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Thermodynamic calculation of the Bi-In-Sb phase diagram

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Abstract: *Phase equilibria of ternary Bi-In-Sb system was investigated by applying CALPHAD method and using literature thermodynamic data for constitutive binary systems. The liquidus surface and isothermal section at 400^0C were calculated. Calculated results were verified experimentally on the alloys samples with the compositions corresponding to the characteristic vertical sections: InSb (1:1)-Bi; BiSb(1:1)-In and BiIn(1:1)-Sb. Phase transitions temperatures were determined by Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC). Microstructure and phase composition investigation were investigated by using Scanning Electronic Microscopy (SEM) with Energy Dispersive Spectrometry (EDS). The experimental and analytical results showed good agreement, concerning the temperatures of phase transitions and phase compositions of alloys concerned.*

Key words: Bi-In-Sb, phase diagrams, thermal analysis, thermodynamic prediction.

1. INTRODUCTION

InSb and GaSb are two examples of so-called narrow band gap semiconductors with high electron mobility. They have gained increasing interest within the last decade.[1-2], because of their high potential for a number of electronic and optoelectronic applications. In the study of Minića et. al. [3] the comparative view of isothermal section at 300^0C is determined by analytical and experimental method. The results were in a good agreement. One of the most powerful methods which can be applied to study thermodynamic properties and phase equilibra of practical alloy systems is the CALPHAD method [4-7]. For metallic solutions, sublattice models developed by Hillert and co-workers have been widely used[8-9]. For the thermodynamic functions of the pure elements in their stable and metastable states, the latest phase stability equations compiled by SGTE [10] were used. The thermodynamic data for the boundary binary systems, used for the calculation of phase equilibria of the ternary Bi-In-Sb systems, were based on the literature data from Boa and Ansara [11] in the case of Bi-In system, Ohtani and Ishida [12] in the case of Bi-Sb system, and Ansara *et al.*[13] in the case of In-Sb system. This thermodynamic data, with some modified and additional thermodynamic parameters, are included in the COST531 database [14] which was used for the calculations in this work. In this paper, the temperatures of phase transition for three vertical sections of ternary Bi-In-Sb system, determined by DSC and DTA method, were presented. The microstructures and the compositions of equilibria phases were obtained by SEM-EDS. The experimentally determined values of the phase transition temperatures were compared to the calculated ones based on optimized thermodynamic data for constitutive binary systems[11-13], by using software package PANDAT 8.1. The results obtained in this work represent a step forward to the complete definition of phase diagram of ternary Bi-In-Sb system, that was incompletely investigated, and have a potential for wide technology application.

2. EXPERIMENT

The alloy samples were prepared from high-purity (99,999%) Bi, In and Sb produced by Alfa Aesar (Germany). Selected samples with compositions from three vertical sections so the molar ratio of two components of 1:1, and molar ratio of the third component was in a range of 0 to 1, with portion of 0,1, are produced by smelting. The samples were prepared as following: the mixtures (~2 g) of the metals were well grained and sealed in quartz tubes under a vacuum and placed in a resistance furnace. The sealed tubes containing the mixed elements were gradually heated to the melting point of Sb ($630,7^0C$). The samples were well stirred and then held at that temperature for 30 minutes. The quartz tubes were taken out of furnace and left for

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cooling in the air to the room temperature. After that, the sealed quartz tubes with the samples which were planned for SEM-EDS analysis were heated in electric resistance furnace until the annealing temperature of 400^{0}C was reached. At this temperature the samples were annealed over a period of 200 h, and than immediately quenched in icy water. The phase transformation temperatures were determined by DTA and DSC methods. The DTA measurements were carried out on Derivatograph MOM Budapest under following conditions: flowing argon atmosphere, sample masses about 1 g, alumina as the reference material, heating rate of 5 ^{0}C /min. The DSC measurements were performed on a SDT Q600 (TA Instruments), under flowing argon atmosphere, with sample masses 50 mg, and heating rate of 5 ^{0}C /min. For microstructure investigation and for phase composition determination was used scanning electron microscopy, SEM (JEOL JSM 6460) with energy dispersive spectrometry, EDS (Oxford Instruments).

3. RESULTS AND DISCUSSION

Based on the values of the thermodynamic parameters the liquidus surface of the Bi-In-Sb ternary system is calculated and plotted in Fig. 1.

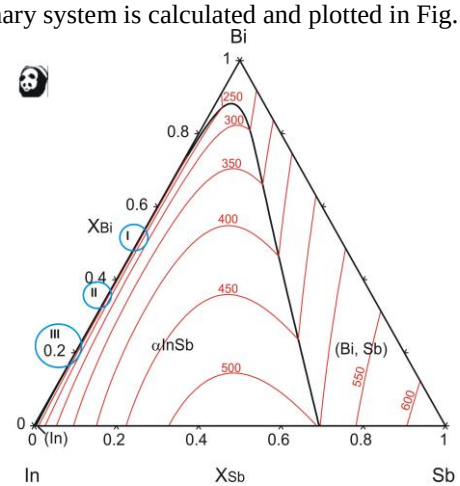


Fig. 1. Calculated liquidus surface of the ternary Bi-In-Sb system

Magnified views of the liquidus surface projection in a vicinity of invariant points are presented on Fig.2. (I)-(III).

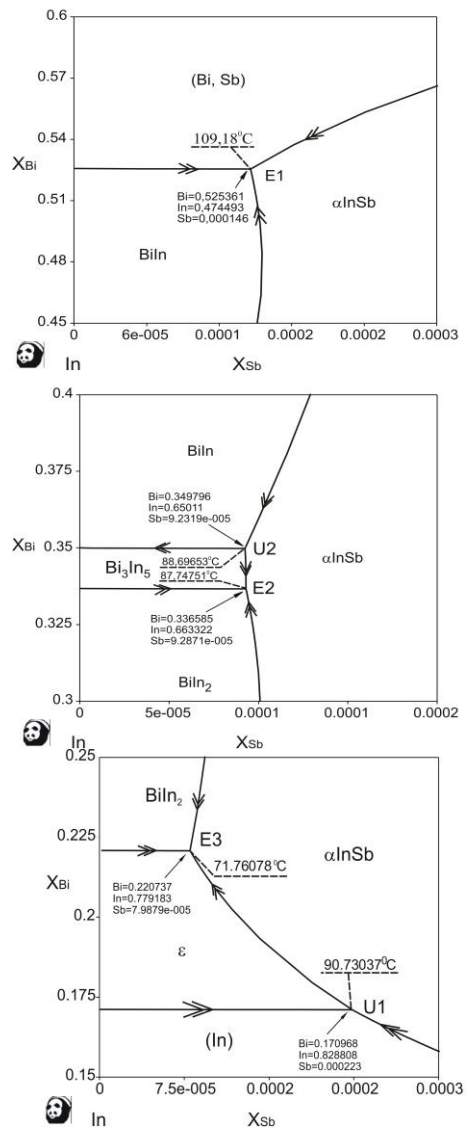


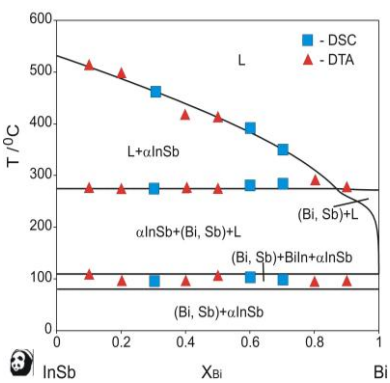
Fig. 2. Magnified views of the liquidus surface projection of Bi-In-Sb ternary system in a vicinity of : I) E1 eutectic point; II) E2 eutectic point; III) E3 eutectic point

The invariant reactions in ternary Bi-In-Sb system are listed in Table 1, as well as the reaction temperatures and the types of those invariant reactions. It can be seen that in ternary Bi-In-Sb system there are five invariant reactions: three eutectic (marked in Table 1 as type E) and two quasi-peritectic (marked as U), and seven regions.

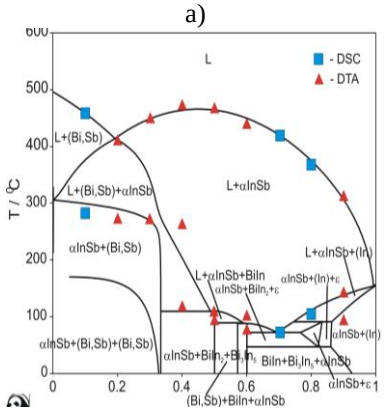
Table 1. Predicted invariant reaction of ternary Bi-In-Sb system

T / ^{0}C	Reaction	Type
109.18	L --> αInSb + (Bi,Sb) + BiIn	E1
90.73	L + (In) --> αInSb + ε	U1
88.69	L + BiIn --> αInSb + Bi_3In_5	U2
87.74	L --> αInSb + Bi_3In_5 + $BiIn_2$	E2
71.76	L --> αInSb + $BiIn_2$ + ε	E3

of primary crystallization (Bi,Sb), αInSb, BiIn, Bi_3In_5, $BiIn_2$, ε and (In), two large regions ((Bi,Sb), αInSb) and five very small regions located on the side of constitutive In-Bi binary system (BiIn, Bi_3In_5, $BiIn_2$, ε, (In)).Three characteristic vertical sections of ternary Bi-In-Sb system were calculated, based on the literature data. The vertical sections were taken from all three corners, Bi, In and Sb with molar ratio equal to In:Sb = 1, Bi:Sb =1 and Bi:In=1, respectively. Calculated phase diagrams for the three vertical sections together with experimentally determined phase transition temperatures by DTA and DSC methods, are presented in Fig. 3.



a)



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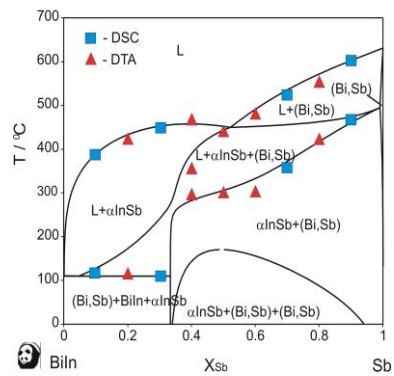
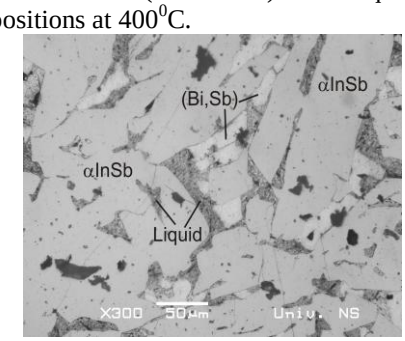


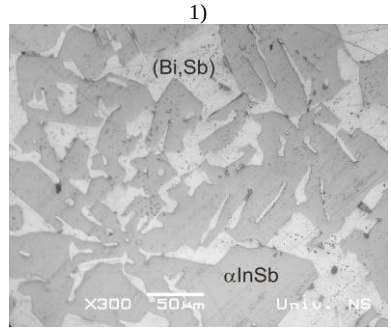
c)

Fig. 3. Calculated phase diagrams for three vertical sections: a)InSb-Bi, b)BiSb-In and, c) BiIn-Sb.

Two samples were investigated using SEM-EDS method and their compositions were presented in Table 2, as well as calculated and experimentally determined (SEM-EDS) equilibrium compositions at 400^{0}C.



1)



2)

Fig. 4. SEM micrograph of the sample 1 and 2

Table 2. Calculated and experimentally determined phase compositions in the ternary Bi-In-Sb system at 400^{0}C

	Overall exp. compo.	Theoretically predicted phases	Exp. determined phases	Phase composition					
				Bi / % at.		In / % at		Sb / % at.	
				exp.	calc.	exp.	calc.	exp.	calc.
1.	25 Bi 25 In 50 Sb	αInSb liquid (Bi,Sb)	αInSb liquid (Bi,Sb)	0.012 44.68 16.02	- 46.34 15.49	48.35 18.04 1.76	50 17.42 0.19	50.45 37.28 82.22	50 36.24 84.32
2.	10 Bi 10 In 80 Sb	(Bi,Sb) αInSb	(Bi,Sb) αInSb	11.89 0.56	12.11 -	0.96 47.94	0.18 50	87.15 51.5	87.61 50

The microstructure of the sample 1 and 2 are shown in Fig. 4. On the microphotograph 1 it can be clearly seen the presence of Liquid , αInSb i (Bi, Sb), and on the microphotograph 2 it can be seen the presence of (Bi,Sb) and αInSb.

The calculated isothermal section of the ternary Bi-In-Sb system at 400^{0}C together with the experimentally determined phase composition for samples 1 and 2 are presented in Fig. 5. It could be seen the existence of the following crystallization fields: single phase field (Liquid); three two-phase fields (Liquid+αInSb; Liquid+(Bi,Sb) and, (αInSb+(Bi,Sb)) and, one three-phase fields (Liquid+αInSb+(Bi, Sb)).

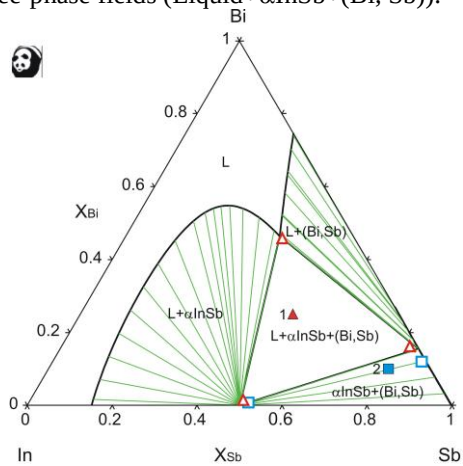


Fig. 5. Isothermal section of the ternary Bi-In-Sb system at 400^{0}C and experimental values of the

The calculated isothermal section of the ternary Bi-In-Sb system at 400^{0}C together with the experimentally determined phase compositions for the samples 1 and 2 (full symbols are referred on the overall composition and empty on the compositions of single phase). It could be

4. CONCLUSION

Phase diagram of the ternary Bi-In-Sb system was calculated using optimized literature data for thermodynamic parameters of the constitutive binary systems by CALPHAD method. It can be concluded that system has five invariant reactions. By experimental verification by determined phase transformation temperatures it can be concluded that the phase diagram is well calculated. There were also obtained good agreements of calculated and experimentally determined phase compositions on two investigated samples, whose compositions were in a region of vertical section at 400^{0}C.

Acknowledgements
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