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Mechanical and Electrical Properties of Alloys and Isothermal Section of Ternary Cu-In-Sb System at 673 K

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Abstract. Lead-free solders with copper represent possible substitution for standard lead-tin solders. 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. The micro structures of the alloys were investigated by application of optic microscopy. By application of CALPHAD method, and software package PANDAT 8.1. there were calculated the isothermal cross sections at 298 K and 673 K. The experimentally obtained phase compositions in microstructures are in a good agreement with phases on calculated cross sections.

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

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1 Introduction

Binary Cu-In system and ternary Cu-In-Sb system have very important role in electronics. The relation between Cu and In in the couples and stable contacts are the main reasons for these systems investigations.

Liu and Mohney [1] have performed thermodynamic calculations to estimate ternary phase diagrams for many of the transition metal-In-Sb systems. The results of their estimates of the phase equilibria in many of the transition metal-In-Sb systems where no diagrams were previously available, describing the approximations made in the calculations were presented here.

Thermodynamic data for the constitutive binary systems included in COST531 thermodynamic database [2] and CALPHAD method [3], enabled calculation of isothermal section at 298 K.

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. Manasijevic et 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-InSb system by EMF method using a zirconia electrolyte.

2 Experimental Procedure

The alloy samples were prepared from high-purity (99.999 mass %) 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 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.

Itabashi et 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

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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
$\eta\prime$	CUIN_ETA	hP4
η	CUIN_ETAP	hP6
$Cu_{11}In_9$	CUIN_THETA	mC20
(In)	TETRAGONAL_A6	tI2
ζ ($Cu_{10}Sb_3$)	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

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

In-$Cu_{0.8}Sb_{0.2}$) at 1200 K. The comparative presentation of experimentally values and calculated values for indium activities for three vertical sections was presented on Figure 1. A good agreement between experimental and calculated values was observed.

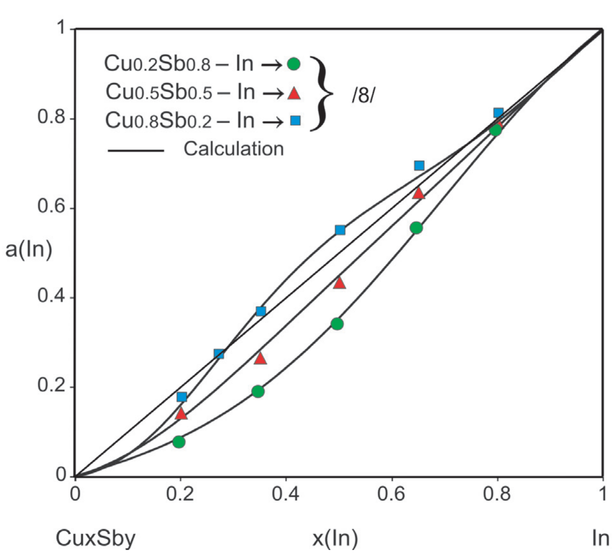

Figure 1. Comparative presentation of experimentally values and calculated values for indium activities for three vertical sections at 1200 K.

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 298 K on Figure 2.

The obtained microstructures were presented on Figure 2.

By observing microstructures showed on Figure 2 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 298 K, presented on Figure 3, 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.

In the next part, the microstructure was analyzed on Scanning Electron Microscope (SEM) with EDS and obtained microstructure was presented on Figure 4. There were three phases on the microstructure, (ZINCBLENDE_B3 + RHOMBO_A7 + CUSB_ETA), and that was confirmed by EDS analysis. The considered sample is sample 2 from the Figure 3. From that figure it can be seen that this sample is from the three-phase region, and it was confirmed by phase analysis at the point.

3.2 Electric Conductivity of Alloys

The electric conductivity (σ) of the ternary Cu-In-Sb system was investigated here. 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. Graphic presentation of the relation of electric conductivity to molar ratio of the alloys was showed on Figure 5.

The electric conductivity for the vertical section Sb-CuIn was given on the Figure 5a). It can be observed that with increasing the molar ration of Sb, the conductivity decreases til 0.2 molar ratio of antimony, and with further increasing the molar ratio of antimony, the electric conductivity is increasing.

The situation is similar with two other vertical sections. Up to the half of molar ratio, the electric conductivity is constant, and by going toward the pure metal composition, it is rapidly increasing.

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

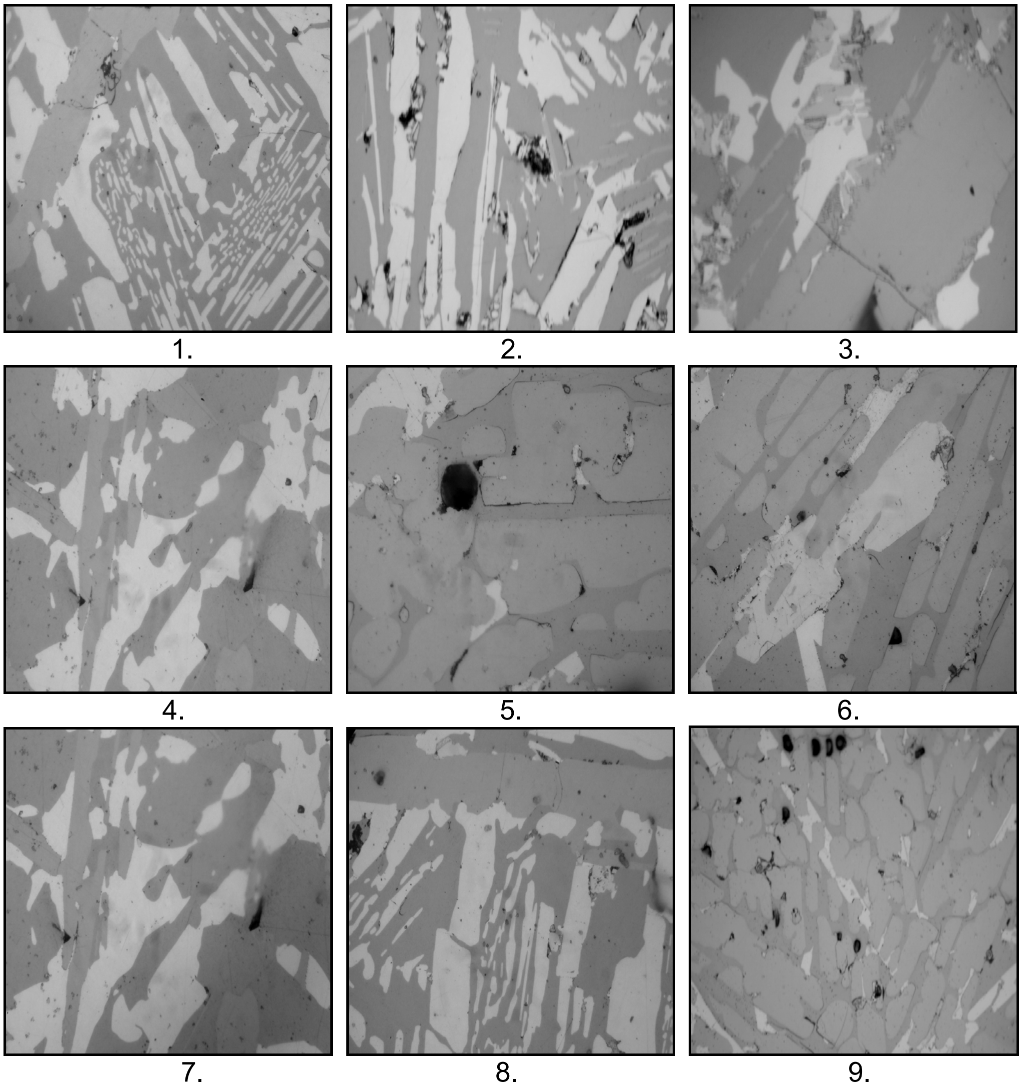

Figure 2. Microstructures of alloys of Cu-In-Sb ternary system, 800×.

quasi linear regression:

$$\hat{Y} = b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 \quad (1)$$

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:

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

$$S = \sum_{i=1}^{N} \varepsilon_i^2 = \sum_{i=1}^{N} [Y_i - (b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3)_i]^2 \quad (3)$$

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

$$\sigma(\mathrm{MS/m}) = 56.8711 * x(\mathrm{Cu}) + 1.2379 * x(\mathrm{In}) + 11.6292 * x(\mathrm{Sb}) - 96.4258 * x(\mathrm{Cu}) * x(\mathrm{In}) - 116.9276 * x(\mathrm{Cu}) * x(\mathrm{Sb}) + 2.8947 * x(\mathrm{In}) * x(\mathrm{Sb}). \quad (4)$$

The mathematic model defined by equation (4) is presented as a graph on Figure 6.

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 $\varepsilon_{\max} = 5.82234$ and less than $3 * E = 6.903237661$ so based on the three

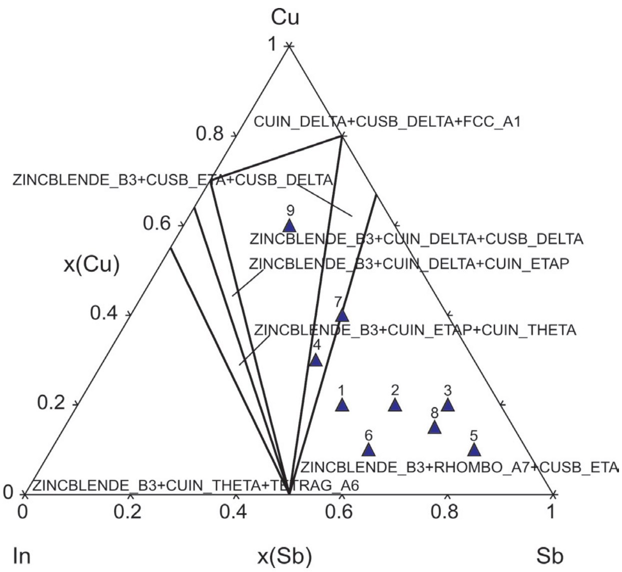

Figure 3. Isothermal section at 298 K of the ternary Cu-In-Sb system.

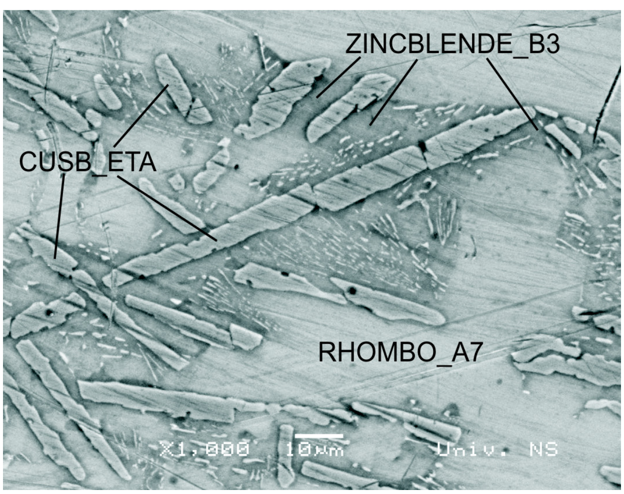

Figure 4. SEM-microstructure

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

Table 2. Alloys compositions and electric conductivities.

σ rule, the assumed functional dependence was considered accurate.

3.3 Mechanical Properties

The Brinell hardness of alloys was determined. The hardness of alloys in three vertical sections: Sb-InCu, In-SbCu and Cu-InSb were investigated. The compositions of the considered alloys and experimentally determined hardness were showed in Table 3. Graphic presentation of the dependance of vertical section hardness vs molar ratios were presented on Figure 7.

Hardness in all three quasi-binary sections tends to raise with increasing molar ratio of corresponding metal. Slightly slower growth can be observed in In-CuSb section. Based on these experimental investigation hardness was determined for whole ternary system.

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

$$\begin{aligned}\mathrm{HB(MN/m^2)} = {} & 282.5354 * x(Sb) + 13.6987 * x(\mathrm{In}) \\ & + 834.7551 * x(\mathrm{Cu}) \\ & + 418.4058 * x(\mathrm{Sb}) * x(\mathrm{In}) \\ & - 1473.1515 * x(\mathrm{Sb}) * x(\mathrm{Cu}) \\ & - 536.8279 * x(\mathrm{In}) * x(\mathrm{Cu}). \qquad (5)\end{aligned}$$

Mathematic model defined by equation (5) was presented as graph on Figure 8.

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 $\varepsilon_{\max} = 94.54563$ less than $3 * E = 138.2538623$ so based on three sigma rule, the assumed functional dependence was considered good.

3.4 Isothermal Section at 673 K

Calculated isothermal section at 673 K 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. The calculated isothermal section was given on Figure 9. with experimentally determined phase composition. By considering Figure 9. and Table 4, it can be concluded that calculated and experimental values are in a good agreement.

On Figure 9, representing isothermal section at 673 K, it can be seen the presence of 22 regions, three of them single phase, ten of them are two-phases, and nine are three-phases regions.

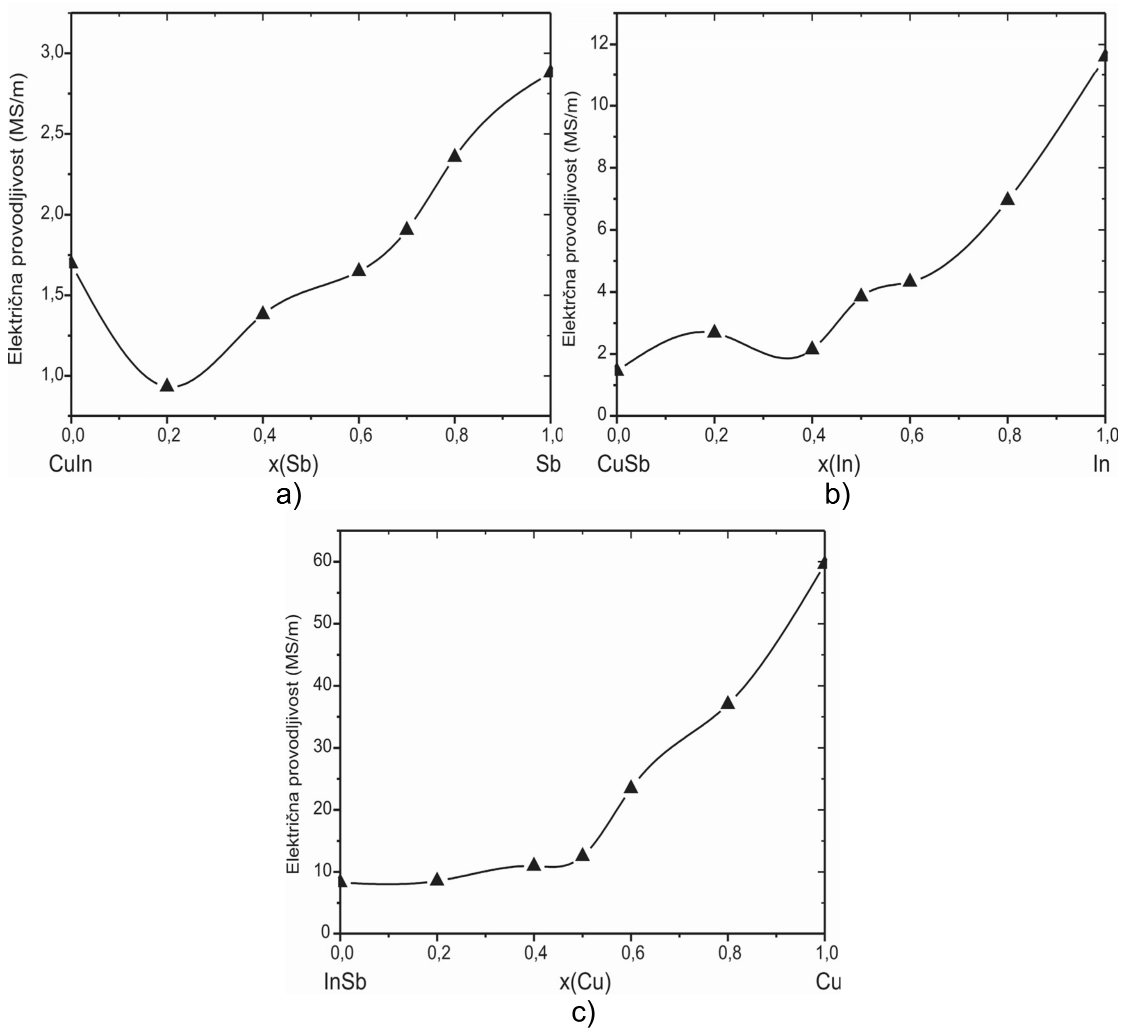

Figure 5. Electric conductivity of ternary Cu-In-Sb system, a) vertical Sb-CuIn section, b) vertical In-CuSb section and c) vertical Cu-InSb section.

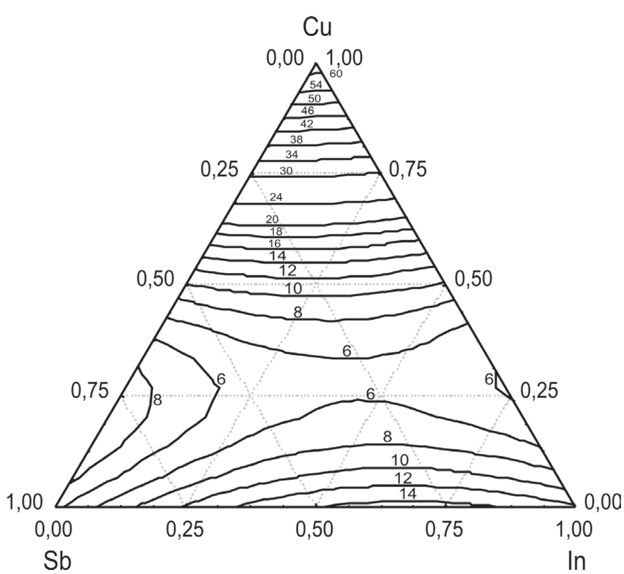

Figure 6. Iso-lines of electric conductivity for the ternary Cu-In-Sb system.

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

Table 3. Alloys compositions and Brinell hardness.

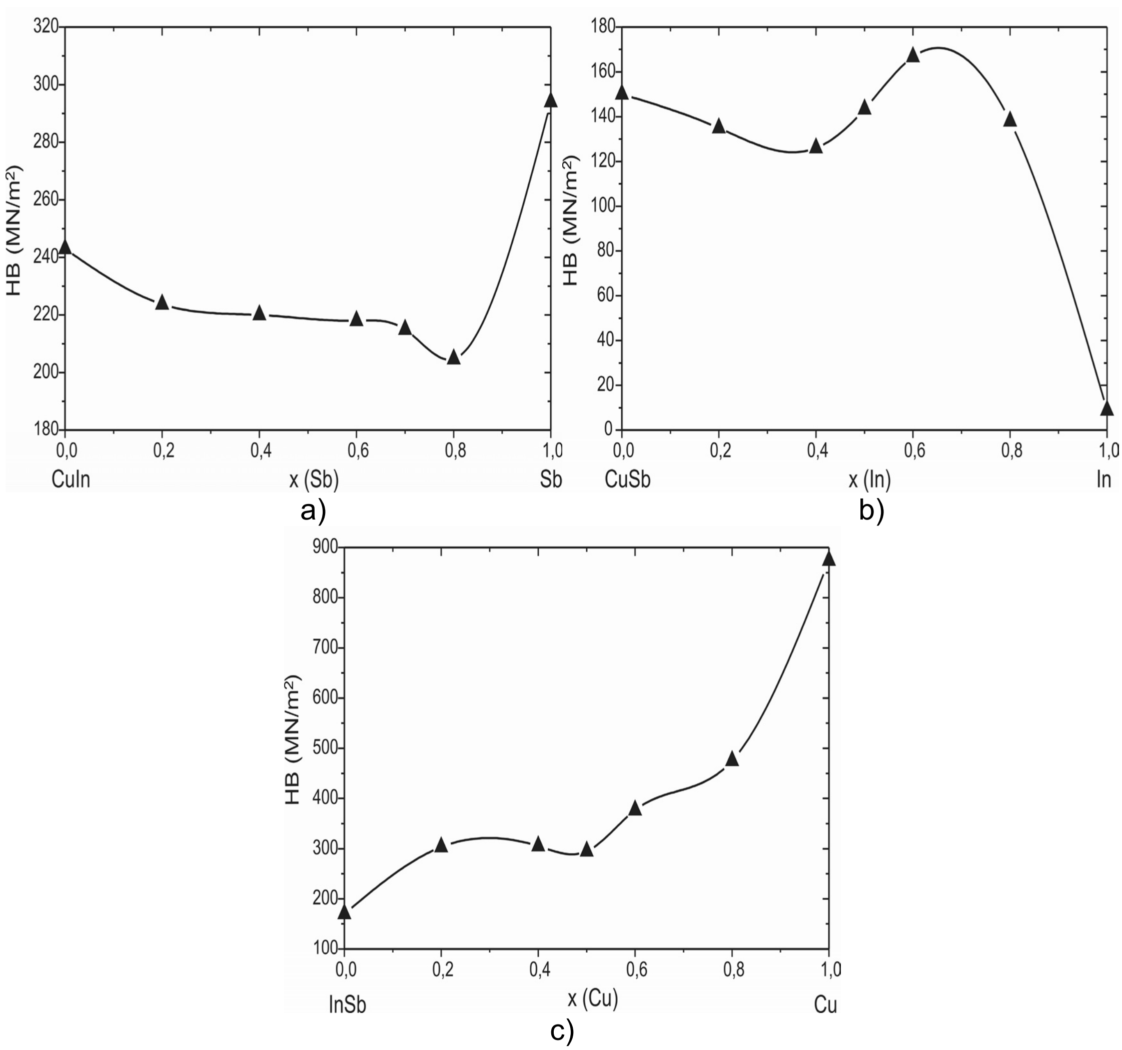

Figure 7. Hardness of alloys of ternary Cu-In-Sb system, a) vertical Sb-CuIn section, b) vertical In-CuSb section and c) vertical Cu-InSb section.

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

Table 4. Calculated and experimentally determined phase compositions in the ternary Cu-In-Sb system at 673 K.

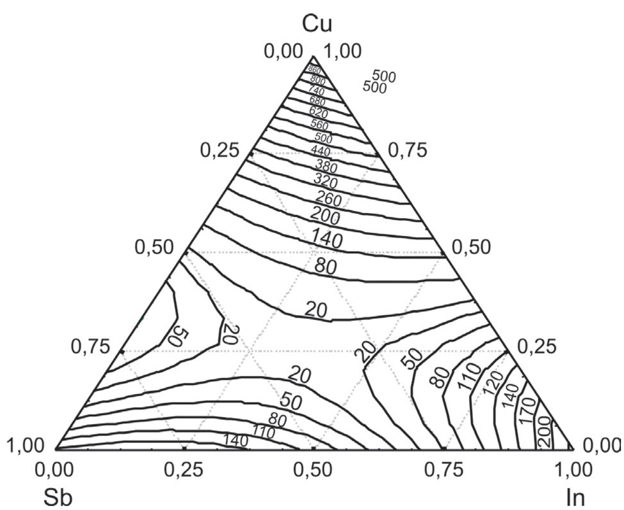

Figure 8. Iso-lines of hardness by Brinel for ternary Cu-In-Sb system.

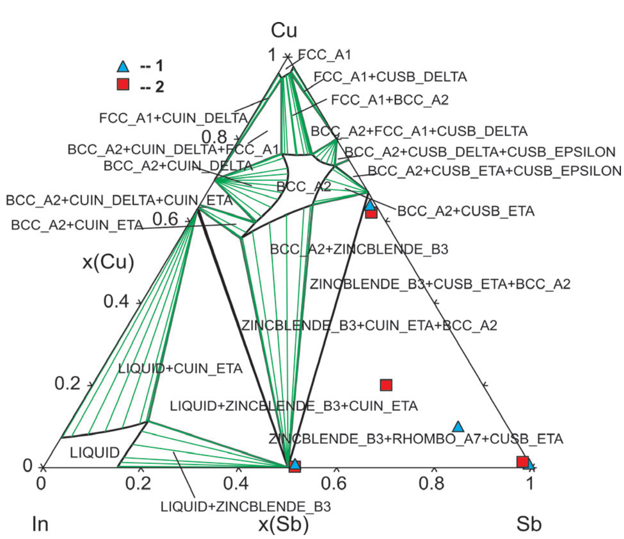

Figure 9. Isothermal section of ternary Cu-In-Sb system at 673 K.

4 Conclusion

Microstructures of the considered alloys and calculated isothermal section at 298 K 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 experimentally determined values for isothermal section at 673 K showed good agreement.

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