

SIZE-DEPENDENT THERMODYNAMIC DESCRIPTION OF THE BINARY Pb-Sn SYSTEM

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Abstract

Recently, a new thermodynamic description of the binary Pb – Sn system was proposed and it seems to be interesting to extend this description on the system, where size of particles plays a key-role. To obtain this goal a set of surface Gibbs energies was calculated and added to Gibbs energies describing bulk phases. The extended thermodynamic description was used for calculation of size-dependent phase diagram of binary Pb-Sn system. Comparison of calculation with limited literature information allows for statement that the proposed model is in good agreement with experiment.

Keywords: Thermodynamics; Nano; Calphad; Lead-free solder.

1. Introduction

The Pb – Sn solder is a classical solder used in electronic industry for years. Nowadays, due to its harmful properties and international regulations [1, 2] it has to be substituted by different lead-free materials. However, due to existence and necessity of repairing of old devices, where Pb-solder was used, the knowledge about equilibrium between Pb solder and Pb-free solders is necessary. Recently, a new thermodynamic description of the binary Pb – Sn system was proposed [3] and it seems to be interesting to extend this description on the system, where size of particles plays a key-role. The CALPHAD [4] method was already used for thermodynamic description of systems made of nano-particles, such as Ag – Sn [5] or Ag – Cu [6]. However, it has to be mentioned here, that this kind of approach is limited to systems containing nano-particles of size 10 nm and bigger [7]. On other hand, the nano-particles play important role in modern materials engineering [8], therefore it seems to be interesting to extend the description [3] into nano-system. The literature information about thermochemical behavior of Pb-Sn nanoparticle is very limited and reveals two papers wrote by the same group, and describing, in fact, the same experiment. Khan et al. [8] analyzed Pb-Sn nanoparticles embedded in pure Al and Al-Cu-Fe icosahedral matrices. In his paper, Khan et al. [9] provided information obtained from X-ray diffraction (XRD),

transition electron microscope (TEM), and different scanning calorimetry (DSC). Based on their observations, authors of this report [9] proposed size-dependent metastable phase diagram of the binary Pb-Sn system that contained only face centered cubic (FCC) and liquid phases. Similarly, Bhattacharya et al. [10] described thermal properties and orientations of three bimetallic Pb – Sn dispersions (Sn82 Pb18, Sn64Pb36, and Sn54Pb46) embedded in aluminum. Based on Bhattacharya et al. [10] paper it is possible to compare calculated size-dependent phase diagram of Pb – Sn system with experimental data; however, it should be emphasis here that calculation is always performed for a specific size of a particle but experiment shows result for particles within a size range. The paper [10] reports only size distribution of Sn82Pb18, which varies from 5nm to 250nm with most of particles in a range 50nm – 150 nm (c.a. 75%), and alloy Sn54Pb46 which size distribution varies from 2 nm to 100 nm with majority in the range 5nm to 10nm (c.a. 60%). In addition, Johnson et al. [11] analyzed nano-inclusions Pb-Sn with composition Pb50Sn50 and Pb25Sn75 embedded in aluminum. The paper [11] describes FCC_A1-BCT_A5 phase equilibrium of nanoparticles with diameter 10 nm. According to Johnson et al. [10] the equilibrium compositions are $x_{pb} = 0.69 \pm 0.04$ and $x_{pb} = 0.08 \pm 0.06$ at room temperature for FCC_A1 and BCT_A5, respectively.

Dedicated to the memory of Professor Dragana Živković

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2. Theoretical background

As it was mentioned in the previous paragraph, the extended CALPHAD approach was used for describing nanosystems before [5, 6]. The concept is based on the assumption, that in a case of nanoparticles the total Gibbs energy of a given phase is a summation of Gibbs energy of bulk and Gibbs energy of a surface.

$$\text{Total } G^\alpha = \text{Bulk } G^\alpha + \text{Surface } G^\alpha \quad (1)$$

The surface Gibbs energy of 1 mole of the given phase is set as a multiplication of molar surface energy σ , and molar surface area A , which for a spherical particle is equal $6V/D$, where V denotes molar volume, D is a diameter of particle, and α is a shape factor. Therefore, the surface Gibbs energy for a spherical particle can be expressed as follows:

$$\text{Surface } G^\alpha = \sigma A = \frac{6\sigma V\alpha}{D} \quad (2)$$

The shape factor varies from 0.333 for nano film to 1.49 for regular tetrahedral [12]. For a spherical particle the shape factor is equal 1, thus for simplification of this paper the spherical shape is assumed and the shape factor is therefore omitted in further calculation.

The Gibbs free energies of pure elements with respect to temperature ${}^0G_i(T) = G_i(T) - H_i^{SER}$ are represented by Equation 3:

$${}^0G_i(T) = a + bT + cT\ln(T) + dT^2 + eT^{-1} + fT^3 + iT^4 + jT^7 + kT^{-9} \quad (3)$$

The ${}^0G_i(T)$ data are referred to the constant enthalpy value of the standard element reference $H_i(T)$ at 298.15 K and 1 bar as recommended by Scientific Group Thermodata Europe (SGTE) [13]. The reference states are: FCC_A1 (Pb), and BCT_A5 (Sn). The ${}^0G_i(T)$ expression may be given for several temperature ranges, where the coefficients $a, b, c, d, e, f, i, j, k$ have different values. The ${}^0G_i(T)$ functions are taken from SGTE Unary (Pure elements) thermodynamic database (TDB) v.5 [13]. Solid and liquid solution phases (FCC_A1, BCT_A5, Liquid) are described by the substitutional solution model [14]:

$$G_m(T) = \sum_i x_i {}^0G_i(T) + RT \sum_i x_i \ln(x_i) + x_i x_j \left(\sum_v {}^vL_{ij} (x_i - x_j)^v \right) \quad (4)$$

where the $x_i x_j \left(\sum_v {}^vL_{ij} (x_i - x_j)^v \right)$ part is the Redlich-Kister polynomial for excess Gibbs free energy.

In a case of nano-particles, the Equations 3 and 4 have to be modified. The Gibbs energy of a pure element will have a formula shown by Equation 5:

$${}^0G_i(T) = a + bT + cT\ln(T) + dT^2 + eT^{-1} + fT^3 + iT^4 + jT^7 + kT^{-9} + \frac{6\sigma_i V_i}{D} \quad (5)$$

and excess Gibbs energy will have a form as follows:

$${}^{xs}G_{i,j} = x_i x_j \left[\sum_v ({}^vL_{ij} + {}^vL_{ij}^{nano}) (x_i - x_j)^v \right] \quad (6)$$

Since the parameter ${}^vL_{ij}$ has a form $A + BT + CT\ln(T)$ then the ${}^vL_{ij}^{nano}$ also should have the same form: $A^{nano} + B^{nano}T + C^{nano}T\ln(T)$. Connection between these parameters and surface Gibbs energy is shown in Equation 7:

$$A^{nano} + B^{nano}T + C^{nano}T\ln(T) = \frac{a^{surf}}{D} + \frac{b^{surf}}{D}T + \frac{c^{surf}}{D}T\ln T \quad (7)$$

where $a^{surf} + b^{surf}T + c^{surf}T\ln T = 6(\sigma_{ij}V_{ij} - x_i\sigma_iV_i - x_j\sigma_jV_j)$, σ_{ij} is a surface free energy of alloy, V_{ij} is molar volume of alloy calculated as a superposition of molar volumes of pure elements multiplied by mole fraction.

The problem appears when there is no experimental information about surface free energy of alloy. In this case, it is possible to apply Butler's equation [15] and calculate value of σ_{ij} as a function of composition and temperature. The Butler's equation has a form:

$$\sigma_{ij} = \sigma_i + \frac{RT}{A_i} \ln \left(\frac{x_i^{surface}}{x_i^{bulk}} \right) + \frac{1}{A_i} ({}^{xs}G_i^{surface} - {}^{xs}G_i^{bulk}) = \sigma_j + \frac{RT}{A_j} \ln \left(\frac{x_j^{surface}}{x_j^{bulk}} \right) + \frac{1}{A_j} ({}^{xs}G_j^{surface} - {}^{xs}G_j^{bulk}) \quad (8)$$

where σ_i is a surface energy of element i , A_i is a surface area of element i , x_j^{bulk} is a mole fraction of element i in bulk, $x_j^{surface}$ is mole fraction of element i in surface, ${}^{xs}G_j^{bulk}$ is a partial Gibbs energy of element i in bulk, and ${}^{xs}G_j^{surface}$ is a partial Gibbs energy of element i in surface.

It is easy to notice, that Equation 8 has two unknowns: mole fraction of surface and surface free energy of alloys. The partial surface excess Gibbs energy can be estimated as 0.85 and 0.84 of a partial bulk excess Gibbs energy for liquids and solids, respectively [16]. The molar surface area of a pure element can be calculated as follows:

$$A_i = 1.091 N_A^{\frac{1}{3}} V_i^{\frac{2}{3}} \quad (9)$$

where N_A is Avogadro's number, and V_i is a molar volume of element i .

Having other variables of Equation 8 calculated from a bulk description it is easy to resolve the equation numerically. In this paper, the Equation 8 was resolved by aid of Matlab software [17]. All other calculations were done using Thermocalc 2017a [18]. In this work, Equation 8 was used for determination of surface energy of all solution phases: Liquid, FCC_A1, and BCT_A5.



3. Result and discussion

For this calculation, the physical properties of liquid and solid Sn were taken from earlier work on Ag – Sn system that was done by Sim and Lee [5]. In a case of properties of Pb, the surface Gibbs energy for a liquid phase was taken from Gasior et al. [19] who determined this property from experiment at temperature range 573 K – 1200 K. According to Tanaka [20], the surface Gibbs energy of liquid is 1.25 times bigger than surface Gibbs energy of liquid at melting temperature; however, the experimental data for different elements reveals that the ratio can be dissimilar. In a case of Pb, the surface Gibbs energy of solid seems to be only 1.01 times bigger than surface Gibbs energy of liquid. Assuming, that

$$\sigma_{Pb}^{solid} = 1.01\sigma_{Pb}^{liquid} \quad (10)$$

it was possible to calculate melting temperature of nano particles Pb as a function of particle size. It should be emphasized here, that the value given in Equation 10 is empirical and was chosen based on experimental data [20]. Result of this calculation is shown in Figure 1. As it can be easily seen, the calculation agrees with experimentally determined melting temperature of Pb. Hence, the Equation 10 was applied in this work. As it was mentioned earlier, the surface tension of solution as a function of composition and temperature was calculated using Matlab software [17]. For calculation of liquid surface tension, the

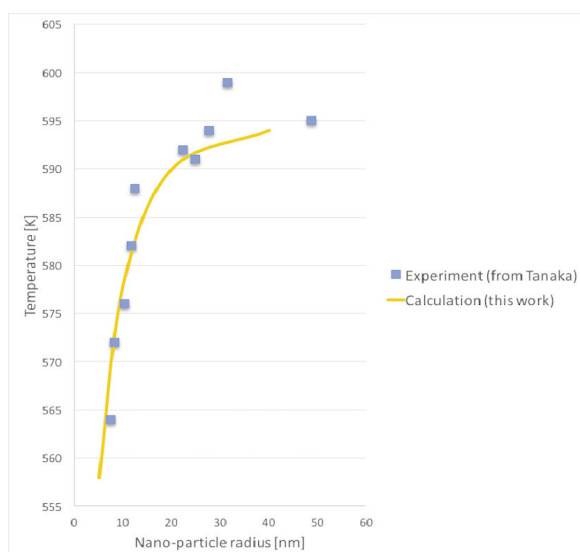


Figure 1. Calculated temperature of melting Pb as a function of particle size superimposed with experimental data given by Tanaka [20].

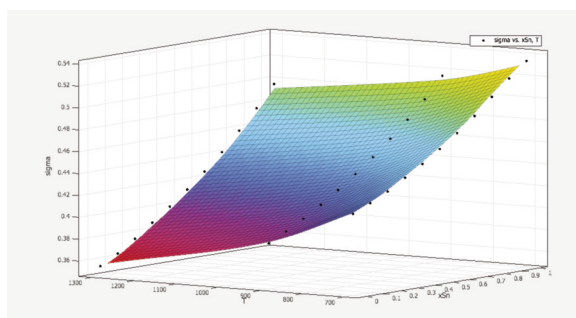


Figure 2. Surface tension of liquid phase fitting using Matlab software [17].

temperature range 700 K – 1300 K was applied in calculation. In a case of solid solution, the temperature range 400 – 600 K was used. The calculated surface tension of liquid as a function of temperature and composition is shown in Figure 2.

All the parameters necessary for calculations, such as Gibbs surface tensions, or molar volumes are gathered in Table 1. Assessed interaction parameters for nano-system and bulk are shown in Table 2 and Table 3, respectively. Based on these equations it was possible to calculate a phase diagram of binary Pb-Sn system as a function of particles size. The calculated phase diagram of binary Pb – Sn system for a bulk, and for 50 nm and 10 nm particles is shown in Figure 3 together with experimental data given by Jeffrey [21], Fisher and Phillips [22], Heumann and Wostmann [23], Stockdale [24], Bhattacharya et al. [10], and Johnson et al. [11].

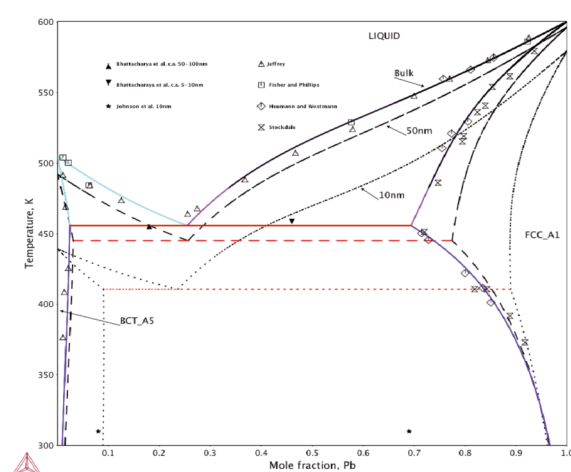


Figure 3. Calculated binary Pb-Sn phase diagram for bulk, 50nm and 10nm superimposed with experimental data given by Jeffrey [21], Fisher and Phillips [22], Heumann and Wostmann [23], Stockdale [24], Bhattacharya et al. [10], and Johnson et al. [11].



Table 1. Physicochemical properties of Pb and Sn used in this work.

Element	Property	Function	Ref.
Pb	σ_{Pb}^{solid}	0.5473-0.0001096*T	This work
	σ_{Pb}^{liquid}	0.4975-0.0001096*T	[17]
	$V_{Pb}^{FCC_A1}$	18.70E-6(1+0.000124(T-600.55))	[17]
	$V_{Pb}^{BCT_A5}$	14.50 E-6(1+0.000124(T-600.55))	This work
	V_{Pb}^{liquid}	19.42E-6(1+0.000124(T-600.55))	[18]
Sn	σ_{Sn}^{solid}	0.671-0.00013(T-504.99)	[5]
	σ_{Sn}^{liquid}	0.5472-0.000065(T-504.99)	[5]
	$V_{Sn}^{FCC_A1}$	1.62E-05	This work
	$V_{Sn}^{BCT_A5}$	1.66E-05	[5]
	V_{Sn}^{liquid}	1.7E-5(1+000087(T-504.99))	[5]

Table 2. Surface Gibbs energies in the binary Pb-Sn system.

Phase	Parameter
Liquid	${}^0G_{Pb}^{Liquid,surface} = \left(\frac{2.985}{D} - \frac{0.0006576 * T}{D} \right) V_{Pb}^{liquid}$
	${}^0G_{Sn}^{Liquid,surface} = \left(\frac{3.2832}{D} - \frac{0.00039 * T}{D} \right) V_{Sn}^{liquid}$
	${}^0L_{Pb,Sn}^{Liquid,surface} = \frac{-2.53E-6}{D} - \frac{1.17E-9}{D} * T$
	${}^1L_{Pb,Sn}^{Liquid,surface} = \frac{-2.754E-6}{D} + \frac{2.676E-9}{D} * T$
FCC_A1	${}^0G_{Pb}^{FCC_A1,surface} = \left(\frac{3.2838}{D} - \frac{0.0006576 * T}{D} \right) V_{Pb}^{FCC_A1}$
	${}^0G_{Sn}^{FCC_A1,surface} = \left(\frac{4.026}{D} - \frac{0.00078 * T}{D} \right) V_{Sn}^{FCC_A1}$
	${}^0L_{Pb,Sn}^{FCC_A1,surface} = \frac{3.704E-5}{D} + \frac{3.043E-8 * T}{D}$
	${}^1L_{Pb,Sn}^{FCC_A1,surface} = \frac{4.969E-5}{D} - \frac{5.918E-8 * T}{D}$
	${}^2L_{Pb,Sn}^{FCC_A1,surface} = \frac{-5.9E-5}{D} + \frac{8.846E-8 * T}{D}$
BCT_A5	${}^0G_{Pb}^{BCT_A5,surface} = (3.2838 / D - 0.0006576T / D) V_{Pb}^{BCT_A5}$
	${}^0G_{Sn}^{BCT_A5,surface} = (4.026 / D - 0.00078T / D) V_{Sn}^{BCT_A5}$
	${}^0L_{Pb,Sn}^{BCT_A5,surface} = \frac{-3.351E-5}{D} + \frac{3.619E-8 * T}{D}$
	${}^1L_{Pb,Sn}^{BCT_A5,surface} = \frac{3.293E-5}{D} - \frac{4.684E-8 * T}{D}$

The data shown by references [20-23] describes bulk phase diagram. It is easy to see that for calculation of bulk, the reproduction of experimental information is good. It is a bit hard to

compare results shown by Bhattacharaya et al. [10] with this work because results given in reference [10] were obtained for particles located inside a range of sizes, what is in contrast to calculation



performed for a particular size of particles. For this work, the most frequent sizes of particles given in Bhattacharaya et al. [10] report were taken. It can be found that calculated phase diagram for two sizes of nanoparticles is, in general, with a good agreement with experimental data. The liquidus lines calculated for two sizes of particles (10nm and 50nm) reproduce well DSC information given by Bhattacharaya et al. [10]. A little different situation can be found in a case of BCT_A5+FCC_A1 equilibrium. Although lead solubility in tin phase given by Johnson et al. [11] is reproduced well by calculation, the calculated solubility of tin in lead phase shows much smaller value than it appears from experiment. However, taking into account temperature of liquidus given by Bhattacharaya et al. [10] for particles with diameter 5-10nm and composition Sn54Pb45 it can be concluded that proposed by Johnson et al [11] solubility of tin in lead equal 0.69 ± 0.04 mole fraction of Pb is overestimated. To the best knowledge of author, there is no more investigation on nanoparticles PbSn thus it is impossible to show more comparison of calculation and experimental data. The composition shifting in cases of nano-phase diagrams is connected to change of Gibbs energies of solid and liquid phases. As it can be seen from Equation 1, the Gibbs energy of surface has to be added Gibbs energy of bulk, therefore the final function has different shape from Gibbs energy of bulk. In consequence, the common tangent lines, which are determined by equilibrium of chemical potentials, are located in different positions, thus the phase diagram of nano-particles looks different from bulk phase diagram.

Table 3. Gibbs energies of phases in the binary Pb-Sn system.

Phase	Parameter	Reference
Liquid	${}^0L_{Pb,Sn}^{Liquid} = 5174.58 + 1.558 * T$	[3]
	${}^1L_{Pb,Sn}^{Liquid} = 331.69$	[3]
FCC_A1	${}^0L_{Pb,Sn}^{FCC_A1} = 4967.51 + 1.809 * T$	[3]
	${}^1L_{Pb,Sn}^{FCC_A1} = 400.16$	[3]
BCT_A5	${}^0L_{Pb,Sn}^{BCT_A5} = 7320.37 + 9.695 * T$	[3]

4. Summary

A thermodynamic description of size-dependent binary Pb-Sn phase diagram was proposed in this

work. Recently optimized Gibbs energies of bulk phases [3] were extended by surface Gibbs energies what allowed for calculation of phase equilibria as functions of particle size. Good agreement between limited experimental data and calculation was found except solubility of tin in lead phase at room temperature. Based on the calculation as well as experimental data it can be concluded, that temperature of eutectic reaction FCC_A1+BCT_A5 = Liquid decreases with particle size decreasing. At the same time, solubility of Sn in FCC_A1 phase as well as solubility of Pb in BCT_A5 phase increasing with decreasing of particle size. The change of phase diagram as a consequence of changing particle size is connected with surface Gibbs energy, which is neglected during calculation of bulk phase diagrams.

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