Savez inženjera metalurgije Srbije i Crne Gore
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ANALYTICAL APPROACH TO THERMODYNAMIC INVESTIGATION OF Au-Sn-Zn ALLOYS

ANALITIČKI PRISTUP TERMODINAMIČKOM ISPITIVANJU Au-Sn-Zn LEGURA

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ABSTRACT

The results of analytical determination of thermodynamic properties for Au-Sn-Zn alloys using general solution model are presented in this paper. Obtained predicted values for activities and other partial and integral molar quantities at 973K were compared with existing experimental literature data, showing good agreement.

Key words: thermodynamics of alloys, lead-free solders, Au-Sn-Zn system, GSM

IZVOD

Rezultati analitičkog odredjivanja termodinamičkih karakteristika Au-Sn-Zn legura, korišćenjem opšteg modela rastvora, predstavljeni su u ovom radu. Predvidjanjem dobijene vrednosti za aktivnosti i druge parcijalne i integralne molarne veličine na 973K uporedjene su sa postojećim eksperimentalnim podacima iz literature i pokazale dobro medjusobno slaganje.

Ključne reči: termodinamika legura, lemovi bez olova, Au-Sn-Zn sistem, GSM

INTRODUCTION

Au-Sn-Zn alloys are interesting as lead-free solder materials and in recent time they are the subject of different researches, including physical, mechanical and thermodynamic properties [1,2].

Considering thermodynamic investigations of these alloys, done up to now, one should conclude that constitutive binaries have been studied in details by numerous investigators and by different experimental techniques [3-13]. Complete data and critical evaluation of thermodynamic properties for Au-Sn, Sn-Zn and Zn-Au binary systems are given by Hultgren [14] and Komarek [15]. Liquid ternary alloys in Au-Sn-Zn system have been researched by Karlhuber et

al. [2] using EMF method and calorimetry in four sections with a constant Au:Sn ratio. Their experiments showed that the addition of Sn to Au-Zn binary system, the compound forming tendency and CSRO (chemical short range order) has an influence on the anomalies of ternary thermodynamic properties typical for Au-Sn-Zn liquid ternary alloys.

In order to investigate mentioned ternary system by thermodynamic predicting, to compare experimental and analytical results, and also, to contribute in more complete knowledge of these new lead-free solders, the results of thermodynamic investigation of Au-Sn-Zn ternary system using general solution model are presented in this paper.

THEORETICAL FUNDAMENTALS

The basic equation of general solution model, derived by Chou, is given as follows [16]:

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

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:

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

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

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

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

$$\xi_{ij} = \eta_i / \eta_i + \eta_j) \qquad (4)$$

where are:

$$\eta_1 = \int_{X_i=0}^{X_i=1} (\Delta G^E_{12} - \Delta G^E_{13})^2\, dX_2$$

$$\eta_{II} = \int_{X_i=0}^{X_i=1} (\Delta G_{21}^E - \Delta G_{23}^E)^2 dX_2$$

$$\eta_{III} = \int_{X_i=0}^{X_i=1} (\Delta G_{31}^E - \Delta G_{32}^E)^2 dX_3, \qquad (5)$$

and

$$X_{I(12)} = x_1 + x_3\xi_{12}$$

$$X_{2(23)} = x_2 + x_1\xi_{23}$$

$$X_{3(31)} = x_3 + x_2\xi_{31} \qquad (6)$$

In all given equations, ΔG^E and ΔG^E_{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 system.

RESULTS AND DISCUSSION

Ternary Au-Sn-Zn system has been investigated in 15 sections. Five sections were taken from Au, Sn and Zn corner, respectively, with following ratios 1:9, 3:7; 1:1; 7:3; 9:1, and with molar content of 0.1 - 0.9 for the third component.

Starting data for the calculation procedure according to general solution model are integral molar Gibbs excess energies and integral molar mixing enthalpies for all three constitutive binaries taken at 973K from Hultgren book [14]. According to Eq.(2) binary solution parameters were calculated, and shown in Table 1, together with the values of similarity coefficients obtained by Eqs. (4-6).

Table 1. Binary solution parameters and similarity coefficients at 973K calculated by GSM

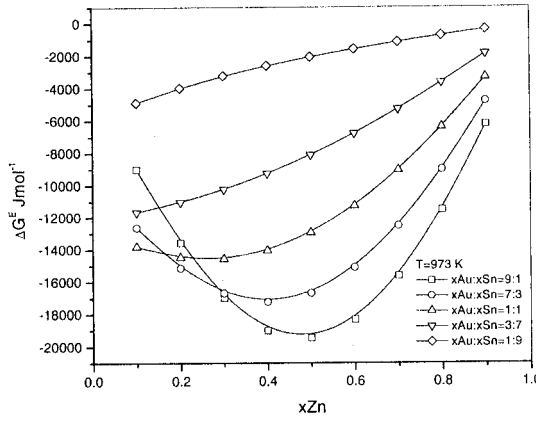
a) for integral molar Gibbs excess energies

A^0_{12}	A^1_{12}	A^2_{12}	A^3_{12}	η_I	ξ_{12}
-50444.8	16810	-4532.25	0	29320549	0.209109
A^0_{23}	A^1_{23}	A^2_{23}	A^3_{23}	η_{II}	ξ_{23}
5995.25	2514	843.75	0	1.11E+08	0.308645
A^0_{31}	A^1_{31}	A^2_{31}	A^3_{31}	η_{III}	ξ_{31}
-81938.8	-3489	12250.75	0	2.48E+08	0.894426

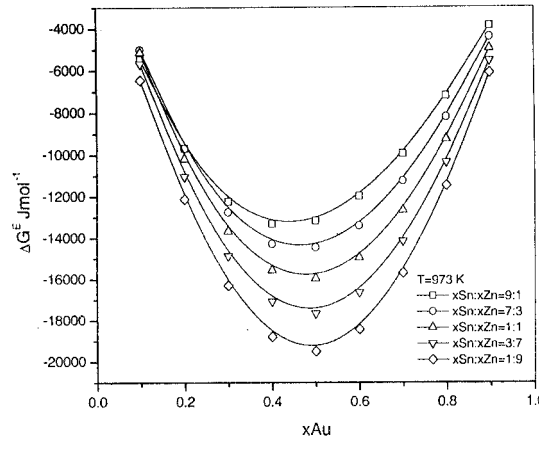
b) for integral molar mixing enthalpies

A^{o}_{12}	A^{1}_{12}	A^{2}_{12}	A^{3}_{12}	η_{I}	ξ_{12}
-42915.1	4684.145	-5207.49	1.58E+04	64419600	0.372084
A^{o}_{23}	A^{1}_{23}	A^{2}_{23}	A^{3}_{23}	η_{II}	ξ_{23}
12931.53	3851.334	2877.428	3518.981	1.09E+08	0.243176
A^{o}_{31}	A^{1}_{31}	A^{2}_{31}	A^{3}_{31}	η_{III}	ξ_{31}
-90869	-6653	24734	-1.73E-11	3.38E+08	0.840055

Based on these data and according to further GSM calculation, ternary interaction coefficients f_{123} were obtained using Eq. (3), which, using Eq. (1), enabled determination of integral molar Gibbs excess energies (Fig.1) and integral molar mixing enthalpies.



a)



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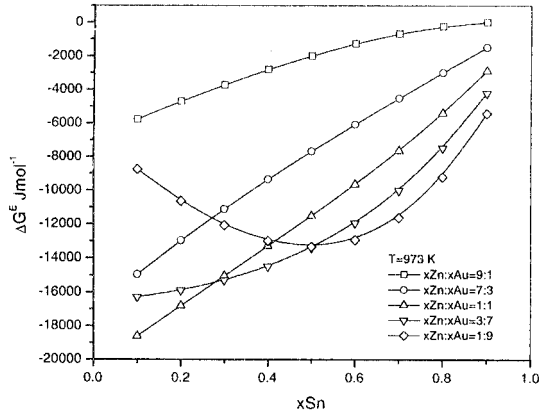
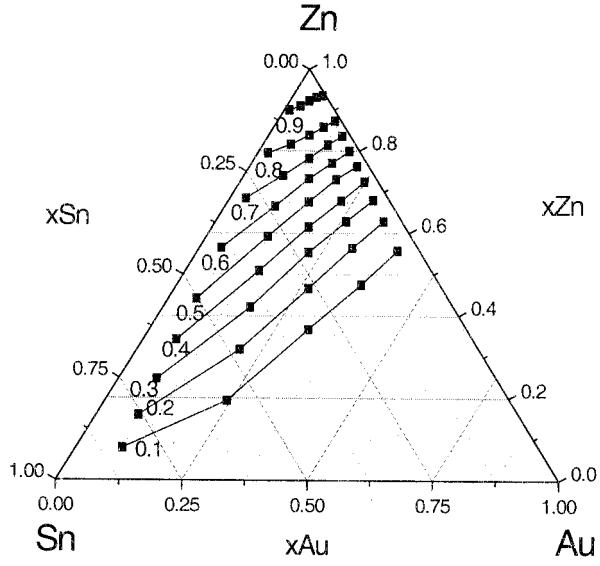


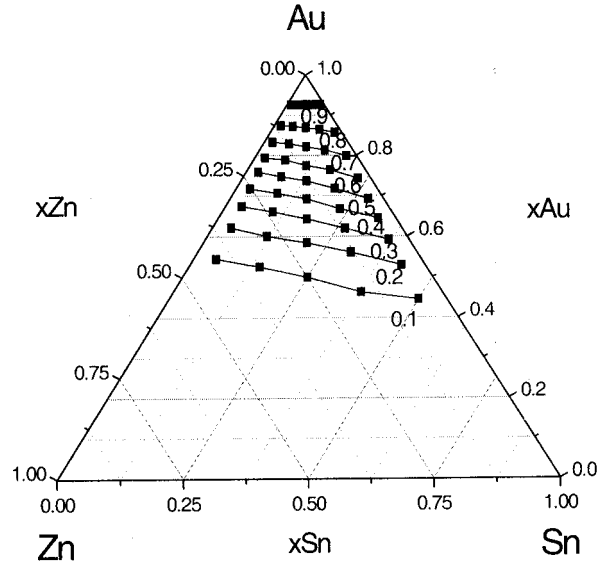
c)

Fig.1. Integral molar Gibbs excess energies at 973K, calculated by GSM, a) sections from Zn corner; b) sections from Au corner c) sections from Sn corner

Activities of all three components in the investigated sections have been determined too, based on ΔG^E values calculated by GSM. Isoactivity curves for gold, tin and zinc at 973K are shown in Fig.2, while iso-lines for integral molar Gibbs energies of mixing are given in Fig.3.



a)



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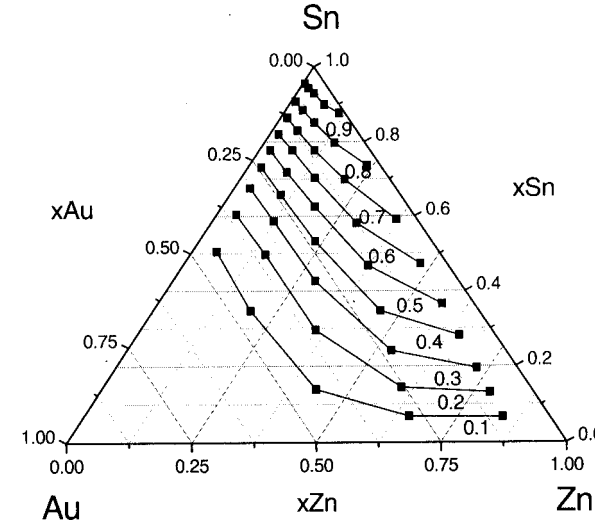


c)

Fig.2. Isoactivity curves in ternary Au-Sn-Zn system at 973K obtained by GSM, a) for zinc; b) for gold; c) for tin

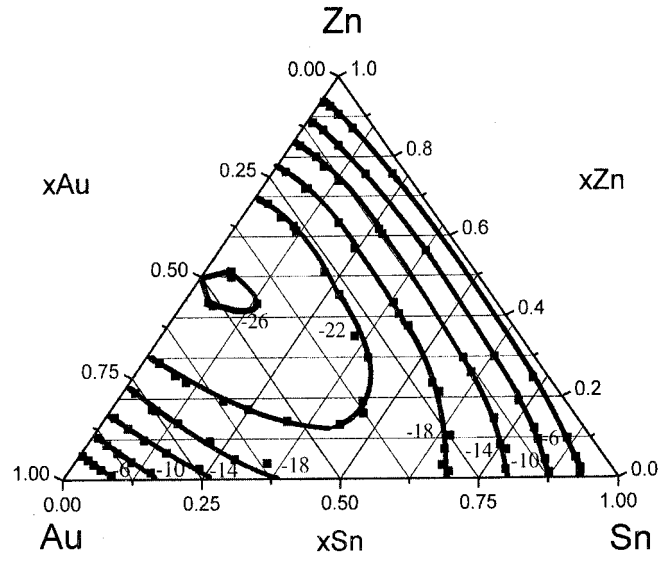
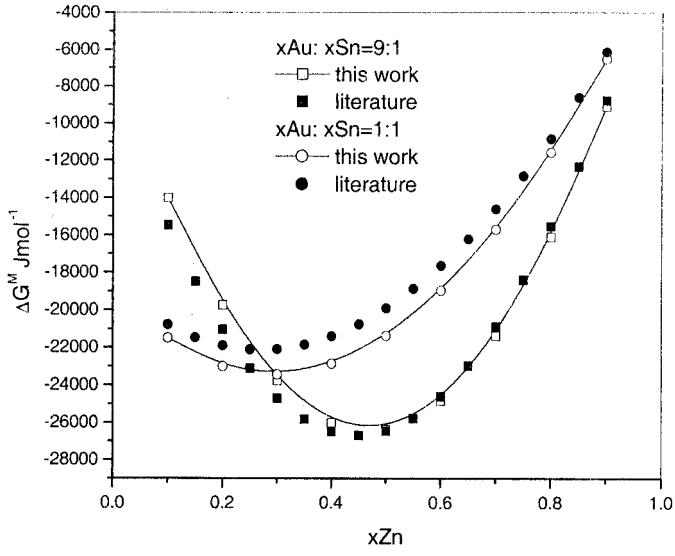


Fig.3. Iso-lines for integral molar Gibbs energie of mixing in ternary Au-Sn-Zn system at 973K (in kJmol^{-1})

As can be seen from Fig. 4, calculated values for both molar mixing Gibbs energies and mixing enthalpies show good agreement with literature [2].

In most of the sections investigated, activity of three constituent elements shows negative deviation from Raoult law. Only in sections with Au:Sn=1:9 and Zn:Au=9:1; 7:3 there is slight positive deviation from ideal behavior. This fact could be also confirmed by Fig.1-b and Fig.2-b, where one can noticed that gold in this system presents the component with greatest capability to mix with the other two coexisting components in the system Au-Sn-Zn. Also, the value of integral molar Gibbs excess energies in all investigated sections (see Fig.1) are negative, with maximum value of –20kJ/mol, while negative values of integral molar Gibbs energies of mixing goes up to –26kJ/mol.

In order to investigate the relation between the results of our work with existing experimental data [2], comparison for integral molar Gibbs energies of mixing, integral molar mixing enthalpies and zinc activities at 973K is shown in Fig.4. It can be seen that relatively good mutual agreement is presented in all three cases.


xAu: xSn=9:1
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xAu: xSn=1:1
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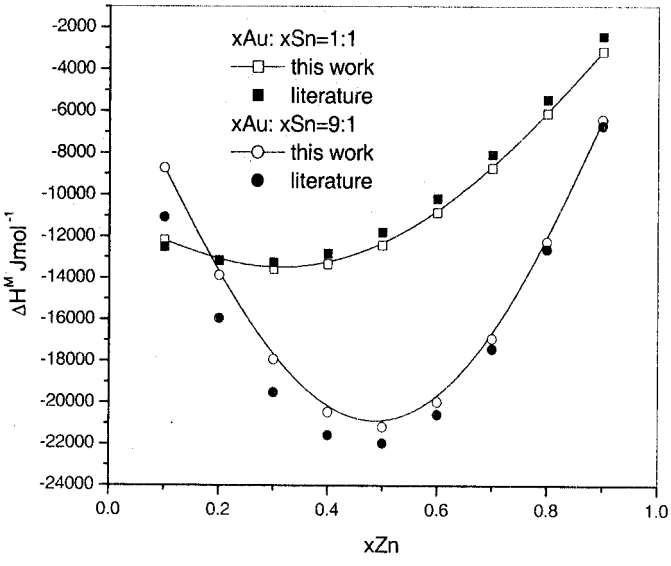
ΔG^M Jmol^{-1}
xZn

a)


xAu: xSn=1:1
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literature
xAu: xSn=9:1
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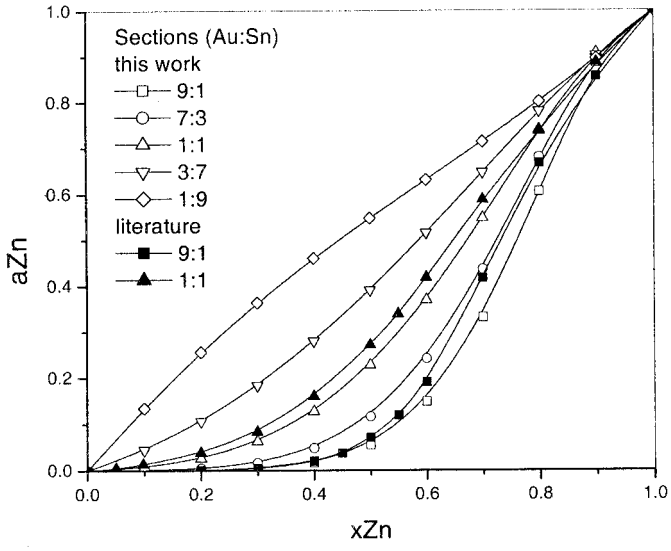
literature
ΔH^M Jmol^{-1}
xZn

b)



c)

Fig.4. Comparison between experimental data [2] and calculated data by GSM in two sections (with Au:Sn ratio of 1:1 and 9:1 at 973K, a) integral molar mixing Gibbs energies; b) integral molar enthalpies of mixing; c) zinc activities

CONCLUSION

Application of general solution model to Au–Sn–Zn liquid alloys gives a detailed set of thermodynamic data which include integral and partial thermodynamic quantities for fifteen sections, diagrams of isoactivity lines for all components and diagram of iso–lines for integral Gibbs energies of mixing at 973 K. Calculated values for chosen are compared with experimentally obtained data and good agreement is noticed.

Results obtained in this work present a contribution to more complete knowledge of thermodynamic properties of Au–Sn–Zn alloys and may be useful for the calculation of the ternary phase diagram of this system, which is of interest as a new lead-free solder material.

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