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Phase equilibria and thermodynamics of the Bi–Cu–In ternary system

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ABSTRACT

Phase equilibria and thermodynamic properties of ternary Bi–Cu–In system were investigated experimentally and by applying CALPHAD method. Calculated values of thermodynamic functions were collated with published experimental thermodynamic results for liquid phase. Calculated isothermal section at 400 °C was compared with experimental SEM/EDS results from this study. Three calculated vertical sections were compared with the DTA/DSC results from this work. Reasonable agreement between thermodynamic prediction and experimental data was observed in all cases.

1. Introduction

In view of environmental and health concerns, the intensive searching for alternative solder alloys to classical lead–tin solder, are still in progress. Knowledge about the phase diagram and the thermodynamic properties of the studied soldering system is required to predict the thermal behavior, the microstructure evolution of the solder itself and the possible interfacial between solder and substrate.

The Bi–Cu–In ternary system is one of the important systems for the development of Pb-free solders. In this paper, the phase relations of the Bi–Cu–In ternary system are investigated experimentally using SEM/EDS and DTA/DSC.

2. Experimental procedure

The alloy samples were prepared from high-purity (99.99 mass%) bismuth, copper and indium produced by Alfa Aesar (Germany). The samples with a total mass of about 2 g were prepared by induction melting of pure metals under argon atmosphere. All alloys were melted several times to ensure homogeneity. The mass losses of samples were less than 1 mass%.

The samples for SEM/EDS analysis were sealed in evacuated quartz tubes and heated in electric resistance furnace until the annealing temperature of 400 °C was reached. The samples were equilibrated over a period of 350 h at this temperature, 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 °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 °C/min.

For microstructure investigation and for phase composition determination scanning electron microscopy, SEM (JEOL JSM 6460) with energy dispersive spectrometry, EDS (Oxford Instruments) was used.

3. Thermodynamic and crystallographic data

Phase diagram of the Bi–Cu–In ternary system was calculated by the calculation of phase diagram (CALPHAD) method [1], using only optimized thermodynamic parameters for constitutive binary systems included in COST531 database [2]. The basic mathematical method used for the calculation of phase equilibria is a constrained minimisation of Gibbs energy for a given temperature, pressure and overall composition. This approach is common for all currently available software packages for the modeling of thermodynamic properties and phase diagrams of multicomponent systems.

The molar Gibbs energy of a phase ϕ can be considered as the sum of a number of different contributions:

$$G_m^{\phi} = G_{ref}^{\phi} + G_{id}^{\phi} + G_E^{\phi} + G_{mag}^{\phi} + G_P^{\phi} + \cdots \quad (1)$$

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Table 1
Considered phases, their crystallographic data and database names [7].

Database name	Common name	Strukturbericht designation	Pearson symbol
LIQUID	Liquid		
FCC_A1	(Cu)	*A*1	*cF*4
RHOMBO_A7	(Bi)	*A*7	*hR*2
BCC_A2	β	*A*2	*cI*2
CUIN_GAMMA	γ	...	*cP*52
CUIN_DELTA	δ	...	*aP*40
CUIN_ETA	η′	$B8_1$	*hP*4
CUIN_ETAP	η	$B8_2$	*hP*6
CUIN_THETA	Cu11In9	...	*mC*20
TETRAG_A6	(In)	*A*6	*tI*2
BIIN	BiIn	*B*10	*tP*4
BI3IN5	Bi3In5	$D8_1$	*tI*32
BIIN_BRASS	BiIn2	$B8_2$	*hP*6
TET_ALPHA1	ε	*A*6 *mod*	*tI*2

where G^{ϕ}_{ref} is the molar Gibbs energy of the weighted sum of the system constituents i (elements, species, compounds, etc.) of the phase ϕ relative to the chosen reference state (typically the Stable Element Reference state—SER),

$$G^{\phi}_{ref} = \sum_{i=1}^{n} x_i \cdot {}^{o}G^{\phi}_{i} \tag{2}$$

and its temperature dependence is given by

$$G(T) = a + bT + cT\ \ln(T) + \sum_{i} d_i T^n \tag{3}$$

where a–d_i are adjustable coefficients.

There is also a contribution to the Gibbs energy from ideal random mixing of the constituents on the crystal lattice, denoted G^{ϕ}_{id},

$$G^{\phi}_{id} = RT\sum_{i=1}^{n} x_i \cdot \ln(x_i), \quad i = 1, \ldots, n \tag{4}$$

for an n-constituent system.

G^{ϕ}_{E} is the excess Gibbs energy, which describes the influence of non-ideal mixing behavior on the thermodynamic properties of a solution phase and is given by the Muggianu extension of the Redlich–Kister formalism [3,4]

$$G^{\phi}_{E} = \sum_{\substack{i,j=1 \\ i\neq j}}^{n} x_i x_j \sum_{z=0}^{m} {}^{z}L(x_i - x_j)^{z} + \sum_{\substack{i,j,k=1 \\ i\neq j\neq k}}^{n} x_i x_j x_k L_{ijk}, \quad z = 0, \ldots, m \tag{5}$$

where the interaction parameters, describing the mutual interaction among constituents i and j, are denoted as ${}^{z}L$. The liquid phase and solid solution phases are modeled in this way, but more complex phases, such as intermetallic compounds, are usually modeled using the compound energy formalism [5].

Additional terms may be necessary for the proper description of the Gibbs energy from Eq. (1). G^{ϕ}_{mag} in Eq. (1) is the magnetic contribution and G^{ϕ}_{P} is the pressure term.

The lattice stabilities (thermodynamic data for pure elements) compiled by Dinsdale [6] and binary thermodynamic data from Ref. [2] were used in this work.

The phases from constitutive binary subsystems considered for thermodynamic binary-based prediction with their crystallographic data are listed in Table 1.

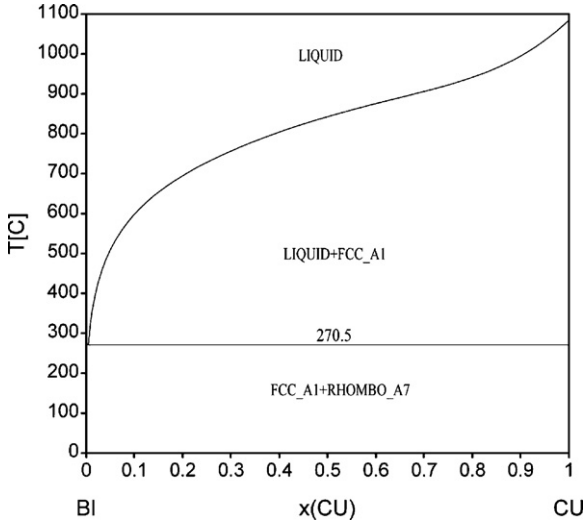

Fig. 1. Calculated phase diagram of the Bi–Cu binary system.

4. Literature data

4.1. Binary systems

The Bi–Cu system is a simple eutectic system showing virtually no mutual solubility of the component elements. The thermodynamic description of this system included in Ref. [2] and used for calculation in this work is taken from Ref. [8]. Calculated phase diagram of the Bi–Cu binary system is shown in Fig. 1.

The thermodynamic description of Bi–In system included in Ref. [2] and used in this work is based on the published data from Boa and Ansara [9].

Calculated phase diagram of the Bi–In binary system is shown in Fig. 2.

The thermodynamic description of Cu–In system used in this work and included in Ref. [2] was taken from Refs. [10,11]. Fig. 3 represents calculated phase diagram of the Cu–In binary system.

4.2. Bi–Cu–In ternary system

There is only one reference on thermodynamics of ternary Bi–Cu–In system by Itabashi et al. [12], in which activities of indium in liquid Bi–Cu–In alloys, along three sections with constant molar

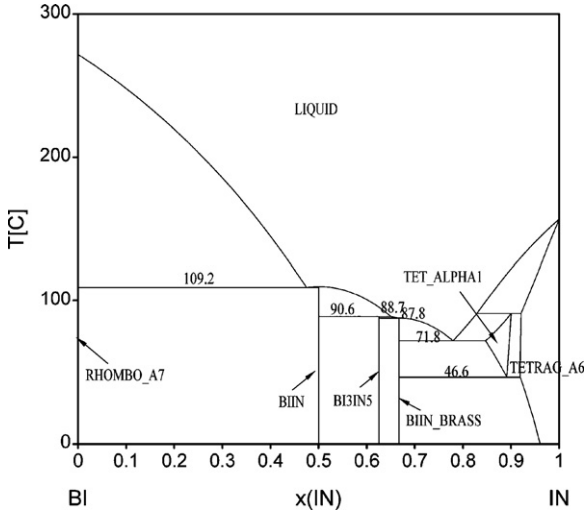

Fig. 2. Calculated phase diagram of the Bi–In binary system.

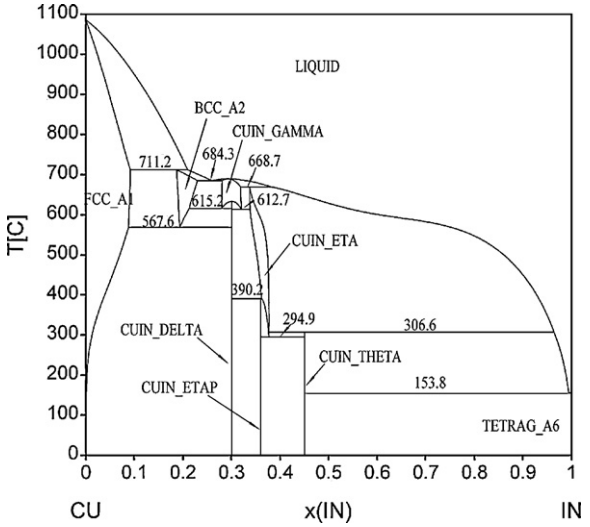

Fig. 3. Calculated phase diagram of the Cu–In binary system.

ratio of Cu/In = 4/1, 1/1 and 1/4 at 982–1259 K, were measured by EMF method using zirconia as solid electrolyte.

5. Results and discussion

Experimental thermodynamic data from the literature and results of SEM/EDS and DTA/DSC measurements from this study were compared with calculated results based on thermodynamic parameter dataset from Ref. [2].

5.1. Thermodynamics of Bi–Cu–In ternary system

The calculated activity of indium in the liquid Bi–Cu–In alloys along sections with Cu/In = 4/1, 1/1 and 1/4 at 1200 K is shown in Fig. 4 together with the experimental results reported by Itabashi et al. [12]. Good agreement between calculated values and the experimental data is observed for all compositions studied. The activity of indium exhibits moderate negative deviation from ideal in considered composition range.

5.2. Isothermal section at 400 °C

There are no published data on the Bi–Cu–In phase equilibria and ternary parameters are not available. Therefore the Bi–Cu–In phase diagram was calculated only on the base of binary thermodynamic data including in the COST531 database [2].

The SEM (scanning electron microscope) with EDS (energy dispersive spectrometry) analyzer was used for determination of composition of coexisting phases. All results from SEM/EDS analysis are given in Table 2.

Predicted isothermal section of the Bi–Cu–In ternary system at 400 °C is shown in Fig. 5.

Two-phase structure was experimentally determined in both investigated samples. Both experimentally determined tie-lines are in agreement with calculated phase diagram.

Microstructure of sample 2 is shown in Fig. 6. Two different phase regions are observed.

Bright phase represents CUIN_ETA phase and its composition is given in Table 2. In this bright phase there is only 0.7 at.% of Bi dissolved. Dark phase represents former liquid phase and its chemical composition given in Table 2 is in correspondence with calculated phase diagram shown in Fig. 5.

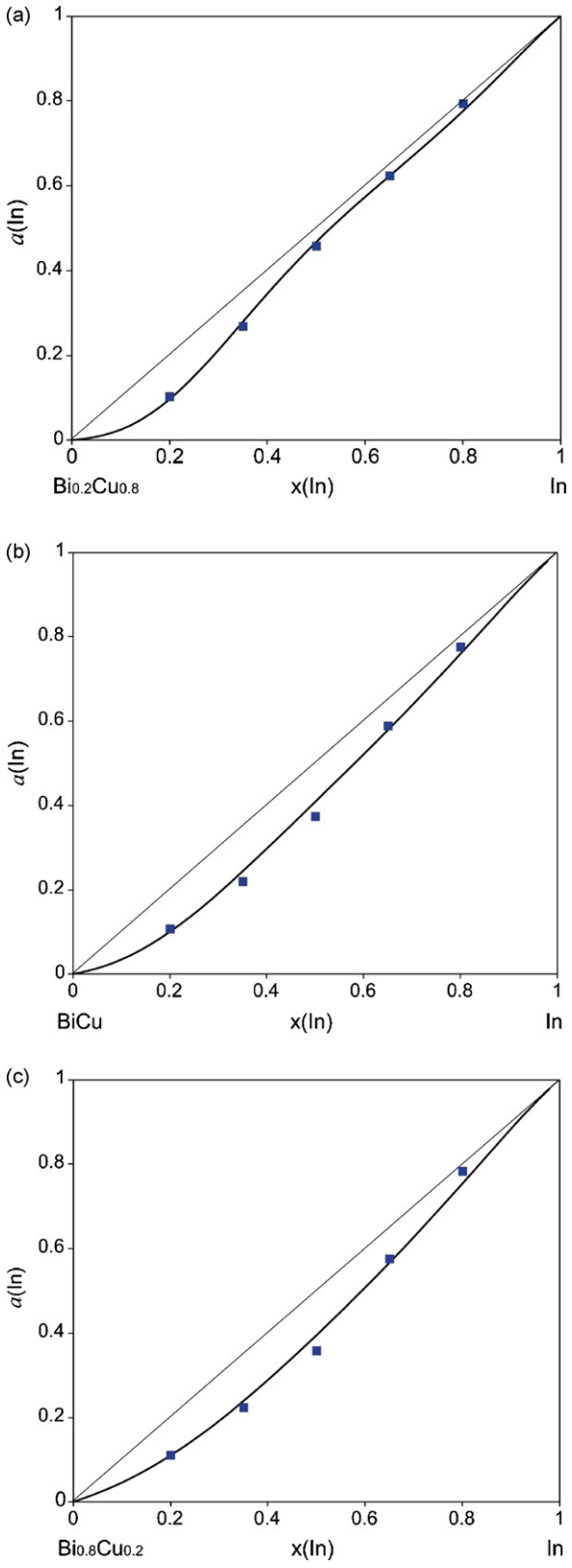

Fig. 4. Calculated and experimentally obtained activity of indium [12] at 1200 K (liquid In reference state): (a) Bi/Cu = 1/4; (b) Bi/Cu = 1/1; (c) Bi/Cu = 4/1.

Table 2
Calculated and experimentally determined phase compositions in the ternary Bi–Cu–In system at 400 °C.

Sample	Overall exp. composition (at.%)			Predicted phases	Experimentally determined phases	Phase composition		
						Bi (at.%) exp.	Cu (at.%) exp.	In (at.%) exp.
1	50 Bi	20 Cu	30 In	CUIN_DELTA; LIQUID	CUIN_DELTA; LIQUID	1.1; 67.4	69.0; 3.3	29.9; 29.2
2	20 Bi	20 Cu	60 In	CUIN_ETA; LIQUID	CUIN_ETA; LIQUID	0.7; 27.1	61.6; 4.9	37.7; 68.0

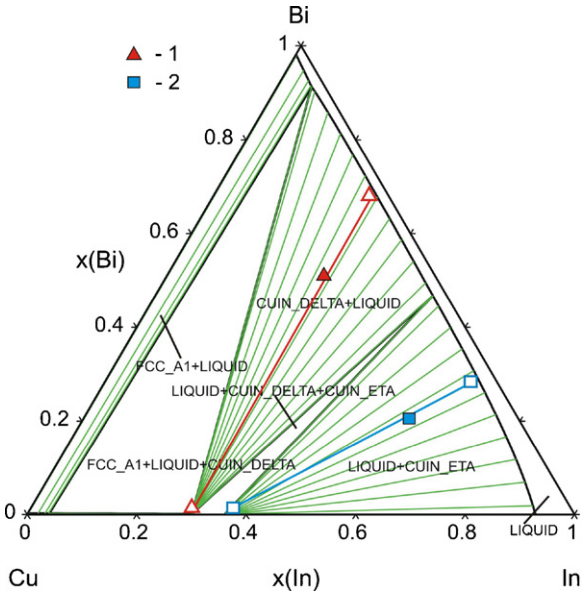

Fig. 5. Predicted phase diagram of the ternary Bi–Cu–In system at 400 °C and experimentally determined phase compositions for the samples 1 and 2 (full symbols are referred on the overall composition and empty on the compositions of single phase).

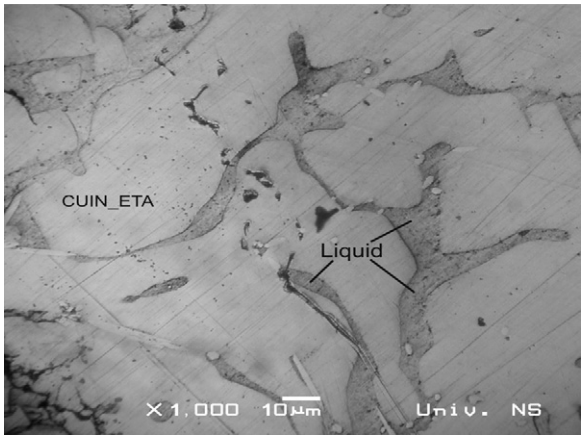

Fig. 6. SEM micrograph of the sample 2.

Table 3
DTA/DSC results for the investigated alloys of the Bi–Cu–In ternary system.

Sample composition	Phase transition temperatures (°C)	
	Liquidus temperature	Other phase transition
x(Bi)		x(Cu)/x(In) = 1/3
0.2	586	85; 159
0.4	576	103; 347
0.6	546	105; 176
0.8	489	103; 183
x(In)		x(Bi)/x(Cu) = 1
0.1	741	273; 545
0.3	651	101; 192; 630
0.5	618	98
0.7	550	85; 210
0.9	380	120
x(Cu)		x(Bi) = 0.5
0.1	545	103; 298
0.15	570	101; 170; 227
0.2	599	103; 190
0.3	587	103; 187
0.4	742	276; 495

5.3. Vertical sections

In order to experimentally study phase transition temperatures of the Bi–Cu–In ternary system, the alloys with overall compositions alongside three chosen vertical sections were investigated by DSC. The analysis of DSC measurements was performed during the heating of samples. The temperatures of invariant phase transitions were taken from the extrapolated onset on heating. The other phase transition temperatures were taken from the peak temperature.

Experimentally determined phase transition temperatures of the examined alloys of ternary Bi–Cu–In system, were presented in Table 3.

The experimentally determined liquidus temperatures are in good agreement with the calculated vertical sections shown in Fig. 7. In majority of investigated samples sharp peaks, at low temperatures, caused by invariant reactions, were detected. In DTA/DSC measurements from this work six invariant reactions were identified and, represented in Table 4. Experimentally detected temperatures of invariant reactions are compared with corresponding calculated values in Table 4.

Table 4
Calculated and experimentally determined invariant reactions from this study.

Calculated temperature, T (°C)	Experimental temperature, T (°C)	Invariant reactions
294.9	292	LIQUID + CUIN_ETA → CUIN_ETAP + CUIN_THETA
266.2	273	LIQUID + FCC_A1 → CUIN_DELTA + RHOMBO_A7
183.7	187	LIQUID + CUIN_DELTA → CUIN_ETAP + RHOMBO_A7
109.2	103	LIQUID → CUIN_ETAP + RHOMBO_A7 + BIIN
95.5	98	LIQUID + CUIN_ETAP → BIIN + CUIN_THETA
87.7	85	LIQUID → CUIN_THETA + BI3IN5 + BIIN_BRASS

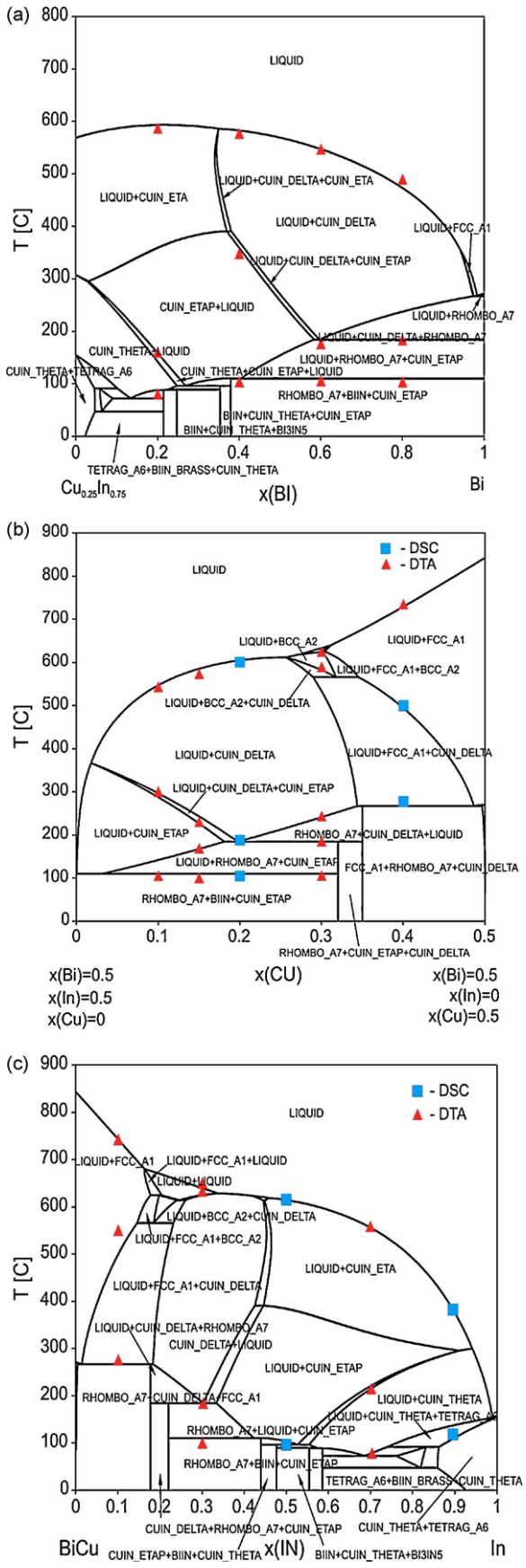

Fig. 7. Calculated vertical sections of the Bi–Cu–In ternary system compared with DTA/DSC results from the present study: (a) Cu:In = 1:3; (b) x(Bi) = 0.5; (c) Bi:Cu = 1:1.

6. Conclusion

Phase diagram of the Bi–Cu–In ternary system has been investigated experimentally, by DTA/DSC and SEM/EDS and analytically, using CALPHAD approach. The calculated isothermal section at 400 °C shows agreement with the results of SEM–EDS analysis. The melting behavior of the different Bi–Cu–In alloys has been determined. Calculated liquidus temperatures show reasonable agreement with DTA/DSC results from the present work.

Acknowledgements

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