MECHANICAL AND ELECTRICAL PROPERTIES OF TERNARY Cu–In–Sb SYSTEM AT 400^{0}C

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Abstract: For the complete definition of the properties of the ternary Bi–Cu–In system, there were performed the investigation of micro structures, hardness by Brinel, and electric conductivity of the alloys. In the range of this ternary system, numerous alloys were tested for three vertical sections, with molar ratio Sb: Cu= 1, Cu:In= 1, Sb:In=.1. By application of CALPHAD method, and software package PANDAT 8.1, there were calculated the isothermal cross section at 25^{0}C and 400^{0}C.

Keywords: Bi–Cu–In ternary system, microstructure, hardness, electric conductivity, isothermal sections.

1. INTRODUCTION

The relation between Cu and In in the couples and stable contacts are the main reasons for these systems investigations [1].

Thermodynamic data for the constitutive binary systems included in COST531 thermodynamic database [2] and CALPHAD method [3], enabled calculation of isothermal section at 25^{0}C.

Thermodynamic data for binary Cu–In system were presented by *X. J. Liu et al.* [4], for the constitutive binary Cu–Sb system by *X. J. Liu et al.* [5] and for binary Sb–In system the thermodynamic data were taken from *I. Ansare* et al. [6]. *D. Manasijevicet al.* [7] has presented comparative quasi-binary sections, where the temperatures of phase transformations determined by (DTA) and calculated values were compared. *S. Itabashi* et al. [8] determined activity of indium in ternary Cu–In-Sb system by EMF method using a Zirconia electrolyte.

2. EXPERIMENT

The alloy samples were prepared from high-purity (99.999%) indium, antimony and copper produced by Alfa Aesar (Germany). The samples mass weight of 4 g were prepared in inductive furnace in Argon atmosphere and cooled on air. The samples used for optic microscopy, electric conductivity measurements and hardness tests

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were prepared by classic metallographic procedure without penetration. The samples of alloy investigated on SEM-EDS were not sealed.

Electron microscopy was done on Scanning Electron Microscopy instrument from JEOL (JSM6460), with Energy Dispersive Spectrometer, EDS by Oxford Instruments.

Optic microscopy was done using Optic microscope OLYMPUS GX41, hardness was measured by Duroscope method using HL-400DL instrument. Electrical conductivity measurements were carried out with SIGMATEST 2.069.

3. RESULTS AND DISCUSSION

Phase names used in this paper with phase names included in thermodynamic data base COST531 [2] with their Pearson's symbols [9] are listed in Table 1.

Table 1. Considered phases, phase's name in the thermodynamic data base and Pearson's symbols [2, 9].

Considered phase	Phase's name in data base	Pearson's symbol
L	LIQUID	-
α(Fcc)	FCC_A1	*cF4*
β(Bcc)	BCC_A2	*cI2*
γ(CuIn)	CUIN_GAMMA	*cP52*
δ (Cu_7In_3)	CUIN_DELTA	*aP40*
η′	CUIN_ETA	*hP4*
η	CUIN_ETAP	*hP6*
$Cu_{11}In_9$	CUIN_THETA	*mC20*
(In)	TETRAGONAL_A6	*tI2*
ξζ($Cu_{10}Sb_3$)	CUSB_ZETA	*hP26*
γ($Cu_{17}Sb_3$)	CUSB_GAMMA	*hP2*
η(Cu_2Sb)	CUSB_ETA	*tP6*
ε(Cu_3Sb)	CUSB_EPSILON	*oP8*
δ(Cu_4Sb)	CUSB_DELTA	*hP?*
(Sb)	RHOMBO_A7	*hR2*
InSb	ZINCBLENDE_B3	*cF8*

Itabashi at al. [8] determined the activities of Indium for three vertical sections (In-$Cu_{0.2}Sb_{0.8}$, In-$Cu_{0.5}Sb_{0.5}$ and In-$Cu_{0.8}Sb_{0.2}$) at 1200K.

3.1. Microstructure analysis

In order to determine microstructure of the alloys of the ternary Cu-In-Sb system, the microstructures for numerous alloys were determined, nine to be precise, and the compositions of the considered alloys were given with quasi binary section at 25^0C on Figure 1.

The obtained microstructures were presented on Figure 1.

By observing microstructures showed on Figure 1 it can be seen that all of them are very similar, and the presence of all three phases in microstructures can be confirmed. The basic of the microstructure is gray phase, than purple phase and light i.e. white phase, in most of the cases the least present in the microstructure. The calculated isothermal section at 25^0C, presented on Figure 2, showed three large regions and four smaller regions. All seven regions have three phases each, every region is three-phase region. This corresponds to the presented microstructures of the alloys.

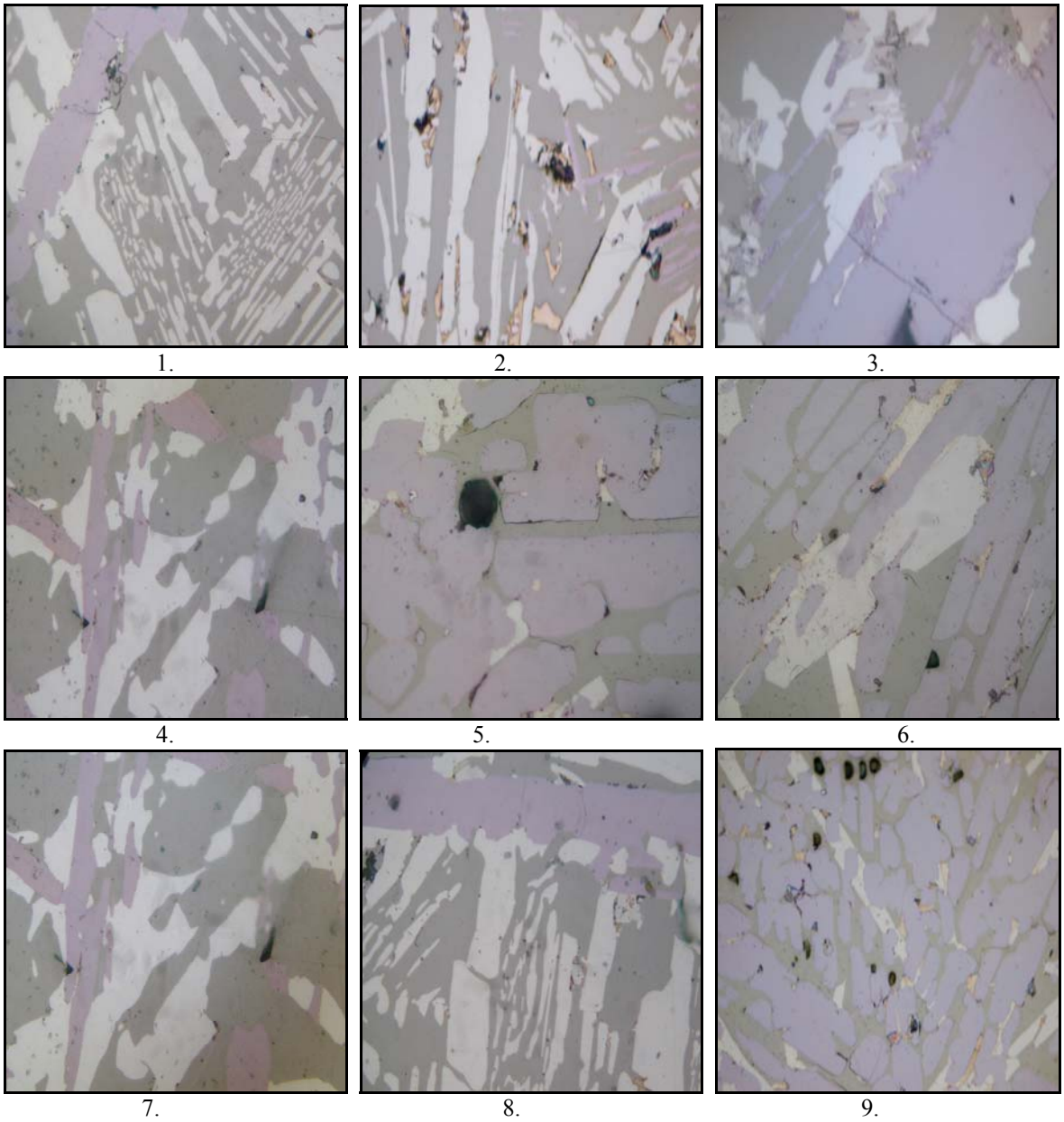

Fig. 1. Microstructures of alloys of Cu-In-Sb ternary system 800X.

3.2. Electric conductivity of alloys

The electric conductivity for three isothermal sections Sb–CuIn, In–CuSb and Cu–InSb was investigated. The compositions of the referring alloys and their electric conductivities were presented in Table 2.

Table 2. Alloys compositions and electric conductivities.

x(Sb)	σ (MS/m)	x(In)	σ (MS/m)	x(Cu)	σ (MS/m)
Sb–CuIn		In–CuSb		Cu–InSb	
0	1.695	0	1.451	0	8.277
0.2	0.932	0.2	2.676	0.2	8.549
0.4	1.38	0.4	2.143	0.4	10.942
0.6	1.649	0.5	3.848	0.5	12.505
0.7	1.904	0.6	4.319	0.6	23.448
0.8	2.356	0.8	6.946	0.8	37.037
1	2.88	1	11..6	1	59.6

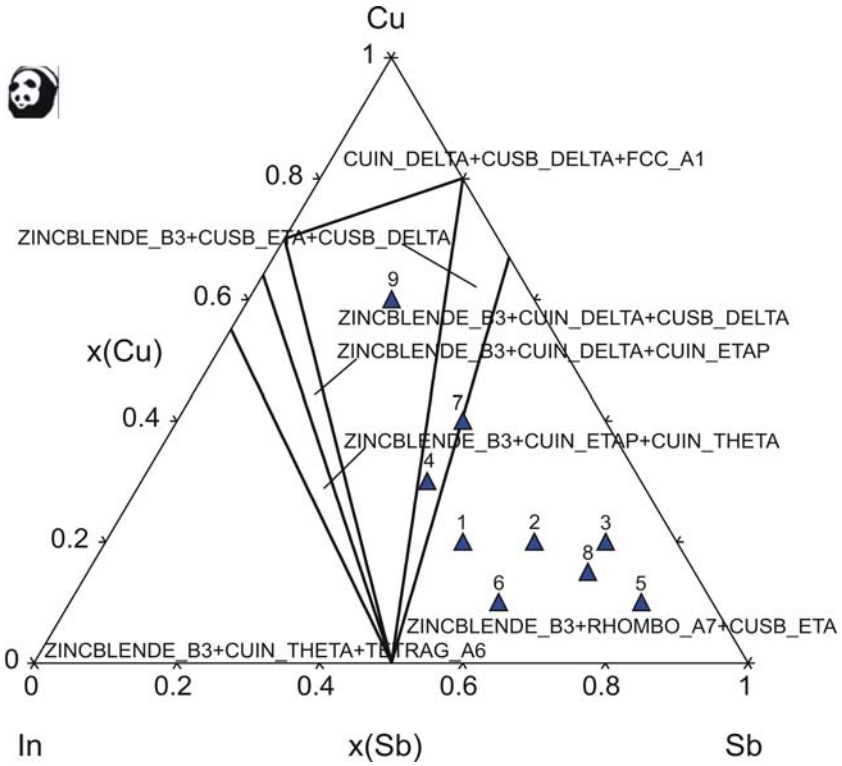

Fig. 2. Isothermal section at 25^0C of the ternary Cu–In–Sb system.

Based on experimentally determined electric conductivities of alloys for three quasi binary sections, the electric conductivity for all ternary Cu-In-Sb system was determined by application of regression model [10]. Theoretic regression model can be presented in a for of multiplied quasi linear regression:

$$\hat{Y} = b_1 X_1 + b_2 X_2 + b_3 X_3 + b_{12} X_1 X_2 + b_{13} X_1 X_3 + b_{23} X_2 X_3 \tag{1}$$

Unknown values of the coefficients of multiplied regression were determined by the least square method, i.e. from the condition that sum of the quadrates of errors:

$$S = S(b_1, b_2, b_3, b_{12}, b_{13}, b_{23}) = \sum_{i=1}^{N} \varepsilon_i^2 = \sum_{i=1}^{N} (Y_i - \hat{Y}_i)^2 \tag{2}$$

$$S = \sum_{i=1}^{N} \varepsilon_i^2 = \sum_{i=1}^{N} \left[Y_i - (b_1 X_1 + b_2 X_2 + b_3 X_3 + b_{12} X_1 X_2 + b_{13} X_1 X_3 + b_{23} X_2 X_3)_i \right]^2 \tag{3}$$

is minimum. The coefficients of regression were determined, and mathematic model, presented by the equation (1) could be written as:

$$\begin{aligned} \sigma(\text{MS/m}) = {} & 56.8711*x(\text{Cu})+1.2379*x(\text{In})+11.6292*x(\text{Sb})-96.4258*x(\text{Cu})*x(\text{In})- \\ & 116.9276*x(\text{Cu})*x(\text{Sb})+2.8947*x(\text{In})*x(\text{Sb}) \end{aligned} \tag{4}$$

For quasi-linear model of multiplied regression given by equation (1) the quadrates of discrepancies of empiric values from regression equation and sum of quadrates of discrepancies was obtained SK=116.4892427. As the absolute value of the greatest discrepancies was ε_{max}=5.82234 and less than 3*E= 6.903237661 so based on the three σ rule, the assumed functional dependence was considered accurate.

3.3 Mechanical properties

The hardness of alloys in three vertical sections: Sb–InCu, In–SbCu i Cu–InSb were investigated. The compositions of the considered alloys and experimentally determined hardness were showed in Table 3.

Table 3. Alloys compositions and hardness by Brinel.

x(Sb)	HB(MN/m^2)	x(In)	HB (MN/m^2)	x(Cu)	HB (MN/m^2)
Sb–CuIn		In–CuSb		Cu–InSb	
0	243	0	150	0	170
0.2	223.7	0.2	135	0.2	303.3
0.4	220	0.4	126	0.4	305
0.6	218	0.5	143.3	0.5	295
0.7	215	0.6	166.7	0.6	376.7
0.8	204.7	0.8	138	0.8	475
1	294	1	8.83	1	874

The mathematic model presented by equation (1) for alloy's hardness by Brinel in the ternary Cu–In-Sb system could be written:

$$HB(MN/m^2) = 282.5354*x(Sb)+13.6987*x(In)+834.7551*x(Cu)+418.4058*x(Sb)*x(In)-1473.1515*x(Sb)*x(Cu)-536.8279*x(In)*x(Cu) \quad (5)$$

For quasi-linear model of multiplied regression, given by equation (1), the quadrates of discrepancies of empiric points from regression equation were calculated, and the sum of discrepancies quadrates was SK= 46723.42994. As absolute value of the largest discrepancy was ε_{max}= 94.54563 less than 3*E= 138.2538623 so based on three sigma rule, the assumed functional dependence was considered good.

3.4. Isothermal section at 400^{0}C

Calculated isothermal section at 400^{0}C was compared to two experimentally investigated samples or two alloys. The samples compositions were given in Table 4, also calculated three-phase region was determined by experiment and by using SEM-EDS.

Table 4. Calculated and experimentally determined phase compositions in the ternary Cu–In–Sb system at 400^{0}C.

Sample	Sample composition [at. %]	Calculated phases	Experimentally determined phases	Experimentally determined phase composition [at. %]		
				Cu	In	Sb
1.	80 Sb 10 Cu 10 In	CUSB_ETA RHOMBO_A7 ZINCBLENDE_B3	CUSB_ETA RHOMBO_A7 ZINCBLENDE_B3	64.78 1.08 1.52	1.1 0.47 47.75	34.22 98.53 50.73
2.	60 Sb 20 Cu 20 In	CUSB_ETA RHOMBO_A7 ZINCBLENDE_B3	CUSB_ETA RHOMBO_A7 ZINCBLENDE_B3	61.91 1.92 0.49	1.99 1.75 48.61	36.1 96.33 50.9

4. CONCLUSION

Microstructures of the considered alloys and calculated isothermal section at 25^{0}C showed presence of three phases. Those three phases are present in all microstructures, just the amount of the single phase is changed. The calculated section showed presence of seven three-phase regions, three of them were large, and four of them were smaller regions.

Electric conductivity showed tendency to stay constant to the half of molar ratio, and after that electric conductivity increased rapidly. Hardness showed tendency of growth a little earlier, so at 0.2 to 0.3 molar ratios,

the sudden raise of hardness was determined. Calculated and experimenatlly determined values for isothermal section at 400^0C showed good agreement.

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