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Pb-free solders: Surface tension calculation of the Ag-Bi-Sn ternary alloys at 873 K

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Abstract

Surface tensions of the Ag-Bi-Sn ternary system alloys are calculated from the surface tensions of the Ag-Bi, Ag-Sn and Bi-Sn sub-binary systems by using geometric models (Kohler, Toop and Hillert). At the same time, the surface tension of the Ag-Bi-Sn ternary alloys at 873K and their sub-binary systems are predicted on the basis of Butler's equation in combination with thermodynamic data. Except for the asymmetric Toop and Hillert models, the agreement between the calculated results and experimental data is quite good using Kohler and Butler's models. With increasing amount of Bismuth the surface tension decreases slightly. The rich-silver cross-section shows that silver has no appreciable effect on increasing the surface tension.

Keywords: Lead-free solders; Surface tension; Geometric models; Ag-Bi-Sn ternary system

1. Introduction

In accordance with the Directives of the European Parliament and of the Council on "waste electrical and electronic equipment" and on "restriction of use of certain hazardous substances", lead is banned from production of new electrical and electronic devices from 1 July 2006 [1]. The traditional lead-tin solders have to be replaced with new solders, free of lead .Other alloys with a melting temperature close to the commonly used Sn-Pb eutectic (183 °C) and having appropriate properties should be found. For industrial usage of a new soldering material, the physical properties (electrical, chemical, thermal, mechanical…) in the solid as well as in the liquid state should be well known.

The surface properties play a key role in joining process. Development of new solders requires data on thermophysical properties such us surface tension which can be obtained experimentally or by numerical modeling, if a reliable data for pure components and simple subsystems are present. Moreover, numerical modeling is sometimes preferred because of growing complexity and cost experiments.

Surface tension data for Ag-Bi, Bi-Sn and Ag-Sn binary alloys have been measured and reported by many authors [2-4]. Therefore, the SURDAT database [5] contains data of surface tension in an extensive range of temperatures and concentrations. However, as far as know, for those alloys systems, there is disagreement between different authors concerning the existence of irregularities in the surface tension isotherms.

The surface tensions of the Ag-Bi-Sn ternary alloys at 873K by using Kohler [6], Toop [7] and Hillert [8] geometric models and Butler's equation [9] are calculated and compared to each other and to the experimental data [10].

2. Thermodynamic modeling of surface tension

2.1. Theoretical background

Geometric models, such as those of Kohler [6], Toop [7] and Hillert [8], originally developed to predict the thermodynamic properties of ternary systems, have been also applied to calculate their thermophysical properties, such as the surface tension, viscosity and molar volume. Having in mind the lack of experimental thermophysical data for many ternary metallic systems, geometric models may be an easy and convenient tool for estimation of those data. The greatest advantage of all aforementioned models is a simple and easy calculation procedure and relatively accurate prediction of

different thermophysical properties. In relation to the surface properties, the surface tension of ternary alloys predicted by geometric models can be subsequently compared with the corresponding results calculated using the model based on Butler's concept [9].

2.2. Application of Butler's equation

In this model, the surface is considered as an additional thermodynamic phase, in equilibrium with the bulk. Based on Butler's model [9], the surface tension of liquid alloys, assuming the regular solution model, can be calculated as:

$$\sigma = \sigma_i + \frac{RT}{S_i} ln \frac{X_i^S}{X_i^b} + \frac{1}{S_i}\{G_i^{E,s}(T, X^s_{j(j=2,3,\dots)}) - G_i^{E,b}(T, X^b_{j(j=2,3,\dots)})\} \quad i = 1,2,3,\dots \qquad (1)$$

Where R, T, σ_i and S_i are the gaz constant, absolute temperature, the surface tension of pure components and the surface area, respectively. $G_i^{E,s}(T, X^s_{j(j=2,3,\dots)})$ and $G_i^{E,b}(T, X^b_{j(j=2,3,\dots)})$ are the partial excess Gibbs energies of a component i in the surface phase and in the bulk phase, respectively.

The molar surface area S_i can be related to the molar volume V_i of the pure liquid and Avogadro's number with the aid of a geometric factor b. The value of 1.09 typical of close packed structures is considered to be also representative of the liquid [11, 12].

$$S_i = bN_A^{1/3}V^{2/3} (\text{m}^2) \qquad (2)$$

Finally, the relationship between excess Gibbs energy of component i in bulk and surface phases is assumed to be equal as follows:

$$G_i^{E,s}(T, X^s_{j(j=2,3,\dots)}) = \beta G_i^{E,b}(T, X^b_{j(j=2,3,\dots)}) \text{ (J/mol)} \qquad (3)$$

β is a parameter corresponding to the ratio of the coordination number Z in the surface phase to that in the bulk phase Z^s/Z^b and is assumed to be equal to 0.83 for liquid [11, 12].

In the present paper, the excess Gibbs energies of the binary subsystems of the Ag-Bi -Sn system are given in the form of Redlich-Kister polynomials [13].

Molar volume and surface tension data required for the calculations in the Ag-Bi-Sn system are presented in Table1.

Table 1: Molar volume and surface tension data of the pure components.

Component	V_i (m^3/mol)	σ_i (m N/m)
Ag	$11.6.10^{-6}(1.0+0.000098(T-1234))$ [14]	$1133.9541 - 0.1904719T$ [16]
Bi	$20.80.10^{-6}$ (1.0+0.000117(T-544.1)) [15]	$405 - 0.0492T$ [17]
Sn	$17.0.10^{-6}(1.0+0.000087(T-504.99))$ [15]	$582.826 - 0.083361T$ [18]

The excess Gibbs energy values for the bulk phase are calculated using Eq1 [19].

$$G^E = \sum_i \sum_{j>1} x_i x_j L_{i,j} + x_i x_{j>i} x_{k>j} L_{i,j,k} \qquad (4)$$

The binary and ternary interaction parameters have a Redlich-Kister type dependency on the composition (Table 2):

$$L_{i,j} = \sum_v (x_i - x_j)^v \; L_{i,j}^v \qquad (5)$$

$$L_{i,j,k} = x_i L_{i,j,k}^0 + x_j L_{i,j,k}^1 + x_k L_{i,j,k}^2 \qquad (6)$$

Table 2: Interaction parameters for the Ag–Bi-Sn system

System	$L^0(T)$	$L^1(T)$	$L^2(T)$	Reference
Ag-Bi	3340.81+39.16749T-5.9698	-5485.45-1.07133T	-3055.34+1.7749T	[20]
Ag-Sn	-5146.7-5.0103T	-15799.3+3.3208T	-6687.5	[21]
Bi-Sn	490+0.966T	-30-0.235T	0	[22]
Ag-Bi-Sn	1700+76.2T	1100+4T	20000-38.95T	[23]

For the surface phase the excess Gibbs energy is modified as in previous example by multiplying the excess energy expression with β = 0.83.

2.3. Application of geometric models

The traditional geometric models can be divided into two types: symmetric (Kohler, Muggianu and Colient models …) and asymmetric (Bonnier, Toop and Hillert models…).

Kohler model:

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. Using Kohler's model [6], the surface tension of ternary alloy systems is given by:

$$\sigma^E = (x_1 + x_2)^2(\sigma^E_{12})\frac{x_1}{x_2} + (x_1 + x_3)^2(\sigma^E_{13})\frac{x_1}{x_3} + (x_2 + x_3)^2(\sigma^E_{23})\frac{x_2}{x_3} \quad (7)$$

Where $\sigma^E_{i,j}$ 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.

The binary contributions are described by using the Redlich-Kister (R-K) [13] Polynomial:

$$\sigma^E = X_1 X_2 \sum_{i=0}^{n} A_i (X_2 - X_1)^v \quad (8)$$

Where A_i is the coefficient of the R-K polynomial. The coefficients of R-K polynomial for excess surface tensions of the three sub-binary alloys at 873K are shown in Table 3.

Table 3: The coefficients of R-K polynomial for excess surface tensions of the Ag-Bi, Ag-Sn and Bi-Sn sub-binary alloys at 873 K.

System	A_0	A_1	A_2
Ag-Bi	-920.812	845.3489	-597.4419
Ag-Sn	-682.7542	403.4695	134.1366
Bi-Sn	-116.2275	64.3142	-42.2286

Toop model:
A numerical method proposed by Toop [7] is asymmetric, and it is given by:

$$\sigma^E = \frac{x_2}{1-x_1}.\sigma^E_{12}(x_1;1-x_1) + \frac{x_3}{1-x_1}.\sigma^E_{13}(x_1;1-x_1) + (x_2+x_3)^2.\sigma^E_{23}\left(\frac{x_2}{x_2+x_3};\frac{x_3}{x_2+x_3}\right) \quad (9)$$

Hillert model:

$$\sigma^E = \frac{x_2}{1-x_1}.\sigma^E_{12}(x_1;1-x_1) + \frac{x_3}{1-x_1}.\sigma^E_{13}(x_1;1-x_1) + \frac{x_2.x_3}{v_{23}.v_{32}}.\sigma^E_{23}(v_{23};v_{32}) \quad (10)$$

With $v_{23} = \frac{(1+x_2-x_3)}{2}$ and $v_{32} = \frac{(1+x_3-x_2)}{2}$

Where σ^E and $\sigma^E_{i,j}$ are the excess surface tension of the ternary system and i-j the binary system, respectively; x_i is the mole fraction of component I in the ternary system. In Table 4, for calculations of the ternary surface tensions, we summarize the excess surface tensions of the sub-binary systems at 873K.

Table 4. Excess surface tensions of the sub-binary systems in the Ag-Bi-Sn ternary alloys at 873K.

Bi-Sn system		Sn-Ag system		Ag-Bi system	
X_{Sn}	σ^E (m N/m)	X_{Ag}	σ^E(m N/m)	X_{Bi}	σ^E (m N/m)
0.0	0.0000	0.0	0.0000	0.0	0.0000
0.1	-18.5695	0.1	-51.2668	0.1	-179.0259
0.2	-27.9874	0.2	-104.7197	0.2	-297.9295
0.3	-31.5341	03	-161.9196	0.3	-320.8574
0.4	-31.4306	0.4	-181.0392	0.4	-273.8446
0.5	-29.0568	0.5	-170.6885	0.5	-230.2028
0.6	-25.1693	0.6	-143.4910	0.6	-182.7829
0.7	-20.1191	0.7	-107.2292	0.7	-126.5805
0.8	-14.0700	0.8	-69.9101	0.8	-28.2855
0.9	-7.2161	0.9	-34.4135	0.9	164.8160
1.0	0.0000	1.0	0.0000	1.0	0.0000

3. Results and discussion

Hindler [10] has reported that with increasing amount of Bi from the Ag-rich to the Bi-rich side (x_{Ag}/x_{Bi}=2/1 to 2/1) the surface tension starts to drop slightly (Figure 1). In order to confirm these results, the calculated values

by using the geometric models and the Butler's equation are shown in Table 5. For comparison, the experimental values are also included.
To verify the influence of amount of Ag and/or Bi, we summarize the three studied sections (x_{Ag}/x_{Bi}=2/1, 1/1 and 2/1) for each model (Figures 2-5).
The calculated results show that the same conclusion has been obtained for the two models (Kohler and Butler; Figures 2-3). In contrary, for the two asymmetric models (Toop and Hillert), the same conclusion has been noted only up to 50 at % Sn. For the concentration more than 50 % in Sn, the phenomenon is reversed. From these results, one can conclude that the Ag-Bi-Sn system can be considered as a symmetric model.

Table 5. Comparison between the calculated surface tensions (N/m) in Ag-Bi-Sn ternary alloys at 873K and the experimental data [10].

x_{Ag}/x_{Bi}=	x_{Sn}	x_{Ag}	x_{Bi}	Expt .data	Kohler .model	Toop.model	Hillert.model	Butler equation
1/1	0	0.5000	0.5000	-----	0.4346	0.4346	0.4346	-----
	0.1	0.4500	0.4500	0.359	0.4268	0.4423	0.4497	0.4276
	0.2	0.4000	0.4000	0.430	0.4130	0.4528	0.4626	0.4020
	0.3	0.3500	0.3500	0.436	0.4180	0.4636	0.4735	0.4437
	0.4	0.3000	0.3000	0.406	0.4323	0.4744	0.4834	0.4734
	0.5	0.2500	0.2500	0.446	0.4501	0.4867	0.4941	0.4963
	0.6	0.2000	0.2000	0.473	0.4676	0.5014	0.5068	0.5146
	0.7	0.1500	0.1500	0.457	0.4823	0.5156	0.5190	0.5295
	0.8	0.1000	0.1000	0.450	0.4943	0.5222	0.5238	0.5415
	0.9	0.0500	0.0500	0.468	0.5034	0.5162	0.5166	0.5504
	1	0.0000	0.0000	-----	0.5100	0.5100	0.5100	0.5100
1 /2	0	0.3334	0.6666	------	0.4174	0.4174	0.4174	------
	0.1	0.3000	0.6000	0.380	0.4064	0.4232	0.4341	0.3600
	0.2	0.2667	0.5333	0.378	0.4034	0.4358	0.4508	0.3755
	0.3	0.2333	0.4667	0.366	0.4133	0.4538	0.4690	0. 3800
	0.4	0.2000	0.4000	0.445	0.4279	0.4746	0.4886	0.4164
	0.5	0.1667	0.3333	0.477	0.4436	0.4963	0.5078	0.4453
	0.6	0.1333	0.2667	0.439	0.4586	0.5143	0.5227	0.4694
	0.7	0.1000	0.2000	0.459	0.4728	0.5235	0.5288	0.4903
	0.8	0.0667	0.1333	0.410	0.4862	0.5213	0.5238	0.5130
	0.9	0.0333	0.0667	0.461	0.4984	0.5115	0.5122	0.5327
	1	0.0000	0.0000	-----	0.5100	0.5100	0.5100	0.5100
2/1	0	0.6666	0.3334	------	0.4583	0.4583	0.4583	-------
	0.1	0.6000	0.4500	0.443	0 .4330	0.4847	0.4889	0.4042
	0.2	0.5333	0.4000	0.459	0.4306	0.4927	0.4981	0.4457
	0.3	0.4667	0.3500	0.512	0.4245	0.4923	0.5007	0.4751
	0.4	0.4000	0.3000	0.509	0.4356	0.4990	0.5038	0.4976
	0.5	0.3333	0.2500	0.506	0.4537	0.5038	0.5077	0.5156
	0.6	0.2667	0.2000	0.522	0.4735	0.5093	0.5122	0.5301
	0.7	0.2000	0.1500	0.529	0.4901	0.5163	0.5181	0.5419
	0.8	0.1333	0.1000	0.573	0.5016	0.5219	0.5228	0.5506
	0.9	0.0667	0.0500	0.551	0.5081	0.5185	0.5187	0.5515
	1	0.0000	0.0000	-----	0.5100	0.5100	0.5100	0.5100

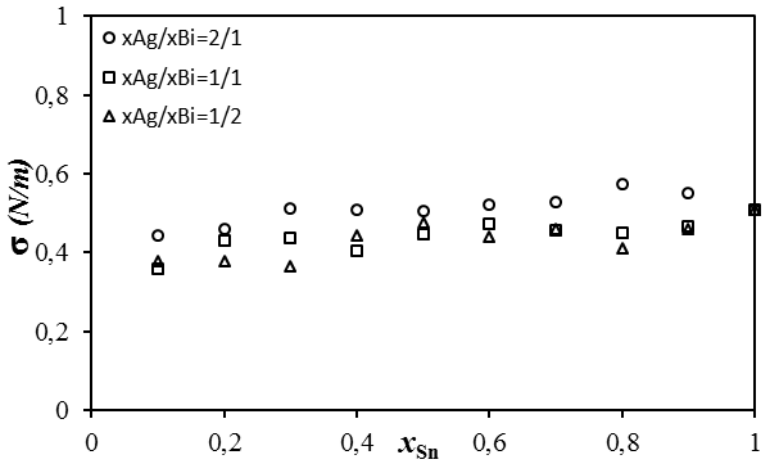

Figure 1. Experimental surface tensions of the liquid Ag-Bi-Sn alloys at 873K [10]

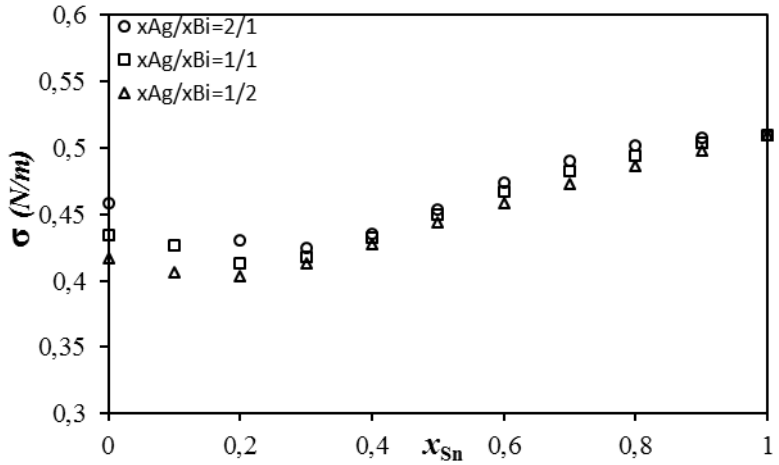

Figure 2. Calculated surface tensions of the liquid Ag-Bi-Sn alloys by using Kohler's model at 873K

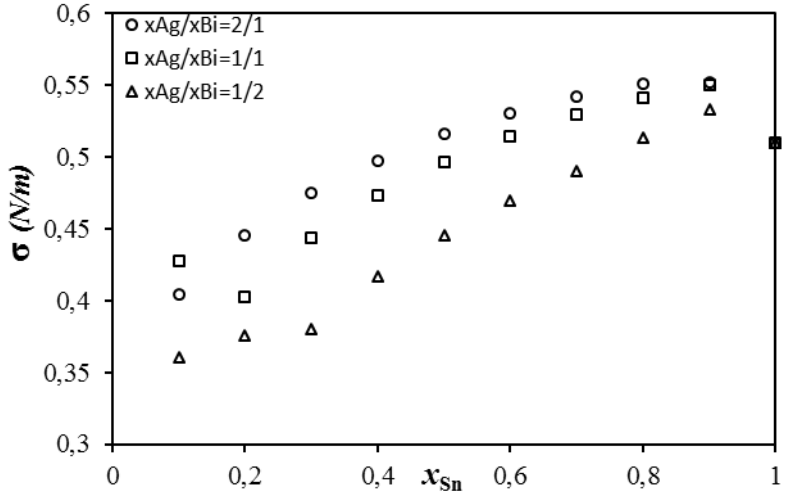

Figure 3. Calculated surface tensions of the liquid Ag-Bi-Sn alloys by using Butler's model at 873K

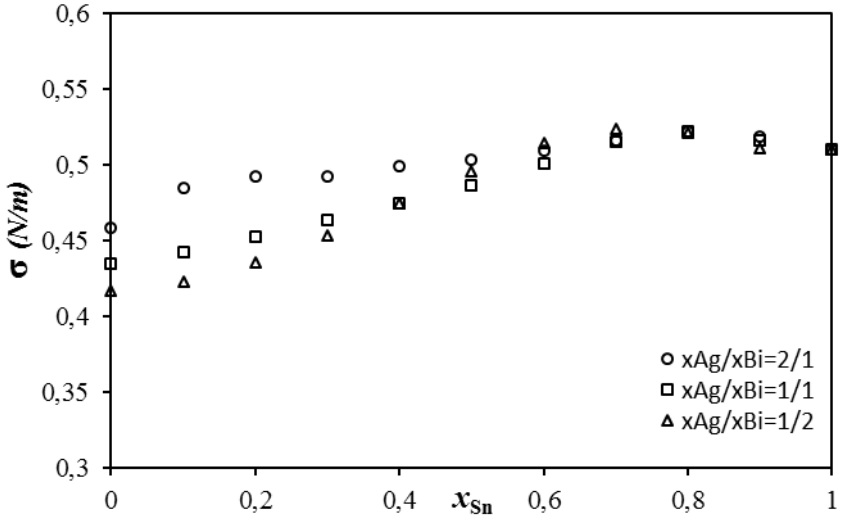

Figure 4. Calculated surface tensions of the liquid Ag-Bi-Sn alloys by using Toop's model at 873K

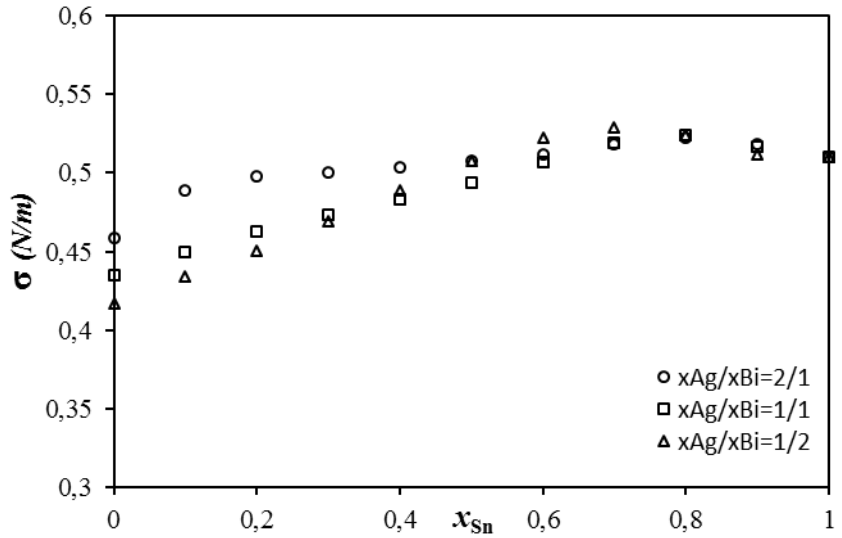

Figure 5. Calculated surface tensions of the liquid Ag-Bi-Sn alloys by using Hillert's model at 873K

Conclusion

The surface tensions of the Ag-Bi-Sn ternary alloys at 873K are calculated by different geometric models, and by using the Butler's equation. Except for the asymmetric Toop and Hillert models, the agreement between the calculated and experimental results is quite good. With increasing amount of Bismuth the surface tension decreases slightly. The silver cross-section (x_{Ag}/x_{Bi} =2/1) shows that silver has no appreciable effect on increasing the surface tension in ternary Ag-Bi-Sn alloys compared to the tin (about 550 mN/m).

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