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STRUCTURAL CHARACTERISTICS OF SOME TERNARY Ag-In-Sn ALLOYS

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ABSTRACT

The Ag-In-Sn system, as one of potential lead-free solder materials, was studied in this paper. The investigated alloys were chosen from two sections, with molar ratio of In:Sn equal to 1:4; 1:2. DTA, XRD, SEM and microhardness investigations were used in order to determine structural characteristics of chosen Ag-In-Sn ternary alloys.

Key words: lead-free solders, Ag-In-Sn, DTA, SEM, XRD, microhardness

INTRODUCTION

Lead has been widely used in all aspects of life for thousands of years. It has been widely used in modern society, also, particularly in microelectronics and presents the base of majority solders up to now. But, this metal is highly toxic and therefore, it should be removed from different materials, especially electonic, according to WEEE [1].

So, the currently used lead-based solders in microelectronics are under way to be replaced by lead-free alloys due to environmental and health concerns. In that purpose, various physical, chemical and mechanical properties of the candidate alloy, as well as the economic aspect have been considered. A significant part of work is to find a substitute for common Pb-Sn solder alloy, which has become complex and widely discussed. The proper alloy must have certain characteristics to satisfy:

- Availability
- No Toxicity
- Melting temperature range
- Wettability
- Other process conditions

Because of their specific properties, the candidates for replacement of Pb-Sn solder alloys are usually tin-based multicomponent alloys, for the investigated binary systems do not satisfy some features (temperature, for example). The question about melting temperature is one of the most difficult problems in the lead-free soldering transition.

The In-Sn and Ag-Sn investigated solder alloys [2, 3] are already in practice, but only in exactly determined conditions. Considering these, it could be expected that Ag-In-Sn ternary system might be one among proper substitutes for common solders.

Thermodynamic characteristics and phase equilibria for the Ag-In-Sn system are investigated from various researchers.

The element activities in the Ag-In-Sn system at 1273, 1373 and 1423 K, were determinated by T. Miki, N. Ogawa, T.Nagasaka and M.Hino [4] (mass spectrometry), and J. Zhang [5], (mass action law, at 1423 K).

Phase equilibria for the system Sn-In-X (X=Ag, Bi, Zn, Sb) was investigated by I. Ohnuma, Y. Cui, J. Liu, et al. [6]. Using Thermo Calc software, the appropriate thermodynamic database was formed, and based on that, invariant reactions of the system, as well as isotermal sections at 373 and 473 K, were given in the paper. Also, the phase equilibria for the Sn-Ag-In system was obtained from experimental values (DSC and optical microscopy) and optimised binary data, by X. J. Liu, Y. Inohana, et al. from Japan, and Z. Moser, W. Gasior i J. Pstrus [7], from Poland.

Based on large experimental work (optical microscopy, DSC, XRD, SEM, microhardness), Ag-In-Sn alloys were investigated by G.P. Vassilev et al. [8], and the isotermal section at 553 K was obtained.

As a contribution to the better knowledge of the properties of mentioned system, the results of investigation of structural characteristics of some Ag-In-Sn alloys are presented in this paper.

EXPERIMENTAL

Two sections (A and B) with constant molar ratio of In:Sn (1:4; 1:2), with 5 samples from each section, were chosen from the concentration range of Ag-In-Sn system. The samples were with constant volume (0,3 cm^3) and with compositions given in Table 1.

Table 1. Composition of Ag-In-Sn alloys for different sections

section	X_i			%at			%mass		
	Ag	In	Sn	Ag	In	Sn	Ag	In	Sn
In:Sn= 1:4 A	0,1	0,18	0,72	10	18	72	9,221	17,679	73,100
	0,2	0,16	0,64	20	16	64	18,615	15,850	65,535
	0,3	0,14	0,56	30	14	56	28,166	13,990	57,844
	0,4	0,12	0,48	40	12	48	37,885	12,097	50,018
	0,5	0,1	0,4	50	10	40	47,778	10,170	42,052
In:Sn= 1:2 B	0,1	0,300	0,600	10	30,0	60,0	9,258	29,583	61,159
	0,2	0,267	0,533	20	26,7	53,3	18,681	26,543	54,776
	0,3	0,233	0,467	30	23,3	46,7	28,254	23,356	48,390
	0,4	0,200	0,400	40	20	40	37,988	20,216	41,796
	0,5	0,167	0,333	50	16,6	33,3	47,936	16,939	35,125

Following experimental techniques were used for the investigation of structural characteristics of chosen alloys: DTA, XRD, SEM and microhardness measurements.

Differential-thermal analysis was carried out in an air atmosphere, with constant heating rate of 10^{o}/min and using Al_2O_3 as the referent material.

In order to determine the microstructure of chosen alloys, scanning electron microscopy (SEM) was used and the recordings were done on the JEOL-JSM T20 scanning microscope. The samples were prepared using the standard procedure and polished ones were etched with $FeCl_3$ solution (32 g $FeCl_3$, 100 ml H_2O_2, 100 ml H_2O).

The identification of the phases in the alloys has been done using X-ray diffraction analysis on Siemens D-500 apparatus, using Cu-anticathode and Ni-filters (40kV, 20mA).

Microhardness for the investigated alloys was determined on the PMT-3 apparatus, for tin matrix and light phase separately.

RESULTS AND DISCUSSION

Following methods of characterization were used for experimental investigation of chosen Ag-In-Sn alloys - DTA, SEM and XRD analysis.

Five samples from each section, A and B, were investigated using DTA and characteristic peak temperatures, determined to be in the range 213÷229 ^{0}C, are presented in Table 2.

Table 2. Characteristic temperatures on DTA curves for investigated Ag-In-Sn alloys

section	X_{Ag}	Temperature on DTA curve, ^{o}C		
		The first peak	The second peak	The third peak
A In:Sn=1:4	0,1		219	384
	0,2		229	410
	0,3		220	427
	0,4		215	465
	0,5		215	514
B In:Sn=1:2	0,1	168	213	383
	0,2		219	408
	0,3		224	386
	0,4		219	378
	0,5		221	422

Obtained DTA curves indicate that the beginning and the end of phase transformation are moved to lower temperatures by the increase of indium and constant silver content in the alloy, which is in an agreement with literature facts – small percent of indium cause lower melting temperature [9].

The increase of indium content in alloy has an influence not only in decreasing melting temperature, but also for the appearance of the peak at 168^{o}C for alloy B1. If

should be noticed that temperature of this peak is close to indium melting point, so it might be a consequence of indium dissolution in the system.

The comparison of experimental DTA results with optimized values in Ref. [7] is presented in Figures 1 and 2.

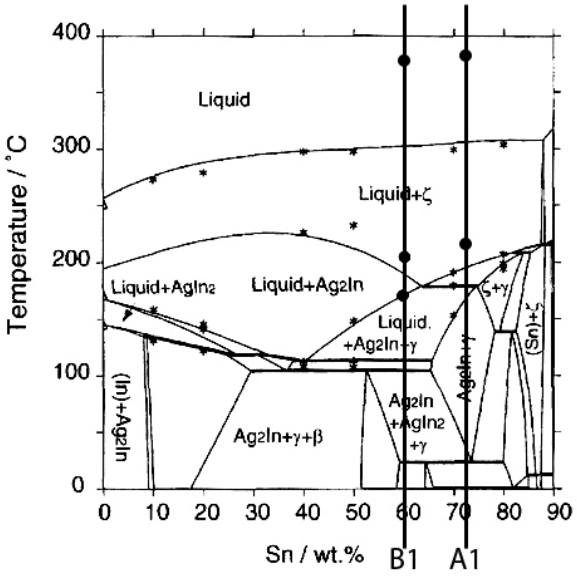


Figure 1. Comparation with optimised values [7] for 10 wt% Ag vertical section

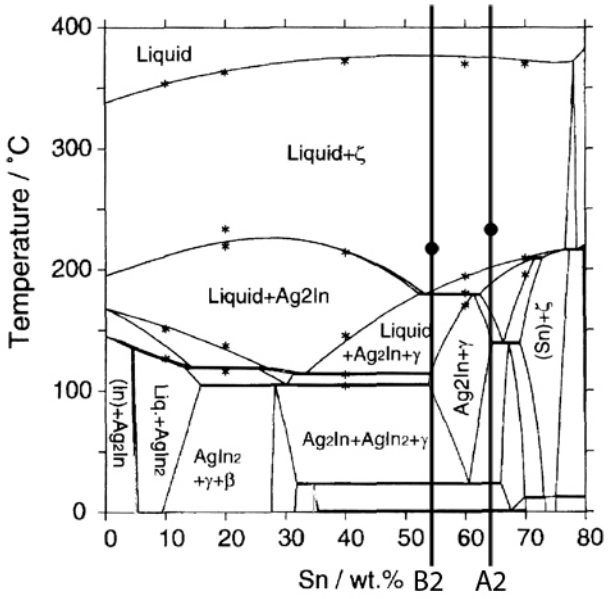
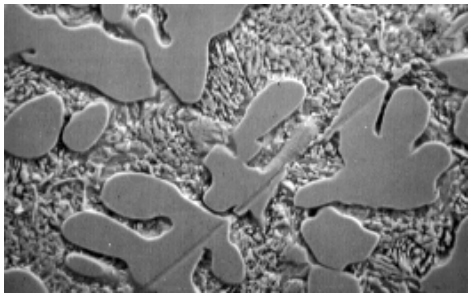
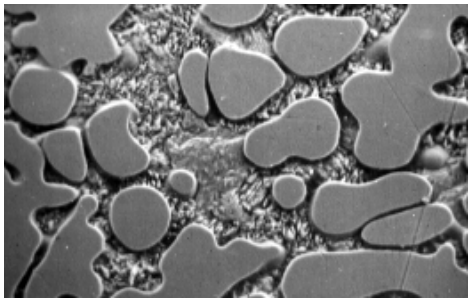


Figure 2. *Comparation with optimised values [7] for 20 wt% Ag vertical section*

Scanning electron microscopy was used in order to determine microstructure of the investigated samples. Dark and light phases are noticeable in the microstructures of chosen alloys, given in Figure 3 for the samples A2 and B4. So, microstructure of all investigated Ag-In-Sn alloys consists of tin matrix (dark area) with primary solution crystals rich on silver and indium (light area), in it. In tin matrix phases (Ag_3Sn) ili (In_3Sn) / ($InSn_4$) are dispersed. Besides that, the fraction of light area (primary solution crystals rich on silver and indium) is increased with silver content in the alloy, and with decrease of tin content in the alloy, the fraction of tin-based phase is decreased.



a) A2 (Ag20In16Sn)



b) B4 (Ag40In20Sn)

Figure 3. SEM microstructure of chosen alloys (Magnification x1000)

The identification of different phases in ternary Ag-In-Sn alloys has been done using X-ray diffraction analysis. These results pointed out that all of investigated alloys had Sn and Ag_3Sn-based matrix with or without addition of other phases, Table 3, while X-ray difractograph for the alloy B5 is shown in Figure 4.

Table 3. XRD analysis for some investigated Ag-In-Sn alloys

alloy	Composition, at%			XRD					
	Ag	In	Sn	Sn	Ag_3Sn	In_3Sn	$InSn_4$	Ag_9In_4	AgIn
A2	20	16	64	+	+				+
A3	30	14	56	+	+				
A5	50	10	40	+	+				
B4	40	20	40	+	+		+		+
B5	50	17	33	+	+				+

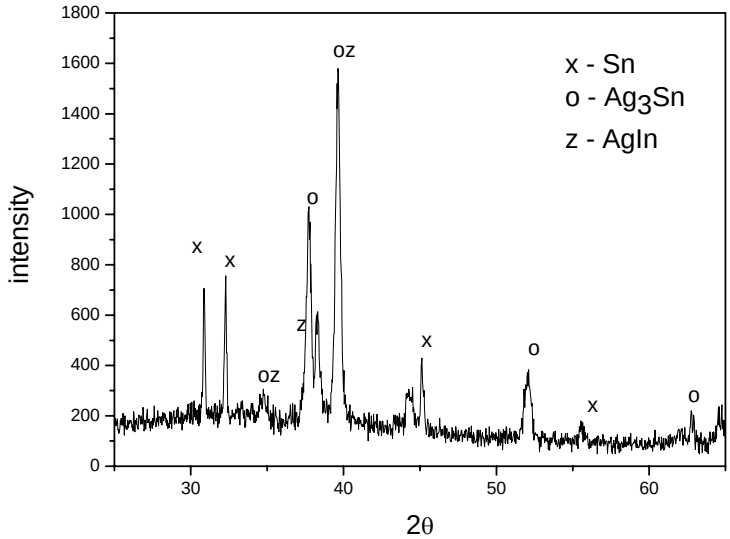


Figure 4 - X-Ray difractograph for alloy B5 (Ag50In17Sn)

The presence In_3Sn phase in Sn matrix is typical for the alloys B1, in distinction to other alloys from section B (β-Sn, Ag_3Sn and Ag-In phase). Concerning section A, alloys A3 and A4 have only β-Sn and Ag_3Sn matrix, due to low content of indium.

The obtained values for microhardness of Ag-In-Sn alloys (Figure 5) confirmed the possibility of intermetallic compound formation in the microstructure (light phase). Generally, microhardness values for light phase are much higher than microhardness for tin matrix. These high values (100 ÷ 250 HV) indicate the presence of primary crystals solution or intermetallic compound in the structure, which is already obtained by results of XRD and SEM analysis.

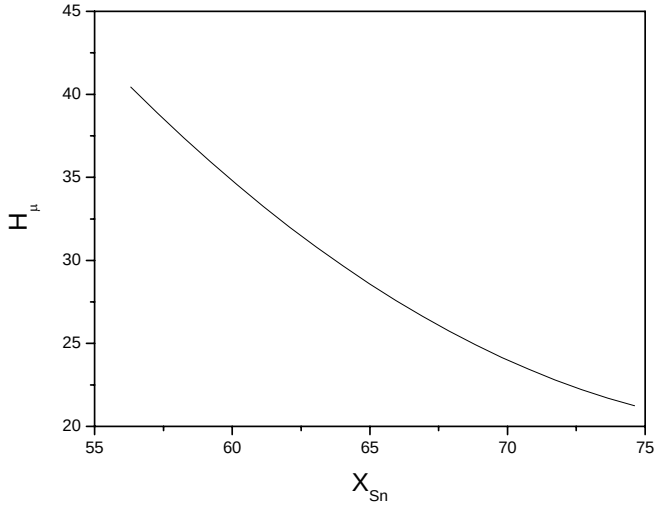


Figure 5. Microhardness for alloys in section A

On the other way, tin matrix has lower microhardness (20 ÷ 40 HV), and decrease of microhardness is caused by increase of tin content in the alloy.

CONCLUSION

Based on DTA curves, the information on characteristic peak temperatures of investigated Ag-In-Sn alloys were obtained. Microstructure of each alloy from sections A and B, with constant molar ratio was determined by scanning electron microscopy. The composition of phases in the microstructure was determined by XRD analysis. As confirmation for previous structural investigations, the micro-hardness values for investigated Ag-In-Sn alloys, are presented.

The indium content in alloy has great influence on the beginning and the end of phase transformations. Considering the results, the most appropriate alloys among investigated sections are the alloys from section A (In:Sn=1:4). The indium content in these alloys is within 10 and 18 at%, which enables indium dissolution, and prevents partial alloy melting. The other reason for low content of indium is high cost price.

Therefore, the alloys, which might be an alternative for the common Pb-Sn solders, are Ag-In-Sn alloys with high percent of tin, small percent of silver and indium. It is just a pre-request, having in mind a great influence of cooling rate and appropriate heat treatment on solder quality, as well as economic factors due to the indium and silver price at market, so further investigations should be carried out in that direction.

REFERENCES

[1] www.univie.ac.at/cost531

[2] Korhonen T.M., Kivilahti J.K., JEM, 27(1998)149

[3] T.B. Massalski, J.L. Muttay, L.H. Benett, H. Baker, Binary alloys phase diagrams, ASM, Metals Park, OH, 1990

[4] Miki T., Ogava N., Nagasaka T., Hino M., Mater. Trans. 42(5)(2001)732

[5] Zhang J., Calphad, 27(1)(2003)9

[6] Ohnuma I., Cui Y., Liu X.J., et al., JEM, 29(2000)1113

[7] Liu X.J., Inohana Y., Takaku Y., Ohnuma I., Kainuma R., Ishida K., Moser Z., Gasior W., Pstrus J., JEM, 31(2002)1139

[8] Vassilev G., Dobrev E., Tedenac J.C., XXXIII Calphad Meeting Abstract PI-8, Krakow, Poland (2004); Vassilev G., Dobrev E., Tedenac J.C., Journal of Alloys and Compounds, (2005)-in print

[9] M.R. Baren, Indium alloys and their engineering applications, Ed. C.E.T. White and H. Okamoto materials park, OH, ASM INTL, 1993, p. 15