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Structural modification and physical properties of Tin-Silver eutectic alloy

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ABSTRACT

The aim of present work was to improve physical and soldering properties of Sn-Ag eutectic alloy by adding cadmium content to it. Structural, electrical resistivity, elastic and soldering properties of $Sn_{96.5-x}Ag_{3.5}Cd_x$ (x=0, 2.5, 4.5, 6.5, 8.5 wt.%) and $Sn_{88}Ag_2Cd_{10}$ rapidly solidified alloys have been investigated. Melting point, contact angle, elastic modulus values of $Sn_{96.5}Ag_{3.5}$ alloy decreased but electrical resistivity increased by adding cadmium content it. Pasty range, internal friction and thermal diffusivity of $Sn_{96.5}Ag_{3.5}$ alloy varied by adding cadmium content. The $Sn_{88}Ag_2Cd_{10}$ alloy has beast soldering properties for electronic application.

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INTRODUCTION

Solder are generally described as a fusible alloys with liquidus temperatures below 400 °C. The element commonly used in solder alloys are Tin (Sn), Lead (Pb), Silver (Ag), Bismuth (Bi), Indium (In), Antimony (Sb) and Cadmium (Cd). Solders are divided into two basic categories: eutectic and non-eutectic. Eutectic solders such as 63Sn- 37Pb have a distinct 183 °C melting point. Non-eutectic solders have a solidus and liquidus region. In electronics, one of the preferred solder used is a eutectic mix of lead and tin. By weight, there is just about 63% tin and 37% lead. It melts at 183 °C. Leadtin (Pb-Sn) solder have been used as a joining material for at least a few millennia and have been the most prominent material for the interconnection and packaging of modern electronic components and devices over the past several decades. The wide spread usage of

KEYWORDS

Structure; Pasty range; Internal friction; Melting point; Contact angle; Elastic modulus; Sn-Ag-Cd alloy.

Pb-Sn solders is due primarily to the combination of low cost and convenient material properties. Most commercial alloys contain cadmium to improve some features, such as hardness, wear resistance, or to lowering melting points of these alloys. Cadmium alloys are used for automatic electrical cut-outs and thermometric alarms. Lead-free solders having high performance and many studies have been made on various alloy-system solders based on Sn, e.g., Sn-9Zn, Sn-3.5Ag, Sn-3Ag-0.5Cu, etc. as likely substitutes^[1-3]. Also the dependence of frequency over a range of 0-3 Hz on Young's modulus and internal friction in Sn-9Zn and Sn-3.5Ag eutectic lead free solder alloys was investigated by T. Ohoak et al^[4]. The progress made in the properties of two lead free solder alloys, Sn-3.5% Ag-1% Zn and Zn-In, are described by M. Mc Cormack et al^[5]. Solidification behaviors of Sn-9Zn-XAg lead-free solder alloys are examined by using scanning electron microscopy, elec-

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tron prope microanalysis, X-ray analysis, computer aided-cooling curve analysis and differential scanning calorimetry^[6]. A review on the microstructure and mechanical properties of Sn-58Bi, Sn-52In and Sn-3.4Ag lead free solder alloys are reported by Glazer^[7]. Several papers [8-10] show that, the eutectic Sn-3.5% Ag is regarded as a good lead free solder alloy for certain aspects such as superior fatigue properties^[11]. Effects of indium addition on solidus and liquidus temperatures, wetting time, wetting force, tensile strength and microhardness of Sn-0.3Ag-0.7Cu lead-free solder alloy were investigated^[12]. Structure, electrical resistivity, wettability, melting point and elastic modulus of 50Sn-50In, 72.2Sn-20In-2.8Ag, 72.5Sn-25In-2.5Ag and 95Sn-5Ag lead free solder alloys have been investigated^[13]. The aim of this work is to study and analysis structure, physical and soldering properties of Sn-Ag eutectic alloy after adding cadmium content.

EXPERIMENTAL WORK

In the present work, $Sn_{96.5-x}Ag_{3.5}Cd_x$ (x= 0, 2.5, 4.5, 6.5, 8.5 wt.%) and $Sn_{88}Ag_2Cd_{10}$ were melted in a muffle furnace using tin, silver and cadmium of purity better than 99.5 %. The resulting ingots were turned and re-melted four times to increase the homogeneity. From these ingots, long ribbons of about 4 mm width and \sim 70 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 cuter. Microstructure of used samples was performed on the flat surface of all samples using an Shimadzu Xray Diffractometer (Dx-30, Japan) of Cu-Ka 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. The electrical resistivity was measured by a conventional double bridge method. The differential thermal analysis (DTA) thermographs were obtained by Shimadzu DTA-50 with heating rate 10 k/min in the temperature range 300-470 °k. All the samples have the same mass, which is 2 mg. The internal friction Q⁻¹ 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^[14–16]:

$$\left(\frac{\mathrm{E}}{\mathrm{\rho}}\right)^{1/2} = \frac{2\pi \mathrm{L}^2 \mathrm{f}_0}{\mathrm{kz}^2}$$

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:

$$\mathbf{D}_{\rm th} = \frac{2\mathbf{d}^2 \mathbf{f}_0}{\pi}$$

where d is the thickness of the sample

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

Where Δf the half width of the resonance curve

RESULTS AND DISCUSSION

X-ray analysis

X-ray diffraction patterns of $Sn_{96.5-x}Ag_{3.5}Cd_x$ (x= 0, 2.5, 4.5, 6.5, 8.5 wt.%) and Sn₈₈Ag₂Cd₁₀ rapidly solidified alloys, Figure (1), show that sharp lines of body-centered tetragonal Sn and very small peaks of hexagonal AgSn detected by x-ray diffractometer, phases. TABLE 1 shows x-ray diffraction analysis, $(2\theta, Intensity, Miller indices (h, k, l), full width half$ maximum, (FWHM)) of $Sn_{96.5-x}Ag_{3.5}Cd_x$ (x=0, 2.5, 4.5, 6.5, 8.5 wt.%) and Sn₈₈Ag₂Cd₁₀ rapidly solidified alloys. From these analysis it obvious that adding Cd content to Sn-Ag alloy caused change in its matrix microstructure such as crystallinity (which is related to intensity of the peak), crystal size (which is related to full width half maximum) and the orientation (which is related to the position of the peak, 2θ).



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TABLE 1 : X-ray analysis of Sn-Ag-Cd rapidly solidified alloys

TABLE1:	X-ray analy	vsis of Sn-A	Ag-Cd rapic	lly solidifie	ed alloys	2θ	d- Å	Int.%	FWHM	Phase	h k l
		Sn _{96.5} A	g 3.5			43.9186	2.06162	22.86	0.2755	βSn	220
20	d- Å	Int.%	FWHM	Phase	hkl	44.9233	2.01782	54.62	0.1771	βSn	211
30.69	2.91365	73.13	0.2165	β sn	200	55.4136	1.65812	12.38	0.3542	βSn	301
32.05	2.79255	100	0.1968	βSn	101	62.5272	1.4855	25.31	0.2755	βSn	112
34.85	2.57445	3.95	0.0010	Ag ₄ Sn	100	63.8176	1.45854	7.83	0.2362	βSn	400
37.60	2.39215	2.12	0.3149	Ag ₄ Sn	002	64.5845	1.44306	17.92	0.3542	βSn	321
39.62	2 27497	5 24	0 2755	Ag ₄ Sn	101	69.0734	1.35984	1.29	0.3936	Ag_4Sn	103
43 87	2.06359	23.17	0.1771	ß sn	220	72.3905	1.30548	11.37	0.2362	βSn	420
44 93	2.00335	52.36	0.0787	βSn	211	73.1404	1.29394	10.3	0.1968	βSn	411
55.34	1.66028	14.04	0.2755	βSn	301	79.5156	1.20545	18.43	0.1378	βSn	312
62.52	1.48570	25.32	0.1181	βSn	112	89.3817	1.0962	8.83	0.2755	βSn	431
63.76	1.45969	6.73	0.1968	βSn	400	95.5608	1.041	5.75	0.2362	βSn	332
72.40	1 30532	10.19	0 1968	ßSn	420	96.6594	1.03207	2.74	0.1968	Ag ₃ Sn	005
73.13	1.29411	9.09	0.2362	βSn	411	97.4547	1.02491	4.28	0.288	βSn	521
79.49	1.20565	17.16	0.2362	βSn	312			Sn ₉₀ Cd _{6.}	5 Ag _{3.5}		-
89.41	1.09594	7.65	0.2362	βSn	431	30.548	2.919	44	0.2558	β sn	200
95.52	1.04130	5.19	0.1574	βSn	332	32.028	2.795	100	0.2952	βSn	101
96.65	1.03211	1.83	0.1968	Ag ₂ Sn	005	38.11	2.361	6.64	0.2755	Ag_4Sn	002
97.42	1.02521	3.75	0.1920	ßSn	521	43.88	2.06323	20.49	0.2755	βSn	220
		Sno4Cd 2	= Ag 25	pon		44.899	2.019	44.32	0.3149	βSn	211
30.73	2 90928	100	0.2165	ß Sn	200	55.27	1.662	9.32	0.3936	βSn	301
32.05	2.79237	92.56	0.2165	ßSn	101	62.52	1.486	20.10	0.2952	βSn	112
33.84	2.64908	2.21	0.4723	Ag ₄ Sn	100	63.79	1.459	3.35	0.2755	βSn	400
39.63	2.27423	3 55	0 3149	Ag ₄ Sn	101	64.577	1.443	10.73	0.3149	βSn	321
43.94	2.06083	17.89	0.1968	ßSn	220	72.41	1.305	5.49	0.2952	βSn	420
44.91	2.01838	50.51	0.1574	βSn	211	73.14	1.294	6.56	0.3149	βSn	411
51.59	1.76318	1.80	0.3936	Ag ₄ Sn	102	79.496	1.206	12.29	0.2165	βSn	312
55.34	1.66008	14.24	0.3542	βSn	301	89.40	1.096	4.82	0.2755	βSn	431
62.54	1.48529	20.03	0.2755	βSn	112	95.53	1.041	3.59	0.1968	βSn	332
63.75	1.460	5.64	0.2362	βSn	400	96.68	1.032	1.05	0.2362	Ag ₃ Sn	005
64.57	1.443	13.66	0.1378	βSn	321	97.44	1.025	2.26	0.3120	βSn	521
72.41	1.30528	7.92	0.1968	βSn	420		2.01.6	$\frac{\operatorname{Sn}_{88}\operatorname{Cd}_{8.}}{\operatorname{Zo}}$	<u>5 Ag_{3.5}</u>	0.0	
73.14	1.29388	8.22	0.2755	βSn	411	30.66	2.916	70.83	0.2755	βSn	200
79.53	1.20532	13.51	0.1378	βSn	312	32.05	2.792	100.00	0.2755	βSn	101
89.40	1.096	5.83	0.2362	βSn	431	38.17	2.358	4.38	0.3936	Ag_4Sn	002
95.53	1.041	3.94	0.1968	βSn	332	43.897	2.063	18.13	0.2755	p Sn	220
96.53	1.032	1.41	0.2362	Ag ₃ Sn	005	44.94	2.017	41.75	0.2755	pSn ogu	211
97.41	1.025	3.40	0.1920	βSn	521	55.38	1.659	11.00	0.2362	pSn ogu	301
		Sno2Cd 4	5 Ag 35	1		62.54	1.485	19.45	0.2952	pSn oSm	112
30.6931	2.91297	84.06	0.2362	βSn	200	03.81 64.562	1.459	5.47 10.75	0.2362	pSn BSn	400 201
32.0381	2.79369	100	0.2165	βSn	101	68.02	1.444	10.75	0.2100	pon Ag Sr	321 102
34.5517	2.59599	1.42	0.4723	Ag ₄ Sn	100	08.93 72 27	1.3021	1.2ð	0.0900	Ag4Sn	103
37.548	2.39543	2.06	0.3149	Ag ₄ Sn	002	12.31 72.14	1.300	5.59	0.2733	pon Ren	420 711
39.4764	2.28275	6.69	0.2755	Ag ₄ Sn	101	70.40	1.294	0.21	0.1908	pon Ben	411 210
22.1701						/9.49	1.200	14.05	0.1908	psn	312

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2θ	d-Å	Int %	FWHM	Phase	h k l
89.42	1.096	5.69	0.1968	βSn	431
95.61	1.041	2.74	0.6298	βSn	332
97.42	1.025	2.43	0.2880	βSn	521
		Sn ₈₈ Cd	10 Ag ₂		
30.6432	2.91518	51.51	0.144	βSn	200
32.0516	2.79023	100	0.216	βSn	101
33.7752	2.65167	1.07	0.576	Ag_4Sn	100
38.7236	2.32345	3.16	0.24	Ag_4Sn	002
43.8921	2.06109	8.15	0.288	βSn	220
44.8699	2.01842	23.33	0.12	βSn	211
45.0033	2.01275	18.75	0.12	βSn	211
55.3135	1.65951	7.24	0.12	βSn	301
62.483	1.48504	14.81	0.12	βSn	112
63.8107	1.45747	2.21	0.288	βSn	400
64.5929	1.4417	6.77	0.336	βSn	321
72.4122	1.30406	4.45	0.192	βSn	420
73.1914	1.29209	4.95	0.288	βSn	411
79.5153	1.20445	10.4	0.144	βSn	312
89.4128	1.09499	3.55	0.24	βSn	431
95.5693	1.04007	2.9	0.24	βSn	332
97.3876	1.02543	1.6	0.192	βSn	521

Soldering properties

Wettability

A property of importance to the manufacturing or product engineer is wettability. Indeed, wettability is defined as the tendency for a liquid metal to spread on a solid surface. Wettability is the precursor of solder ability, which describes the solder's ability to form an actual joint on a circuit board. Wettability is quantitatively assessed by the contact angle formed at the solder substrate's flux triple point. The contact angles of $Sn_{96.5-x}Ag_{3.5}Cd_x$ (x= 0, 2.5, 4.5, 6.5, 8.5 wt.%) and $Sn_{88}Ag_2Cd_{10}$ rapidly solidified alloys on Cu substrate are shown in TABLE 2. From these results, it is clear that adding Cd content to Sn-Ag alloy due a significant change in contact angle, wettability, of it and $Sn_{88}Ag_2Cd_{10}$ alloy have adequate contact angle, leading to their spreading on the substrate.

Melting point and pasty range

The melting point of $Sn_{96.5-x}Ag_{3.5}Cd_x$ (x=0, 2.5, 4.5, 6.5, 8.5 wt.%) and $Sn_{88}Ag_2Cd_{10}$ rapidly solidified alloys was measured and then seen in TABLE (3), because it is very important for industrial applications. Also

TABLE 2: Contact angles of $Sn_{965,x}Ag_{35}Cd_x$ (x=0, 2.5, 4.5
6.5, 8.5 wt.%) and Sn _{ee} Ag ₂ Cd ₁₀ alloys on Cu substrate

Alloy	θ°
Sn _{96.5} Ag _{3.5}	34±4
$Sn_{94}Ag_{3.5}$ Cd _{2.5}	30.5±1
Sn ₉₂ Ag _{3.5} Cd _{4.5}	30±1
Sn ₉₀ Ag _{3.5} Cd _{6.5}	34±3
Sn ₈₈ Ag _{3.5} Cd _{8.5}	36.5±3
$Sn_{88}Ag_2 Cd_{10}$	25±2.1

thermo-graphs, Figure (2), of $Sn_{96.5-x}Ag_{3.5}Cd_x$ (x=0, 2.5, 4.5, 6.5, 8.5 wt.%) and $Sn_{88}Ag_2Cd_{10}$ alloys which have a little variations in the shape of Exo-thermal peaks, (That means a change in internal structure caused after adding Cd content) and that agrees with the results seen in x-ray diffraction analysis. The melting temperature of Sn-Ag alloy decreased after adding cadmium content.

The solidus temperature is defined as the temperature at which the first deviation from the base line appears (Figure 2). The deviation signals that a phase change is taking place. Thus the solidus temperature has been reached The tangent line, drawn in by the DSC, is an approximation of the solidus temperature. The liquidus temperature is defined as the temperature at which the graph returns to the baseline. The end of the deviation signifies the end of the phase change, i.e. the alloy has reached the liquid phase and the liquidus temperature. The tolerance on the values from the chart is ± 2 °C. The appearance of the DSC output is severely affected by the scan rate. Scan rate is the speed at which the temperature is increased during the scan. The pasty range is the difference between solidus and liquidus points which is seen in TABLE 3.. The pasty range value of Sn-Ag alloy varied after adding cadmium content.

TABLE 3 : melting point and pasty range of $Sn_{96.5x}Ag_{3.5}Cd_x$ (x= 0, 2.5, 4.5, 6.5, 8.5 wt.%) and $Sn_{88}Ag_2Cd_{10}$ alloys

Alloy	Melting Point (°C)	Pasty Range (°C)
Sn _{96.5} Ag _{3.5}	222.17	0
Sn ₉₄ Ag _{3.5} Cd _{2.5}	221.91	27.64
Sn ₉₂ Ag _{3.5} Cd _{4.5}	221.35	34.88
Sn ₉₀ Ag _{3.5} Cd _{6.5}	220.35	28.99
Sn ₈₈ Ag _{3.5} Cd _{8.5}	219.75	32.05
Sn ₈₈ Ag ₂ Cd ₁₀	216.58	29.31













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Electrical resistivity

Electrical resistivity value of Sn-Ag alloy is increased after adding cadmium content as seen in TABLE 4. That is because cadmium atoms is dissolved in the Sn-Ag matrix playing as the scattering center for conduction electrons which increases their resistivity.

TABLE 4 : electrical resistivity of $Sn_{96.5-x}Ag_{3.5}Cd_x$ (x= 0, 2.5, 4.5, 6.5, 8.5 wt.%) and $Sn_{88}Ag_2Cd_{10}$ alloys

Alloy	ρ x10 ⁻⁸ (Ω.m)
Sn _{96.5} Ag _{3.5}	19.9
Sn ₉₄ Ag _{3.5} Cd _{2.5}	22.90
Sn ₉₂ Ag _{3.5} Cd _{4.5}	27.05
Sn ₉₀ Ag _{3.5} Cd _{6.5}	30.78
Sn ₈₈ Ag _{3.5} Cd _{8.5}	33.2
$Sn_{88}Ag_2 Cd_{10}$	41.46

TABLE 5 : elastic modului of $Sn_{96.5.x}Ag_{3.5}Cd_x$ (x= 0, 2.5, 4.5, 6.5, 8.5 wt.%) and $Sn_{88}Ag_2Cd_{10}$ alloys

Alloy	E (Gpa)	B (Gpa)	μ (Gpa)
Sn _{96.5} Ag _{3.5}	36.33	42.94	13.36
Sn ₉₄ Ag _{3.5} Cd _{2.5}	30.18	35.42	11.11
Sn ₉₂ Ag _{3.5} Cd _{4.5}	29.1	33.91	10.72
Sn ₉₀ Ag _{3.5} Cd _{6.5}	27.95	32.34	10.30
Sn ₈₈ Ag _{3.5} Cd _{8.5}	25.11	28.86	9.26
$Sn_{88}Ag_2 Cd_{10}$	24.77	28.28	9.15

TABLE 6 : Internal friction and thermal diffusivity of $Sn_{96.5.}$ $_xAg_{3.5}Cd_x$ (x= 0, 2.5, 4.5, 6.5, 8.5 wt.%) and $Sn_{88}Ag_2Cd_{10}$ alloys

alloy	Q-1	$D_{th} x 10^{-4} \text{ cm}^2/\text{sec}$
Sn _{96.5} Ag _{3.5}	$0.097 \pm .02$	2.19±0.32
$Sn_{94}Ag_{3.5}Cd_{2.5}$	$0.069 \pm .0088$	1.80 ± 0.51
$Sn_{92}Ag_{3.5} Cd_{4.5}$	$0.046 \pm .018$	2.82±1.1
$Sn_{90}Ag_{3.5} Cd_{6.5}$	$0.068 \pm .019$	2.63 ± 0.55
Sn ₈₈ Ag _{3.5} Cd _{8.5}	$0.058 \pm .012$	1.61 ± 0.31
$Sn_{88}Ag_2Cd_{10}$	$0.070 \pm .023$	3.69±0.19

Elastic properties

Elastic modului Sn- Ag alloy is decreased by adding cadmium content as shown in TABLE 5. That is because the dissolved Cadmium atoms on grain boundary/ or the formed in Sn- Ag matrix affecting on bond matrix which decreasing elastic modulus of Sn- Ag alloy.

The resonance curves of $Sn_{96.5-x}Ag_{3.5}Cd_x$ (x=0, 2.5,

4.5, 6.5, 8.5 wt.%) and $Sn_{88}Ag_2Cd_{10}$ alloys are shown in Figure 3. Calculated Internal friction and thermal diffusivity values are seen in TABLE 6. The results show that, internal friction value of Sn-Ag eutectic alloy decreased by adding cadmium content but thermal diffusivity value is varied.







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CONCLUSION

- 1 Adding cadmium content caused change in Sn-Ag matrix microstructure.
- 2 Elastic modulus, internal friction and melting point values of Sn-Ag eutectic alloy decreased but electrical resistivity value increased after adding cadmium content to it.
- 3 Contact angle, pasty range and thermal diffusivity values of Sn-Ag eutectic alloy varied after adding cadmium content to it.
- 4 $Sn_{88}Ag_2Cd_{10}$ alloy has best soldering properties for electronic applications.

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