Phase equilibria investigation and characterization of the Au-In-Sb system

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Abstract. The Au-In-Sb system belongs to the group of potential candidates for lead-free solder materials. The results of phase equilibria investigation and characterization of the alloys in the Au-InSb section are presented in this paper. The investigations were performed using different experimental methods – thermal analysis, optical microscopy and SEM-EDX, hardness and electrical conductivity measurements, and also, using ThermoCalc software based on adequate thermodynamic calculation.

Introduction

Gold and gold alloys are widely applied in modern technical branches – electronics, communications, space and aero technologies, chemistry and medical science, etc. They are known for good mechanical and thermal properties, as well as corrosion consistency. Owing to formation of low temperature eutectic with other elements, gold alloys are often used as welding alloys in electronics [1].

The Au-In-Sb system belongs to the group of potential candidates for lead-free solder materials in the frame of indium-based lead-free solders. They are considered as a possible alternative to conventional Pb-bearing solders in step soldering, which are required for high density packaging of multi-chip modules demanding a number of solders with melting points over a wide temperature range [2]. Therefore, mentioned gold-based system is the subject of different investigations lately, for its phase diagram of ternary Au-In-Sb system is of importance in predicting the interface reactions between In-based solders and Au-substrate, which can provide a tool for design a potential interface [2].

Phase equilibria of this system has been firstly studied by Kubiak and Schubert [3] and Tsai and Williams [4], during eighties. Based on these results, a compilation on the Au-In-Sb phase diagram determination has been done in the book "Phase Diagrams of Ternary Gold Alloys" of Prince and collaborators [5]. Recently, phase diagram of the Au-In-Sb system has been calculated using thermodynamic modeling and presented in literature by Liu et al. [6], as well as the data on condensed phase equilibria in transition metal-In-Sb systems and predictions for thermally stable contacts to InSb [7].

In the frame of thermodynamic research, which presents important base for modern phase equilibria investigation, there were a lot of references considering both ternary Au-In-Sb system and constitutive binaries. So, the experimental determination of the enthalpies of mixing of liquid In–Sb alloys using a sensitive calorimeter at 953 K was presented by Predel and Oehme [8], while Kameda and Tanabe [9] gave the results of electromotive force measurements. Thermodynamic assessment of this system was performed by Ansara et al. [10] and Cui et al. [11], while the phase equilibria of the In-Sb system has been investigated by Liu et al. [12] and Goryacheva et al. [13]. For liquid Au-In alloys, Castanet et al. [14] have determined thermodynamic activities by an EMF method, and the phase diagram of the Au-In system have been assessed by Okamoto et al. [15] and Shunk [16]. Concerning the Au-Sb system, Okamoto et al. [17] have calculated phase equilibria of this system using experimentally obtained thermodynamic data, as well Vogel et al. [18]. Using partial enthalpies of mixing for liquid Au-Sb alloys determined by EMF measurements [19] and vapor pressure measurements as the basis, the enthalpy of mixing have been calculated by Hino et al. [20]. The most recent investigation of the Au-Sb system is given in Ref. [21].

Having in mind this literature survey at one side, and latest demand for new lead-free gold-indium-based solders at the other side [23], the results of phase equilibria and characterization of the AuIn-Sb section in the Au-In-Sb system are presented in this paper. The investigations were performed using different experimental methods – differential thermal analysis, optical microscopy, hardness and electrical conductivity measurements, aiming to contribute to the better knowledge of the investigated Au-In-Sb lead-free solder candidate.

Experimental

Investigated samples were chosen in the AuIn-Sb section of the Au-In-Sb system. The samples were prepared using metals - gold, indium and antimony of 99.99% purity. The composition and masses of chosen samples are given in Table 1.

Table 1. Composition and masses (in g) of the investigated samples

Alloy	x_{Sb}	x_{Au}	x_{In}	m_{Sb}	m_{Au}	m_{In}
A1	0	0.5	0.5	0	3.8032	2.2145
A2	0.05	0.475	0.475	0.2304	3.5396	2.0623
A3	0.2	0.4	0.4	0.8693	2.8122	1.6386
A4	0.28	0.36	0.36	1.1813	2.4569	1.4317
A5	0.4	0.3	0.3	1.6169	1.9610	1.1429
A6	0.65	0.175	0.175	2.4158	1.0520	0.6129
A7	0.85	0.075	0.075	2.9678	0.4326	0.2468

DTA measurements have been carried out on the Derivatograph 1500 (MOM Budapest) apparatus under following conditions - air atmosphere, heating rate 10 ^{o}C/min, T_{max}=1073 K. As a referent material during measurements was used Al_2O_3. In order to test reproducibility of the results every measurement run was repeated, but no significant temperature deviation was found between the first series and repeated series of DTA measurements.The precision of the measurement in the investigated temperature interval was ±5 ^{o}C.

SEM-EDX analysis was performed on Philips microscope XL-300 type with EDX of resolution of 1 nm on 30 kV and 5 nm on 1 kV, extinction voltage of 0.2-30 kV and magnification of 2000x.

Microstructure analysis of investigated samples was performed by optic microscopy, using a Reichert MeF2 microscope (magnification x500). Solution of 1:1 HNO_3 was applied for structure development.

Electrical conductivity of investigated materials was measured using the standard apparatus - SIGMATEST 2.069 (Foerster) eddy current instrument for measurements of electrical conductivity of non-ferromagnetic metals based on complex impedance of the measuring probe with diameter of 8mm.

Hardness measurements were done using standard procedure according to Vickers.

Results and Discussion

The results of the DTA heating measurements, including liquidus temperatures and other peak temperatures, are presented in Table 2.

Table 2. The results of DTA investigation

Alloy	Composition, at%Sb	Temperature, °C	
		Liquidus	Other peak temperatures
A1	0	514	/
A2	5	490	418
A3	20	420	387
A4	28	377	359
A5	40	419	382
A6	60	524	384
A7	85	589	390

Based on starting thermodynamic data for the constitutive binary systems, taken from COST531 Thermodynamic Database [23], thermodynamic modeling was done according to standard procedure [24]. The phases occurring in the system are [23] – liquid (constituents Au, In,Sb), FCC (Au) (constituents Au, In, Sb:Va), BCT_A5 (constituents In,Sb), RHOMBOHEDRAL_A7 (constituents Au,In,Sb), TETRAGONAL_A5 (constituents In,Sb), $AuSb_2$ (constituents Au:Sb,In), $AuIn_2$ (constituents In,Sb:Au) and AuIn (constituents Au:In, Sb). As Liu et al. [6] already determined, AuIn-Sb can not compose pseudobinary system, because when AuIn and Sb combine, reactions must happen when annealed.

The phase diagram of the investigated section AuIn-Sb has been calculated using ThermoCalc software and is presented in Fig.1, together with experimentally determined DTA points.

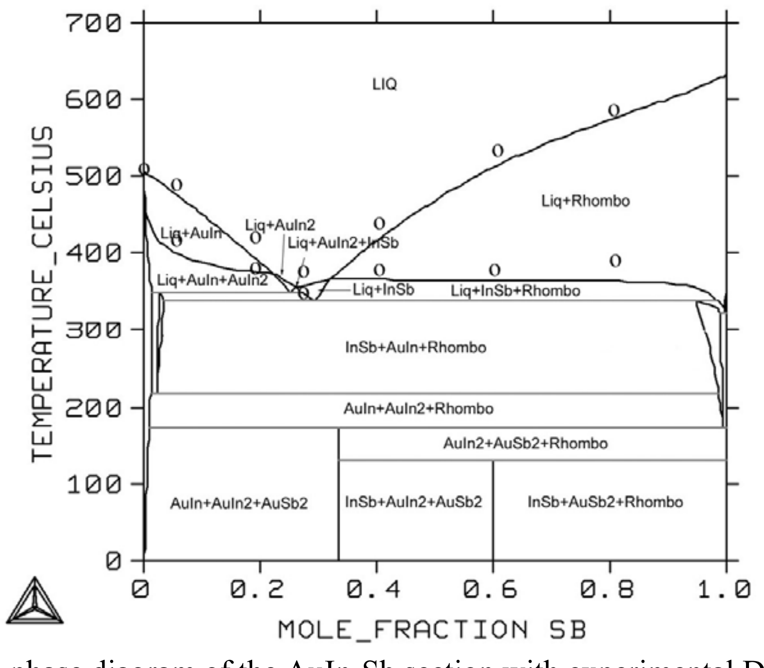

Fig.1. Calculated phase diagram of the AuIn-Sb section with experimental DTA points (circles)

It could be noticed that calculated phase diagram is in good agreement with DTA experiments, as well as with the results on phase equilibria available in literature [6] at the moment.

Further characterization of the investigated alloys in the Au-In-Sb system, have been done using SEM-EDX, optic microscopy, hardness and electrical conductivity measurements.

The results of SEM-EDX analysis are presented in Fig.2 and Table 3, while characteristic microphotographs recorded by optic microscopy are given in Fig.3.

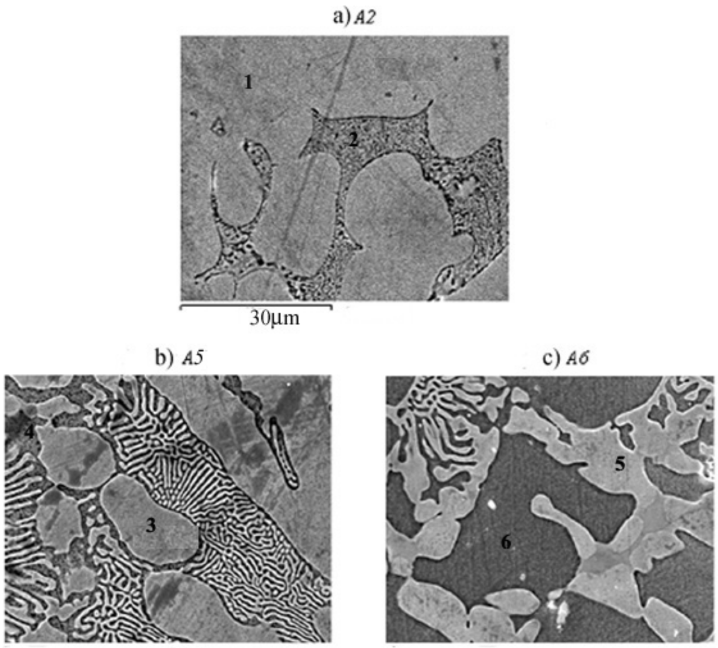

Fig.2. SEM microphotographs for the samples A2 (a), A5 (b) and A6 (c)

Table 3. The results of EDX analysis for the samples A2, A5 and A6

Sample	Phase (in Fig.1)	Experimental composition		
		at% Au	at% In	at% Sb
A2	1	55.4	44.6	/
	2	59.31	23.74	16.95
A5	3	53.97	46.03	/
	4	2.37	/	97.63
A6	5	55.46	44.54	/
	6	/	/	100

The results of hardness measurements are shown in Table 4 in Fig.4. It may be noticed that at concentration $x_{Sb} = 0.05$ hardness shows maximum peak, while in the concentration range over this composition hardness decreases.

Table 4. The results of hardness measurements

Alloy	x_{Sb}	HV5
A1	0	99.4
A2	0.05	126
A3	0.2	94.7
A4	0.28	89.13
A5	0.4	94.57
A6	0.65	79.93
A7	0.85	57.77

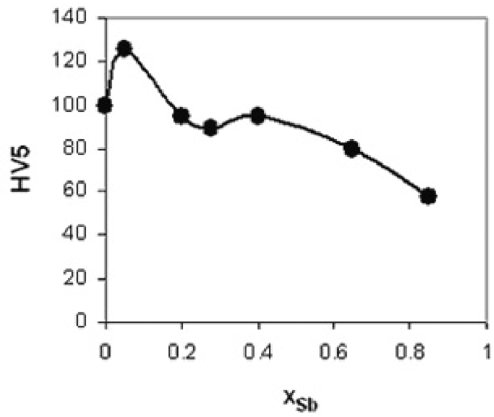

Fig. 4 Hardness vs. composition

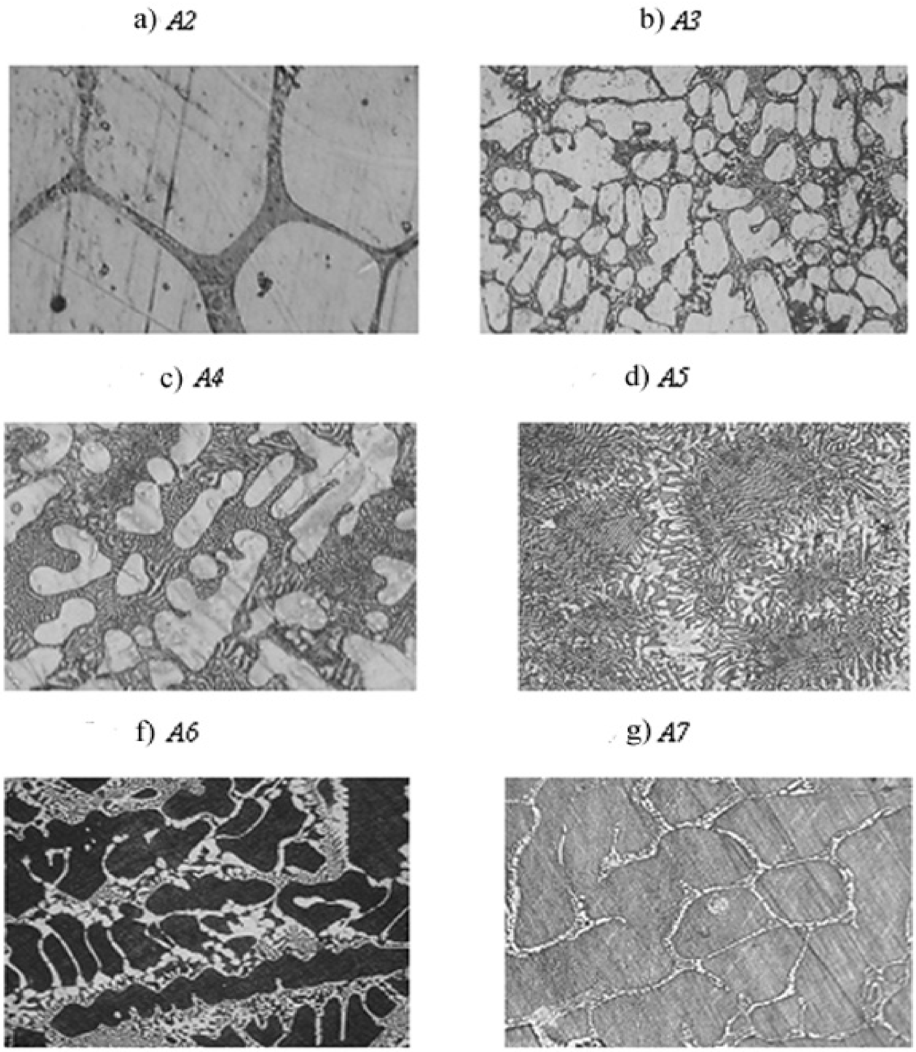

Fig.3. Characteristic optical microphotographs (magnification 500x) for:
a) A2, b) A3, c) A4, d) A5, e) A6, f) A7

The results of electrical conductivity measurements are presented in Table 5 (three measuring series) and Fig.5, where electrical conductivity dependence on composition is showed. As can be seen, the electrical conductivity decreases rapidly with antimony concentration increase in the investigated alloys.

Table 5. Measured values of electrical conductivity for investigated Au-In-Sb alloys

Alloy	Electrical conductivity (MS/m)		
A1	12.94	12.77	12.99
A2	7.396	7.546	7.339
A3	5.660	5.664	5.572
A4	5.533	5.522	5.536
A5	4.287	4.283	4.268
A6	2.667	2.633	2.644
A7	0.5475	0.6700	0.4948

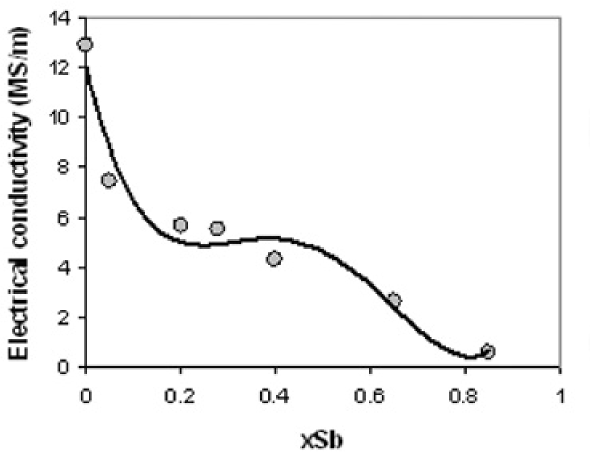

Fig.5. Electrical conductivity vs. composition

Conclusions

The Au-In-Sb alloys, from the section AuIn-Sb, has been characterized using different experimental methods, such as DTA, SEM-EDX, optic microscopy, hardness and electrical conductivity measurements. Phase diagram of this section has been calculated by thermodynamic modeling based on constitutive binary systems data using ThermoCalc software, and confirmed by DTA and SEM-EDX results. Measured values of hardness and electrical conductivity show rapid decrease by antimony content increase in the investigated alloys.

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