Investigation of the Thermodynamic Model and Ternary Interaction Parameter Influence for Sn-Ag-Bi Liquid Alloys

Dragana Živković[1*], Iwao Katayama[2], Hiromi Yamashita[2], Dragan Manasijević[1], Živan Živković[1]

[1]University of Belgrade, Technical Faculty, VJ12, 19210 Bor, Serbia
E-mail: dzivkovic@tf.bor.ac.yu
[2]Osaka University, Graduate School of Engineering, Osaka, Japan

Received: October 11, 2006 **Accepted:** October 20, 2006

Abstract: The results of thermodynamic model and ternary interaction parameter influence investigation for the Sn-Ag-Bi system are presented in this paper. The calculation of thermodynamic properties was done using general solution model, Hillert and Toop model for the liquid alloys at 900K in the following sections: Sn-AgxBiy Ag-BixSny, and Bi-AgxSny (where x:y is equal to molar ratio of 1:1, 1:3 and 3:1). Based on the calculation results, the most accurate thermodynamic data for the Sn-Ag-Bi system was obtained using asymmetric Hillert model including ternary interaction parameter.

Keywords: thermodynamics, phase diagrams, ternary alloys, Ag-Bi-Sn system, lead-free solders

* Corresponding author: Dr Dragana Živković, Phone/Fax: .+381 30 424 547,

Introduction

Due to the importance of the ternary Sn-Ag-Bi system as potential lead-free solder material[1,2], different investigations have been done in order to determine its phase equilibria and thermodynamic properties. Kattner et al.[3] calculated the phase diagram from the referent thermodynamic data of binary systems, which are numerous[4-9]. Hassam et al.[10] experimentally investigated liquidus surface of this ternary system, while the more complete analysis of the Sn-Ag-Bi ternary phase diagram and optimization of the ternary thermodynamic Redlich-Kister parameters, based on available binary thermodynamic data, was done by Ohtani et al.[11]. The data on calculated liquidus projection and invariant equilibria in the Sn-Ag-Bi system can also be found in[12].

In the frame of experimental thermodynamic investigations of the liquid Sn-Ag-Bi alloys, Hassam et al.[13] determined enthalpies of formation and Katayama et al.[14] measured tin activities using fused salt EMF method.

The aim of this work was identification of the most accurate thermodynamic model to describe thermodynamic behavior of liquid Sn-Ag-Bi alloys and also, investigation of the ternary interaction influence in the example of Sn-Ag-Bi system.

Scientific paper

THEORETICAL FUNDAMENTALS

The calculations in this work have been done using general solution model [15], Hillert model [16] and Toop model [17]. Such obtained data were compared with the results of application of Redlich-Kister-Muggianu model [18], using the data on evaluated ternary thermodynamic parameters by OHTANI ET AL. [11].

The basic theoretical interpretations of these models are given:

- General solution model[15]

$$G^E = x_1x_2\,(A^o_{12} + A^1_{12}\,(x_1\text{-}x_2) + A^2_{12}\,(x_1\text{-}x_2)^2) + x_2x_3\,(A^o_{23} + A^1_{23}\,(x_2\text{-}x_3) + A^2_{23}\,(x_2\text{-}x_3)^2) + x_3x_1\,(A^o_{31} + A^1_{31}\,(x^3\text{-}x^1) + A^2_{31}\,(x_3\text{-}x_1)^2) + fx_1x_2x_3 \quad (1)$$

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

$$\Delta G^E_{ij} = X_iX_j\,(A^o_{ij} + A^1_{ij}\,(X_i - X_j) + A^2_{ij}\,(X_i - X_j)^2 + ... + A^n_{ij}\,(X_i - X_j)^2) \quad (2)$$

where X_i and X_j indicate the mole fraction of component "i" and "j" in "ij" binary system. The function f is the ternary interaction coefficient expressed by

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

where ξ_{ij} are the similarity coefficients defined by hi called the deviation sum of squares:

$$\xi_{ij} = hi / (hi + hj) \quad (4)$$

where are

$$\eta_I = \int_{X_i=0}^{X_i=1} (\Delta G^E_{12} - \Delta G^E_{13})^2\,dX_1$$

$$\eta_{II} = \int_{X_i=0}^{X_i=1} (\Delta G^E_{21} - \Delta G^E_{23})^2\,dX_2 \quad (5)$$

$$\eta_{III} = \int_{X_i=0}^{X_i=1} (\Delta G^E_{31} - \Delta G^E_{32})^2\,dX_3$$

and

$$X_{1(12)} = x_1 + x_3\xi_{12}$$
$$X_{2(23)} = x_2 + x_1\xi_{23} \quad (6)$$
$$X_{3(31)} = x_3 + x_2\xi_{31}$$

- Hillert model[16]

$$G^E = \frac{x_2}{1-x_1}\Delta G^E{}_{12}(x_1;1-x_1) + \frac{x_3}{1-x_1}\Delta G^E{}_{13}(x_1;1-x_1) + \frac{x_2x_3}{v_{23}v_{32}}\Delta G^E{}_{23}(v_{23};v_{32}) \quad (7)$$

where is: $v_{ij} = 1/2\ (1+x_i-x_j)$

- Toop model[17]

$$G^E = \frac{x_2}{1-x_1}\Delta G^E{}_{12}(x_1;1-x_1) + \frac{x_3}{1-x_1}\Delta G^E{}_{13}(x_1;1-x_1) + (x_2+x_3)^2\Delta G^E{}_{23}\left(\frac{x_2}{x_2+x_3};\frac{x_3}{x_2+x_3}\right) \quad (8)$$

In all given equations, G^E and $\Delta G^E{}_{ij}$ correspond to the integral molar quantity for ternary and binary systems, respectively, while x_1, x_2, x_3 correspond to the mole fraction of components in investigated ternary system.

Results and discussion

Basic data for the calculation were thermodynamic data for the constitutive subsystems in the ternary Sn-Ag-Bi system. The values of integral molar Gibbs excess energies, $\Delta G^E{}_{ij}$, for the binary systems Ag-Bi, Bi-Sn and Sn-Ag were taken from the Version 1.1 of the COST 531 Database for Lead Free Solders[9], according to the references[3,5,7,8]. The Redlich-Kister parameters for the liquid phase of the constitutive binaries are given in Table 1.

Table 1. Redlich-Kister parameters for the liquid phase of the constitutive binary systems

System	$L^o(T)$	$L^1(T)$	$L^2(T)$
Ag-Sn	-5146.7-5.0103T	-15799.3+3.3208T	-6687.5
Ag-Bi	3340.81+39.16749T-5.969876TlnT	-5485.45-1.07133T	-3055.34+1.77449T
Bi-Sn	490+0.966T	-30-0.235T	0

Related similarity coefficients were determined according to Equations.(4-6) at investigated temperature of 900K and their values are: $\xi_{Bi\text{-}Sn} = 0.033$; $\xi_{Sn\text{-}Ag} = 0.447$ and $\xi_{Ag\text{-}Bi} = 0.973$. They are also shown graphically in Figure 1.

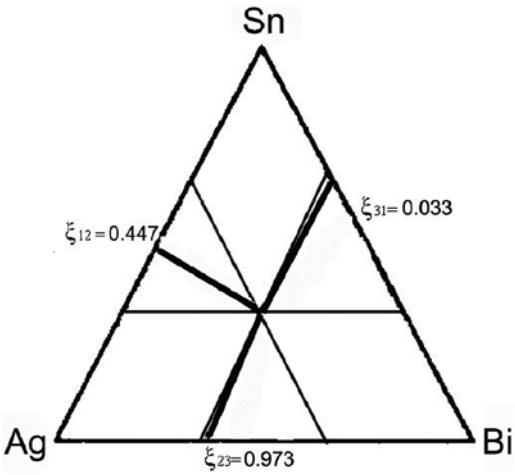

Figure1. The selected binary compositions for three binaries in the investigated ternary system according to general solution model at 900K (shown as bold solid lines)

The similarity coefficient concept, given in Figure 1, pointed out to the asymmetric behavior of the investigated system Sn-Ag-Bi, which was the main reason for choosing asymmetric models - Hillert and Toop, as the additional predicting methods used in this paper.

Furthermore, the comparison with available literature data - the results of Redlich-Kister-Muggianu model (using the data on evaluated ternary thermodynamic parameters by OHTANI ET AL.[11]) and the experimental EMF results of KATAYAMA ET AL.[14], was done. The illustration of the comparison between calculated and experimentally determined tin activities[14], in the form of lngSn vs. composition, is shown in Figure 2 for the sections Sn-AgxBiy (x:y equal to 3:1, 1:1 and 1:3) at 900K.

The comparison shows that calculated results differ slightly comparing to each other. Although not uniform for all sections, the agreement with experimental points[14] is fairly well comparing to the RKM literature data[11] including optimized ternary interaction parameter.

In order to accurately examine the deviation between used models at one side and experimental data[14] at the other side, the root mean square deviation analysis was applied to tin activities data:

$$RMS = 1/N \times [\Sigma(a_{Sn\ exp} - a_{Sn\ calc})^2]^{1/2} \qquad (10)$$

where are: RMS - root mean square deviation, N – the number of counting points, $a_{Sn\ exp}$ – experimental, literature results[14] and $a_{Sn\ calc}$ – calculated values for tin activity. The results of this analysis, done for the investigated three sections with molar ratio Ag:Bi=3:1, 1:1 and 1:3, are presented in Table 2, pointing out that Hillert model is the most adequate model for thermodynamic description of ternary Sn-Ag-Bi system, which was expected (Figure 1.) since investigated Sn-Ag-Bi system behaves asymmetrically.

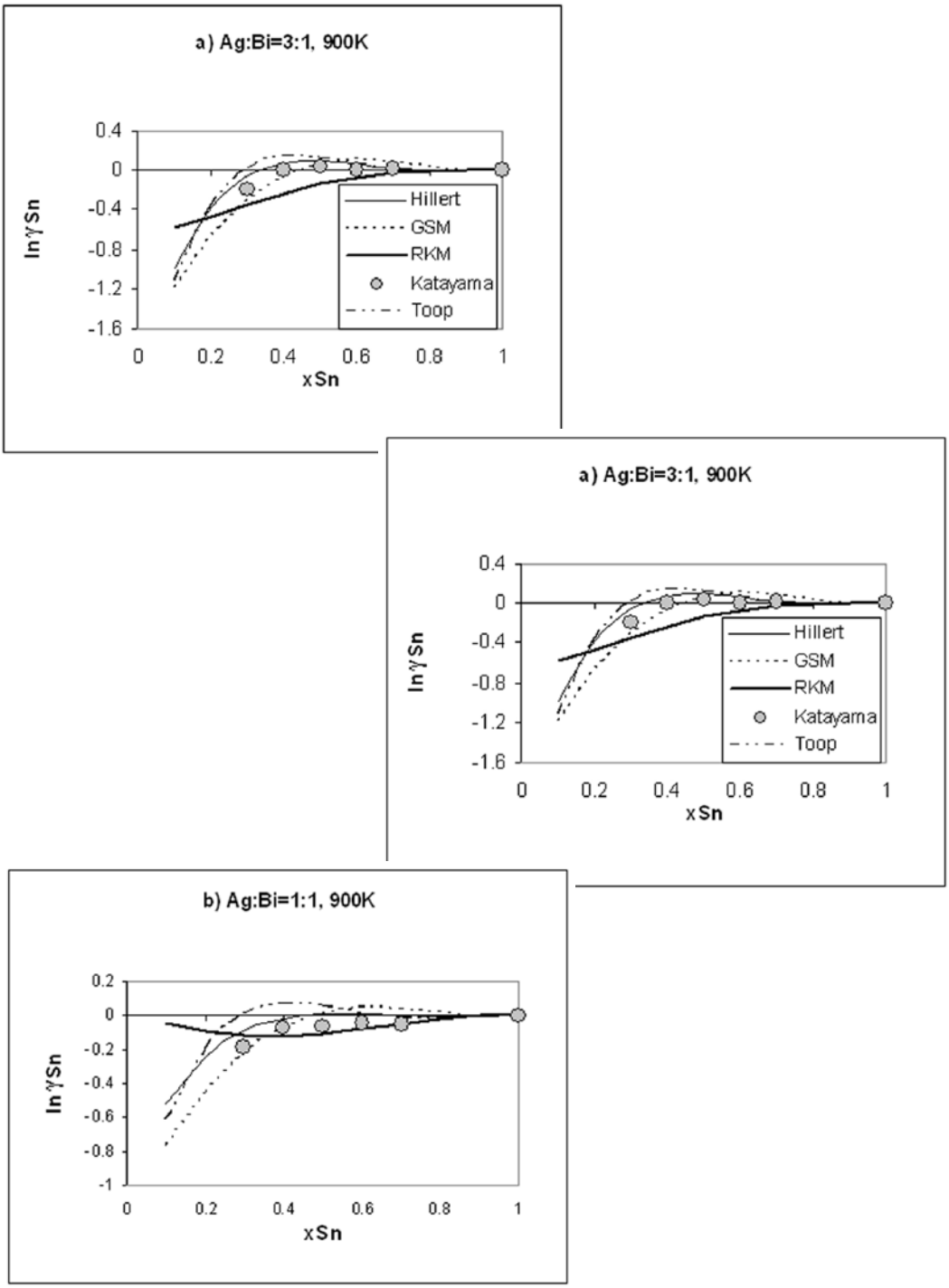

Figure 2. The comparison between calculated and derived lngSn from experimental data[14] for the sections Sn-AgxBiy (x:y equal to 3:1 – a, 1:1 – b and 1:3 -c) at 900K

Table 2. The results of the root mean square deviation analysis

Model	RKM	GSM	Toop	Hillert
St	0.008035	0.007063	0.089173	0.005085

Therefore, thermodynamic calculations in the investigated ternary system Bi-Sn-Ag (taken as 1-2-3 in order) were carried out at 900K according to Hillert model, Equation 7, in the following sections: Sn-Ag_xBi_y Ag-Bi_xSn_y, and Bi-Ag_xSn_y, where x:y is molar ratio equal to 1:1, 1:3 and 3:1. The values of calculated integral molar Gibbs excess energies for liquid alloys, in chosen sections, are given in the form of polynomial expressions in Table 3.

Table 3. Integral molar excess Gibbs energies, (given as $G^E = A + Bx_i + Cx_i^2 + ...$, J/mol) for liquid alloys in different sections in the Sn-Ag-Bi system at 900K

G^E (J/mol) = $A + Bx_i + Cx_i^2 + Dx_i^3 + Ex_i^4$					
Section (i:j)	A	B	C	D	E
Ag:Bi=1:1	510.89	-7596.5	19853	-19927	7159
Ag:Bi=3:1	-293.04	-14586	46831	-51199	19250
Ag:Bi=1:3	915.81	-5778.7	13480	-13120	4505.4
Bi:Sn=1:1	335.15	-2640	7953.8	-30020	24375
Bi:Sn =3:1	279.97	-3594.7	10606	-39114	31821
Bi:Sn =1:3	216.67	-230.49	4623	-23223	18625
Sn:Ag=1:1	-2159.9	6480.1	-4121.4	-200.13	/
Sn:Ag=3:1	-690.93	2359.4	-1438.3	-227.99	/
Sn:Ag=1:3	-3542.2	10111	-4288	-3351.4	1070.8

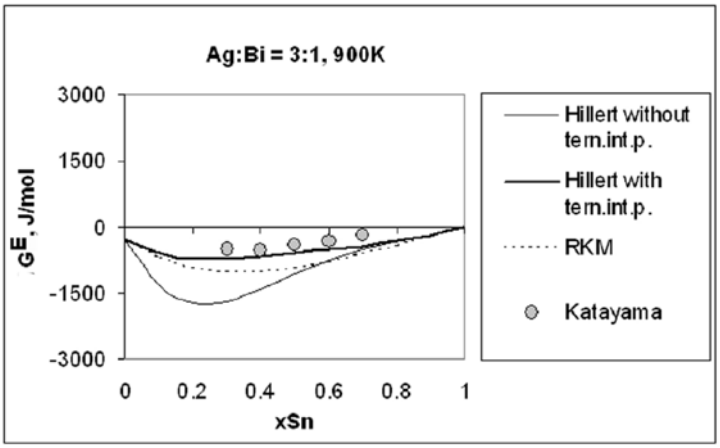

Figure 3. Investigation of the ternary interaction parameter influence on GE values

The influence of the ternary interaction parameter for the liquid phase, given in[11] as: $L^{l}_{Ag,Bi,Sn} = x_{Ag}(1700+76.2T) + x_{Bi}(11000+4T) + x_{Sn}(20000-38.95T)$, was also investigated. The comparison between the values for the integral molar Gibbs excess energies for the section Ag:Bi=3:1 at 900K, calculated using Hillert model with and without ternary interaction parameter and literature data – obtained by Redlich-Kister-Muggianu model using the data on evaluated ternary thermodynamic parameters[11] and experimental ones[14], are shown in Figure 3.

The best agreement with experimental values[14] was observed for the calculated Hillert results including ternary interaction parameter. Therefore, it may be concluded that the most accurate thermodynamic data on the Sn-Ag-Bi system could be obtained using asymmetric Hillert model including ternary interaction parameter.

Conclusions

The results of thermodynamic properties and phase diagram prediction in the Sn-Ag-Bi system are presented in this paper. The calculation of thermodynamic properties was done using general solution model, Hillert and Toop model for the liquid alloys at 900K in sections Sn-Ag_xBi_y Ag-Bi_xSn_y, and Bi-Ag_xSn_y, where x:y is equal to 1:1, 1:3 and 3:1. The calculated results were compared with available referent data and the results of the root mean square deviation analysis pointed out to the Hillert model, including ternary interaction parameter, as the most adequate model for thermodynamic description of ternary Sn-Ag-Bi system.

References

[1] http://www.pb-free.com/ica_authored_papers/low_alpha_solders.pdf

[2] N.C. Lee: Advancing Microelectronics, 26 (5) (1999) 29.

[3] U. Kattner, W.J. Boetthinger,: J.Electron.Mater., 23 (7) (1994) 603.

[4] R. Hultgren et al.: Selected values of the Thermodynamic Properties of Binary Alloys, Metals Park, OH, ASM, 1973.

[5] C.S. Oh, J.H. Shim, B.J. Lee, D.N. Lee: J.Alloys Comp., 238 (1996) 155.

[6] B.J. Lee, C.S. Oh, J.H. Shim: J.Electron.Mater., 25 (1996) 983.

[7] H. Ohtani, K. Ishida: J.Electron.Mater., 23 (8) (1994) 747.

[8] D. Malakhov et al.: Mater. Trans., 43 (2002) 1879.

[9] Version 1.1 of the COST 531 Database for Lead Free Solders

[10] S. Hassam, E. Dichi, B. Legendre: J.Alloys Comp., 268 (1998) 199.

[11] H. Ohtani, I. Satoh, M. Miyashita, K. Ishida: Mater. Trans. JIM, 42 (5) (2001) 722.

[12] www.metallurgy.nist.gov/phase/solder/agbisn.html

[13] S. Hassam, M. Gambino, J. P.bros, Z. Metallknd.: 85 (7) (1994) 460.

[14] I. Katayama, T. Tanaka, S. Akai, K. Yamazaki, T. Iida: Materials Science Forum (in print)

[15] K.C. Chou: Calphad, 19(3) (1995) 315.

[16] M. Hillert: Calphad, 4 (1980) 1.

[17] G.W. Toop: Trans.Met.Soc. AIME, 233 (1965) 850.

[18] O. Redlich, A.T. Kister: Ind.Eng.Chem., 24 (1948) 345.