The Surface Tension and Density of Liquid Ag–Bi, Ag–Sn, and Bi–Sn Alloys

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Summary. The sessile drop method has been used to measure density and surface tension for pure Ag, Bi, Sn, and their mixtures. For pure metals and Bi–Sn alloys negative temperature coefficients of surface tension have been obtained. In case of Ag–Bi and Ag–Sn alloys the temperature coefficients of surface tension take negative or positive values depending on composition. Experimental values of the surface tension for Ag–Bi, Ag–Sn, and Bi–Sn are compared with those computed from *Butler*'s model. A relatively good agreement is observed.

Introduction

Ag–Bi–Sn alloys are regarded as potential lead-free solders, which can be used in various applications, especially in the field of electronics. The surface tension of such solder is a very important parameter. Unfortunately, the literature data for this ternary system are limited to very narrow composition and temperature range [1]. There is noticeable disagreement among existing data for limiting binary systems. Therefore the aim of this project was to determine the surface tension and density of limiting binaries Ag–Bi, Ag–Sn, and Bi–Sn alloys.

Results of Density and Surface Tension
Measurements of Ag, Bi, and Sn

The results obtained for the density (ρ) and surface tension (σ) of pure Ag, Bi, and Sn are listed in Table 1. They are in good agreement with the average values suggested by *Keene* [4].

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Table 1. Surface tension σ and density ρ for Ag, Bi, and Sn

	$\sigma = A + B \cdot T$ $\overline{\text{mN} \cdot \text{m}^{-1}}$	R^2	$\rho = A + B \cdot T$ $\overline{\text{g} \cdot \text{cm}^{-3}}$	R^2
Ag	$1163.7 - 0.2040T$	0.9928	$10.180 - 0.000714T$	0.9636
Bi	$431.4 - 0.0800T$	0.9983	$10.726 - 0.001200T$	0.9709
Sn	$636.5 - 0.1101T$	0.9785	$7.118 - 0.000507T$	0.9766

Results of Surface Tension and Density Measurements of Ag–Bi, Ag–Sn, and Bi–Sn Alloys

The results of the measurements of Ag–Bi alloys are presented in Table 2.

They suggest negative values of $\partial\sigma/\partial T$ for alloys with lower silver contents ($x_{\text{Ag}} = 0.1$ and $x_{\text{Ag}} = 0.3$) and positive values for alloys with higher silver contents ($x_{\text{Ag}} = 0.5$, 0.7, and 0.9). These findings are supported by the results reported by *Metzger* [5] and disagree with the data given by *Gasior et al.* [6]. This phenomenon is possibly due to the increase of the silver content in the surface layer at the expense of bismuth when the temperature is increased.

In the case of Ag–Bi at a given composition, the *Gibbs* adsorption equation takes the form of Eq. (1) where $n = n_{\text{Ag}}^{(b)} + n_{\text{Bi}}^{(b)} = n_{\text{Ag}}^{(s)} + n_{\text{Bi}}^{(s)}$ is total number of moles in the surface and bulk phase, A is the surface, and $\overline{S}_{\text{Ag}}$ is partial molar entropy of silver, $x_{\text{Ag}}^{(s)}, x_{\text{Bi}}^{(s)}$ and $x_{\text{Ag}}, x_{\text{Bi}}$ are the molar fractions in the surface and bulk phase respectively.

$$\left(\frac{\partial\sigma}{\partial T}\right)_{\text{comp, P}} = \frac{n}{A}\left[\frac{x_{\text{Ag}}}{x_{\text{Bi}}}\left(x_{\text{Bi}}^{(s)} - x_{\text{Bi}}\right) - \left(x_{\text{Ag}}^{(s)} - x_{\text{Ag}}\right)\right] \cdot \left(-\overline{S}_{\text{Ag}}\right) \qquad (1)$$

As $\overline{S}_{\text{Ag}}$ is positive, the sign of $\partial\sigma/\partial T$ depends on the sign of the expression in the squared brackets. It can be proved that at certain compositions $\partial\sigma/\partial T$ adopts positive values if the silver content of the surface phase increases with increasing temperature.

The molar volume of Ag–Bi alloys shows slightly positive deviation from additivity and is in fairly good agreement with values computed from the data of *Gasior et al.* [6].

The densities and surface tensions of Ag–Sn alloys are listed in Table 3. The molar volumes calculated from measured densities vary linearly with the composition and are in fairly good agreement with data reported by *Moser et al.* [7] and *Lauermann* and *Metzger* [8].

Table 2. Surface tension σ and density ρ for Ag–Bi alloys

x_{Ag}	$\sigma = A + B \cdot T$ $\overline{\text{mN} \cdot \text{m}^{-1}}$	R^2	$\rho = A + B \cdot T$ $\overline{\text{g} \cdot \text{cm}^{-3}}$	R^2
0.1	$423.7 - 0.0743T$	0.9907	$9.948 - 0.000771T$	0.9514
0.3	$416.5 - 0.0549T$	0.9348	$10.192 - 0.000914T$	0.9692
0.5	$350.5 + 0.0127T$	0.3584	$10.283 - 0.000993T$	0.9542
0.7	$395.7 + 0.0330T$	0.9292	$10.211 - 0.001000T$	0.9952
0.9	$655.0 + 0.0277T$	0.4702	$9.613 - 0.000700T$	0.9513

Table 3. Surface tension σ and density ρ for Ag–Sn alloys

x_{Ag}	$\sigma = A + B \cdot T$ $\overline{\text{mN} \cdot \text{m}^{-1}}$	R^2	$\rho = A + B \cdot T$ $\overline{\text{g} \cdot \text{cm}^{-3}}$	R^2
0.1	$576.5 - 0.0632T$	0.9424	$7.346 - 0.000535T$	0.9894
0.3	$650.9 - 0.1043T$	0.9877	$7.771 - 0.000640T$	0.9910
0.5	$539.9 + 0.0334T$	0.4625	$8.933 - 0.001353T$	0.9357
0.7	$592.4 + 0.0350T$	0.6407	$9.094 - 0.000670T$	0.9700
0.9	$967.9 - 0.1278T$	0.9797	$9.118 - 0.000356T$	0.8533

Table 4. Surface tension σ and density ρ for Bi–Sn alloys

x_{Sn}	$\sigma = A + B \cdot T$ $\overline{\text{mN} \cdot \text{m}^{-1}}$	R^2	$\rho = A + B \cdot T$ $\overline{\text{g} \cdot \text{cm}^{-3}}$	R^2
0.1	$437.8 - 0.0771T$	0.9908	$9.943 - 0.001043T$	0.9512
0.3	$430.1 - 0.0732T$	0.9804	$9.433 - 0.000750T$	0.9950
0.5	$439.0 - 0.0593T$	0.9690	$8.798 - 0.000920T$	0.9631
0.7	$463.6 - 0.0583T$	0.9356	$7.805 - 0.000608T$	0.9752
0.9	$504.0 - 0.0474T$	0.8874	$7.157 - 0.000508T$	0.9783

The surface tension of Ag–Sn alloys decreases with increasing temperature for some compositions ($x_{Ag} = 0.1$, 0.3, and 0.9), whereas for others ($x_{Ag} = 0.5$ and 0.7) an opposite tendency is observed. This phenomenon is also apparent from the data reported by *Lauermann et al.* [9] and *Lee et al.* [10], whereas the values given by *Moser et al.* [7] do not exhibit such behaviour.

The results obtained for Bi–Sn alloys are listed in Table 4. The measured densities of Bi–Sn alloys are lower than those reported by *Moser et al.* [1]. The surface tension of Bi–Sn decreases linearly with increasing temperature for all investigated alloys of Bi–Sn.

Modelling of the Surface Tension of Ag–Bi, Ag–Sn, and Bi–Sn Alloys

Assuming equilibrium between the bulk phase of a binary alloy and its surface layer which is treated as a true "phase", the surface tension can be described as shown by Eq. (2) [11] where $a_i^{(s)}$, $a_i^{(b)}$ are the activities of the ith component in the surface and in the bulk phase, respectively, A_i^0 is the molar surface of the pure component, and A_i is its partial molar surface in the alloy.

$$\sigma_{i-j} = \frac{A_i^0}{A_i}\sigma_i + \frac{RT}{A_i}\ln\frac{a_i^{(s)}}{a_i^{(b)}} = \frac{A_j^0}{A_j}\sigma_j + \frac{RT}{A_j}\ln\frac{a_j^{(s)}}{a_j^{(b)}} \tag{2}$$

R is the gas constant and T is the absolute temperature.

This method was for the first time developed by *Butler* [12] under the assumption that the difference in composition between the surface "phase" and the bulk phase is restricted to the first layer of molecules. Equation (2) is simplified if the partial molar areas are equal to the molar surface areas of the components ($A_i = A_i^0$). This was the assumption used in the calculations.

Table 5. Calculated *Redlich-Kister* coefficients for Ag–Bi and Bi–Sn mixtures

Mixture	$L^{(0)}/\text{J} \cdot \text{mol}^{-1}$	$L^{(1)}/\text{J} \cdot \text{mol}^{-1}$	$L^{(2)}/\text{J} \cdot \text{mol}^{-1}$	Literature
Ag–Bi	$7072.6 - 4.1292T$	$-9349.2 - 3.4517T$	$-3421.9 + 1.0133T$	[14, 15]
Bi–Sn	$581.6 + 1.3422T$	$12.4 - 0.0376T$	$15.1 + 0.3851T$	[16, 17]

The thermodynamic properties of investigated alloys were described by *Redlich-Kister* polynomials [13]. The respective parameters for Ag–Bi and Bi–Sn alloys were calculated using literature data. They are given in Table 5. The parameters for Ag–Sn alloys were taken from literature [18].

There is an assumption that the absolute value of partial excess *Gibbs* energy of a component in the surface layer is smaller than in the bulk phase because atoms in the surface layer have lower coordination numbers than in the bulk phase.

Therefore the partial excess *Gibbs* energy of the *i*th component in the surface layer can be expressed as given by Eq. (3) where the constant is an adjustable parameter.

$$\Delta G_i^{Ex(s)} = \text{const} \times x_j^{2(s)} \left[L_{i-j}^{(0)} + L_{i-j}^{(1)}(x_j^{(s)} - 3x_i^{(s)}) \right.$$
$$\left. + L_{i-j}^{(2)}(x_j^{(s)} - x_i^{(s)})(x_j^{(s)} - 5x_i^{(s)}) + \ldots \right] \qquad (3)$$

Some authors assume that the adjustable parameter is equal to the ratio of the coordination number of the surface atoms to the coordination number of the atoms in the bulk phase (const $= z^{(s)}/z^{(b)}$). However, the surface region is in a very turbulent state, because there is two-way traffic of molecules condensing and evaporating on the surface. As surface molecules possess a much higher energy
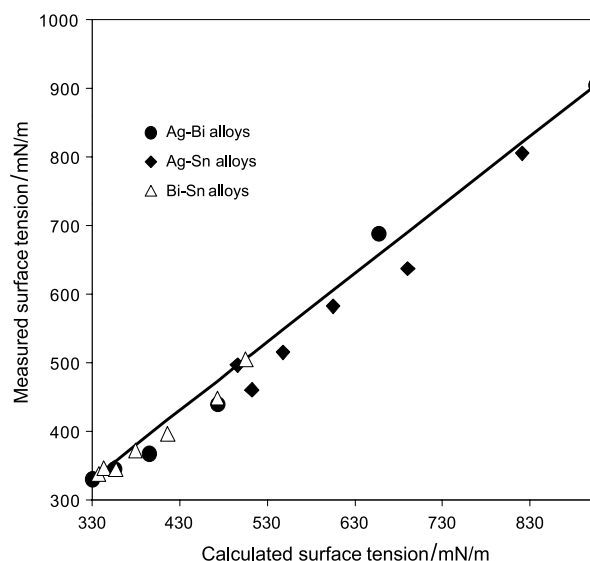

Fig. 1. Comparison of the experimental surface tensions of Ag–Bi, Ag–Sn, and Bi–Sn with those calculated from the model; calculations were carried out at 1273 K for Ag–Bi and Ag–Sn alloys and at 1173 K for Bi–Sn alloys

than molecules in the bulk, it is reasonable to expect that the surface mixture is close to ideal one. Consequently, the adjustable parameter was assumed to be zero.

The calculated surface tensions of Ag–Bi, Ag–Sn, and Bi–Sn are compared in Fig. 1.

Conclusion

The density and the surface tensions of the binary alloys Ag–Sn, Ag–Bi, and Sn–Bi were measured with the sessile drop method. The values of the densities are smaller than the literature values based on the maximum bubble pressure method. At certain compositions the surface tension of Ag–Bi decreases linearly with increasing temperature. For other compositions an opposite tendency is observed. This phenomenon is likely to occur if there is a big difference between surface tensions of alloy components. In such case, according to *Gibbs* adsorption equation, there is an adsorption of the component with lower surface tension into the surface layer. An increase in temperature increases the surface concentration of the component with the higher surface tension, which may lead to an increase of alloy's surface tension.

In case of Ag–Sn alloys the surface tension decreases with increasing temperature for some alloys ($x_{Ag} = 0.1$, 0.3, and 0.9), whereas others exhibit the opposite trend ($x_{Ag} = 0.5$ and 0.7). However, it is worth to point out that in nearly all cases with positive temperature coefficients, the correlation coefficients (R) are much lower than in those cases where negative coefficients prevail (see Tables 2–4). The surface tension of Sn–Bi, in general, shows a linear temperature dependence.

Experimental

The sessile drop method in conjunction with X-ray radiography and digital X-ray image processing was used to measure the density and surface tension of liquid pure metals (Ag, Bi, Sn) as well as Ag–Bi, Ag–Sn, and Bi–Sn alloys. A graphite plate was employed as substrate material. The experimental apparatus has been described elsewhere [2]. It consists of a furnace with Superkanthal heating elements combined with an Exposcop 8000 X-ray radiographic unit. The coordinates of points on the drop's surface were determined with the help of a computer program. These points were used to determine the density and the surface tension of the samples. The calculation of the surface tension was based on the method developed by *Rotenberg et al.* [3]. For our measurements, metals of high purity (Ag 99.995%, Bi 99.999%, and Sn 99.99%) were used.

Acknowledgements

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