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Thermo-mechanical and wetting behavior of modified SnAg3.5eutectic solder alloy

Abu Bakr El-Bediwi, Amira El-Shafei, Mustafa Kamal
Metal Physics Lab., Physics Department, Faculty of Science, Mansoura University, Egypt
baker_elbediwi@yahoo.com

Abstract

Effects of adding bismuth content on structure, thermo-mechanical and wetting behavior of $SnAg_{3.5}$ eutectic alloy have been investigated. Matrix structure of $SnAg_{3.5}$ eutectic alloy, such as crystallinity, crystal size and lattice parameters, changed after adding bismuth content which effect on all measured properties. Melting temperature of $SnAg_{3.5}$ eutectic alloy decreased after adding bismuth content. Elastic modulus and contact angle of $SnAg_{3.5}$ eutectic alloy varied after adding bismuth content. The $Sn_{66.5}Ag_{3.5}Bi_{30}$alloy has the best solder properties for electronic applications such as lower melting temperature, contact angle and elastic modulus.

Key words

elastic modulus; contact angle; thermal properties; microstructure; eutectic alloy

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1. Introduction

The solder alloys are binary, ternary and some are even quaternary alloys. Since the properties of the binary Pb-free solders cannot fully meet the requirements for applications in electronic packaging, additional alloying elements were added to improve the performance of these alloys. The melting point of a solder should be low enough to avoid thermal damage to the assembly being soldered and high enough for the solder joint to bear the operating temperatures.Tin- silver based solders have been considered as the first choice for a lead free solder due to its excellent mechanical properties. The eutectic composition for this solder is Sn-3.5wt%Ag and the eutectic temperature is 221 ºC. Its microstructural studies have confirmed the presence of the fine Ag_3Sn needles and β-Sn matrix [1].Addition of Bi into Sn-Ag eutectic alloy reduces its melting temperature effectively and also improves the wettability [2-4]. Addition of small amount of Cu has been found to be advantageous for this binary Sn-3.5Ag solder. The eutectic Sn-Ag-Cu solder properly wets the substrate. Now a day it is widely used in aircraft and automotive industries, where the solder joints are subjected to thermal stresses. Its mechanical properties have been found to be better than that of Sn-Pb solders. Researchers have conducted many experiments to find the exact eutectic composition for this ternary alloy, but still there is a little controversy. The eutectic temperature for this composition has been found to be 2170C [5].The creep rupture properties of Sn–3.5Ag based ternary alloys with varying amounts of Cu or Bi were investigated using rolled and heat-treated bulk specimens. The results show that, The 0.75% Cu specimen have lowest creep rate, while the 10% Bi specimen have highest creep rate [6]. In the present study, we have examined three typical Sn–Ag–Cu near-eutectic alloys, Sn–3.0Ag–0.5Cu,Sn–3.5Ag–0.7Cu and Sn–3.9Ag–0.6Cu, as standard lead-free solders. The effects of strain rates and cooling speeds on various properties of the alloys were investigated [7]. The effects of rare earth Ce doping on the properties of SnAgCu solder alloys were studied [8]. The addition of 0.03% (mass fraction) rare earth Ce into SnAgCu solder may improve its mechanical properties, but slightly lower its melting temperature. It is found that SnAgCuCe solders show higher creep resistance than SnAgCu alloys. The effect of cadmium content on structure, elastic modulus, electrical resistivity, thermal diffusivity and internal friction of SnAg eutectic alloy have been investigated [9]. The aim of this work was to investigate the effects of adding bismuth content on structure, elastic modulus, thermal diffusivity, internal friction, melting temperature and wetting behavior of $SnAg_{3.5}$ eutectic alloy.

2. Experimental work

The tin- sliver- bismuth alloy was molten in the muffle furnace using high purity, more than 99.95%, bismuth, tin and silver. 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 × 10^5k/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 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 [10- 12].

3. Results and discussions

Structure

X-ray diffraction patternsof $Sn_{96.5-x}Ag_{3.5}Bi_x$ (x= 0, 6, 12, 18, 24 and 30 wt. %) rapidly solidified alloys have lines corresponding to β- Sn, Ag_3Sn and hexagonal Bi phases as shown in Figure (1a). The analysis of x-ray patterns show that, adding different ratio of bismuth content to $Sn_{96.5}Ag_{3.5}$alloy caused a change in its matrix microstructure such as lattice parameters and formed crystal structure (crystallinity, crystal size and the orientation) as seen in Table (1a).Lattice parameters, (a and c), and unit volume cell of β- Sn phase in $Sn_{96.5-x}Ag_{3.5}Bi_x$alloys were determined and then listed in Table (1b). Also lattice parameter, a, and unit volume of β- Snin $Sn_{96.5}Ag_{3.5}$increased after adding bismuth content. That is because some Biatoms dissolved in matrix alloy forming solid solution and other accumulated forming Bi phase.

Scanning electron micrographs, SEM, of $Sn_{96.5-x}Ag_{3.5}Bi_x$ (x= 0, 6, 18 and 30 wt. %) alloys show heterogeneity structure as shown in Figure (1b). Microstructure of $Sn_{96.5-x}Ag_{3.5}Bi_x$alloys show β- Sn matrix, needle Ag_3Sn and spherical Bi atoms and that agree with x-ray results.

Thermal properties

Thermal analysis is often used to study solid state transformations as well as solid-liquid reactions. 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 2(a) shows DSC thermographs for $Sn_{96.5-x}Ag_{3.5}Bi_x$ (x= 0, 6, 12, 18, 24 and 30 wt. %)alloys. A little variation in the exo-thermal peaks shape which related to a change inmatrixalloy after adding Bi content. The melting temperature and other thermal properties of $Sn_{96.5-x}Ag_{3.5}Bi_x$alloys are listed in Table 2(a). Melting temperature of $Sn_{96.5}Ag_{3.5}$ alloy decreased after adding Bi content.

Wettability

Wetting is the ability of a liquid to maintain contact with a solid surface, resulting from intermolecular interactions when the two are brought together. Low contact angle, less than 90°, usually indicates that wetting of the surface is very favorable and the fluid will spread over a large area of the surface but high contact angle, greater than 90°, generally means that wetting of the surface is unfavorable so the fluid will minimize contact with the surface and form a compact liquid droplet. Table (2b) shows the contact angles of $Sn_{96.5-x}Ag_{3.5}Bi_x$alloys on Cu substrate. The contact angle of $Sn_{96.5}Ag_{3.5}$alloy increased after adding Bi content up to 24% and then decreased. The photographs of spreading $Sn_{96.5-x}Ag_{3.5}Bi_x$molten alloys on Cu substrate in air are shown in Figure (2b).

Mechanical properties

The elastic constants are directly related to atomic bonding and structure. Elastic modului of $Sn_{96.5-x}Ag_{3.5}Bi_x$alloys are listed in Table (3). Elastic modulus of $Sn_{96.5}Ag_{3.5}$alloydecreased after adding Bi content except 12 and 18% it's increased. That is because adding Bi content to $Sn_{96.5}Ag_{3.5}$ alloy changed its matrix microstructure which effects on atomic bonding.

The resonance curves $Sn_{96.5-x}Ag_{3.5}Bi_x$alloys are shown in Figure (3). Calculated internal friction and thermal diffusivity values of $Sn_{96.5-x}Ag_{3.5}Bi_x$alloys are seen in Table (3). Internal friction of $Sn_{96.5}Ag_{3.5}$alloydecreased after adding Bi content.

Conclusions

Matrix microstructure such as unit cell and formed crystal of $Sn_{96.5}Ag_{3.5}$alloy changed after adding Bi content. Melting point and internal friction of $Sn_{96.5}Ag_{3.5}$alloy decreased after adding Bi content. Elastic modulus, thermal parameters and contact angle of $Sn_{96.5}Ag_{3.5}$alloy varied after adding Bi content. The $Sn_{66.5}Ag_{3.5}Bi_{30}$alloy has the best solder properties for electronic applications such as lower melting temperature, contact angle and elastic modulus.

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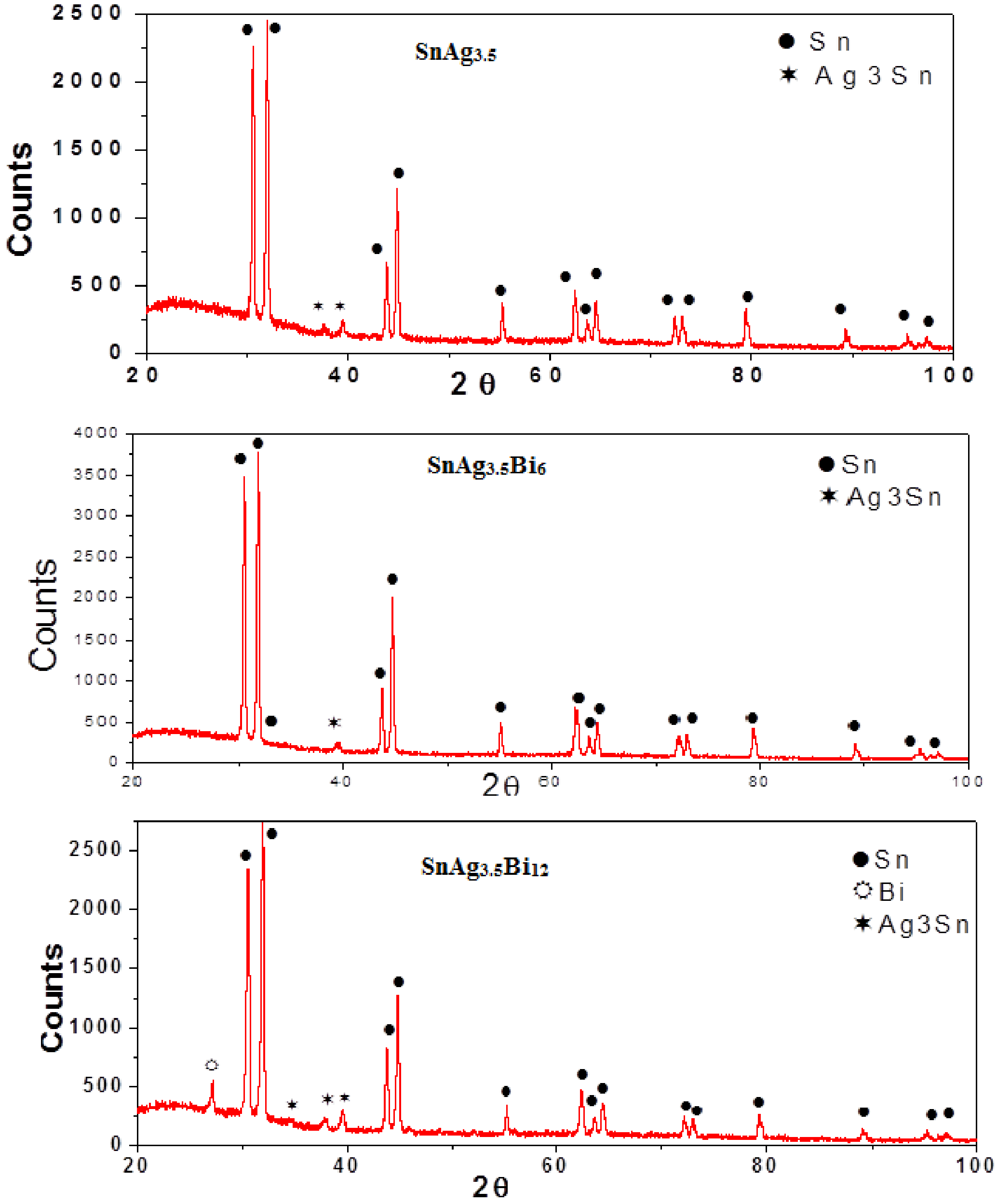

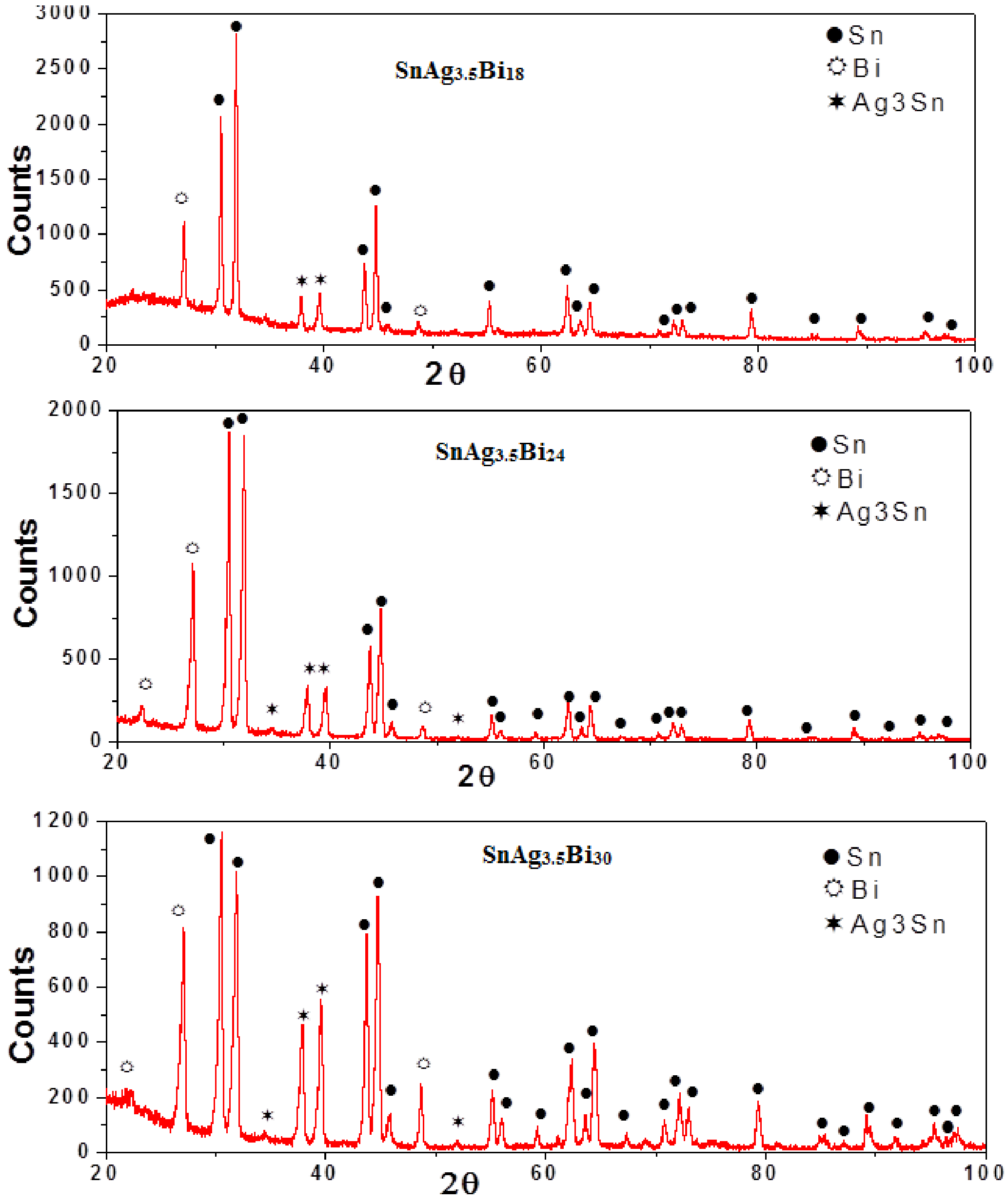

Figure 1a:- x-ray diffraction patterns of $Sn_{96.5-x}Ag_{3.5}Bi_x$alloys

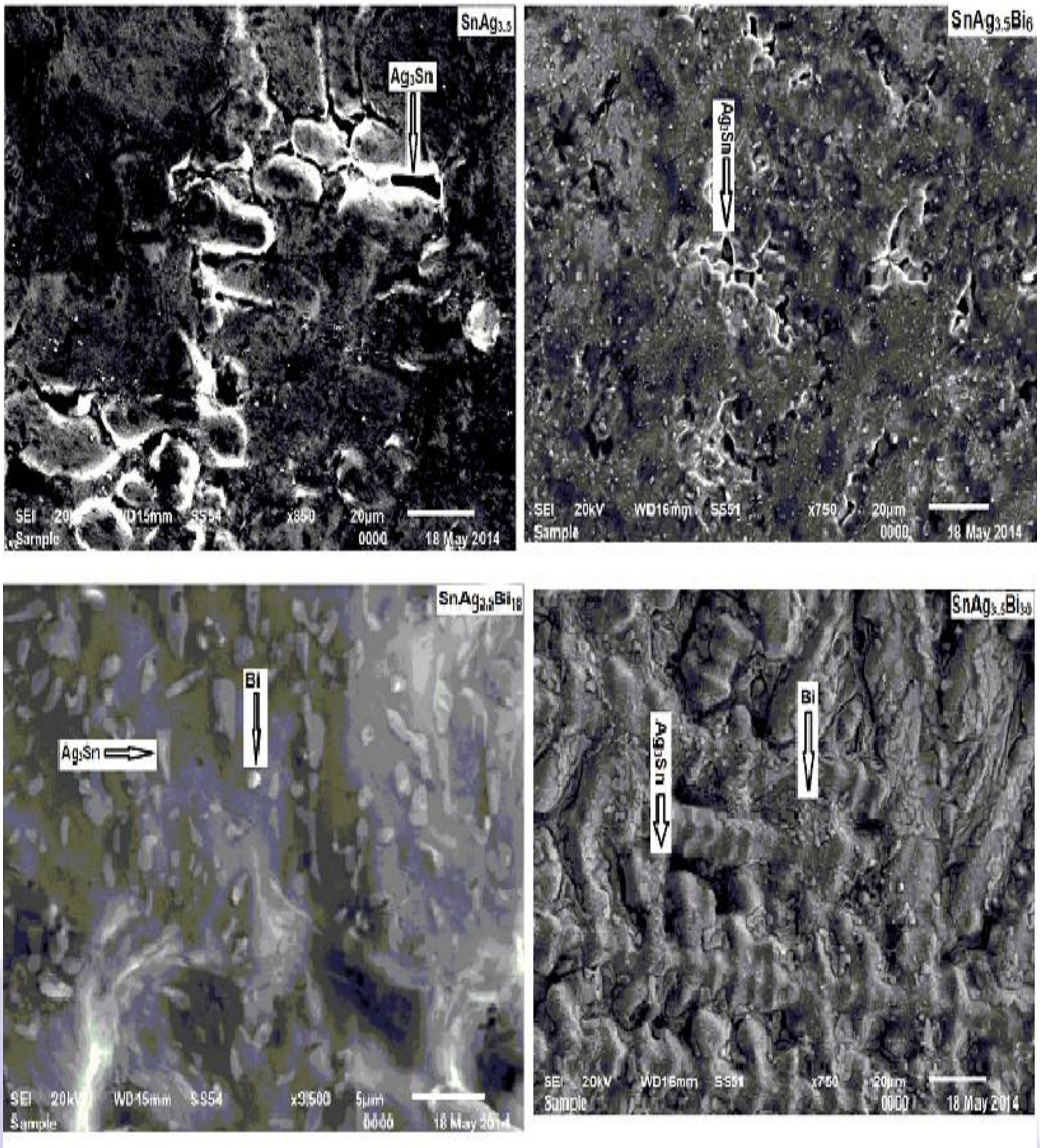

Figure 1b:- SEM of $Sn_{96.5-x}Ag_{3.5}Bi_{x}$alloys

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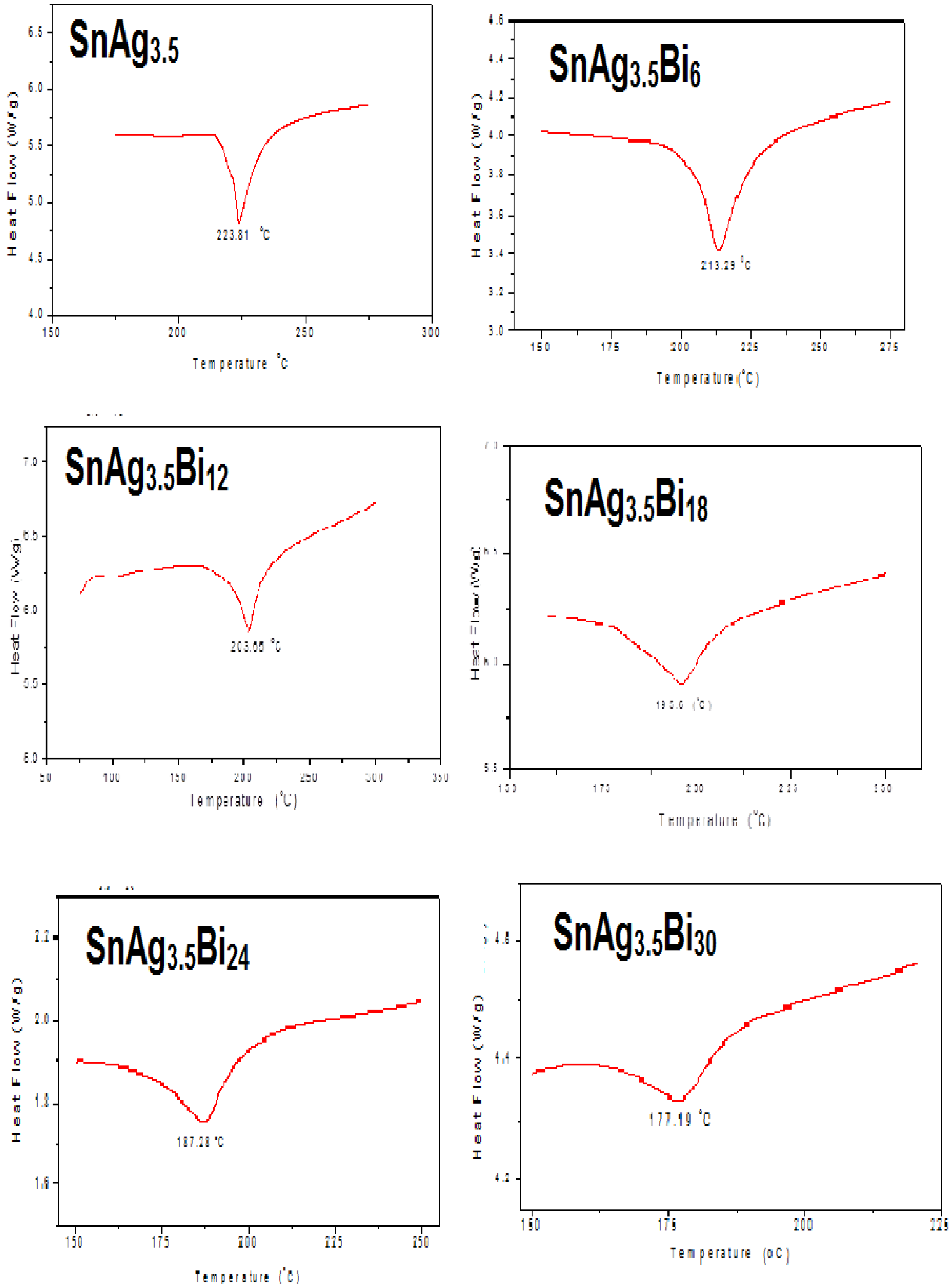

Figure 2a:- DSC thermographs of $Sn_{96.5-x}Ag_{3.5}Bi_x$alloys

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Figure 2b:- Photographs of $Sn_{96.5-x}Ag_{3.5}Bi_x$molten alloys on Cu substratein air

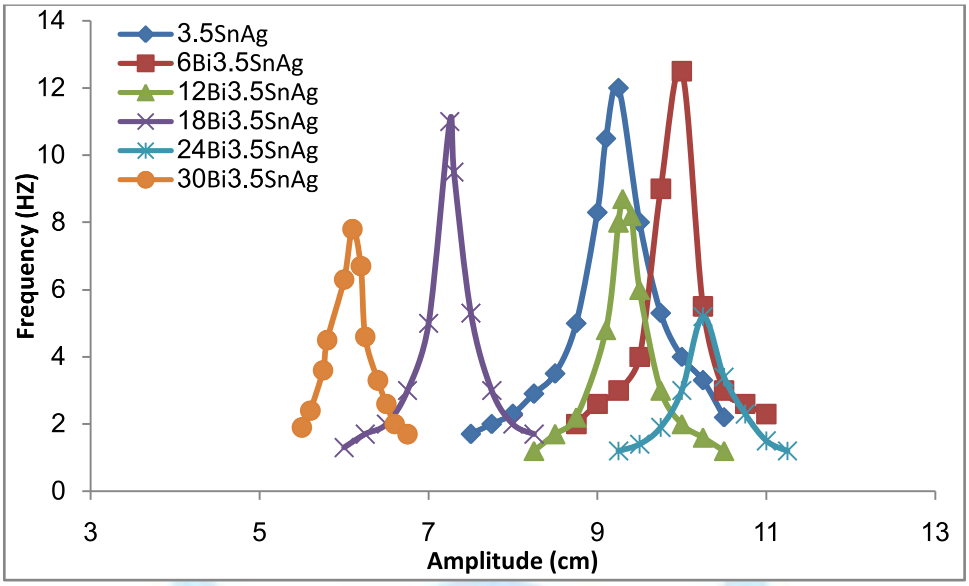

Figure 3:- resonance curves of $Sn_{96.5-x}Ag_{3.5}Bi_x$alloys

Table 1a:-x-ray analysis of $Sn_{96.5-x}Ag_{3.5}Bi_x$alloys

$SnAg_{3.5}$				$SnAg_{3.5}Bi_6$			
2θ	Area	FWHM	τÅ	2θ	Area	FWHM	τÅ
30.5625	419.32	0.2165	366.937	30.5526	90.34	0.2362	336.333
31.9859	514.29	0.2362	336.333	31.9449	100	0.216	367.786
37.5561	24.68	0.6298	126.138	32.0629	49.5	0.096	827.519
39.5036	23.01	0.2362	336.335	39.5382	2.53	0.384	206.881
43.8454	125.4	0.2362	336.336	43.7456	21.81	0.288	275.843
44.8673	194.23	0.1771	448.576	44.7675	51.79	0.168	472.873
55.2738	76.27	0.2755	288.362	55.1846	10.83	0.288	275.846
62.4617	84.1	0.2362	336.344	62.3667	16.51	0.192	413.773
63.6882	33.06	0.1968	403.682	63.6115	6.19	0.288	275.849
64.5709	44.27	0.1378	576.522	64.404	11.65	0.168	472.885
72.359	37.51	0.1968	403.688	72.1615	5.62	0.288	275.853
73.1213	32.46	0.1574	504.738	72.9011	6.24	0.192	413.780
79.4521	41.2	0.1574	504.744	79.2624	9.46	0.24	331.028
89.3488	20.72	0.1574	504.754	89.1117	4.63	0.192	413.793
95.5001	16.9	0.144	551.731	95.2757	3.32	0.192	413.798
97.3837	19.05	0.192	413.800	97.0716	1.91	0.384	206.899

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SnAg$_{3.5}$Bi$_{12}$			
2θ	Area	FWHM	τÅ
27.1481	51.74	0.2362	336.332
30.5083	525.64	0.2558	310.562
31.9147	635.89	0.2558	310.562
34.5328	17.61	0.4723	168.202
37.9169	16.84	0.2362	336.334
39.5025	47.25	0.3149	252.278
43.6951	78.76	0.1181	672.673
44.783	270.82	0.2362	336.337
55.1854	53.5	0.2362	336.341
62.3394	70.02	0.1968	403.681
63.5442	20.85	0.1968	403.682
64.3591	64.21	0.2755	288.366
72.1601	32.33	0.2362	336.349
72.9502	23.69	0.1968	403.688
79.2561	43.04	0.2362	336.353
89.0869	13.04	0.1574	504.754
95.2694	14.47	0.2362	336.364
97.1882	25.62	0.576	137.933

SnAg$_{3.5}$Bi$_{18}$			
2θ	Area	FWHM	τÅ
27.2011	155.75	0.2165	366.936
30.5292	194.38	0.1181	672.665
31.9513	450.13	0.1771	448.570
37.9422	51.51	0.1968	403.669
39.6415	64.99	0.2362	336.335
43.7802	108.64	0.1771	448.575
44.7452	175.45	0.1771	448.576
45.867	19.97	0.3149	252.279
48.6967	22.98	0.2755	288.359
55.2282	76.28	0.2755	288.362
62.3763	98.16	0.2362	336.344
63.5815	31.08	0.2362	336.345
64.4166	102.74	0.3542	224.293
70.8912	16.35	0.3149	252.288
72.1711	21.27	0.1574	504.738
72.9924	36.53	0.2362	336.349
79.3238	47.97	0.1968	403.693
85.2119	18.75	0.9446	84.107
89.1624	16.92	0.1574	504.754
95.3219	18.5	0.2362	336.364
97.2974	26	0.576	137.933

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$SnAg_{3.5}Bi_{24}$			
2θ	Area	FWHM	τÅ
22.3746	28.23	0.2952	269.110
27.1518	209.81	0.2362	336.332
30.5285	432.25	0.2558	310.562
31.9257	425.87	0.2558	310.562
34.4912	9.53	0.4723	168.202
37.8821	83.04	0.3149	252.278
39.6098	70.36	0.2755	288.357
43.6942	116.27	0.2362	336.336
44.7481	167.83	0.2362	336.337
45.7569	17.7	0.2362	336.337
48.7718	21.96	0.3542	224.289
51.927	5.73	0.4723	168.205
55.1892	36.27	0.2755	288.362
56.0325	11.65	0.2755	288.362
59.2132	7.97	0.2755	288.363
62.3198	45.58	0.2362	336.344
63.6265	11.44	0.1968	403.682
64.2929	35.66	0.2362	336.345
67.3153	4.73	0.3149	252.287
70.7134	10.21	0.433	183.477
72.1151	20.32	0.2362	336.349
72.8539	14.01	0.1968	403.688
79.2192	23.52	0.2165	366.959
85.0131	10.18	0.7872	100.924
89.0318	10.94	0.2165	366.966
91.7617	5.22	0.4723	168.217
95.273	7.75	0.2362	336.364
97.2544	16.17	0.768	103.450

$SnAg_{3.5}Bi_{30}$			
2θ	Area	FWHM	τÅ
22.4755	15.33	0.3149	252.275
27.1264	187.57	0.2755	288.354
30.5419	287.06	0.2952	269.112
31.9653	249.82	0.3149	252.276
34.5284	10.69	0.4723	168.202
37.9173	126.29	0.3346	237.424
39.6347	160.21	0.3542	224.287
43.7275	235.34	0.3149	252.278
44.7852	277.47	0.3346	237.4260
45.885	32.34	0.3542	224.288
48.6866	48.82	0.2362	336.338
51.9243	5.62	0.3149	252.281
55.1519	45.07	0.2362	336.341
56.0054	22.98	0.2362	336.341
59.183	18.48	0.3542	224.292
61.1063	4.24	0.2362	336.344
62.3444	66.94	0.2362	336.344
63.5945	23.05	0.2558	310.573
64.4052	132.76	0.3936	201.841
67.3111	11.3	0.3149	252.287
69.0701	6.8	0.3149	252.287
70.7474	19.95	0.2362	336.348
72.1306	28.5	0.1771	448.592
72.9167	28.59	0.2362	336.349
74.8997	7.54	0.6298	126.145
79.2855	44.82	0.2755	288.373
84.8872	11.13	0.3149	252.294
87.0822	6.27	0.3149	252.296
89.1293	21.68	0.2165	366.966
91.7125	10.24	0.3149	252.298
95.2868	12.32	0.1771	448.612
96.4002	4.36	0.1968	403.707
97.3277	37.14	0.768	103.450

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Table 1b:-lattice parameters, unit cell volume and crystal size of $Sn_{96.5-x}Ag_{3.5}Bi_x$ alloys

Tetragonal Sn					
Alloys	ave. particle size (A^o)	a (Å)	c (Å)	c/a	Unit cell volume ($Å^3$)
$Sn_{96.5}Ag_{3.5}$	402.438	5.84	3.186	0.546	10.707
$Sn_{90.5}Ag_{3.5}Bi_6$	373.796	5.849	3.039	0.519	11.259
$Sn_{84.5}Ag_{3.5}Bi_{12}$	345.044	5.854	3.192	0.545	10.738
$Sn_{78.5}Ag_{3.5}Bi_{18}$	352.93	5.853	3.111	0.532	11.0137
$Sn_{72.5}Ag_{3.5}Bi_{24}$	282.037	5.857	3.2014	0.547	10.714
$Sn_{66.5}Ag_{3.5}Bi_{30}$	278.686	5.854	3.19	0.545	10.743

Table 2a:-melting point and thermal parameters of $Sn_{96.5-x}Ag_{3.5}Bi_x$ alloys

Sample	Melting point °C	T_1(K)	T_2(K)	$\Delta H \times 10^4$ (j/Kg.K)	Cp (J/Kg.K)	ΔS (J/Kg.K)
$SnAg_{3.5}$	223.81	492.94	509.85	4.5240	2675.34	90.25
$SnAg_{3.5}Bi_6$	213.29	477.75	498	5.3520	2642.96	109.74
$SnAg_{3.5}Bi_{12}$	203.65	466.49	481.6	2.9730	1967.57	62.73
$SnAg_{3.5}Bi_{18}$	195.6	455.8	476.78	2.1160	1008.58	45.39
$SnAg_{3.5}Bi_{24}$	187.28	443.83	473	1.8250	625.64	39.83
$SnAg_{3.5}Bi_{30}$	177.19	439.64	460.87	0.5666	266.89	12.59

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Table 2b:-contact angles of $Sn_{96.5-x}Ag_{3.5}Bi_x$alloys

Alloys	Contact angles (θº)
$Sn_{96.5}Ag_{3.5}$	26±2
$Sn_{90.5}Ag_{3.5}Bi_6$	34±2
$Sn_{84.5}Ag_{3.5}Bi_{12}$	33.5±2
$Sn_{78.5}Ag_{3.5}Bi_{18}$	30±2
$Sn_{72.5}Ag_{3.5}Bi_{24}$	33.5±2
$Sn_{66.5}Ag_{3.5}Bi_{30}$	23.5±2

Table 3:-elastic moduliinternal friction and thermal diffusivity of $Sn_{96.5-x}Ag_{3.5}Bi_x$alloys

Sample	E GPa	B GPa	µ GPa	Q^{-1}	D_{tH}x10^{-4} $cm^2.Sec^{-1}$
$SnAg_{3.5}$	49	53.7	18.2	0.0455	4.25
$SnAg_{3.5}Bi_6$	46	50.4	17.1	0.0276	5.71
$SnAg_{3.5}Bi_{12}$	53.8	59	20	0.0280	4.29
$SnAg_{3.5}Bi_{18}$	54	59.2	20	0.0342	1.95
$SnAg_{3.5}Bi_{24}$	43	47.1	15.9	0.0305	7.92
$SnAg_{3.5}Bi_{30}$	28	30.7	10.4	0.0448	2.48