

On the variation of surface tension with composition in liquid Pb-Sn alloys

In a recent paper, Demeri *et al.* [1] have measured the contact angle and surface tension of Pb-Sn alloys on fused silica substrates by the sessile drop technique. Their results indicate a non-linear variation of surface tension with composition at various temperatures and an absolute minimum surface tension at the eutectic alloy, ~ 62 wt % Sn. They suggest that this non-linear behaviour may be a result of preferential adsorption of one of the components at the surface. Similar observations have also been made for the liquid Au-Sn system by Kaufman and Whalen [2]. The purpose of this note is to provide some comment on the non-linear behaviour of surface tension with composition in liquid Pb-Sn alloys.

Following the treatment of Kaufman and Whalen [2], the extent of the surface referred to in the real system is a volume which surrounds the inhomogeneous part of the system. Preferential segregation of one or more constituents of a system to this volume may occur spontaneously if this action lowers the energy of the system [3]. Positive adsorption is characterized by excess amounts of the adsorbed components in the surface region. Adsorption may be described by surface excess quantities Γ_i [2],

$$\Gamma_i = (m_i^\sigma - m_i)/A \quad (1)$$

where m_i^σ is the mole concentration of the *i*th component in the region of the discontinuity, m_i the mole concentration of the *i*th component in the bulk liquid, and A the area of phase contact. At constant temperature any variation in surface tension must result from, or be accompanied by, a change in chemical potential of one of the components. For the Pb-Sn binary system the pertinent Gibbs adsorption isotherm may be written as

$$d\sigma = -\Gamma_{Sn}d\mu_{Sn} - \Gamma_{Pb}d\mu_{Pb} \quad (2)$$

where μ_i is the chemical potential of the *i*th component.

We now select an area of surface containing one mole of matter to be compared with one mole from the bulk liquid so that

$$\begin{aligned} m_{Pb}^\sigma + m_{Sn}^\sigma &= 1 \\ m_{Pb} + m_{Sn} &= 1. \end{aligned} \quad (3)$$

It follows from Equations 1 and 3 that

$$\Gamma_{Sn} = -\Gamma_{Pb}. \quad (4)$$

Further, if Equations 2 and 4 are combined with the Gibbs-Duhem equation, one obtains

$$d\sigma = -\frac{\Gamma_{Sn}}{m_{Pb}} d\mu_{Sn}. \quad (5)$$

If data were available, from measured slopes of surface tension versus chemical potential one could calculate the surface excess of Sn, Γ_{Sn} , in Pb-Sn alloys using Equation 5 and, following the same type of energy considerations as Kaufman and Whalen [2], calculate free energies of adsorption. Preferential adsorption of Sn at the surface is characterized by positive values of Γ_{Sn} in a plot of Γ_{Sn} versus mole fraction Sn, while negative values represent preferential adsorption of Pb at the surface. Maxima or minima surface tension have zero values of Γ_{Sn} , c.f. Equation 5. Unfortunately, there appear to be insufficient data to calculate Γ_{Sn} from Equation 5 for liquid Pb-Sn alloys. However, it seems not unlikely that these calculations would indicate the formation of compounds or compound-like arrangements in the liquid state; of particular interest would be that or those compounds at the eutectic composition. Supportive of this possibility is that the extrema concentrations of Demeri *et al.* [1] are temperature independent.

The above is an argument which, in order to be verified, must be checked against experimental results for the liquid Pb-Sn system. Thus, we suggest that data be taken so that plots of surface tension versus chemical potential, and hence Γ_{Sn} versus mole fraction Sn, can be obtained. Further effort should also be directed toward an understanding of the minimum of surface tension at the eutectic alloy composition.

References

1. M. DEMERI, M. FARAG and J. HEASLEY, *J. Mater. Sci.* **9** (1974) 683.
2. S. M. KAUFMAN and T. J. WHALEN, *Acta Metallurgica* **13** (1965) 797.
3. J. W. GIBBS, "Collected Works", Vol. I (Yale University Press, New Haven, 1948) p. 219.

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