied. The greater of the hardness is the greatest of the resistance to deformation. The Vickers hardness of binary $Bi_{75}Pb_{25}$, $Bi_{87.5}Sn_{12.5}$, $Bi_{87.5}Cd_{12.5}$ and ternary $Bi_{62.5}Pb_{25}Sn_{12.5}$, $Bi_{75}Sn_{12.5}Cd_{12.5}$, $Bi_{62.5}Pb_{25}Cd_{12.5}$ melt spun alloys at 10 gram force and indentation time 5 sec are shown in TABLE 6. Vickers hardness value of melt spun alloys is affected by structural change, formed phase such as intermetallic compound and solid solution. The minimum shear stress (τ_m) value of bismuth based binary and ternary rapidly solidified alloys was calculated using the equation[20]:-

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

Where ν is Poisson's ratio of the elements in the alloy and then listed in TABLE 6.

TABLE 6 : Vickers hardness and minimum shear stress of melt spun alloys

Alloys	H_V Kg\mm^2	μ_n Kg\mm^2
$Bi_{75}Pb_{25}$	1.29±13.02	0.5±4.3
$Bi_{87.5}Sn_{12.5}$	1.97±15.28	0.98±5.04
$Bi_{87.5}Cd_{12.5}$	0.76±17.87	0.4±5.9
$Bi_{62.5}Pb_{25}Sn_{12.5}$	1.89±6.57	0.9±2.17
$Bi_{75}Sn_{12.5}Cd_{12.5}$	1.56±20.52	0.81±6.77
$Bi_{62.5}Pb_{25}Cd_{12.5}$	0.46±6.98	0.23±2.3

Thermal properties

Thermal analysis is often used to study solid state transformations as well as solid-liquid reactions. The magnitudes of thermal properties depend on the nature of solid phase and on its temperature.

The differential scanning calorimetry (DSC) thermographs were obtained by SDT Q600 (V20.9 Build 20) with heating rate 10 °C /min in the temperature range 0-400 °C. Figure 4 shows the DSC thermographs for the binary $Bi_{75}Pb_{25}$, $Bi_{87.5}Sn_{12.5}$, $Bi_{87.5}Cd_{12.5}$ and ternary $Bi_{62.5}Pb_{25}Sn_{12.5}$, $Bi_{75}Sn_{12.5}Cd_{12.5}$, $Bi_{62.5}Pb_{25}Cd_{12.5}$ melt spun alloys. From these graphs the melting point of binary $Bi_{75}Pb_{25}$, $Bi_{87.5}Sn_{12.5}$, $Bi_{87.5}Cd_{12.5}$ and ternary $Bi_{62.5}Pb_{25}Sn_{12.5}$, $Bi_{75}Sn_{12.5}Cd_{12.5}$, $Bi_{62.5}Pb_{25}Cd_{12.5}$ melt spun alloys are determined. From these thermographs, it's obvious that, binary $Bi_{75}Pb_{25}$, $Bi_{87.5}Sn_{12.5}$ and $Bi_{87.5}Cd_{12.5}$ melt spun alloys did not have a single melting point. That is mean that, these composition are not the eutectic composition, these alloys have a mixture of phases\with different melting point or one phase with forming a solid solution. Ternary $Bi_{62.5}Pb_{25}Sn_{12.5}$, $Bi_{75}Sn_{12.5}Cd_{12.5}$ and $Bi_{62.5}Pb_{25}Cd_{12.5}$ melt spun alloys have a single melting point that is mean that, these compositions are the eutectic composition.

CONCLUSION

1) X-ray diffraction patterns and its analysis for binary and ternary melt spun alloys show that, these

alloys consisted of two phases, Bi& Sn, Bi& Cd, Bi& pb_7Bi_3 or more with forming solid solution. These crystal structure phases, (shape, size and position) is dependent on the alloy composition.

2) Electrical resistivity, mechanical properties and thermal behavior of melt spun bismuth based alloys affected by forming hexagonal pb_7Bi_3 phase and solid solution.

3) After studying and analyzing physical properties of melt spun bismuth based alloys, the next research will concentrated on produce new fusible alloys with superior properties for soldering and bearing by adding different alloying elements such as silver, copper, zinc and indium with reducing lead and cadmium.

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