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International Journal of Current Research
Vol. 7, Issue, 06, pp. 17305-17311, June 2015

INTERNATIONAL JOURNAL OF CURRENT RESEARCH

ISSN: 0975-833X

RESEARCH ARTICLE

NEW TIN-BISMUTH BASED LEAD FREE SOLDER ALLOYS WITH SUPERIOR PROPERTIES FOR INDUSTRIAL APPLICATIONS

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ARTICLE INFO

Article History:
Received 26th March, 2015
Received in revised form
12th April, 2015
Accepted 29th May, 2015
Published online 30th June, 2015

Key words:
Wetting behavior,
Structural,
Thermal parameters,
Electrical resistivity,
Mechanical properties.

ABSTRACT

Our research contained thermal behavior (DSC thermographs and thermal parameters), wetting properties (spreading behavior and contact angles), microstructure (x-ray analysis and scanning electron micrographs) and empirical solder applications (photo graphs of soldering electronic device) of new ternary tin- bismuth- X (X= Cu and Ag), quaternary tin- bismuth- X (X = Zn-In, Zn-Cu, Cu-In, Sb-In and Ag- In) and penta tin- bismuth- X (X=Ag-In-TiO_2) solder alloys. Also it contained all measured physical properties (thermal, mechanical, electrical and soldering properties) of new tin-bismuth based alloys. The $SnAg_{3.5}Bi_{30}In_2$ and $SnAg_{3.5}Bi_{30}In_2$ $(Tio2)_{1.5}$ alloys have best properties such as low coast, lower melting temperature (174 °C) contact angles (15 and 13°) and high strengthens (elastic modulus and Vickers hardness) compared to tin- lead commercial solder alloy for electronic industry. Significant decreased in melting temperature (~ 60 °C)of SnAg and SnCu alloys after adding alloying elements. Also all new tin- bismuth based lead free solder alloys have low melting temperature, high strengthens and adequate wetting behavior compared to tin- lead commercial solder alloy.

Citation: Abu Bakr El-Bediwi, Amira El-Shafei and Mustafa Kamal, P., 2015. "New tin-bismuth based lead free solder alloys with superior properties for industrial applications", *International Journal of Current Research,* 7, (6), 17305-17311.

INTRODUCTION

There are many different types of solder being used by industry. Lead-free solders in commercial use may contain tin, copper, silver, bismuth, indium, zinc, antimony, and traces of other metals. Most lead-free replacements for conventional Sn60/Pb40 and Sn63/Pb37 solder have melting points from 5 to 20 °C higher, though solders with much lower melting points are available. Solder alloys are categorized as either soft or hard. Soft solders typically contain tin and lead, although indium, cadmium, and bismuth are also found in soft solders. Hard solders contain metals such as gold, zinc, aluminum, and silicon. Amore rigorous classification is based on the melting temperature where soft solders melt below approximately 350 °C while hard solders melt above 350 °C. Due to the inherent toxicity of lead (Pb), environmental regulations around the world have been targeted to eliminate the usage of Pb-bearing solders in electronic assemblies. Sn-Bi alloy has the highest ultimate tensile strength while both Sn-Ag and Sn-Zn alloys exhibited higher ductility than the Sn-Pb and Sn-Bi alloys (Osório *et al.,* 2013). Adding Bi to Sn-Ag-Cu ternary alloys greatly reduced the loss in strength due to aging. Also adding bismuth increases strength (Witkin, 2012).

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Thermal properties and microstructure of $Bi_{58}Sn_{42}$, $Bi_{53}Sn_{26}Cd_{21}$, $In_{70}Sn_{30}$, $Sn_{50}In_{50}$ and $Sn_{53}Bi_{37}In_{10}$ solder alloys have been studied and analyzed (Chriastelova *et al.,* 2008). Bismuth-silver alloy ($Bi_{89}Ag_{11}$) has been identified as a viable Pb-free power die-attach solder (Lalena *et al.,* 2002). Structure, electrical resistivity and elastic modulus of $SnSb_7$ and $SnSb_7X$ (X = Cu, Ag, or Cu and Ag) rapidly solidified alloys have been investigated (Bediwi, 2004). Also structure, hardness, mechanical and electrical transport properties of Sn_{90-x} Sb_{10} Bi_x (x = 0, or x ≥1) alloys have been studied and analyzed (Bediwi *et al.*, 2004). Adding 1.5% Bi and 1.5% Cu to Sn 5%Sb alloy improved both strength and ductility of the base alloy (Esfandyarpour, 2011).

Adding copper to Sn–Ag solder alloys enhances the corrosion resistance of alloys which exhibit improved passivity behavior compared to $Sn_{73.9}Pb_{26.1}$ solder. Also increasing the copper content from 0.8 to 6.7 % improves the corrosion behavior of Sn–Ag solders (Rosalbino *et al.,* 2008). Microstructure, thermal properties, corrosion and oxidation resistance of Sn-9Zn-0.5Ag-1In solder alloy were studied (Chang *et al.,* 2006). Adding 1% of In to Sn-9Zn-0.5Ag alloy decreased melting point of alloy and enhanced adhesion strength of alloy on Cu substrate. Electrical resistivity increased but elastic modulus, internal friction and melting point deceased by adding cadmium content to $SnZn_9$ alloy (El-bediwi *et al.,* 2004).

Also Sn-In-Ag system offers several advantages such as good wettability (Frear, 1996 and Artaki *et al.,* 1994), good corrosion behavior (Oulfajrite *et al.,* 2003) and very satisfying interaction with the substrate, especially with copper (Choi *et al.,* 1999). The microstructures and tensile properties of Sn-3.0wt.%Ag-0.5wt.%Cu, Sn-3.5wt.%Ag-0.7wt.%Cu and Sn-3.9wt.%Ag-0.6wt.%Cu, prepared under three different cooling conditions were evaluated after casting (Kim, 2002). The aim of our research was to produce new free lead alloy with superior soldering properties such as low coast, low melting point, good wettability, strengthens and corrosion resistance for electronic applications.

Experimental work

A high purity, more than 99.95%, elements tin, bismuth, lead, indium, cadmium, zinc, silver, copper, antimony and titanium oxide were used in this work. The used alloys, tin- bismuth- X (X= Cu and Ag), tin- bismuth- X (X = Zn-In, Zn-Cu, Cu-In, Sb-In and Ag- In) and tin- bismuth- X (X=Ag-In-TiO_2), were molten in the muffle furnace. 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 made using an Shimadzu x–ray diffractometer (Dx–30, Japan)of Cu–K_α radiation with λ=1.54056 Å at 45 kV and 35 mA and Ni–filter in the angular range 2θ ranging from 20 to 100° in continuous mode with a scan speed 5 deg/min. Scanning electron microscope JEOL JSM-6510LV, Japan was used to study microstructure of used samples**.** 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 of used alloys. Internal friction Q^{-1} and the elastic constants of used alloys were determined using the dynamic resonance method (Cullity, 1959; Sppinert and Teffit, 1961 and Schreiber, 1973).

RESULTS AND DISCUSSION

Microstructure

X-ray diffraction patterns of tin- bismuth- X (X= Cu and Ag), tin- bismuth- X (X = Zn-In, Zn-Cu, Cu-In, Sb-In and Ag- In) and tin- bismuth- X (X=Ag-In-TiO_2) alloys have lines corresponding to tetragonal Sn and rhombohedral Bi phases. The results show that, the shape of formed phases (intensity, broadness and position) of tin- bismuth based alloys changed after adding different alloying elements.

That is mean that, all additive materials (Cu, Ag, Zn-In, Zn-Cu, Cu-In, Sb-In, Ag- In and Ag-In-TiO_2) dissolved in Sn matrix formed a solid solution/or and other accumulated atoms formed a traces of detected/or not detected phases (SnBi, SnSb, InSn and AgSn) as shown in Figure 1.

Scanning electron microscope

Scanning electron micrographs, SEM, of tin- bismuth- X (X= Cu and Ag), tin- bismuth- X (X = Zn-In, Zn-Cu, Cu-In, Sb-In and Ag- In) and tin- bismuth- X (X=Ag-In-TiO_2) alloysare shown in Figure 2. SEM analysis of used new tin-bismuthbased alloys showed heterogeneity micro-structure, which related to the formation of non-equilibrium phases. That is meant that, β-Sn and rhombohedral Bi phaseswith detectable\or non detectable traces of intermediate phases with various chemical compositions were detected and that is agreed with x-ray analysis.

Thermal properties

Thermal analysis is often used to study solid state transformations as well as solid-liquid reactions. Figure 3 shows DSC thermographs of tin- bismuth- X (X= Cu and Ag), tin- bismuth- X (X = Zn-In, Zn-Cu, Cu-In, Sb-In and Ag- In) and tin- bismuth- X (X=Ag-In-TiO_2) alloys. Adding materials (Cu, Ag, Zn-In, Zn-Cu, Cu-In, Sb-In, Ag- In and Ag-In-TiO_2) to tin- bismuthbased alloy caused little variation in exothermal peaks.

Wetting behavior

Wetting is a property of liquid to spread over a solid substrate, i.e., the tendency for a liquid solder to wet the substrate. It tells how a liquid and a solid are having an intimate contact between them. Wettability is characterized by the degree and rate of wetting. Degree of wetting depends on the contact angle formed at the interface as well as on the surface energy of interface. The rate of wetting is determined by how quick the liquid wets the surface and spreads over the substrate. Wettability is quantitatively assessed by the contact angle formed at the solder substrate's flux triple point. The spreading of tin- bismuth- X (X= Cu and Ag), tin- bismuth- X (X = Zn-In, Zn-Cu, Cu-In, Sb-In and Ag- In) and tin- bismuth- X (X=Ag-In-TiO_2) alloyson pure Cu substrate at room temperature in air are shown in Figure4.

Physical properties

Physical properties of tin- bismuth- X (X= Cu and Ag), tin-bismuth- X (X = Zn-In, Zn-Cu, Cu-In, Sb-In and Ag- In) and tin- bismuth- X (X=Ag-In-TiO_2) alloys were measured using different experimental techniques are listed in Table 1. The results show that, all measured physical properties such as elastic moduli, internal friction, Vickers hardness, electrical resistivity, melting temperature and contact angle of tin-bismuth based alloys correlated to alloy composition (microstructure of alloy). Also elastic modulus, Vickers hardness and melting temperature values of used alloys lower than the values of commercial lead- tin solder alloy.

Soldering process

Soldering is a process in which two or more metal items are joined together by melting and flowing a filler metal into the joint, the filler metal having a relatively low melting point. In the electronics industry lead-tin (Pb-Sn) solder is a very important material but Pb is toxic and has adverse effects on the environment and human beings. Laws have been proposed to eliminate Pb from electronic devices and components.

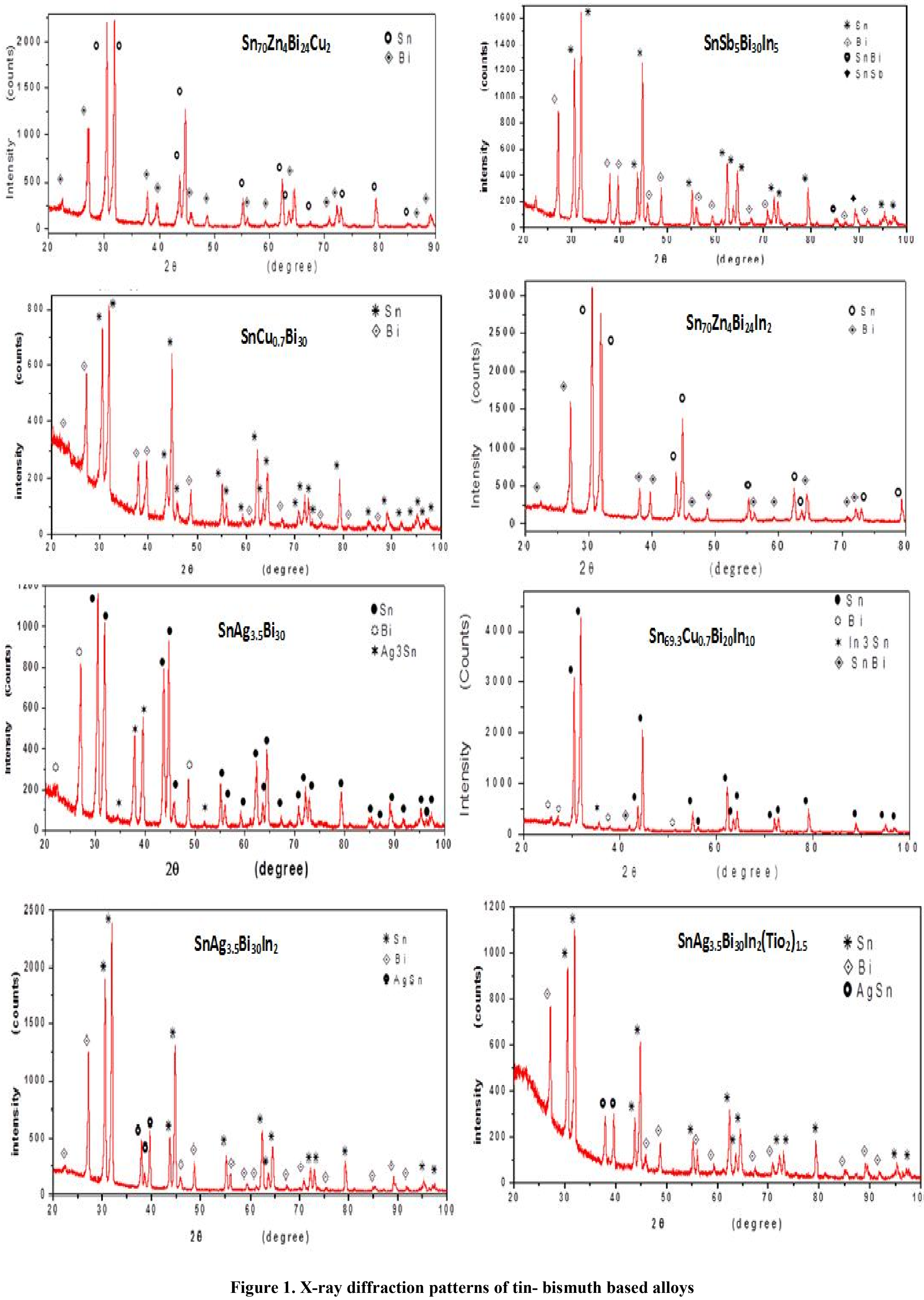

Figure 1. X-ray diffraction patterns of tin- bismuth based alloys

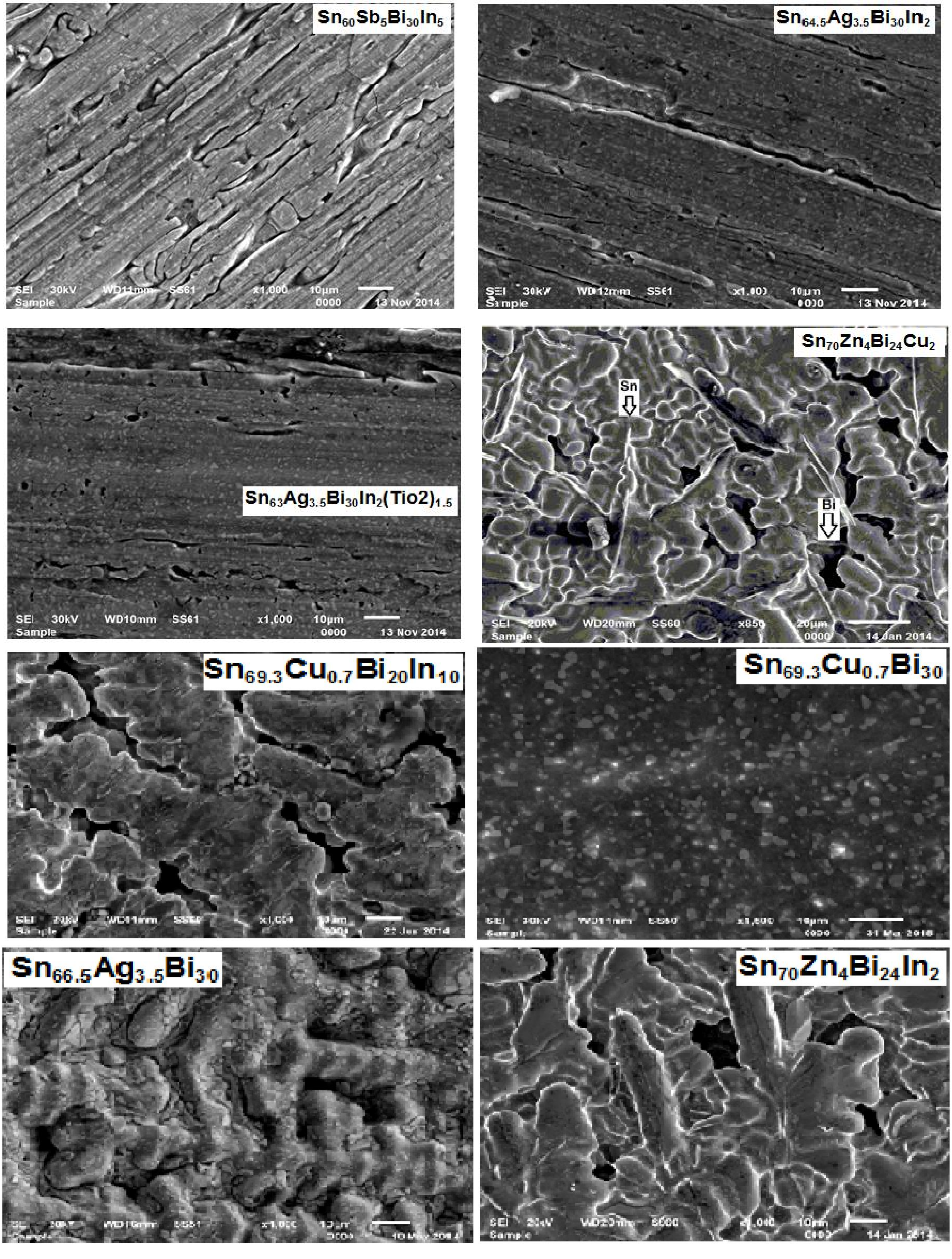

Figure 2. SEM of tin- bismuth based alloys

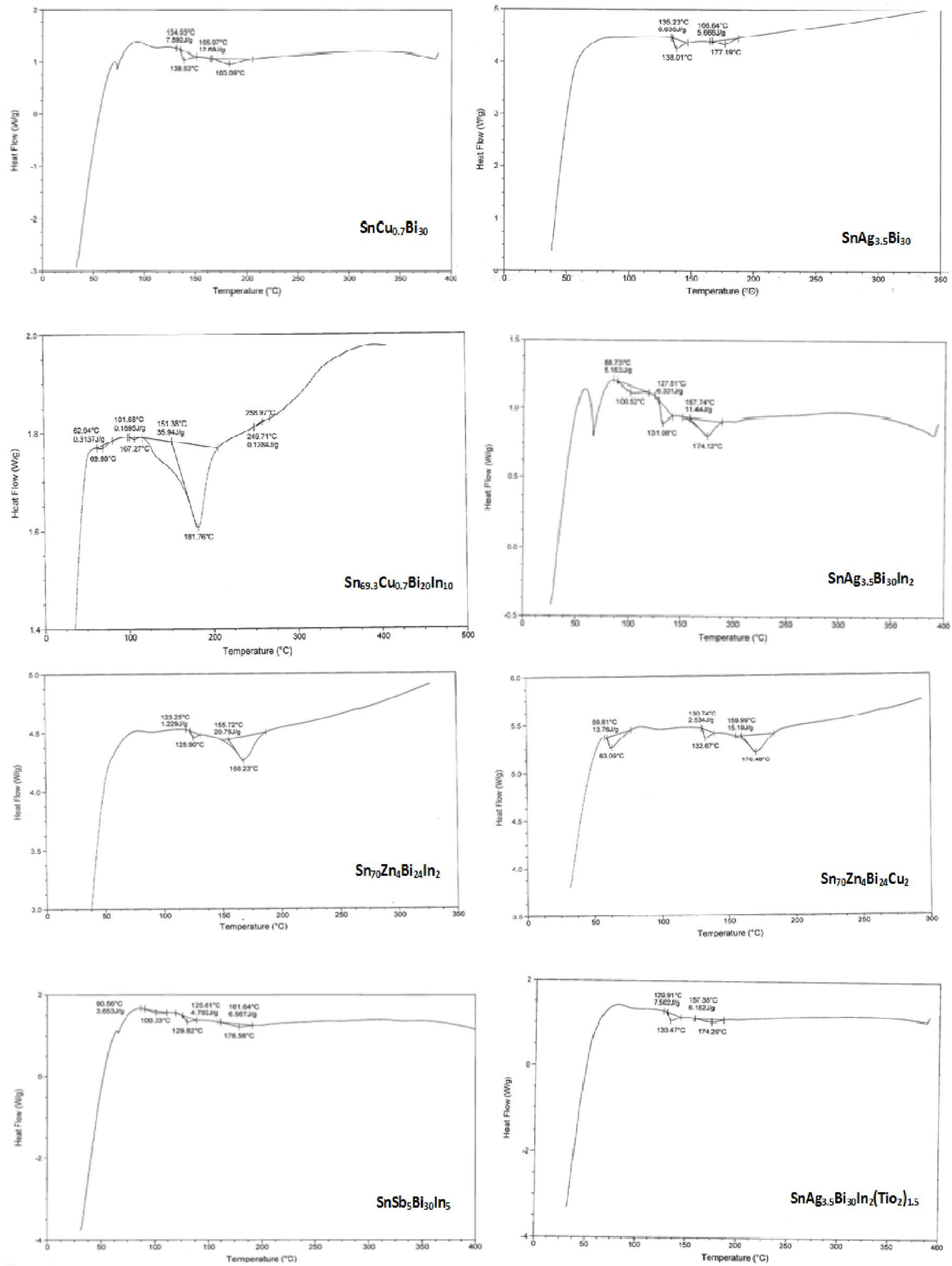

Figure 3. DSC of tin- bismuth based alloys

Figure 4. Photo graphs for tin- bismuth based alloysspreading on cupper substrate in air

Table 1. Physical properties of tin- bismuth based alloys

Alloys	Density (gm/cm^3)	Young modulus (Gpa)	Shear modulus (Gpa)	Bulk modulus (Gpa)	Internal friction	Thermal diffusivity (m^2/sec)	Vickers Hardness (Kg/mm^2)
$SnAg_{3.5}Bi_{30}$	8.681	28	10.4	30.7	0.045	2.48	25.28
$SnCu_{0.7}Bi_{30}$	7.85	46.33	17.15	51.78	0.006	8.73	25.87
$SnZn_4Bi_{24}In_2$	7.198	24	8.88	26.7	0.013	25.2	22.47
$SnZn_4Bi_{24}Cu_2$	7.6	40.9	15.2	44.8	0.041	2.03	23.1
$SnCu_{0.7}Bi_{20}In_{10}$	8.077	36.9	13.7	40.6	0.015	1.94	26.75
$SnSb_5Bi_{30}In_5$	8.063	33	12.4	32.45	0.0075	32.2	22.32
$SnAg_{3.5}Bi_{30}In_2$	7.98	34.5	12.75	39.14	0.01	10.5	23.12
$SnAg_{3.5}Bi_{30}In_2(Tio2)_{1.5}$	7.91	28.25	10.45	31.77	0.01	31.7	17.01

Alloys	Resistivity $x10^{-8}\Omega.cm$	Melting Point (ºC)	Thermal Conductivity ($W.m^{-1}.K^{-1}$)	Contact angle
$SnAg_{3.5}Bi_{30}$	73.76	177.19	2.07	23.5
$SnCu_{0.7}Bi_{30}$	97.11	183.09	1.5	24.5
$SnZn_4Bi_{24}In_2$	103.7	168.23	1.48	28
$SnZn_4Bi_{24}Cu_2$	49.7	170.48	3.06	30
$SnCu_{0.7}Bi_{20}In_{10}$	108.3	181.76	1.42	32
$SnSb_5Bi_{30}In_5$	128.27	178.56	1.14	22
$SnAg_{3.5}Bi_{30}In_2$	97.39	174.12	1.49	15.5
$SnAg_{3.5}Bi_{30}In_2(Tio2)_{1.5}$	121.39	174.2	1.2	13

Figure 5. Photo graphs for soldering process of tin- bismuth based alloys in electronic devices

The harmful effect of lead on human body and environment has promoted many research and experiments on lead free solders for electronic applications. The new lead free solders should have some desirable properties like wettability, low melting temperature, corrosion resistance, good electrical conductivity and good mechanical and material properties. Soldering process (soldering process in electronic device) photo graphs of tin- bismuth- X (X= Cu and Ag), tin- bismuth- X (X = Zn-In, Zn-Cu, Cu-In, Sb-In and Ag- In) and tin- bismuth- X (X=Ag-In-TiO_2)alloys are shown in Figure 5. Theses soldering process checked after three months, the connection (Filler\or solder alloy) still very strong.

Conclusion

All new tin- bismuth based lead free solder alloys have best soldering properties such as low melting temperature, high strengthens and adequate wetting behavior compared to tin- lead commercial solder alloy. The $SnAg_{3.5}Bi_{30}In_2(Tio2)_{1.5}$ alloy has best properties such as low coast, lower melting temperature (174 °C) contact angle (13°) and high strengthens compared to tin- lead commercial solder alloy for electronic industry.

REFERENCES

Artaki, I., A. M. Jackson, P. T. Vianco, 1994. *J. Electron. Mater*. 23 (8) 757.

Chang, T. C., J. W. Wang, M. C. Wang, M. H. Hon, 2006. *J. alloys & Comp*.

Choi, W. K., H .M. Lee, J. Korean., 1999. Phys. Soc. 35 340.

Chriastelova, J. and M. Ozvold, 2008. J. of alloys and compounds 457 323.

Cullity, B. D. 1959. Element of x-ray diffraction, Ch.10 297.

El- Bediwi, A. B., E. Gouda, M. Kamal, 2004. AMSE, 65, n° 1, Modeling C.

El-Bediwi, A. B. 2004. Radia. Eff. Def. Sol. 159 125.

El-bediwi, A., M. El-Bahay and M. Kamal, 2004. Radia. Eff. Def.Sol. 159 491.

Esfandyarpour, M. J., R. Mahmudi, 2011. Mate. Sci. Eng. A 530 402.

Frear, D. R. 1996. *J Metals* 48 (5) (1996) 49.

Kim, K. S., S. H. Huh, K. Suganum, 2002. Mater. Sci. Eng. A333 106.

Lalena, J. N., N. F. Dean and M. W. Weiser, 2002. *J. Electronic Mater*. 31: 11.

Osório, W. R., L. C. Peixoto, L. R. Garcia, N. M. Noël andA. Garcia, 2013. *J. of Alloys and Compounds*, 572 97.

Oulfajrite, H., A. Sabbar, M. boulghallat, A. Touaiti, R. Lbibb, A. Zrineh, 2003. Mater. Lett. 57 4368.

Rosalbino, F., E. Angelini, G. Zanicchi, R. Marazza, 2008. 109: 2–3 386–391.

Schreiber, E., O. L. Anderson and N. Soga, 1973. Elastic Constants and their Measurement, McGraw-Hill Book Company, Ch. 4.

Sppinert S. and W. E. Teffit, 1961. ASTM, Proc. 61 1221.

Witkin, D. B. 2012. Mater. Sci. & Eng., 532 212–220.

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