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The Surface Tension of Binary Alloys: Simple Models for Complex Phenomena[1]

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Surface segregation is the key to understanding the surface tension γ of alloys. The basic phenomena can be demonstrated qualitatively by using the ideal solution model. For a binary system, this model is first used to explain the temperature dependence of the surface tension. A simple criterion is established for sign reversal of the temperature coefficient. The ideal solution model is then extended to include the effect of compound formation. A simple explicit equation is proposed which fits existing data surprisingly well.

KEY WORDS: binary alloy; compound formation; ideal solution; liquid metal; surface segregation; surface tension.

1. INTRODUCTION

The surface tension γ of binary liquid alloys has been the subject of numerous publications. Using Butler's equation [1], it can be derived from the surface tensions of the pure elements and bulk thermodynamic data of the alloy [2]. Although not free from intrinsic simplifications, it has been widely used. Two prominent examples are the publications of Yeum et al. [3] and of Frohberg and coworkers [4]. A more sophisticated multilayer model was later developed by Chatain and coworkers [5]. All these models can be solved only numerically; an explicit analytical expression does not exist. On the other hand, the ideal solution model [6] provides a simple analytical formula. In its original form, it is known to be applicable to weakly interacting systems only. Nevertheless, it describes the gross physical features correctly, in particular, surface segregation.

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In the ideal solution model, the surface concentrations $c^s_{A,B}$ of a binary alloy of components A and B are given by

$$c^s_A = \frac{c_A}{c_A + c_B/S_0}, \quad c^s_B = \frac{c_B}{c_B + c_A S_0} \tag{1}$$

where c_A, c_B are the bulk concentrations, and S_0 is the surface segregation factor given by

$$S_0 = e^{\frac{A(\gamma_B - \gamma_A)}{RT}} \tag{2}$$

Here, it has been assumed that the molar volumes of both components are identical, $V_A = V_B = V$; consequently, $A = A_A = A_B$ is the (average) molar surface area [7]: $A = 1.09 V^{2/3} \mathrm{N}_\mathrm{A}^{1/3}$. $\mathrm{N_A}$ is Avogadro's constant: $\mathrm{N_A} = 6 10^{23}\,(\mathrm{mol})^{-1}$, R is the gas constant ($\mathrm{R} = 8.3\,\mathrm{N\,m\,mol^{-1}\,K^{-1}}$), and T is the temperature. In practice, V is an effective molar volume and is used as a fitting parameter.

Using the surface concentrations, the surface tension of the alloy can be written as

$$\gamma(T) = c^s_A(T)\gamma_A(T) + c^s_B(T)\gamma_B(T) \tag{3}$$

where $\gamma_{A,B}(T)$ are the surface tensions of the pure components.

Within this model, two effects will be discussed: In contrast to the behavior of the pure elements, the surface tension of an alloy may have a positive temperature coefficient, i.e., $\partial\gamma/\partial T > 0$. This is due to the fact that, at low temperatures, the surface is covered entirely by the component with lower surface tension, and $\partial\gamma/\partial T$ is negative, following the temperature dependence of the surface tension of this component. At high temperatures, the surface concentrations of the two components equal those of the bulk phase (which are temperature independent) and, consequently, $\partial\gamma/\partial T$ is a weighted average of the temperature coefficients of the two components, and is therefore also negative. At intermediate temperatures, however, there will be a transition from the lower limit of γ to the upper limit. This transition region may or may not display a positive temperature coefficient $\partial\gamma/\partial T > 0$. It depends on the competition between energetic and entropic effects. In other words, the system can lower its energy by segregating the component with lower surface tension at the surface, but entropy is maximized when such a concentration profile is homogenized.

In systems forming intermetallic compounds in the solid phase, a surface depletion is often observed in contrast to the predictions of the ideal solution model. This effect can be understood by assuming that clusters of the intermetallic composition also prevail in the liquid phase. The success of thermodynamic association models [8], which are based on the existence of such clusters, supports this view. If these clusters exist, they bind the otherwise surface- active component, preventing it from segregating at the surface. In other words, there is a competition between surface segregation and cluster formation, controlled again by entropy and energy considerations. By allowing the ideal solution model to account for cluster formation, we present an extension of this model, capable of describing surface depletion. Both models will be discussed and compared to experimental data.

2. TEMPERATURE DEPENDENCE

In the following, we assume $\gamma_A < \gamma_B$ and introduce $\Delta\gamma_{BA} = \gamma_B - \gamma_A > 0$. This means that component A is surface active in component B. By taking the temperature derivative of Eq. (3) which we denote by a prime, we obtain, after eliminating $c_A^s = 1 - c_B^s$,

$$\gamma' = c_B^{s'}\Delta\gamma_{BA} + c_B^s \Delta\gamma'_{BA} + \gamma'_A \tag{4}$$

In this equation, the first term is positive and describes the increase in surface tension with temperature due to the entropic effect. The last term is negative and dominates at high temperatures. The second term can have either sign, but will be generally small and can therefore be neglected. The temperature T_γ of the surface tension maximum, $\gamma‘(T_\gamma) = 0$, is therefore (implicitly) given by

$$c_B^{s'} = -\frac{\gamma'_A}{\Delta\gamma_{BA}} \tag{5}$$

For the surface tension of the two components we assume a linear temperature dependence with the same temperature coefficient γ_0. For such a model, the second term in Eq. (4) vanishes identically. This is not a serious restriction of generality, at least as long as the surface tensions of the pure components do not intersect. Such a behavior has not been observed for liquid metals. Consequently, we can write

$$\gamma_{A,B}(T) = \gamma_{A,B}^0 - \gamma'_0 T \tag{6}$$

where γ_A^0, γ_B^0, and γ_0‘ are positive numbers and $\Delta\gamma_{BA} = \gamma_B^0 - \gamma_A^0$. Inserting Eq. (6) into Eq. (3), and defining $\Delta\gamma_A(T) = \gamma(T) - \gamma_A^0$, we arrive at the following equation:

$$\Delta\gamma_A(T) = -\gamma'_0 T + \Delta\gamma_{BA}\, c_B^s(T) \tag{7}$$

Next, we introduce a dimensionless temperature *t*;

$$t = \frac{RT}{A \Delta\gamma_{BA}} \tag{8}$$

and replace $\gamma_0' = -\frac{d\gamma}{dT}$ by $\dot{\gamma}_0 = -\frac{d\gamma}{dt} = \gamma_0' \frac{A\,\Delta\gamma_{BA}}{R}$. Finally, we divide Eq. (7) by $\dot{\gamma}_0$ and obtain the following equation for the dimensionless surface tension $g(t) = \Delta\gamma_A(T)/\dot{\gamma}_0$:

$$g(t) = -t + \frac{\Delta g}{1 + \frac{c_A}{c_B} e^{1/t}} \tag{9}$$

Here, $\Delta g = \Delta\gamma_{BA}/\dot{\gamma}_0 = R/(A\gamma_0')$. The function $g(t)$ describes the difference between the surface tension of the alloy and that of the surface active component in units of the dimensionless temperature coefficient. It contains only two parameters, namely Δ_g and c_A/c_B, the ratio of the bulk concentrations. It is interesting to note that Δ_g does in fact not depend on $\Delta\gamma_{BA}$, the difference of the surface tensions of the two components.

Starting from Eq. (9), it is now straightforward to discuss the temperature derivative $\dot{g} = dg/dt$. It is given by

$$\dot{g} = -1 + \Delta g \frac{\frac{c_A}{c_B}}{\left(1 + \frac{c_A}{c_B} e^{1/t}\right)^2} \frac{e^{1/t}}{t^2} \tag{10}$$

From the condition $\dot{g} = 0$, we obtain

$$t\left(e^{-1/2t} + \frac{c_A}{c_B} e^{1/2t}\right) = \sqrt{\Delta g \frac{c_A}{c_B}} \tag{11}$$

If this criterion is satisfied, there will be extrema of the surface tension. The left hand side of Eq. (11) is a convex function of t which diverges for $t = 0$ and $t = \infty$. For $c_A > 0$ it has a minimum > 0. Therefore, Eq. (11) has either no solution or two solutions. This means that depending on the value of the square root on the right-hand side, the surface tension is either a monotonic function, or it has both a minimum and a maximum.

In order to derive an explicit result, we neglect $e^{-1/2t}$ on the left-hand side and arrive at the following criterion for the appearance of a positive temperature coefficient of the surface tension:

$$\Delta g > \Delta g^* = 1.85 \frac{c_A}{c_B} \tag{12}$$

where we have used the fact that the function $xe^{1/x}$ has a minimum at $x=1$ with a value of e. The temperature t_γ, at which the maximum occurs, is approximately given by

$$t_\gamma = \sqrt{\Delta g\, c_A\, c_B} \tag{13}$$

In Fig. 1 the surface tension as given by Eq. (9) is plotted for $c_A = 0.7$ and three different values of Δg. The lowest curve corresponds to $\Delta g = 0.5\Delta g^*$, the second curve represents $\Delta g = \Delta g^*$, while the upper curve is given by $\Delta g = 2\Delta g^*$, where Δg^* is the critical value for the occurrence of extrema. The dashed line shows the surface tension of component 1 which is a lower bound for $g(t)$. Numerically, we find $\Delta g^* = 4.7$, while Eq. (12) predicts $\Delta g^* = 4.3$. As can be seen from Fig. 1, the maximum for $\Delta g = 2\Delta g$ occurs at $t_\gamma = 1.1$, while Eq. (13) yields $t_\gamma = 1.3$.

Positive temperature coefficients for the surface tension have been reported by many authors, and also a maximum in the surface tension as a function of temperature has been observed. Such an example is shown in Fig. 2 for a NiFe alloy, probably measured under high oxygen partial pressure [9]. To the author's best knowledge, a minimum in the surface tension

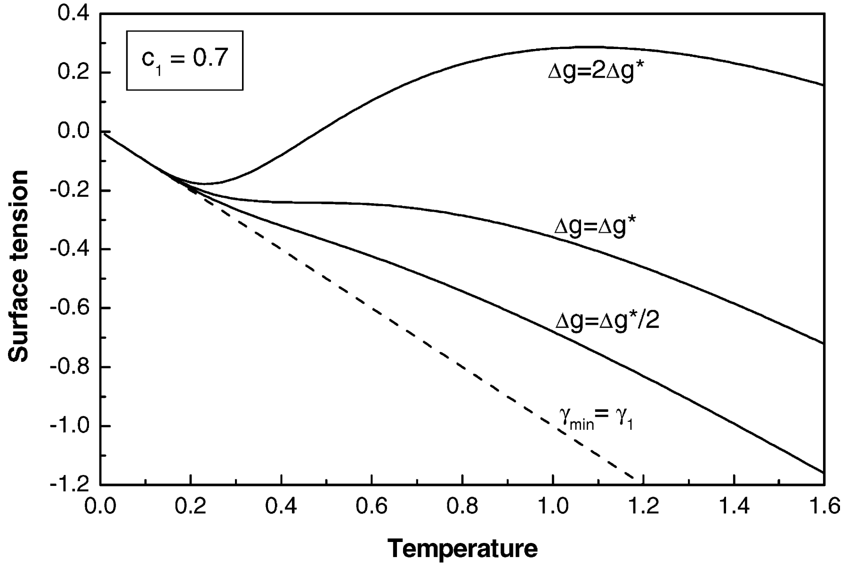

Fig. 1. Surface tension of a binary alloy as a function of temperature in dimensionless units. Curves are plotted for $c_A = 0.7$. Dashed curve, $\gamma_{\min}$, corresponds to the surface tension of component A. The other curves correspond to $\Delta g = 0.5\Delta g^*$, $\Delta g = \Delta g^*$, and $\Delta g = 2\Delta g^*$ where Δg^* is the threshold value for the occurrence of extrema.

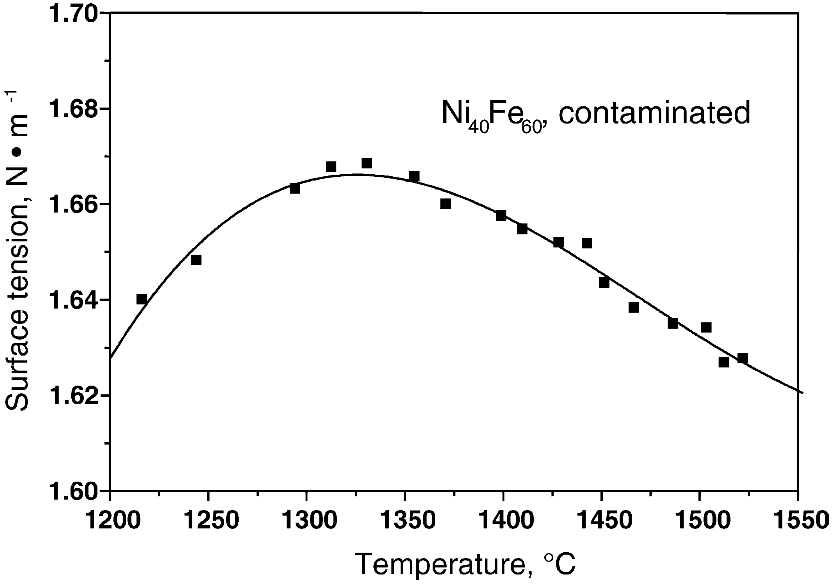

Fig. 2. Surface tension of a $Ni_{40}Fe_{60}$ alloy contaminated by oxygen.

has not been reported for metallic systems. This may be due to the fact that the temperature of the minimum is so low, that the sample solidifies before it reaches that temperature.

3. COMPOUND FORMATION

As before, we assume component A to be surface active, i.e., $\gamma_A < \gamma_B$ and $S_0 > 1$. The surface segregation factor S_0 is the ratio between the energy gained by surface segregation and the thermal energy. The idea is to modify this factor by taking into account the fact that some of the surface-active atoms may be bound in clusters. For these, the energy gain by surface segregation must include the energy required to break a cluster of the form $A_n B_m$. Consequently, we replace S_0 by S_{AB};

$$S_{AB} = e^{\frac{A(\gamma_B - \gamma_A) - f(n+m)c_A^n c_B^m}{RT}} \tag{14}$$

Here f is the molar binding energy of the cluster. The factor $(n + m)$ ensures that f remains independent of cluster size. The factor $c_A^n c_B^m$ describes the probability for such a cluster. The maximum probability occurs at

$$c_A^{\max} = \frac{n}{n+m} \tag{15}$$

This means that the deviation from ideal behavior is largest at the concentration of the intermetallic phase. Inserting Eq. (14) into Eq. (1), and Eq. (1) into Eq. (3), we finally obtain our model;

$$\gamma = \frac{\gamma_A c_A}{c_A + c_B e^{-\frac{A(\gamma_B-\gamma_A)-f(n+m)c_A^n c_B^m}{RT}}} + \frac{\gamma_B c_B}{c_B + c_A e^{\frac{A(\gamma_B-\gamma_A)-f(n+m)c_A^n c_B^m}{RT}}} \tag{16}$$

In order to get a feeling for the behavior of the model, we have plotted Eq. (16) in Fig. 3 for three different cases: A_3B_1, AB, A_1B_3, as a function of concentration c_B. We have chosen $\gamma_A = 1, \gamma_B = 2, A\gamma_A/(RT) = 1$, and $f/(RT) = 5$ for all three cases. For comparison, the ideal solution model ($f = 0$) is also shown. Surface tension values below the diagonal, $c_A\gamma_A + c_B\gamma_B$, correspond to surface segregation; values above it result

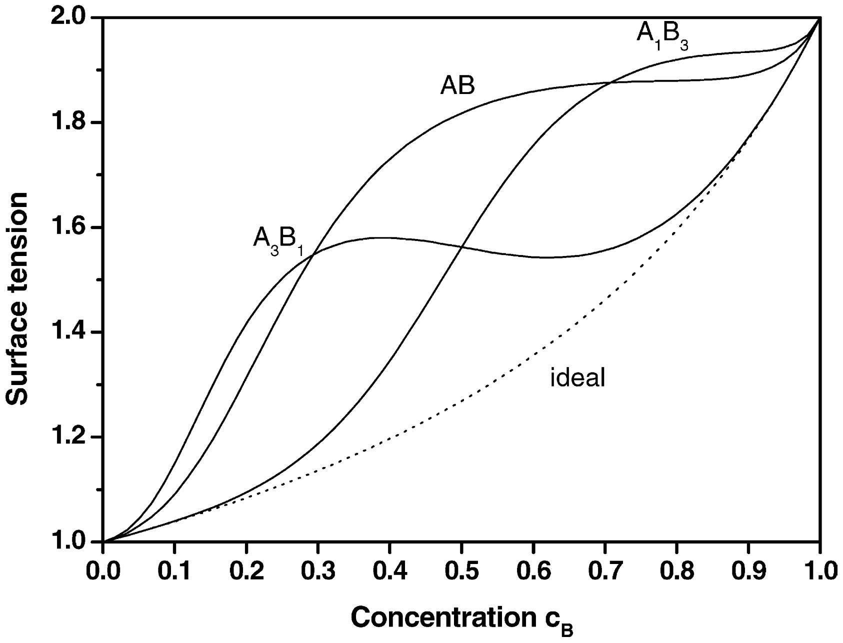

Fig. 3. Surface tension of a hypothetical binary alloy as a function of concentration. Dotted line corresponds to the ideal solution model, and full lines represent the present model, assuming compounds of the form A_1B_3, AB, and A_3B_1. Model parameters are the same for all three curves.

from surface depletion of component A. Whereas the ideal solution model predicts surface segregation for all concentrations, the present model is indeed capable of describing surface depletion near the intermetallic composition.

To check the model against a real system, we have chosen Ni-Al, where experimental data are available [10, 11]. The Ni-Al system displays several intermetallic phases in the solid [12], and one has to make a choice of which one is to be modeled. Obviously, this is the one with the highest binding energy, i.e., with the highest liquidus temperature in the phase diagram. In the case of the Ni-Al system, this is $Ni_{50}Al_{50}$. Figure 4 shows the experimental data and our fit using Eq. (16) with $n = m = 1$. The fit was performed using the Levenberg–Marquardt algorithm and resulted in the following values of the fit parameters: $\gamma_{Al} = 0.738\,\mathrm{N\,m^{-1}}$, $\gamma_{Ni} = 1.725\,\mathrm{N\,m^{-1}}$, $\gamma_{Al}A/(\mathrm{R}T) = 1.268$, and $f/(\mathrm{R}T) = 5.334$. As can be seen, the fit is excellent.

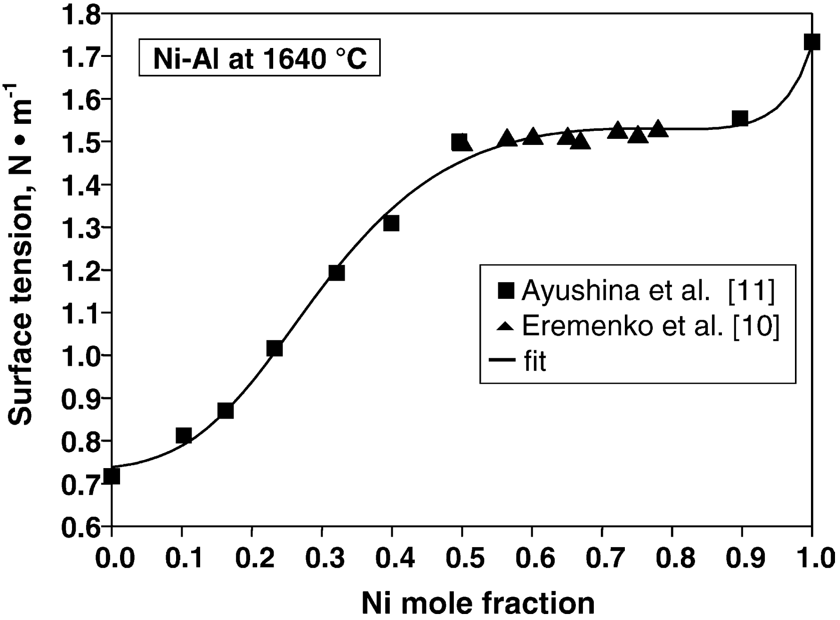

Fig. 4. Surface tension of the Ni-Al system at 1640°C. Open squares are data from Eremenko et al. [10], open triangles are data from Ayushina et al. [11], and the full line is a fit with the present model, assuming NiAl clusters.

4. CONCLUSION

In conclusion, the simple models presented here show correctly the gross features of the surface tension of binary alloys. The ideal solution model predicts a sign reversal for the temperature coefficient correctly, and it can handle compound formation, when the probability for cluster formation is built in phenomenologically. It should be stressed that this is a model, not a rigorous theory. Nevertheless, although not intended for this purpose, it fits experimental data surprisingly well. The coefficients determined from fitting have, however, no physical relevance, and can only be used to parameterize experimental data sets.

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