13th International Research/Expert Conference
"Trends in the Development of Machinery and Associated Technology"
TMT 2009, Hammamet, Tunisia, 16-21 October 2009

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

Dragana Živković[a], Duško Minić[b], Dragan Manasijević[a], Ana Kostov[c], Nada Talijan[d]

[a]University of Belgrade, Technical Faculty
VJ 12, 19210 Bor
Serbia

[b]University of Priština,
Faculty of Technical Sciences
38220 Kosovska Mitrovica, Serbia

[c]Mining and Metallurgy Institute
Zeleni bulevar 35, 19210 Bor
Serbia

[d]University of Belgrade, ICTM-CMM
Karnegijeva 4, Belgrade
Serbia

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, SEM-EDX analysis, 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 our research group [3], which has recently 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 agens for structure development. For SEM-EDX analysis, JEOL JSM-6460 scanning electron

microscope with EDX analyzer was used. Hardness measurements were done using standard procedure according to Brinell. 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:

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

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:

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

The function f is the ternary interaction coefficient expressed by

$$f = (2\xi_{12} - 1)\{A^2_{12} ((2\xi_{12} - 1)x_3 + 2(x_1 - x_2)) + A^1_{12}\} + (2\xi_{23} - 1)\{A^2_{23} ((2\xi_{23} - 1)x_1 + 2(x_2 - x_3)) + A^1_{23}\} + (2\xi_{31} - 1)\{A^2_{31} ((2\xi_{31} - 1)x_2 + 2(x_3 - x_1)) + A^1_{31}\} \quad \text{... (4)}$$

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.

4. 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 1673K.
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 constitutional binaries in the investigated Cu-Bi-Sb system are presented in Table 1. 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 2.

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

(a)

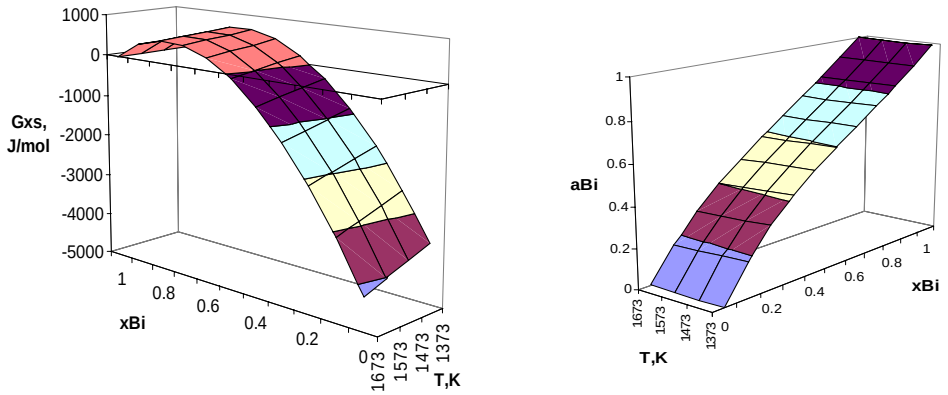
System	Bi-Cu	Bi-Sb	Cu-Sb
A^o_{ij} (T)	20747.5-5.85*T	2230+0.06*T	-16154.82+23.99549*T-4.0284*T*ln(T)
A^1_{ij} (T)	-4925+2.55*T	/	-35130.8+50.3301*T-5.2316*T*ln(T)
A^2_{ij} (T)	4387.5-2.3*T	/	-29263.28+15.3192*T
A^3ij (T)	/	/	-2300.89
A^4ij (T)	/	/	8873.94

(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	0.920	0.049

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 1673K, 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.



a) *b)*

Figure 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

It may be seen that G^{xs} is positive only in the case of bismuth content higher then 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 -4.5kJ/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 60at%Bi, approaching to ideal line with further increasing of bismuth content.

Obtained thermodynamic results are in accordance with the Cu-Bi-Sb system phase equilibria [3]. The phase diagram of the investigated vertical section with molar ratio of Cu:Sb=3:7, calculated according to CALPHAD method [9], using ThermoCalc software and optimized thermodynamic data from COST531 Database for lead-free solders [4], is shown in Fig.2.

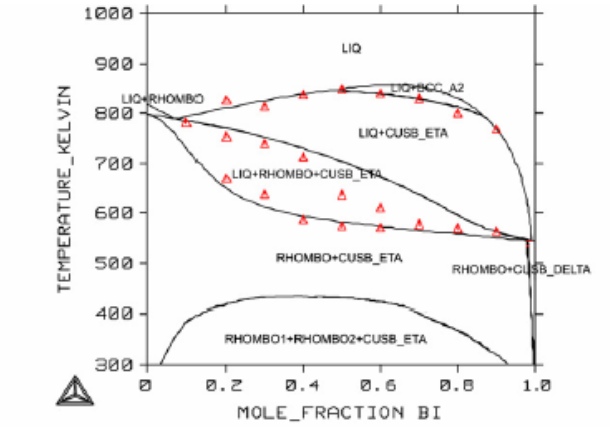


Figure 2. Phase diagram of investigated section from bismuth corner with molar ratio of Cu:Sb=3:7

SEM-EDX analysis confirms given phase diagram. The results for the investigated sample with 40at%Bi indicate to the presence of the following phases - RHOMBO (Sb and Bi rich solid solution) and CUSB_ETA (η-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 CUSB_ETA – 66Cu, 34Sb.
The results of optic microscopy are shown in Fig.3. Microstructure of the investigated samples (Fig.3) shows presence of dark phase responding to Cu_2Sb and light gray phase related to Bi-Sb rich solid solution.

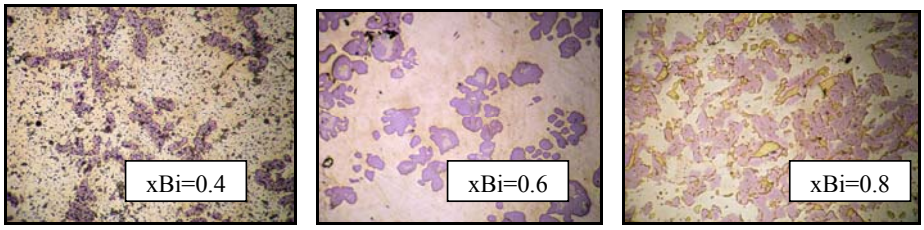


Figure 3. Microphotographs of selected samples from the Bi-Cu30Sb70 section

The results of hardness and electroconductivity are presented in Fig.4. As can be seen, hardness values of investigated alloys, obtained in the range from 40 to 90HB, increase with the increase of bismuth content, having a sharp decrease in value at the composition of 40%atBi. The electroconductivity shows opposite trend - decreasing uniformly with bismuth content increase.

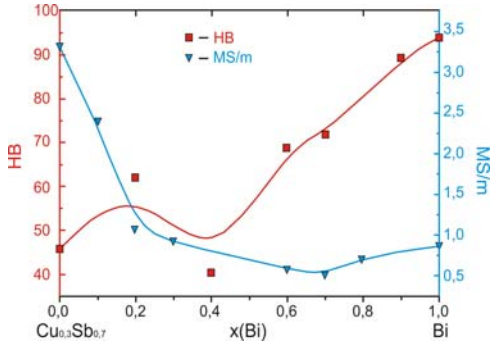


Figure 4. The results of hardness and electroconductivity measurements

5. CONCLUSIONS

The contribution to the thermodynamic analysis, phase equilibria, structural, mechanical and electric properties of the Bi-Cu-Sb alloys as a potential lead-free solder material is given in this work.

6. AKNOWLEDGEMENT

This work was supported by Ministry of Science and Technological Development of the Republic of Serbia (Projects No.19011 and 142043) and performed in the frame of the EU action COST MP0602.

7. REFERENCES

[1] http://www.univie.ac.at/cost531
[2] http://cost602.ipm.cz
[3] D. Manasijević, D. Minić, D. Živković, D. Rajnović, Intermetallics, 16 (2008) 107-112.
[4] A.T. Dinsdale, A.Kroupa, J. Vizdal, J. Vrestal, A. Watson, A. Zemanova, COST531 Database for Lead-Free Solders, Ver.2.0, Unpublished research, 2006.
[5] O. Teppo, J. Niemela, P.Taskinen, Thermochim. Acta, 173 (1990) 137.
[6] X. J. Liu, C. P. Wang, I. Ohnuma, R. Kainuma, K. Ishida, J. Phase Equilib., 21 (5) (2000) 432.
[7] H. Ohtani, K. Ishida, J. Electron. Mater., 23 (8) (1994) 747.
[8] Chou K.C., CALPHAD, 19 (3) (1995) 315.
[9] N. Saunders, A. P. Miodownik, CALPHAD (A Comprehensive Guide), Elsevier, London, 1998.