Calculation of thermodynamic properties for ternary Ag–Cu–Sn system

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Abstract: Results of thermodynamic properties calculations for the liquid alloys in ternary Ag–Cu–Sn system are presented in this paper. The general solution model has been used for the thermodynamic prediction in the sections from each component corner, with the molar ratio of the other two components 1:9, 3:7, 1:1, 7:3, 9:1, for which characteristic thermodynamic quantities have been obtained at temperature 1473 K.

Key words: Ag–Cu–Sn alloys, thermodynamics, general solution model

Introduction

The Ag–Cu–Sn system is fundamental to the development of technology of lead-free solder alloys. Recent legislations in many countries to eliminate the use of lead containing solder alloys have created renewed interest in this system, especially in the Sn rich region.

This system has rather already been investigated. Thus, Yen and Chen[1] have determined phase equilibria of the Ag–Sn–Cu ternary system experimentally as well as using the calculation of phase diagram (CALPHAD) method. Ohnuma et al.[2] have presented the phase equilibria and the related thermodynamic properties of the Sn–Ag–Cu alloys using a thermodynamic database for micro-soldering alloys that consists of the elements Pb, Bi, Sn, Sb, Cu, Ag, Zn and In. Hirose et al.[3] have investigated joint strength and interfacial microstructure between Sn–Ag–Cu and Sn–Zn–Bi solders and Cu substrate. Dutkiewicz et al.[4] have investigated rapid quenching and mechanical alloying of eutectic Ag–Cu–Sn alloys. He and Ding[5] have investigated Ag–Cu–Sn brazing filler metals. Also, Moon et al.[6] have investigated experimentally and made thermodynamic assessment of Sn–Ag–Cu solder alloys.

The latest thermodynamic assessment of Ag–Cu–Sn ternary system is work of Gisby and Dinsdale[7] carried out prior the COST 531 Action[8] and included in COST 531 Database for Lead Free Solders[9] and

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in COST 531 Atlas of Phase Diagrams for Lead-Free Soldering[10]. The calculated binary systems and liquidus projection of ternary Ag–Cu–Sn system according to Reference[10] are shown in Figure 1. The phase diagram of the Ag–Cu binary system is rather simple without intermediate phases and the phase diagrams of the Ag–Sn and Cu–Sn are complex with appearance of many intermediate phases.

In this paper, in order to investigate thermodynamic behavior of liquid Ag–Cu–Sn alloys and its relationship with phase structure of solidified alloys, several integral and partial thermodynamic functions were calculated using Chou's general solution model. Obtained results were discussed in connection with a mutual reactivity of the components in investigated ternary system.

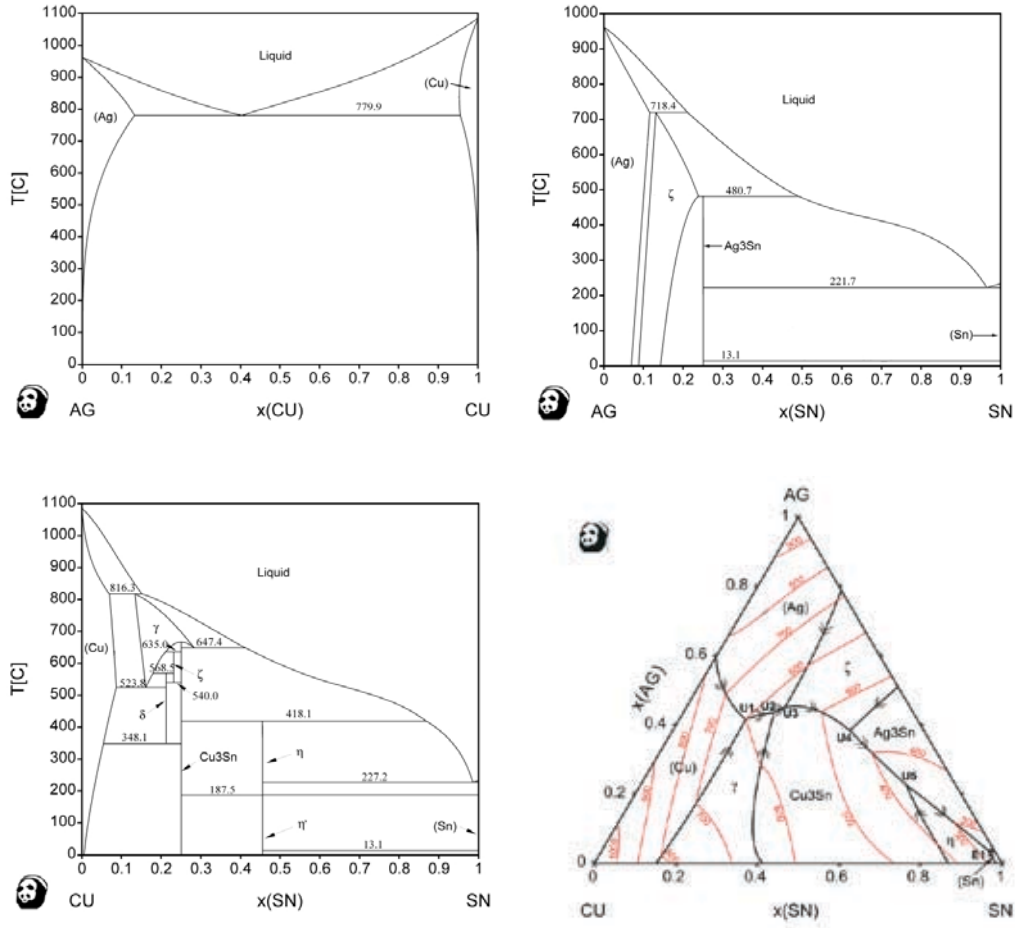

Figure 1. Phase diagrams of the boundary binary systems, and the liquidus projection of the ternary Ag–Cu–Sn system[10]

THEORETICAL FUNDAMENTALS

There are several traditional models to extrapolate thermodynamic properties of the ternary system based on the three constitutive binary systems, which are classified, according to HILLERT[11], into two categories: symmetrical (KOHLER[12], MUGGIANU[13]) and asymmetrical (TOOP[14], HILLERT[11]).

The use of a symmetrical model when an asymmetrical model is more appropriate can often give rise to errors. Categorization of the investigated ternary system in the one of these two categories is, in some cases and in the lacking of the adequate experimental data, uncertain task. Also, a different choice of an arrangement of the three components to the three apexes of triangle in the case of the asymmetric model application will lead to a different result of the ternary Gibbs energy of mixing. From this reasons CHOU[15,16] proposed a new model, based on the "similarity coefficient concept", which advantage is that its application does not require predetermination if a system is symmetrical or not, neither choice of the symmetric and asymmetric components in the particular ternary system. The correctness of this model has already been confirmed in some practical examples[17–19]. Therefore this model is applied for the calculation of the thermodynamic properties of the liquid Ag–Cu–Sn ternary system.

The basic equation of general solution model developed by CHOU is given as follows (in detail see References[15,16]):

$$\Delta G^E = x_1x_2\,(A^o_{12} + A^1_{12}\,(x_1\text{-}x_2) + A^2_{12}\,(x_1\text{-}x_2)^2) + x_2x_3\,(A^o_{23} + A^1_{23}\,(x_2\text{-}x_3) + A^2_{23}\,(x_2\text{-}x_3)^2) + x_3x_1\,(A^o_{31} + A^1_{31}\,(x_3\text{-}x_1) + A^2_{31}\,(x_3\text{-}x_1)^2) + f x_1x_2x_3 \quad (1)$$

where ΔG^E is an integral excess Gibbs energy for a ternary system, x_1, x_2, x_3 are the mole fractions of a ternary alloy, A^o_{ij}, A^1_{ij}, A^2_{ij} are regular-solution type parameters for binary system "ij" and can be temperature dependent.

The function f is the ternary interaction coefficient expressed by:

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

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

$$\xi_{ij}=\eta_i/(\eta_i+\eta_j) \quad (3)$$

where are:

$$\eta_I = \int_0^1 (\Delta G^E_{12} - \Delta G^E_{13})^2\,dX_1$$

$$\eta_{II} = \int_0^1 (\Delta G^E_{21} - \Delta G^E_{23})^2\,dX_2$$

$$\eta_{III} = \int_0^1 (\Delta G^E_{31} - \Delta G^E_{32})^2\,dX_3 \quad (4)$$

and

$$X_{1(12)} = x_1 + x_3\xi_{12}$$
$$X_{2(23)} = x_2 + x_1\xi_{23}$$
$$X_{3(31)} = x_3 + x_2\xi_{31} \quad (5)$$

Results and discussion

The thermodynamic calculation were performed using general solution model, in the sections from each component corner with the molar ratio of the other two components 1:9, 3:7, 1:1, 7:3, 9:1 at chosen temperature 1473 K. This temperature is appropriate for analysis of atomic interaction in liquid phase because it is not too high. The starting data values of Redlich-Kister parameters of the liquid phases of the binary systems Ag–Cu, Ag–Sn, and Cu–Sn are shown in Table 1.

For the calculation of integral excess Gibbs energy using Chou's model we arbitrary adopted following settings of components: Ag-component 1, Cu-component 2 and Sn-component 3. Therefore the Redlich-Kister parameters (named with L_{ij} in Table 1) for the Ag(1) – Cu(2) and Cu(2) – Sn(3) binary systems are identical to regular-solution type parameters appearing in Chou's model (named with A_{ij} in Eqs. 1,2). Only for the second parameter in the Sn(3) – Ag(1) binary system stands following relation $A_{ij} = -L_{ij}$. Calculated regular-solution type parameters for constitutive binaries, deviation sum of squares and similarity coefficients for the ternary Ag–Cu–Sn system at 1473 K are presented in Table 2.

Using the values from Table 1 and Equation 1 ΔG^E functions for boundary binary systems and chosen ternary sections at 1473 K were calculated and shown in Figure 2.

Table 1. The Redlich-Kister parameters for boundary binary systems

Parameter	Ag–Cu[20,21]	Ag–Sn[22]	Cu–Sn[23]
L^0_{ij}	+ 17384.37 – 4.46438 T	– 5146.7 – 5.0103T	– 9002.8 – 5.8381 T
L^1_{ij}	+ 1660.74 – 2.31516T	– 15799.3 + 3.3208 T	– 20100.4 + 3.6366 T
L^2_{ij}	-	– 6687.5	– 10528.4

Table 2. Regular-solution type parameters for Ag–Cu, Cu–Sn and Sn–Ag binaries, deviation sum of squares and similarity coefficients for the ternary Ag–Cu–Sn system at 1473 K (Ag–Cu–Sn set in 1–2–3 order).

A^0_{AgCu}	A^1_{AgCu}	A^2_{AgCu}	η_I	$\xi_{Ag\text{-}Cu}$
10808.34	1749.491	0	2.01E+07	0.391709
A^0_{CuSn}	A^1_{CuSn}	A^2_{CuSn}	η_{II}	$\xi_{Cu\text{-}Sn}$
– 17602.3	– 14743.29	– 10528.4	3.12E + 07	0.881417
A^0_{SnAg}	A^1_{SnAg}	A^2_{SnAg}	η_{III}	$\xi_{Sn\text{-}Ag}$
– 12526.9	10907.76	– 6687.5	4200970	0.172818

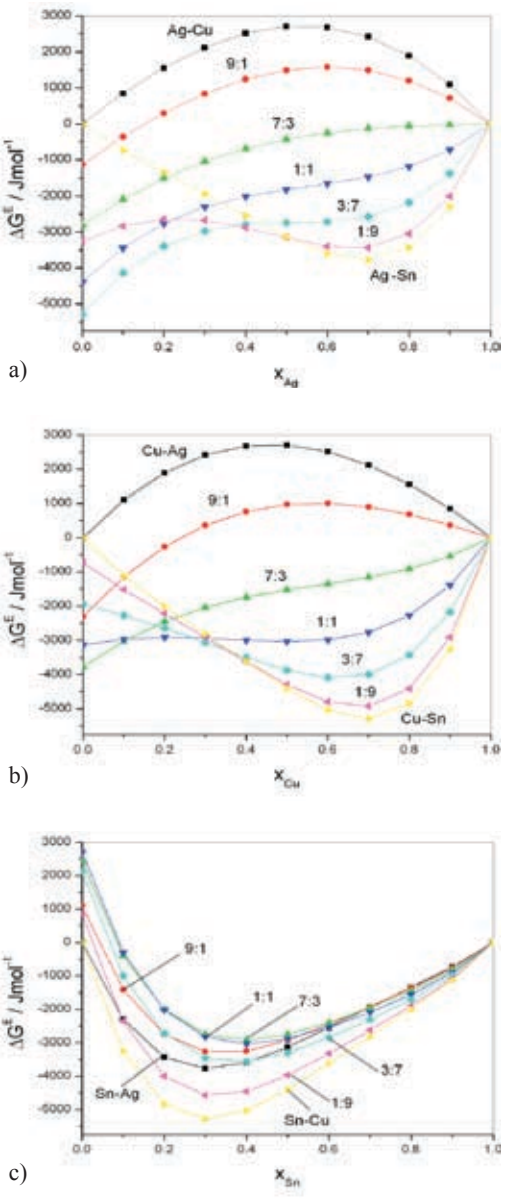

Figure 2. Dependence of ΔGE on molar fraction of Xi for three binary systems and chosen ternary sections at 1473 K (a – Ag-corner, b – Cu-corner, c – Sn-corner)

In Figure 2 it can be observed that Cu–Ag binary system has positive values ΔG^E in whole concentration range, while the other two constitutive binary systems have negative values ΔG^E. According to this, chemical interaction between atoms Sn on one side and atoms Cu and Ag on the other side is much stronger than chemical interaction between atoms Cu and Ag. This causes that in solid state Ag and Cu do not make any new intermediate phases while Sn with both Cu and Ag forms a series of intermediate phases. This tendency is held in ternary system. According to the liquidus projection of the Ag–Cu–Sn system, shown in Figure 1, for the alloys with low concentration of Sn, primary crystallization phases are solid solutions based on Ag and Cu and for alloys with moderately and high concentration of Sn primary crystallization phases are intermediate phases based on Sn.

According to calculated dependence of G^{xs} of composition, and using equations (4) and (5), partial thermodynamic quantities have been obtained.

$$G^{xs}_i = G^{xs} + (1 - x_i)\,(\partial G^{xs}/\partial x_i) \qquad (6)$$

$$G^{xs}_i = RT \ln(a_i / x_i) \qquad (7)$$

Dependence of the partial molar Gibbs free energies on composition of each component at 1473K is shown in Figure 3.

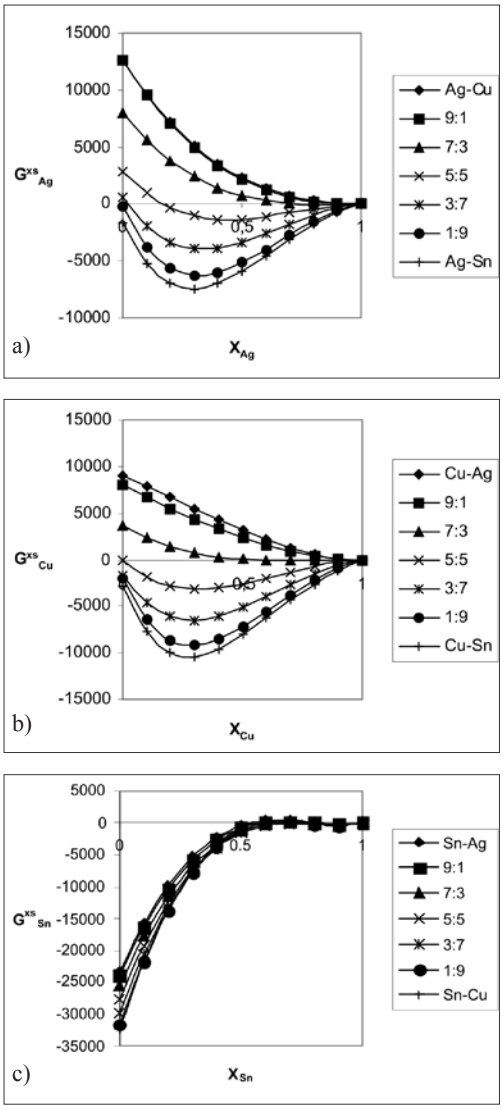

Figure 3. Dependence Gxsi on composition of components for all observed sections in Cu–Ag–Sn system at 1473 K(a – Ag-corner, b – Cu-corner, c – Sn-corner)

Further calculation involves determining the dependence of activity of components of composition in the observed sections of the ternary Cu–Ag–Sn system.

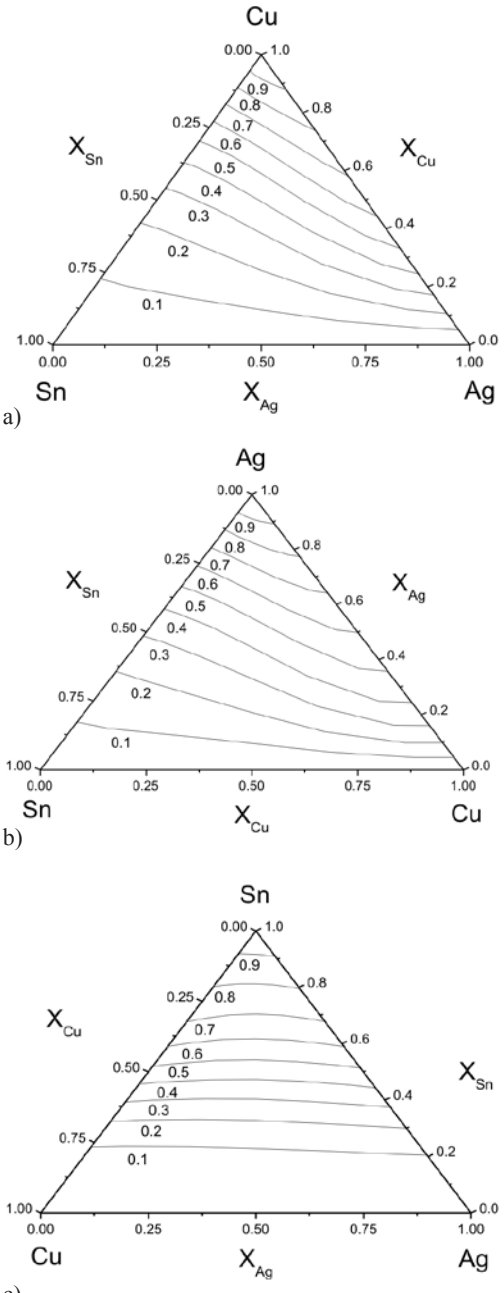

Figure 4. Iso-activity lines for Cu (a), Ag (b), and Sn (c) in ternary Cu–Ag–Sn system at 1473 K

The calculated activities of the components in Cu–Ag–Sn system at 1473K indicate that activities of Ag and Cu decrease rapidly with increase of Sn content in ternary alloys. Minimum of thermodynamic activity Ag and Cu achieve in boundary Ag–Sn and Cu–Sn systems which is in agreement with their strong chemical affinity toward Sn. Variation of Ag and Cu concentration in ternary Ag–Cu–Sn alloys has much less influence on Sn activity.

Iso-activity lines for Cu, Ag, and Sn at 1473 K that illustrate previously mentioned facts are shown in Figure 4.

Conclusions

Thermodynamic analysis of the liquid Cu–Ag–Sn alloys has been carried out with geometrical Chou's general solution model for predicting the thermodynamic quantities of ternary alloys according to known thermodynamic quantities of the constituting binary systems. Integral excess Gibbs free energies for fifteen distinguished sections at 1473 K have been calculated. Further calculation has involved obtaining of the partial molar Gibbs free energies, and diagrams of iso-activity lines for all three components have been constructed.

It has been determined that thermodynamic properties of the constituting binary systems define thermodynamic behavior of the ternary system alloys, and that chemical affinities between the elements in binary systems remain in ternary alloys, as well.

Presented results can be used for comparison with future experimental results in order to determine the deviation and to define ternary interaction parameters.

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References

[1] Yen, Y., Chen, S. (2004): *Journal of Materials Research* 19 (8), pp. 2298–2305.

[2] Ohnuma, I., Miyashita, M., Anzai, K., Liu, X. J., Ohtani, H., Kainuma, R., Ishida, K. (2000): *J. Electron. Mater.*, 2000, 29 (10), pp. 1137–1144.

[3] Hirose, A., Yanagawa, H., Ide, E., Kobayashi, K. F. (2004): *Science and Technology of Advanced Materials*, 5 (1-2), pp. 267–276.

[4] Dutkiewicz, J., Lityfiska, L., Swiatek, R. (1995): *Journal of Materials Processing Technology*, 53, pp. 131–138.

[5] He, Z., Ding, L. (1997): *Materials Chemistry and Physics*, 49, pp. 1–6.

[6] Moon, K. W., Boettinger, W. J., Kattner, U. R., Biancaniello, F. S., Handwerker, C. A. (2000): *Journal of Electronic Materials*, 29 (10), pp. 1122–1136.

[7] Gisby, J. A., Dinsdale, A. T. *unpublished research*.

[8] Lead-free Solder Materials-COST Action 531 (http://www.univie.ac.at/cost531/)

[9] Dinsdale, A. T., Kroupa, A., Vízdal, J., Vrestal, J., Watson, A., Zemano-

va, A. (2008): *COST531 Database for Lead-free Solders, Ver. 3.0*, unpublished research.

[10] Dinsdale, A. T., Watson, A., Kroupa, A., Vrestal, J., Zemanova, A., Vizdal J. (Eds.) (2008): *COST Action 531-Atlas of Phase Diagrams for Lead-free Solders*, Vol. 1, Brno, Czech Republic.

[11] Hillert, M. (1980): *Calphad* 4, p. 1.

[12] Kohler, F. (1960): *Monatsh. Chem.* 91, p.738.

[13] Muggianu, Y. M., Gambino, M., Bross, J. P. (1975): *J. Chimie Physique* 72, p.83.

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

[15] Chou, K. C. (1995): *Calphad*, 19 (3), pp. 315–325.

[16] Chou, K. C., Li, W. C., Li, F., He, M. (1996): *Calphad*, 20, p. 395.

[17] Katayama, I., Yamazaki, K., Nakano, M., Iida, T. (2003): *Scan. J. Metall*., 32.

[18] Živković, D., Katayama, I., Kostov, A., Živković, Ž. (2003): *J. Thermal Analysis and Calorimetry*, 71, p. 567.

[19] Živković, D., Živković, Ž., Šestak, J. (1999): *Calphad,* 23, p. 113.

[20] Hayes, F. H., Lukas, H. L., Effenberg, G., Petzow, G. (1986): *Z. Metallkde.* 77, pp. 749–754.

[21] Lukas, H. L. (1998): *Unpublished work.*

[22] Shim, J. H., Oh, C. S., Lee, B. J., Lee, D. N. (1996): *J. Alloys and Compounds*, 238, pp.155–166.

[23] Liu, X. J., Liu, H. S., Ohnuma, I., Kainuma, R., Ishida, K., Itabashi, S., Kameda, K., Yamaguchi, K. (2001): *J. Electron. Mater*., 30(9), p. 1093.