

THERMODYNAMIC ANALYSIS AND CHARACTERIZATION OF ALLOYS IN Bi–Cu–Sb SYSTEM

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Abstract

The results of thermodynamic analysis and characterization of some alloys in Bi-Cu-Sb lead-free solder system are presented in this paper. Thermodynamic analysis was done using general solution model, while optic microscopy, hardness and electroconductivity measurements were used in order to determine structural, mechanic and electric characteristics of selected samples in section from bismuth corner with molar ratio Cu:Sb=3:7.

Keywords: Lead-free solder materials; Bi-Cu-Sb system; Thermodynamics; Characterization.

1. Introduction

Significant scientific efforts have been done recently in the field of development and design of advanced lead-free solder materials for high temperature application [1,2]. Specific attention in these researches has

been directed to the copper-antimony-based alloys, among which Bi–Cu–Sb alloys are especially interesting for technological application.

The Bi–Cu–Sb system has not been explored from the thermodynamic and phase equilibria point of view, except the work of

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our research group [3], which has presented experimental study and thermodynamic calculation of this system phase equilibria. On the other hand, thermodynamic characteristics of binary constituent systems are numerous and well known, and their optimized values (included in the COST531 Database for lead-free solders [4]) are given – for Cu–Bi system by Teppo et al. [5], for Cu–Sb system by Liu et al. [6], and for Bi–Sb system by Ohtani and Ishida [7].

As a contribution to more complete knowledge of mentioned lead-free material, the results of thermodynamic analysis and characterization of some alloys in the Bi–Cu–Sb system are presented in this paper.

2. Experimental

The metals used for the preparation of selected samples were bismuth, copper and antimony of 99.99% purity. Investigated alloys were taken in the section from bismuth corner with molar ratio Cu:Sb equal to 3:7, and with composition of bismuth equal to 0.1; 0.2; 0.3; 0.4; 0.6; 0.7; 0.8 and 0.9. For experimental investigation used in this work, optic microscopy, hardness and electroconductivity measurements were applied.

Microstructure analysis of investigated samples was performed by optical microscopy, using a Reichert MeF₂ microscope. The samples were prepared without using of etching agents for structure development.

Electrical conductivity of investigated materials was measured using three series of measurements on 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.

All experiments were performed in an air atmosphere.

3. Theoretical fundamentals

Basic theoretic fundamentals of general solution model are given by Chou [8], and present one of the well known thermodynamic predicting methods. The main expression for the calculation of integral molar Gibbs excess energies, G^{xs} , for the system “ijk”, is given as follows:

$$G^{xs} = x_i x_j (A_{ij}^0 + A_{ij}^1 (x_i - x_j) + A_{ij}^2 (x_i - x_j)^2) + x_j x_k (A_{jk}^0 + A_{jk}^1 (x_j - x_k) + A_{jk}^2 (x_j - x_k)^2) + x_k x_i (A_{ki}^0 + A_{ki}^1 (x_k - x_i) + A_{ki}^2 (x_k - x_i)^2) + f x_i x_j x_k \quad \dots (1)$$

where A_{ij}^0 , A_{ij}^1 , A_{ij}^2 are parameters for binary system “ij” independent of composition, only relying on temperature, which have been used in the regular type equation, such as:

$$G^{xs}_{ij} = X_i X_j (A_{ij}^0 + A_{ij}^1 (X_i - X_j) + A_{ij}^2 (X_i - X_j)^2 + \dots + A_{ij}^n (X_i - X_j)^n) \quad \dots (2)$$

where X_i and X_j indicate the mole fraction of component “i” and “j” in “ij” binary system, as:

$$X_{i(ij)} = x_i + x_k \xi_{ij} \quad \dots (3)$$

The function f is the ternary interaction coefficient expressed by

$$f = (2\xi_{12} - 1) \{A_{12}^2 ((2\xi_{12} - 1)x_3 + 2(x_1 - x_2)) + A_{12}^1\} + (2\xi_{23} - 1) \{A_{23}^2 ((2\xi_{23} - 1)x_1 + 2(x_2 - x_3)) + A_{23}^1\} + (2\xi_{31} - 1) \{A_{31}^2 ((2\xi_{31} - 1)x_2 + 2(x_3 - x_1)) + A_{31}^1\} \quad \dots(4)$$

where ξ_{ij} are the similarity coefficients, defined to be calculated according to the procedure of general solution model [8].

In all given equations, G^{xs} and G^{xs}_{ij} correspond to the integral molar excess Gibbs energies for ternary and binary systems, respectively, while x_1 , x_2 , x_3 correspond to the mole fraction of components in investigated ternary alloys.

3. Results and discussion

The thermodynamic calculation in ternary Cu-Bi-Sb system was performed along the line of a constant Cu:Sb molar ratio of 3:7, in a temperature range from 1373 to 1673 K.

The starting data for the calculation

according to general solution model were taken from the references [5–7]. The Redlich-Kister parameters (in J/mol) for the liquid phase of the constitutional binaries in the investigated Cu–Bi–Sb system are presented in Table 1a.

Based on these starting data, similarity coefficients were determined according to the procedure of general solution model [8] and their values are shown in Table 1b.

Further calculation was carried out for selected alloys in investigated section in the Bi–Cu–Sb ternary system in the temperature range from 1373 to 1673 K, according to the fundamentals of general solution model [8], as given by Eqs.(1–4). The results of the thermodynamic predictions, including integral molar Gibbs excess energy and bismuth activities, are given in Fig.1 as a graphic illustration of 3D dependence on temperature and composition.

It may be seen that G^{xs} is positive only in the case of bismuth content higher than

Table 1. Redlich-Kister parameters for the liquidus phase of constitutional binaries (a) and calculated similarity coefficients at different temperatures (b) in the ternary system Bi–Cu–Sb

a)

System	Bi-Cu	Bi-Sb	Cu-Sb
A_{ij}^0 (T)	$20747.5 - 5.85 * T$	$2230 + 0.06 * T$	$- 16154.82 + 23.99549 * T - 4.0284 * T * \ln(T)$
A_{ij}^1 (T)	$- 4925 + 2.55 * T$	/	$- 35130.8 + 50.3301 * T - 5.2316 * T * \ln(T)$
A_{ij}^2 (T)	$4387.5 - 2.3 * T$	/	$- 29263.28 + 15.3192 * T$
A_{ij}^3 (T)	/	/	$- 2300.89$
A_{ij}^4 (T)	/	/	8873.94

b)

T, K	ξ_{Cu-Bi}	ξ_{Bi-Sb}	ξ_{Sb-Cu}
1373	0.653	0.872	0.073
1473	0.643	0.889	0.065
1573	0.634	0.905	0.057
1673	0.624	0.92	0.049

60at% (Fig.1a), while negativity is typical for almost all compositions and for whole investigated temperature range. The minimum value of G^{xs} is equal to -4.5 kJ / mol, while the maximum occurs at about 0.6 kJ / mol.

That indicates to significant attraction between the components of the system, which is in accordance with phase diagram

characteristics for the constitutive binaries [5–7].

Derived partial quantities confirm given statements. Dependence of bismuth activity vs. composition (Fig.1b) shows uniform change of activity values and positive deviation from Raoult law in composition part up to 60 at % Bi, approaching to ideal line

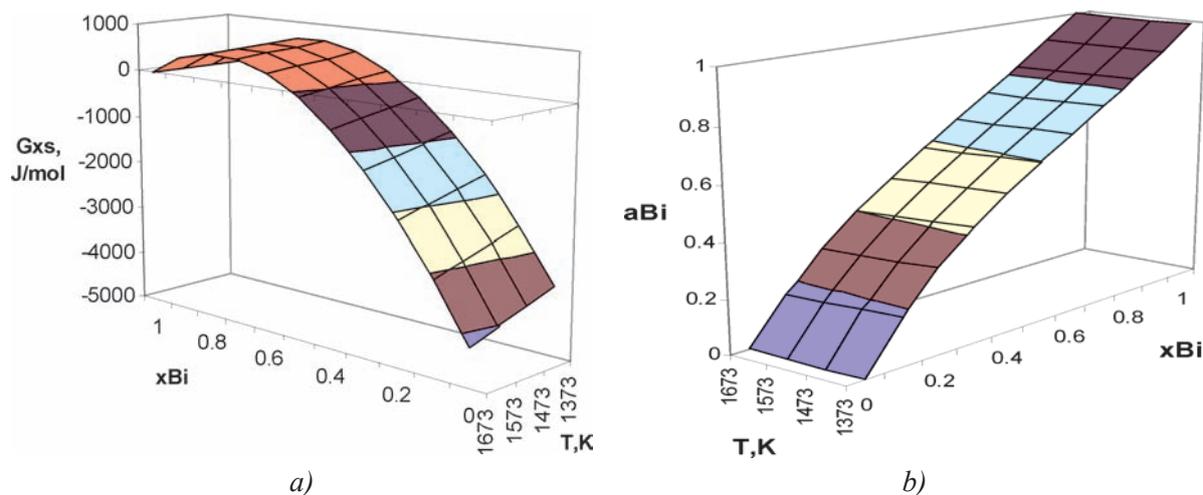


Fig.1. Dependence of the integral excess Gibbs energy (a) and bismuth activities (b) on composition and temperature for investigated section Bi:Sb=3:7 in the range of 1373–1673K

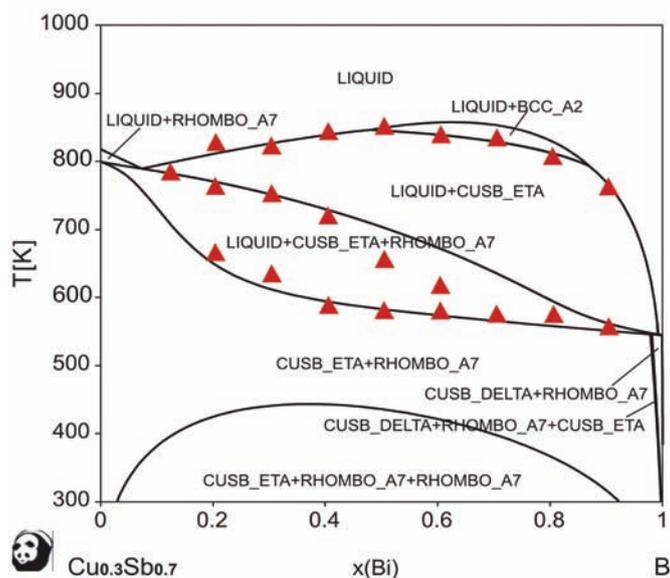


Fig.2. Phase diagram of investigated section from bismuth corner with molar ratio of Cu:Sb=3:7[3] (triangles respond to experimental DTA measurements)

with further increasing of bismuth content.

Obtained thermodynamic results are in accordance with the Cu-Bi-Sb system phase equilibria [3], as can be seen in Fig.2.

The presence of the following phases was determined in [3] – RHOMBO (Sb and Bi

rich solid solution) and CUSB_ETA (h-phase or Cu_2Sb), with overall experimental composition (in at%) for investigated sample of 39Bi, 18Cu and 43Sb, while experimental composition of presented phases was (in at%): RHOMBO – 28Bi, 3Cu, 69Sb and

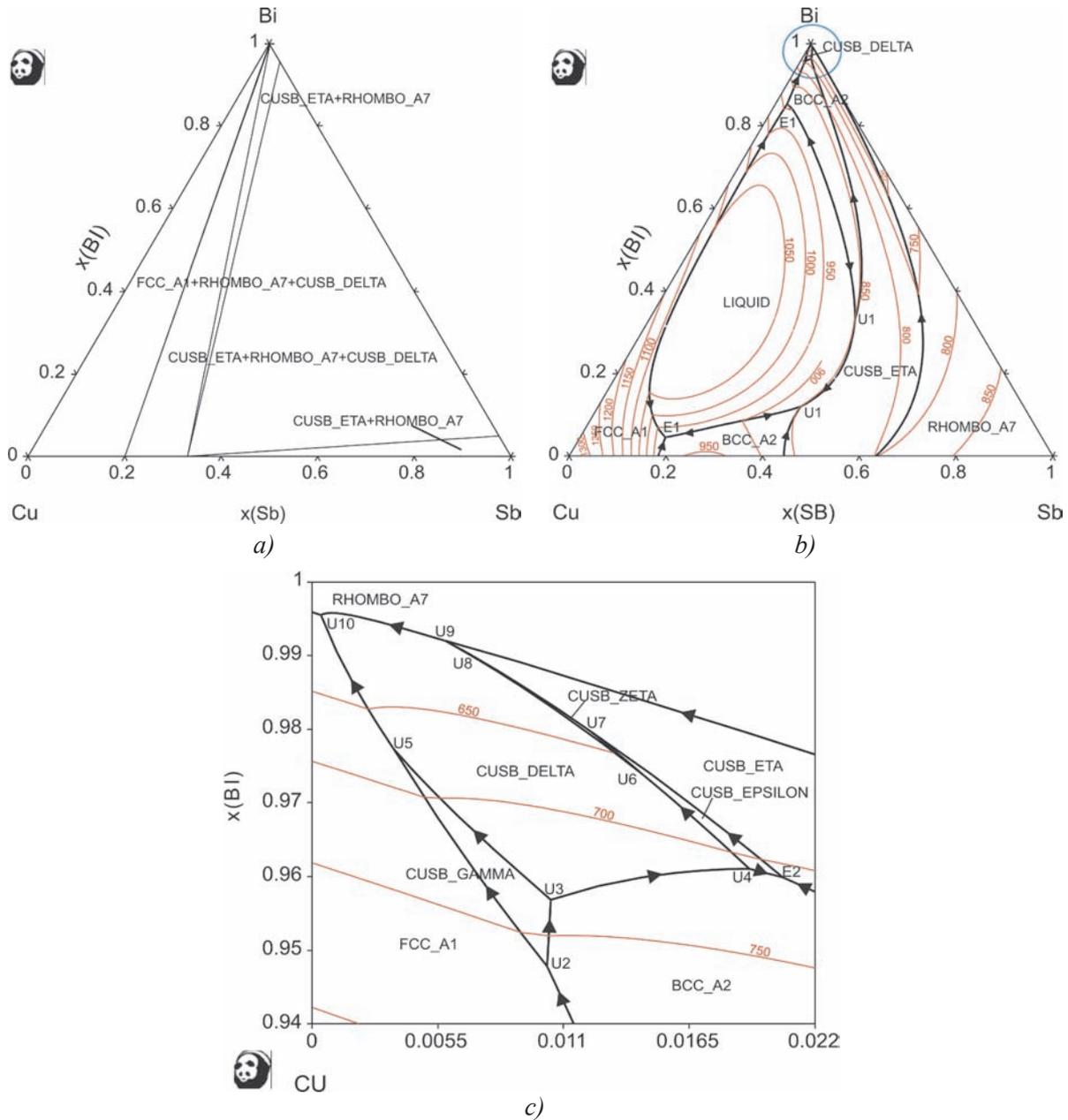


Fig.3. Isothermal section (a), calculated liquidus projection at 298K (b) and detailed Bi-corner part signed in liquidus projection (c) of Bi-Cu-Sb system

CUSB_ETA – 66Cu, 34Sb, as was confirmed by SEM – EDX analysis in [3].

Further in this work, the isothermal section at 298 K, liquidus projection and its detailed Bi–corner part of investigated Bi–Cu–Sb system were calculated following CALPHAD methodology [9] and using PANDAT software, using optimized thermodynamic data from COST531 Database for lead-free solders [4]. Obtained results are shown in Fig.3.

In the frame of characterization of

investigated samples, the results of optic microscopy are shown in Fig.4. Microstructure of the investigated samples (Fig.4) shows presence of dark phase responding to Cu_2Sb and light gray phase related to Bi-Sb rich solid solution.

The results of hardness and electroconductivity are presented in Fig.5. As can be seen, hardness values of investigated alloys, obtained in the range from 40 to 90 HB, increase with the increase of bismuth content, having a sharp decrease

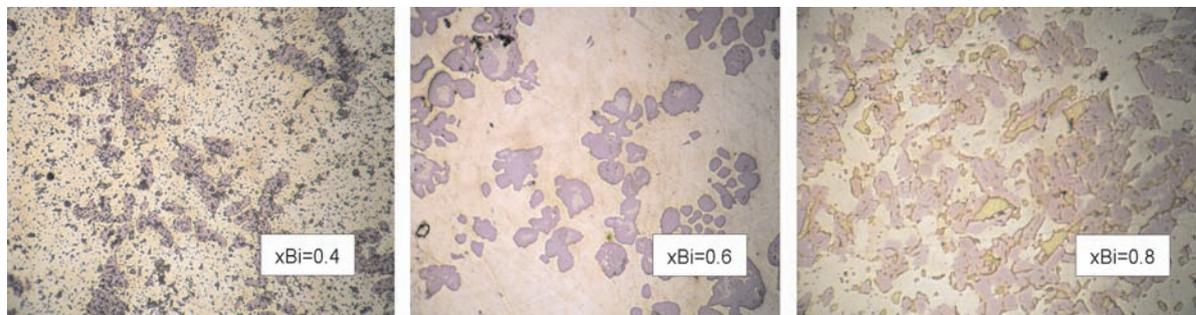


Fig.4. Microphotographs of selected samples from the Bi-Cu30Sb70 section

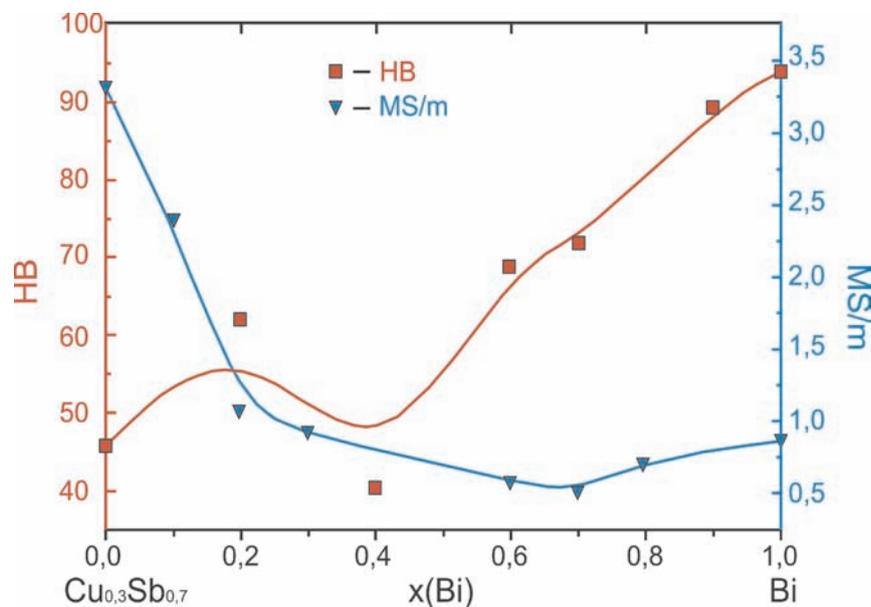


Fig.5. The results of hardness and electroconductivity measurements

in value at the composition of 40 % at Bi. The electroconductivity shows opposite trend – decreasing uniformly with bismuth content increase.

4. Conclusions

Thermodynamic analysis, phase equilibria, structural, mechanical and electric properties of the Bi–Cu–Sb are presented in this work, as a contribution to the better knowledge of recently investigated Bi-Cu-based lead-free solder materials [10].

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