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Pb-free solders: Surface tension calculation of Au-Bi-Sn ternary alloys at different temperatures (Part I)

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Abstract

In this paper, the surface tension of liquid Au-Bi-Sn alloys has been calculated using Kohler and Toop models. In addition, the surface tension of the Au-Bi-Sn ternary alloys over a wide temperature range (673-1273K) and their sub-binary systems are predicted on the basis of Guggenheim equation. Three selected cross-sections with the constant gold to bismuth ration of 1:1, 1:2 and 2:1 have been studied. The results show that the surface tension increases with increasing tin and decreases with increasing temperature for the three studied models. The calculated values of the surface tension of the liquid Au-Bi-Sn alloys at 673 K are compared with the experimental data available in literature. The best agreement is observed for the values obtained by Guggenheim equation.

Keywords: Pb-free solders, Surface tension, Geometrical models, Au-Bi-Sn, Guggenheim equation

1. Introduction

According to WEEE (Waste Electrical and Electronic Equipment Directive) [1], lead, as a highly toxic metal, has been removed from different materials, especially electronic, although it was widely used in industry, particularly in microelectronics. Therefore, lead-based solders are under way to be replaced by lead-free alloys, so significant work has been done and is still going on to find a substitute for common Pb-Sn solder alloy. Due to the specific properties of Pb-Sn solder alloys, the candidates for their replacement are usually tin-based multicomponent alloys, since the investigated binary systems do not satisfy some features (temperature, for example). A candidate lead-free solder alloy must fulfill some requirements: suitable melting temperature and solidification behavior, good wettability, and excellent mechanical properties [2, 3]. In this work, Au-Bi-Sn alloys have been proposed as promising lead-free solders.

Thermo-physical data are of great importance for the development of a lead-free solder database, for the design of new lead-free solders, and for the prediction of their physical and chemical properties such as surface tension and viscosity [4]. The surface tension of the liquid Au-Bi-Sn alloys has been measured by Zhongnan et al. [5] using the sessile drop method at different temperatures along two cross sections of x_{Au}/x_{Bi}=1/1 and 1/2. However, experimental researches on thermo-physical properties for the Au–Bi–Sn system are still scare. Generally, relatively high investigating temperatures and the evaporation of some metals could make experimental measuring difficult and expensive. That is the main reason for applying geometrical models to predict the surface tension of the Au-Bi-Sn ternary based on the Bi-Sn, Au-Sn, and Au-Bi sub-binary information.

The surface tension data for Bi-Sn binary alloys has been measured by many authors [6-9]. The thermo-physical properties of Au–Sn liquid alloys system have been investigated by a quasi-lattice structural model for the chemical complexes [10–12] as well as by the quasi-chemical approximation for regular solution [13-15]. According to our survey, no data has been reported on the physical properties for Au-Bi binary alloys.
In this work, the surface tension for ternary Au-Bi-Sn liquid alloys was calculated over a wide temperature range (673-1273K) using Kohler [16], Toop [17] geometric models and Guggenheim equation [18]. The predicted results are compared to each other and to the experimental one [5].

2. Theoretical fundamentals

2.1. Surface tension calculation of liquid Au-Bi-Sn system

The equation [18] given by Guggenheim for the surface tension of a perfect ternary solution is:

$$\exp\left(-\frac{\sigma_M A}{RT}\right) = x_1 exp\left(-\frac{\sigma_1 A}{RT}\right) + x_2 \exp\left(-\frac{\sigma_2 A}{RT}\right) + x_3 exp\left(-\frac{\sigma_3 A}{RT}\right) \quad (1)$$

Where σ_M is the surface tension of the mixture, σ_1, σ_2 and σ_3 are surface tensions of the individual components of the alloy, and A is the molar surface area which is defined by:

$$A = f N_A^{1/3} \left(\frac{M}{\rho}\right)^{2/3} \quad (2)$$

$$\rho = \sum x_i \rho_i \qquad M = \sum x_i M_i$$

ρ and ρ_i are the densities of liquid alloy and pure component i, respectively. M and M_i are atomic weights of the liquid alloy and pure component i, respectively (Table 1).
Here N_A is the Avogadro number, f is the atomic arrangement factor for the liquid surface (1.09 for close packing and 1.12 for body cantered cubic packing). Since A_1=A_2=A_3=A_{alloy}, calculation of A for the main component of the alloy only will be required.

Table 1: Volume molar, density and atomic mass of the pure components

component	V_i (m^3/mol)	ρ_i *(g/cm^3)*	M_i *(g/mol)*
Au	11.310^{-6}(1.0+0.00008(T-1337.33)) [19]	18.92-0.00123 [19]	196.9665
Bi	$20.80.10^{-6}$ (1.0+0.000117(*T*-544.1)) [20]	10.73-0.0012T [21]	208.9804
Sn	$17.0.10^{-6}$(1.0+0.000087(*T*-504.99)) [20]	7.118-0.00051*T* [21]	118.6900

2.2 .Equation for the excess surface tension of sub-binary systems

The composition dependence of the surface tension of mixtures can be represented in terms of the excess surface tension σ^E defined as:

$$\sigma^E = \sigma - \sigma^i \quad (3)$$

Where σ is the surface tension of a binary liquid system, σ^i is the surface tension of the ideal solution. σ^i can be obtained from the following equation:

$$\sigma^i = X_1\sigma_1 + X_2\sigma_2 \quad (4)$$

Where X_i is the molar fraction of a component i, and σ_i is the surface tension of pure liquid i. The surface tensions are shown in table 2.
The excess surface tension values $\sigma_{i,j}^E$ of the two sub-binary systems Au-Sn and Bi-Sn are taken from previous work of Novakovic et al. [22] and SURDAT – Database of Pb – free soldering materials [23-24], respectively.

Table 2: Surface tension of the pure components.

Component	σ_i (N/m)	Reference
Au	1.3246-0.00014102T	[22]
Bi	0.405 - 0.0000492T	[24]
Sn	0.582826 - 0.000083361T	[24]

The surface tensions of the third sub-binary Au-Bi alloys are calculated based on Butler's model [25]. According to this model, the surface tension in A-B binary liquid alloy is expressed as follows:

$$\sigma = \sigma_A + \frac{RT}{S_A}\ln\frac{1-x_B^S}{1-x_B^B} + \frac{1}{S_A}\left(G_A^{E,S}(T,x_B^S) - G_A^{E,B}(T,x_B^B)\right) \quad (5)$$
$$= \sigma_B + \frac{RT}{S_B}\ln\frac{x_B^S}{x_B^B} + \frac{1}{S_B}\left(G_A^{E,S}(T,x_B^S) - G_A^{E,B}(T,x_B^B)\right)$$

Where R is the gas constant, T is the temperature, σ_i is the surface tension of the liquid for pure element i, S_i is the molar surface area in a monolayer the liquid phase for pure element i, which can be obtained from $S_i = 1.091\, N_0^{1/3} V_i^{2/3}$where $N_0$is Avogadro's number, and V_i is the molar volume of the liquid for pure element i.$G_i^{E,S}(T,x_B^S)$ And $G_i^{E,B}(T,x_B^B)$ are the partial excess Gibbs energies of a component *i* in the surface phase and in the bulk phase, respectively.
The excess term in the surface phase, $G_A^{E,S}(T,x_B^S)$ can be expressed as:

$$G_i^{E,S}(T,x_B^S) = 0.83 G_i^{E,B}(T,x_B^B) \quad (6)$$

Where $G_i^{E,S}(T,x_B^B)$ can be obtained from thermodynamic parameters. The numerical value of 0.83 is recommended by Tanaka and Iida [26].
The excess Gibbs energy values for the bulk phase are calculated using Eq (5) ([27]:

$$G^E = \sum_i \sum_{j>1} x_i^B\, x_j^B\, L_{i,j} \quad (7)$$

The binary and ternary interaction parameters [28] have a Redlich-Kister type dependency on the composition:

$$L_{i,j} = \sum_\nu (x_i - x_j)^\nu\; L_{i,j}^\nu \quad (8)$$

The excess surface tension σ^E of melts is defined as the difference between the true surface tension and the corresponding value calculated from the ideal solution model (Eq. (3)).
Using Kohler's model [16], the surface tension of ternary alloy systems is given by:

$$\sigma^E = (x_1+x_2)^2(\sigma_{12}^E)_{\frac{X_1}{X_2}} + (x_1+x_3)^2(\sigma_{13}^E)_{\frac{X_1}{X_3}} + (x_2+x_3)^2(\sigma_{23}^E)_{\frac{X_2}{X_3}} \quad (9)$$

Where σ_{ij}^E denotes the excess surface tension of the binary system i-j for the ratio $X_i/X_j = x_i/x_j$. x_i and X_i represent the molar fraction of a component i in the ternary and binary systems, respectively

Toop model
A numerical method proposed by Toop [17] is asymmetric, and it is given by:

$$\sigma^E = \frac{x_2}{1-x_1}.\sigma_{12}^E(x_1;1-x_1) + \frac{x_3}{1-x_1}.\sigma_{13}^E(x_1;1-x_1) + (x_2x_3)^2.\sigma_{23}^E\left(\frac{x_2}{x_2+x_3};\frac{x_3}{x_2+x_3}\right) \quad (10)$$

3. Results and discussion

3.1. Surface tension in the liquid Au-Bi-Sn ternary alloys

The linear equations describing the dependence on temperature of the surface tension are collected in the Table 3.

Table 3: Temperature dependence of surface tension (N/m) of Au-Bi-Sn in the temperature range 673*K*-1273*K*

x_{Sn}	Kohler	Toop	Guggenheim
	x_{Au}/x_{Bi} = 1/1		
0.0	0.514-0.00007*T	0.489-0.00004*T	0.479-0.00006*T
0.1	0.478-0.00004*T	0.488-0.00003*T	0.482-0.00005*T
0.2	0.464-0.00003*T	0.495-0.00002 *T	0.485-0.00005*T
0.3	0.451-0.00001*T	0.503-0.00002 *T	0.489-0.00004*T
0.4	0.463-0.00001*T	0.511-0.00002 *T	0.494-0.00004*T
0.5	0.475-0.00001*T	0.522-0.00003*T	0.501-0.00004*T
0.6	0.496-0.00002*T	0.539-0.00004*T	0.510-0.00004*T
0.7	0.527-0.00004*T	0.562-0.00006*T	0.522-0.00005*T
0.8	0.567-0.00006*T	0.592-0.00008*T	0.536-0.00005*T
0.9	0.616-0.00001*T	0.629-0.00013* T	0.556-0.00006*T
1.0	0.648-0.00013*T	0.646-0.00013*T	0.582-0.00008*T
	x_{Au}/x_{Bi} = 1/2		
0.0	0.459-0.00006*T	0.449-0.00005*T	0.431-0.00003*T
0.1	0.418-0.00002*T	0.438-0.00003*T	0.437-0.00003*T
0.2	0.429-0.00001*T	0.445-0.00002*T	0.444-0.00003*T
0.3	0.424-0.000007*T	0.461-0.00002*T	0.452-0.00005*T
0.4	0.442-0.00001*T	0.480-0.00003*T	0.461-0.00003*T
0.5	0.467-0.00002*T	0.501-0.00004*T	0.472-0.00003*T
0.6	0.500-0.00004*T	0.526-0.00005*T	0.485-0.00004*T
0.7	0.540-0.00007*T	0.556-0.00007*T	0.501-0.00004*T
0.8	0.587-0.00009*T	0.591-0.00009*T	0.521-0.00005*T
0.9	0.642-0.0001*T	0.631-0.0001*T	0.547-0.00006*T
1.0	0.642-0.00013*T	0.646-0.00013*T	0.582-0.00008*T
	x_{Au}/x_{Bi} = 2/1		
0.0	0.602-0.00008*T	0.557-0.00004*T	0.541-0.00009*T
0.1	0.570-0.00008*T	0.572-0.0003*T	0.536-0.00008*T
0.2	0.548-0.00006*T	0.574-0.00002*T	0.532-0.00007*T
0.3	0.527-0.00004*T	0.568-0.00002*T	0.526-0.00005*T
0.4	0.512-0.00005*T	0.560-0.00001*T	0.525-0.00005*T
0.5	0.508-0.00004*T	0.556-0.00002*T	0.526-0.00004*T
0.6	0.514-0.00002*T	0.559-0.00003*T	0.529-0.00004*T
0.7	0.534-0.00005*T	0.571-0.00005*T	0.607-0.0013*T
0.8	0.567-0.00005*T	0.594-0.00007*T	0.543-0.00005*T
0.9	0.613-0.00009*T	0.628-0.0001*T	0.554-0.00006*T
1.0	0.646-0.00013*T	0.646-0.00013*T	0.569-0.00007*T

Based on the models Kohler and Toop and Guggenheim's equation, surface tensions of Au-Bi Sn alloys were calculated.

As an example, Figure 1 shows the temperature dependence of calculated surface tensions, using Kohler's model, along the cross section $x_{Au}/x_{Bi} = 1/2$) with $0 \leq x_{Sn} \leq 1$.

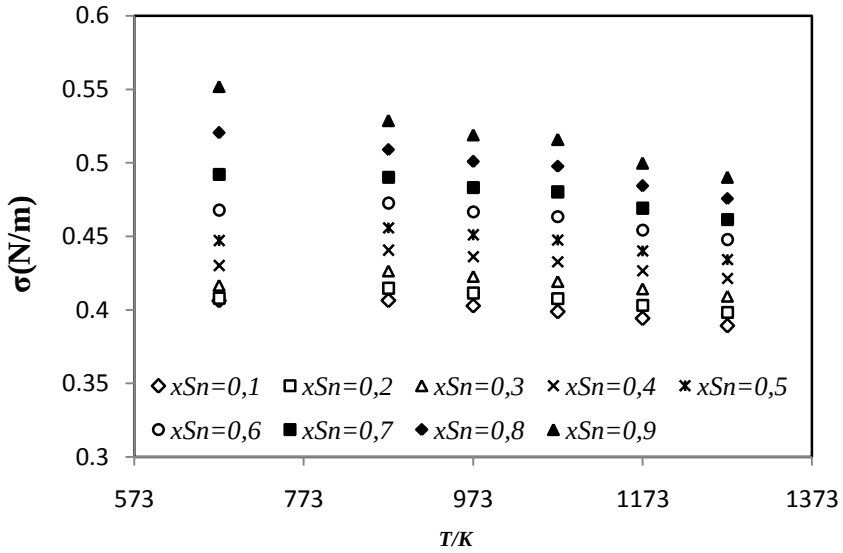

Figure 1: Temperature dependence of surface tension for fixed ration Au/Bi=1/2 using Kohler's model

As it can be seen, the linear dependence on temperature is obtained. On the other hand, for each temperature, the surface tension increases as the concentration of tin increases. It should be noted that the same behavior was obtained with the Toop's model and Guggenheim's equation.

Figures 2 and 3 show the comparison between our calculated values of surface tension and those measured by Zhongnan et al.[5] along those two cross-section x_{Au}/x_{Bi} =1/2 (Fig.2) and x_{Au}/x_{Bi} =1/1(Fig.3). For comparison, in the same figures we have added, the surface tensions of Pb-Sn electronic solder alloys.

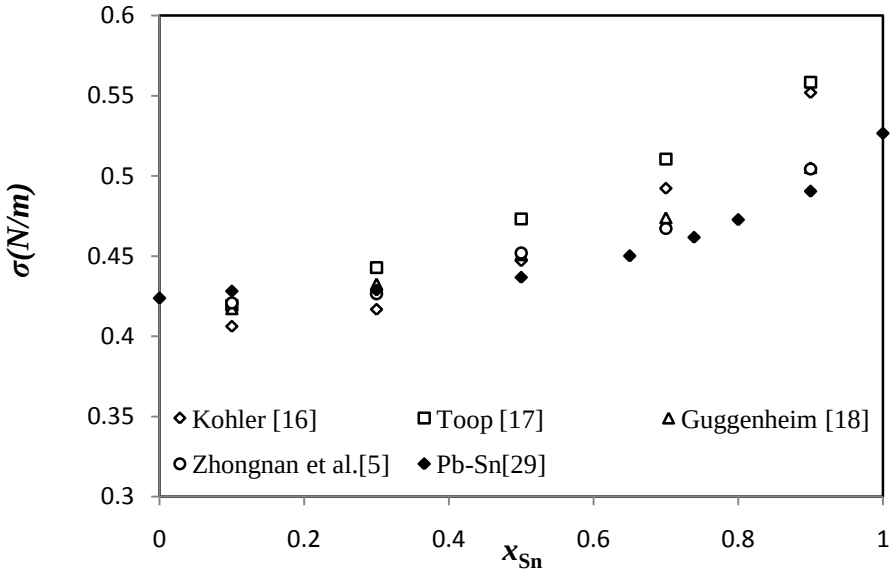

Figure 2: Comparison between the calculated and experimental [5] surface tension of Au-Bi-Sn for x_{Au}/x_{Bi}=1/2 alloys, together with the experimental values of Pb-Sn [29] at 673K

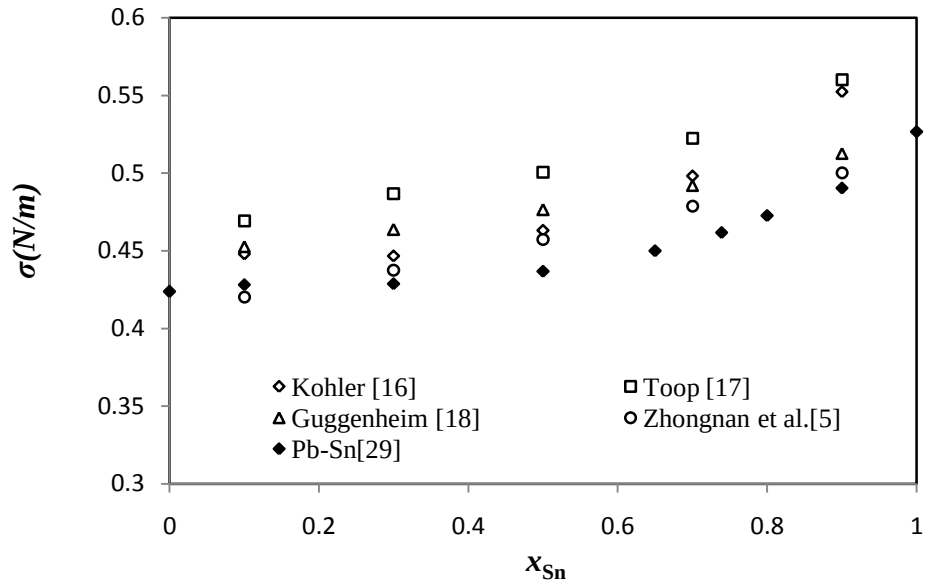

Figure 3: Comparison between the calculated and experimental [5] surface tension of Au-Bi-Sn for x_{Au}/x_{Bi}=1/1 alloys, together with the experimental values of Pb-Sn [29] at 673K

Generally, the surface tensions calculated with Guggenheim's equation are in good agreement with those obtained experimentally [5].The calculated values from Kohler and Toop models are slightly higher than the experimental ones.

Finally, one can conclude, that both our calculated results and the measured ones [5] are higher than those of Pb-Sn alloys at 673K.

Additionally, if one takes the root mean square deviation corresponding to experimental results for each traditional model:

$$S = \frac{1}{N}\sqrt{\sum_{i=1}^{N}\left(\sigma_{th,i} - \sigma_{exp,i}\right)^2}$$

Where $\sigma_{th,i}$ and $\sigma_{exp,i}$ represent the surface tension of Au-Bi-Sn alloys a fixed composition i for a theoretical model and an experimental results, respectively, while N is the total number of investigated alloys, the calculations of square deviation are summarized in Table 3.

Table 3: Calculated square deviation values S between theoretical and experimental [5] surface tension.

T /K	$\mathbf{S_k}$	$\mathbf{S_T}$	$\mathbf{S_G}$
673K	0.0072914	0.01006514	0.00500995
973K	0.00888233	0.01455414	0.00014139
1173K	0.00846496	0.01435922	0.00550678
1273K	0.00157272	0.01931717	0.009952542

From these S-values, Guggenheim's equation (S_G) gives the minimum values, except for 1273 K where Kohler gives the best agreement. One can conclude that at high temperatures, the ternary Au-Bi-Sn system has a symmetric behavior and the Kohler model gives the best results.

Conclusion

In this work, the surface tensions of liquid Au-Bi-Sn alloys were calculated using the Kohler, Toop and Guggenheim equations. The calculations were performed at different temperatures by adding tin to three different sections with x_{Au}/x_{Bi} = 1/2, 1/1 and 2/1. The results show that the tension de surface decreases with increasing temperature and increases with Sn-compositions. This finding would be helpful for further experimental data. The calculation square deviation values between theoretical and experimental show that the Guggenheim's equation gives the best agreement. The work of this paper (Part I) will be complemented by the study of some physic-chemical properties, such as viscosity, molar volume, and density of liquid Au-Bi-Sn alloys, which will be the second part of this study (Part II).

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