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THERMODYNAMIC ANALYSIS AND CHARACTERIZATION OF Bi-Cu-Sn ALLOYS AS ADVANCED LEAD-FREE SOLDER MATERIALS FOR HIGH TEMPERATURE APPLICATION

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ABSTRACT
Due to the frequent use of Cu as a substrate material in electronics, it is of importance to understand the interactions between these solders and the substrate, based on the knowledge of the phase equilibria, thermodynamics and other characteristics of the Bi–Cu–Sn system.
The results of thermodynamic analysis and characterization of Bi-Cu-Sn alloys as advanced lead-free solder materials for high temperature application are presented in this paper. The research inlcudes analytical investigations done by thermodynamic predicting according to GSM method and experimental investigations performed by differential thermal analysis, optical microscopy, hardness and electroconductivity measurements.
Keywords: thermodynamics, characterization, Bi-Cu-Sn alloys, lead-free solder materials

1. INTRODUCTION

The Bi-Cu-Sn ternary system belongs to the group of systems recently studied from the point of view of interaction of solder with substrates [1-4], although not completely investigated yet.
Few studies of Bi-Cu-Sn ternary system have been performed regarding thermodynamics and phase equilibria. The liquidus projection, Sn-rich part of the system and calculated invariant equilibria of the Bi-Cu-Sn system, extrapolated from binary thermodynamic descriptions, have been presented by Kattner [5]. Enthalpies of mixing of liquid ternary Bi-Cu-Sn alloys at 800 ^{o}C in a large composition range were reported by Ipser at al. [6] and Flandorfer et al. [7]. The activity of bismuth in liquid dilute Cu-Sn-Bi alloys by the method of equilibrium saturation with metal vapour, at 1373 K was determined by Wnuk and Romanowska [8]. The latest results are the results of Kopyto et al. [9], who performed the electromotive force measurement in order to obtain thermodynamic properties of liquid Bi-Cu-Sn alloys, as well as the results of Manasijević et al. [10].
Having in mind the lack in complete knowledge of the investigated system properties, the results of thermodynamic analysis and characterization of chosen Bi-Cu-Sn ternary alloys - obtained by GSM TD predicting, thermal, structural and mechanical investigations, were presented in this work.

2. EXPERIMENTAL

All samples were prepared from Bi, Cu and Sn of 99.99 % purity. The samples were prepared by induction melting under argon atmosphere. The samples were homogenized at 300 ^{o}C for 2 h and slowly cooled down to the room temperature at a rate less than 5 K/min.
The DTA measurements were carried out with the Derivatograph (MOM Budapest) apparatus under following conditions: argon atmosphere, sample masses about 2 g, heating rate 10 K/min and alumina

as the reference material. Microstructure analysis of investigated samples was performed by optical microscopy, using a Reichert MeF2 microscope. Electrical conductivity was measured using three series of measurements on the standard apparatus SIGMATEST 2.069 (Foerster), while hardness measurements were done according to standard procedure. The samples were prepared without using of etching agens for structure development. All experiments were performed in an air atmosphere.

3. THEORETICAL FUNDAMENTALS

Basic theoretic fundamentals of general solution model are given by Chou [11], 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:

$$G^{xs} = x_i x_j (A^o_{ij} + A^1_{ij} (x_i - x_j) + A^2_{ij} (x_i - x_j)^2) + x_j x_k (A^o_{jk} + A^1_{jk} (x_j - x_k) + A^2_{jk} (x_j - x_k)^2) + x_k x_i (A^o_{ki} + A^1_{ki} (x_k - x_i) + A^2_{ki} (x_k - x_i)^2) + f x_i x_j x_k \quad \text{... (1)}$$

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

$$G^{xs}_{ij} = X_i X_j (A^o_{ij} + A^1_{ij} (X_i - X_j) + A^2_{ij} (X_i - X_j)^2 + ... + A^n_{ij} (X_i - X_j)^2) \quad \text{... (2)}$$

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

$$X_{i(ij)} = x_i + x_k \xi_{ij}.$$

The function f is the ternary interaction coefficient expressed by

$$f = (2\xi_{12} - 1)\{A^2_{12} ((2\xi_{12} - 1)x_3 + 2(x_1 - x_2)) + A^1_{12}\} + (2\xi_{23} - 1)\{A^2_{23} ((2\xi_{23} - 1)x_1 + 2(x_2 - x_3)) + A^1_{23}\} + (2\xi_{31} - 1)\{A^2_{31} ((2\xi_{31} - 1)x_2 + 2(x_3 - x_1)) + A^1_{31}\}, \quad \text{... (3)}$$

where ξ_{ij} are the similarity coefficients, defined to be calculated according to the procedure of general solution model [11].

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.

4. RESULTS AND DISCUSSION

The thermodynamic calculation in ternary Cu-Bi-Sn system was performed along the line of a constant Bi:Cu molar ratio of 1:1, 1:3 and 3:1 at the temperature of 1273K.

The starting data for the calculation according to general solution model were taken from [12]. The Redlich-Kister parameters (in J/mol) for the liquid phase of the constitutional binaries in the investigated Cu-Bi-Sn system are presented in Table 1. Based on these starting data, similarity coefficients were determined according to the procedure of general solution model [11] and their values were: $\xi_{Cu\text{-}Bi} = 0.108$, $\xi_{Bi\text{-}Sn} = 0.692$ and $\xi_{Sn\text{-}Cu} = 0.787$.

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-Sn

System	Bi-Cu	Bi-Sn	Cu-Sn
A^o_{ij} (T)	20747.5-5.85*T	500+1.5*T	-9002.8-5.8381*T
A^1_{ij} (T)	-4925+2.55*T	-100-0.135*T	-18936.316+2.339*T
A^2_{ij} (T)	4387.5-2.3*T	/	-14122.6+52.942T-7.057TlnT

Further calculation was carried out for selected alloys in selected sections in the Bi-Cu-Sn ternary system at investigated temperature 1273K, according to the fundamentals of general solution model [11], as given by Eqs.(1-3). The results of the predictions, including integral molar Gibbs excess energy and calculated tin activities, are given in Table 2 and Fig.1, respectively.

Table 2. Integral molar Gibbs excess energies, G^{xs} (in J/mol) obtained by GSM

Section	Tin molar content, xSn								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
Bi-Cu=1:1	1580	494	-128	-446	-578	-608	-578	-495	-326
Bi:Cu=1:3	128	-1321	-1979	-2133	-2000	-1734	-1417	-1067	-634
Bi:Cu=3:1	1566	1010	650	419	265	152	63	5	-36

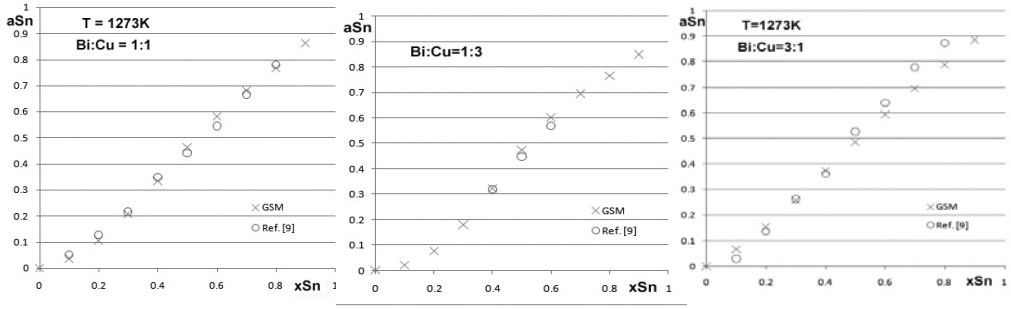

Figure 1. Tin activities in selected section of the Bi-Cu-Sn system at 1273K obtained by GSM

It may be noticed that there is a slight deviation from Raoult law in all three investigated sections, with a small change at a certain tin composition from negative to positive behaviour. Also, comparison of calculated results from this work with experimental literature data [9], shown in Fig.1, indicates to a good mutual agreement. Having in mind the lack of complete experimental thermodynamic results for searched system, it is important to know that general solution model can adequately describe its thermodynamic behaviour.

In the frame of the alloys characterization, thermal analysis has been done and the results of the measurements are given in Table 3, including characteristic phase transition temperatures – liquidus and other peak temperatures obtained by DTA in three investigated Bi-Cu-Sn sections.

Table 3. DTA results for the investigated alloys of the Bi-Cu-Sn ternary system

Sample composition (in at%)	T (K)	
	Liquidus temperature	Other peak temperature
Bi:Cu=1:1		
Bi40Cu40Sn20	996	413, 482, 506, 948
Bi35Cu35Sn530	949	417, 473
Bi30Cu30Sn40	938	413, 466, 526
Bi25Cu25Sn50	865	417, 560
Bi15Cu15Sn70	757	413, 457, 632
Bi:Cu=3:1		
Bi60Cu20Sn20	920	414, 473, 501
Bi30Cu10Sn60	760	414
Bi15Cu5Sn80	619	412, 460
Bi:Cu=1:3		
Bi17.5Cu52.5Sn30	938	471
Bi15Cu45Sn40	918	413, 546
Bi12.5Cu37.5Sn050	861	413, 575
Bi7.5Cu22.5Sn70	752	413, 642

The results of optical microscopy are presented in Fig.2, while the results of electroconductivity and hardness measurements are shown in Fig.3.

5. CONCLUSION

The results of thermodynamic analysis and characterization of selected alloys in Bi-Cu-Sn system are shown in this paper. The results of GSM predicting showed good mutual agreement with available literature data, while other experimentally obtained results of DTA, LOM, electroconductivity and hardness measurements present a contribution to the better knowledge of that potential lead-free solder material for high temperature application.

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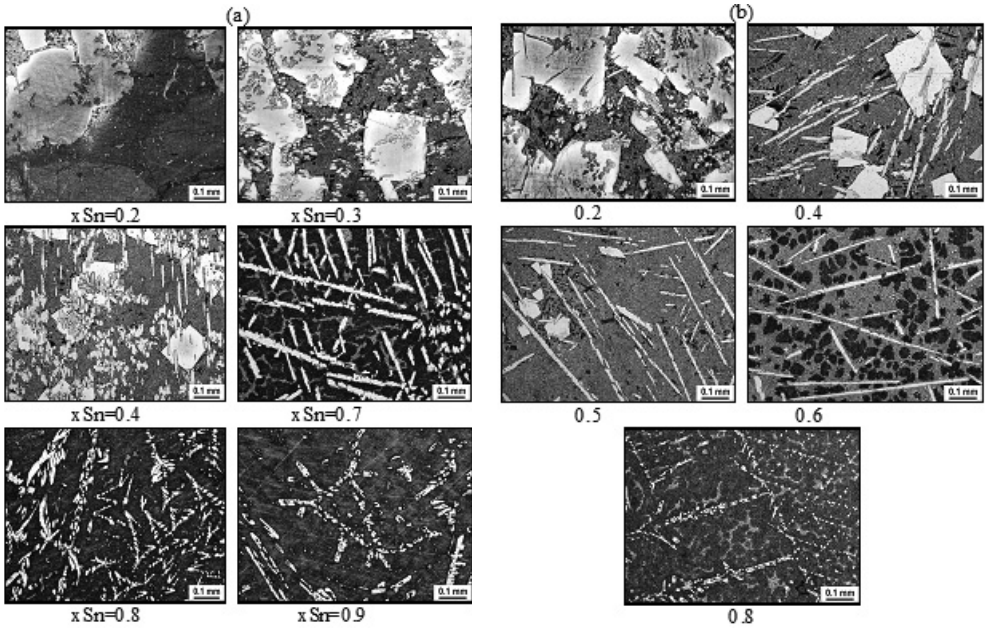

Figure 2. Microphotographs of the alloys in the sections with molar ratio Bi:Cu=1:1 (a) and 3:1 (b)

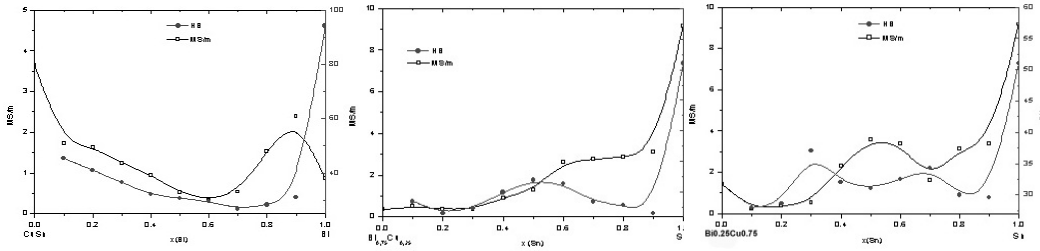

Figure 3. Hardness and electroconductivity of the alloys in the sections with molar ratio Bi:Cu=1:1 (a), 3:1 (b) and 1:3 (c)

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