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Comparative thermodynamic analysis of the Pb–$Au_{0.7}Sn_{0.3}$ section in the Pb–Au–Sn ternary system

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Abstract

The results of comparative thermodynamic analysis of Pb–$Au_{0.7}Sn_{0.3}$ section in Pb–Au–Sn system are presented in this paper. Investigation was done comparatively by calorimetric measurements and thermodynamic calculation according to the general solution model. Thermodynamic parameters, such as partial and integral molar quantities, were determined at different temperatures. The comparison between experimental and calculated results showed mutual agreement. Demixing tendency of lead, presented in the positive deviation from ideal behavior, was confirmed through the study of concentration fluctuation in the long-wavelength limit. Also, chosen alloys in the investigated section were characterized using SEM-EDX analysis.

Keywords: Alloy thermodynamics; Ternary systems; Pb–Au–Sn alloys

1. Introduction

Gold and gold alloys are widely applied in modern technical branches—electronics, communications, space and aero technologies, chemistry and medical science, etc. They are known for good mechanical and thermal properties, as well as corrosion consistency. Owing to the formation of low temperature eutectic with other elements, gold alloys are often used as welding alloys in electronics [1].

Solder alloys for gold jewelry and other gold and gold-plated objects are being investigated too [2,3]. For that purpose, different low-temperature systems based on gold are interesting and one among them is ternary Pb–Au–Sn system [4–6].

Considering thermodynamic data, the results of investigation of constitutive binary systems Pb–Au, Au–Sn and Pb–Sn are numerous [7–17] and the most complete literature data can be found in the books by Hultgren et al. [18] and Massalski et al. [19], as well as in the COST 531 Database for Lead Free Solders [20], recently. Thermodynamics of ternary Pb–Au–Sn system has been investigated by the authors of this paper [21,22], but these existing data comprise the Pb–AuSn section investigations only.

As a contribution to the more complete thermodynamic description of Pb–Au–Sn alloys, the results of thermodynamic testing of the Pb–$Au_{0.7}Sn_{0.3}$ section are presented in this paper.

2. Experimental

The Oelsen calorimetry method, described in detail in Refs. [23–26], was used for the experimental thermodynamic analysis of a section in the ternary Pb–Au–Sn system with a constant molar ratio of Au:Sn = 7:3.

The water equivalent for the calorimeter used was determined by a standard method using dissolved Na_2CO_3 and its value was 3314 J/K.

SEM analysis was performed on Philips microscope XL-300 type with EDX of resolution of 1 nm on 30 kV and 5 nm on 1 kV, extinction voltage of 0.2–30 kV and

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Table 1
The composition of experimentally investigated alloys

Alloy no.	x_{Pb}	x_{Au}	x_{Sn}	m_{Pb} (g)	m_{Au} (g)	m_{Sn} (g)
1	1	0	0	11.4000	0	0
2	0.9	0.07	0.03	10.0520	1.3457	0.3549
3	0.7	0.21	0.09	7.5118	3.8813	1.0231
4	0.5	0.35	0.15	5.1621	6.2225	1.6413
5	0.3	0.49	0.21	2.9853	8.3945	2.2145
6	0.1	0.63	0.27	0.9609	10.4225	2.7487
7	0	0.70	0.30	0	11.3692	2.9986

magnification of 1500× and 5000×. Solution (40 ml HNO_3 + 30 ml CH_3COOH + 160 ml H_2O + 2–3 drops of H_2O_2) was used as an etching agent for the samples prepared according to the standard metallographic procedure.

All experiments were carried out in an air atmosphere, with Pb, Au and Sn metals of 99.99 mass% purity. Composition and masses of the experimentally investigated alloys in the Pb–$Au_{0.7}Sn_{0.3}$ section are given in Table 1, having constant total volume for all samples according to the requirements of the method used. The samples were cooled in the furnace to the room temperature.

3. Results and discussion

The equilibria of the Au–AuSn–Pb partial ternary system has been investigated by Humpston and Evans [27], who determined four ternary transition reactions (Au63.5Pb26Sn10.5 at 655.5 K, Au42.5Pb47.5Sn10 at 527 K, Au30.5Pb60.5Sn9 at 497 K and Au20.5Pb75.5Sn4 at 487 K), a ternary eutectic equilibrium (Au15Pb84Sn1 at 484 K) and a four-phase monotectic equilibrium (Au64Pb9Sn27 at 530.5 K, where compositions are given in atomic percents).

The phase diagram of the section Pb–Au_2Sn [27], which is compositionally very near to the investigated section with a constant molar ratio of Au:Sn = 7:3 in the ternary Pb–Au–Sn system, is presented in Fig. 1.

In the frame of structural analysis of the alloys in investigated section, SEM-EDX analysis was done for the samples with x_{Pb} = 0.3 and 0.9. SEM images for the sample with

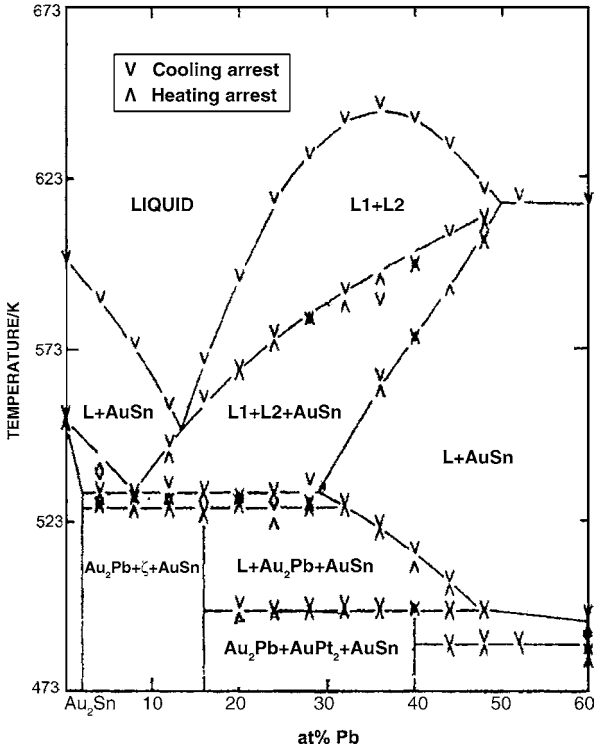

Fig. 1. Au/Sn-rich portion of isopleth between Au_2Sn and Pb [27].

Table 2
The results of experimental determination of composition by SEM/EDX analysis

Sample	Experimental composition (at.%)	Experimentally determined phases	The compositions of phases (at.%)		
			Pb	Au	Sn
xPb = 0.3	3 (Pb)	$AuPb_2$	33.1	66.8	0.1
	49 (Au)	Au_2Pb	67.1	32.6	0.3
	21 (Sn)	AuSn	0.6	50.3	49.1

x_{Pb} = 0.3 are given in Fig. 2, while the results of experimental determination of composition by EDX analysis are presented in Table 2.

Obtained results show the presence of three phases: dark phase responding to Au_2Pb, gray phase responding to $AuPb_2$

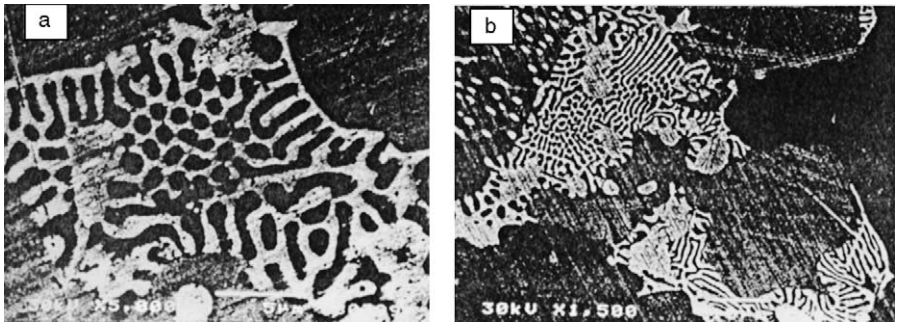

Fig. 2. SEM images of the investigated sample with x_{Pb} = 0.3 (enlargement: a, 5000×; b, 1500×).

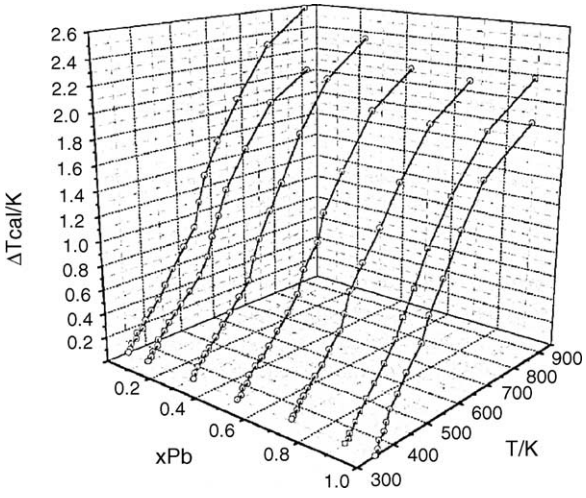

Fig. 3. Enthalpy space diagram.

and light phase responding to AuSn. Noticed structure is in agreement with the literature data [27] and phase diagram presented in Fig. 1, consisting of ($Au_2Pb + AuPb_2 + AuSn$) mixture, which occurs at lower temperatures in the composition range from about 16 up to 40 at.% Pb.

Thermodynamic analysis of the investigated section in the Pb–Au–Sn system was done according to the Oelsen procedure [23–26]. Based on the cooling curves obtained by calorimetric measurements, temperature changes of the calorimeter were determined for all samples in the temperature range up to 873 K. According to these data, the enthalpy space diagram and enthalpy isotherm diagram were constructed and presented in Figs. 3 and 4, respectively. (It should be noted that in presented diagrams 1 K corresponds to the water equivalent to be 3314 J/K.)

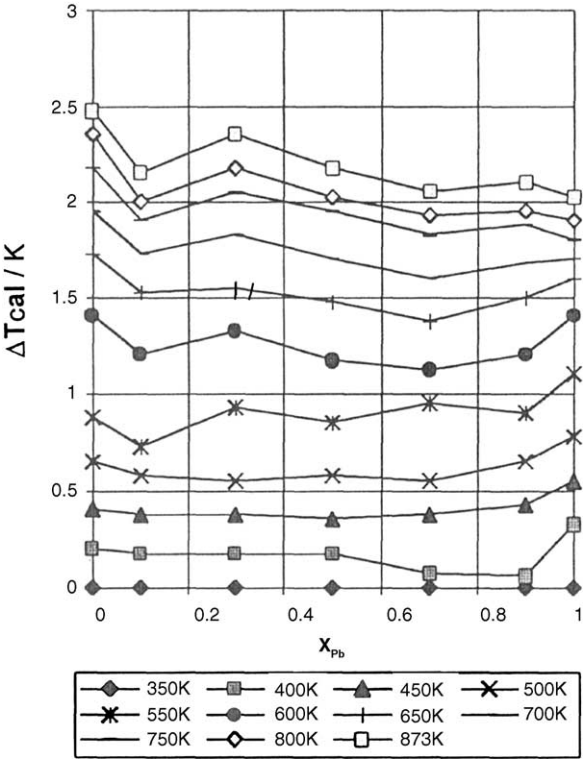

Fig. 4. Enthalpy isotherm diagram.

Table 3
The results of the Oelsen quantitative thermodynamic analysis at different temperatures

T (K)	Alloy no.	x_{Pb}	a_{Pb}	γ_{Pb}	G^{M}_{Pb} (J/mol)	G^{XS}_{Pb} (J/mol)
873	1	1	1	1	0	0
	2	0.9	0.906	1.007	−716	51
	3	0.7	0.750	1.071	−2088	498
	4	0.5	0.640	1.280	−3239	1792
	5	0.3	0.500	1.667	−5031	3709
	6	0.1	0.220	2.200	−10990	5723
	7	0	0	/	/	/
773	1	1	1	1	0	0
	2	0.9	0.905	1.006	−664	40
	3	0.7	0.740	1.057	−2003	369
	4	0.5	0.630	1.260	−3073	1537
	5	0.3	0.495	1.650	−4677	3331
	6	0.1	0.215	2.150	−10224	5091
	7	0	0	/	/	/
673	1	1	1	1	0	0
	2	0.9	0.902	1.002	−600	12
	3	0.7	0.735	1.050	−1792	284
	4	0.5	0.610	1.220	−2877	1157
	5	0.3	0.480	1.600	−4272	2735
	6	0.1	0.205	2.050	−9223	4178
	7	0	0	/	/	/

The basic equation in Oelsen thermodynamic analysis [23] is given as:

$$\frac{G_i^{M}}{T} = \int_{1/T_0}^{1/T} H_{x,T}\, \mathrm{d}\left(\frac{1}{T}\right) = R \ln a_i \quad (1)$$

where G_i^{M} is the partial molar Gibbs energy for component i, T_0 the starting temperature, T the final temperature, $H_{x,T}$ the enthalpy value measured in the Oelsen calorimeter for the temperature change from T_0 to T, R the gas constant and a_i is the activity of the component i. Further calculation in the thermodynamic analysis was done based on Eq. (1) and the results of the graphic planimetry, which enabled the determination of lead activities, activity coefficients and partial molar quantities at 873, 773 and 673 K. The results are given in Table 3.

A positive deviation from Raoult law is noticed for the partial thermodynamic quantities of lead at all temperatures and in the whole concentration range of the Pb–$Au_{0.7}Sn_{0.3}$ section, indicating to demixing tendencies of lead related to the other two components in the system.

General solution model for ternary systems [28,29] was used as a thermodynamic method for predicting the quantities in the chosen section of the Pb–Au–Sn ternary system. According to this model, integral molar excess Gibbs energies for ternary system can be expressed based on the known

Table 4
Binary A_{ij}^{k} parameters for each constitutive binary system at 873 K according to [17]

System *ij*	A_{ij}^{0}	A_{ij}^{1}	A_{ij}^{2}
Pb–Au	9622.1	2374.3	−1417.2
Au–Sn	−50276	−16079	−2875.1
Sn–Pb	5489.3	−80.504	479.3

binary thermodynamic values, as follows:

$$\Delta G_{123}^{XS} = x_1x_2[A_{12}^{0} + A_{12}^{1}(x_1 - x_2) + A_{12}^{2}(x_1 - x_2)^2] + x_2x_3[A_{23}^{0} + A_{23}^{1}(x_2 - x_3) + A_{23}^{2}(x_2 - x_3)^2] + x_3x_1[A_{31}^{0} + A_{31}^{1}(x_3 - x_1) + A_{31}^{2}(x_3 - x_1)^2] + fx_1x_2x_3 \quad (2)$$

where A_{ij}^{0}, A_{ij}^{1}, A_{ij}^{2} are the parameters for each "*ij*" binary system, independent of composition and only relying on temperature, *f* the ternary interaction coefficient, dependent on the similarity coefficients [28,29] for constitutive binary systems Pb–Au, Au–Sn and Sn–Pb, and x_1, x_2, x_3 are the mole fractions of the components present in the investigated ternary system, where Pb–Au–Sn is in order 1–2–3.

The values of integral molar Gibbs excess energies for the constitutive binary systems Pb–Au, Au–Sn and Sn–Pb at 873 K, taken from the data book by Hultgren et al. [18], were used as the starting binary thermodynamic data for the calculation according to the general solution model. Characteristic A_{ij}^{k} parameters for each binary system are shown in Table 4.

Obtained values for the integral molar excess Gibbs energies in the Pb–$Au_{0.7}Sn_{0.3}$ section at 873 K may be presented in the analytical form of a dependence on composition, as:

$$\Delta G_{123}^{XS} = -8284.4x_{Pb}^{2} + 20303x_{Pb} - 12026 \quad (3)$$

In further step, partial excess thermodynamic quantities were derived using the following equation:

$$G_i^{XS} = \Delta G_{123}^{XS} + \left(\frac{\partial \Delta G_{123}^{XS}}{\partial x_i}\right)(1 - x_i) \quad (4)$$

which enabled determination of the corresponding activity coefficients and activities. These thermodynamic quantities for the Pb–$Au_{0.7}Sn_{0.3}$ section at 873 K are given in Table 5.

Table 5
Calculated partial molar quantities in the Pb–$Au_{0.7}Sn_{0.3}$ section at 873 K

Alloy no.	x_{Pb}	a_{Pb}	γ_{Pb}	G_{Pb}^{M} (J/mol)	G_{Pb}^{XS} (J/mol)	ΔDG_{123}^{XS} (J/mol)
1	1	1	1	0	0	0
2	0.9	0.909	1.010	−695	70	−478
3	0.7	0.776	1.108	−1842	747	−1870
4	0.5	0.663	1.327	−2980	2051	−3933
5	0.3	0.517	1.724	−4785	3953	−6696
6	0.1	0.246	2.462	−10174	6538	−10074

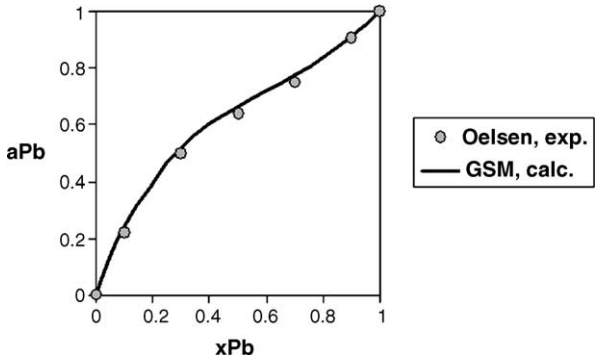

Fig. 5. Dependence of a_{Pb} on the composition at 873 K determined experimentally using Oelsen calorimetry and predicted according to general solution model.

Lead activities for the section Pb–$Au_{0.7}Sn_{0.3}$ at 873 K are shown in Fig. 5. They are obtained by the experiment (Oelsen calorimetry) and by *i*th model calculation (general solution model).

Both results by the experiment and calculation method are in a good accordance and show positive deviation from ideal behavior. It is obvious, having in mind thermodynamic characteristics of the constitutive binaries that tin has a stronger affinity to gold, than to lead. That leads to a greater thermodynamic probability of Au–Sn solution formation than Pb–Au or Pb–Sn, and in agreement with the observed thermodynamic behavior of the liquid alloys in Pb–$Au_{0.7}Sn_{0.3}$ section in the Pb–Au–Sn system.

In order to confirm the above-mentioned statement, the energetics of mixing in the liquid alloys has been analysed through the study of concentration fluctuation in the long-wavelength limit, $S_{cc}(0)$, connected with the microscopic information on liquid alloys [30]. The presence of chemical order is indicated by $S_{cc}(0) < S_{cc}(0,id)$, while on the contrary, if $S_{cc}(0) > S_{cc}(0,id)$, the segregation and demixing in liquid alloys takes place.

Using the experimental values for lead activity presented in this study, $S_{cc}(0)$ at 873 K was calculated using following equation:

$$S_{cc}(0) = \frac{(1 - x_{Pb})a_{Pb}}{\partial a_{Pb}/\partial x_{Pb}} \quad (5)$$

and the mixing behaviour of liquid alloys in the Pb–$Au_{0.7}Sn_{0.3}$ section can be deduced from the deviation of $S_{cc}(0)$ from $S_{cc}(0,id)$, as shown in Fig. 6.

The $S_{cc}(0)$ values in Fig. 6 clearly indicate that $S_{cc}(0) > S_{cc}(0,id)$ in the whole concentration range, which implies a tendency for homocoordination (i.e. like atoms Pb–Pb tend to pair as nearest neighbours) and indicate a demixing tendency presented in the investigated section of the Pb–Au–Sn system, confirming the above mentioned explanations of the positive deviation from ideal behaviour.

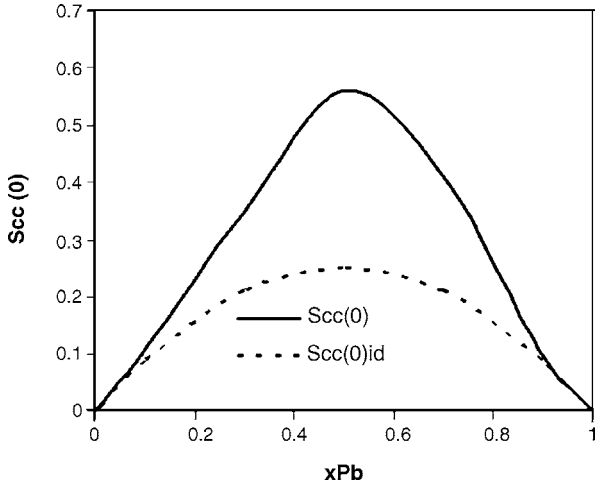

Fig. 6. The concentration fluctuation in the long wavelength limit, $S_{cc}(0)$ for the liquid alloys in Pb–$Au_{0.7}Sn_{0.3}$ section at 873 K.

4. Conclusions

Comparative thermodynamic analysis of Pb–$Au_{0.7}Sn_{0.3}$ section in the Pb–Au–Sn system was done experimentally using Oelsen's calorimetry and by thermodynamic predicting using general solution model. Results of the comparative analysis of the obtained thermodynamic parameters showed positive deviation from the Raoult's law in the entire concentration area, as well as a good mutual agreement. Demixing tendency, existing in the system, was confirmed through the study of concentration fluctuation in the long-wavelength limit.

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