Surface tension of compound forming liquid binary alloys: A simple model

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Surface tension γ of binary liquid alloys has been a subject of numerous publications, with the main emphasis on the role of surface active components. This is the component with the lowest surface tension, which tends to segregate at the surface thereby lowering the total energy of the system. Using Butler's equation [1], the surface tension of alloys can be derived from the surface tension of the pure elements and bulk thermodynamic data of the alloys [2, 3]. In practice, the latter are not always available and one is forced to use models that do not require such inputs, e.g., the ideal solution model [4]. This model predicts surface segregation qualitatively and correctly. Unfortunately, it can only be applied to relatively simple systems with weak interactions. In particular, the ideal solution model cannot explain surface depletion of the surface active species, often observed in systems forming intermetallic compounds in the solid phase. This effect can be understood by assuming that clusters of the intermetallic composition prevail in the liquid phase too. The success of thermodynamic association models [5], which are based on the existence of such clusters, supports this hypothesis. If these clusters exist, they bind the otherwise surface active component, preventing it from segregating at the surface. Consequently, there is a competition between surface segregation and cluster formation, which is controlled by entropy and energy considerations.

In the following we consider a binary alloy A–B, which shows one intermetallic phase in the solid state, of the form $A_{\mathrm{n}}B_{\mathrm{m}}$. We start by writing the surface tension γ of A–B as:

$$\gamma = c_{\mathrm{A}}^{\mathrm{s}}\gamma_{\mathrm{A}} + c_{\mathrm{B}}^{\mathrm{s}}\gamma_{\mathrm{B}} \tag{1}$$

where $\gamma_{\mathrm{A}}, \gamma_{\mathrm{B}}$ are the surface tensions of the two components, and $c_{\mathrm{A}}^{\mathrm{s}}, c_{\mathrm{B}}^{\mathrm{s}}$ are the surface concentrations of the two components. In this equation, two assumptions have clearly been made: (i) It is assumed that equal amounts of the two species A and B create equally large surface areas i.e., the influence of different molar volumes is neglected, and (ii) it is assumed that each atom of a given species contributes the same amount to the surface tension, regardless of its local environment. In other words, the energy of a broken bond of a surface atom is independent of the local structure. Of course, both effects would have to be included in a rigorous theory, but for the sake of simplicity, they are neglected here.

For the surface concentrations the ideal solution model gives:

$$c_{\mathrm{A}}^{\mathrm{s}} = \frac{c_{\mathrm{A}}}{c_{\mathrm{A}} + c_{\mathrm{B}}/S_0}, \quad c_{\mathrm{B}}^{\mathrm{s}} = \frac{c_{\mathrm{B}}}{c_{\mathrm{B}} + c_{\mathrm{A}}S_0} \tag{2}$$

where $c_{\mathrm{A}}, c_{\mathrm{B}}$ are the bulk concentrations of components A and B, and S_0 is the surface segregation factor given by:

$$S_0 = e^{\frac{\mathrm{A}(\gamma_{\mathrm{B}}-\gamma_{\mathrm{A}})}{\mathrm{RT}}} \tag{3}$$

A is the molar surface area [6]: $A = 1.09\ v^{2/3}\ N_{\mathrm{A}}^{1/3}$. $N_{\mathrm{A}} = 6 \times 10^{23}\ (\mathrm{mol})^{-1}$ is Avogadro's constant and R is the gas constant: $R = 8.3$ (Nm/mol K). In the derivation of Equation 2 it has been assumed, as discussed above, that the molar volumes of both components are identical, $v_{\mathrm{A}} = v_{\mathrm{B}} = v$. In practice, v is the effective molar volume and is used as a fitting parameter.

In the following we assume component A to be surface active, i.e., $\gamma_{\mathrm{A}} < \gamma_{\mathrm{B}}$ and $S_0 > 1$. The surface segregation factor 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 be reduced by the energy required to break a cluster of the form $A_{\mathrm{n}}B_{\mathrm{m}}$. Consequently, we replace S_0 by S_{AB}:

$$S_{\mathrm{AB}} = e^{\frac{\mathrm{A}(\gamma_{\mathrm{B}}-\gamma_{\mathrm{A}})-\mathrm{f}(\mathrm{n}+\mathrm{m})\mathrm{c}_{\mathrm{A}}^{\mathrm{n}}\mathrm{c}_{\mathrm{B}}^{\mathrm{m}}}{RT}}. \tag{4}$$

here f represents the molar binding energy of the cluster. The factor $(n + m)$ ensures that f remains independent of cluster size. The factor $c_{\mathrm{A}}^{\mathrm{n}}c_{\mathrm{B}}^{\mathrm{m}}$ describes the probability for such a cluster. The maximum probability occurs at:

$$c_{\mathrm{A}}^{\max} = \frac{n}{n + m}. \tag{5}$$

This means that the deviation from ideal behavior is largest at the concentration of the intermetallic phase.

Inserting Equation 4 into Equation 2, and Equation 2 into Equation 1, we finally obtain our model:

$$\gamma = \frac{\gamma_{\mathrm{A}}c_{\mathrm{A}}}{c_{\mathrm{A}} + c_{\mathrm{B}}e^{-\frac{A(\gamma_{\mathrm{B}}-\gamma_{\mathrm{A}})-f(n+m)c_{\mathrm{A}}^{\mathrm{n}}c_{\mathrm{B}}^{\mathrm{m}}}{\mathrm{RT}}}} + \frac{\gamma_{\mathrm{B}}c_{\mathrm{B}}}{c_{\mathrm{B}} + c_{\mathrm{A}}e^{\frac{A(\gamma_{\mathrm{B}}-\gamma_{\mathrm{A}})-f(n+m)c_{\mathrm{A}}^{\mathrm{n}}c_{\mathrm{B}}^{\mathrm{m}}}{\mathrm{RT}}}}. \tag{6}$$

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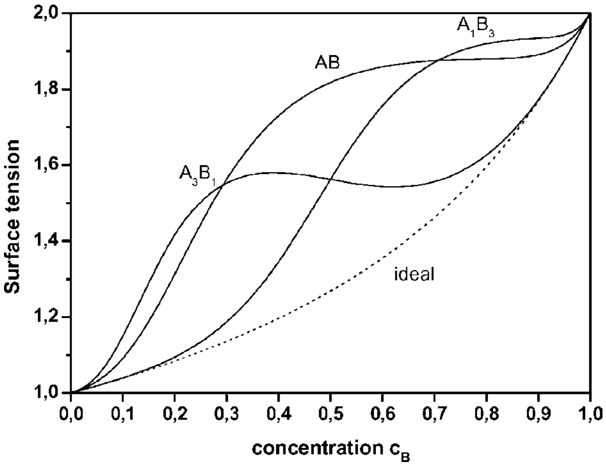

Figure 1 The surface tension of a hypothetical binary alloy as the function of concentration. The dotted line corresponds to the ideal solution model, the full lines represent the present model, assuming compounds of the form A_1B_3, AB, A_3B_1, respectively. The model parameters are the same for all 3 curves.

In order to get a feeling of the behavior of the model we have plotted, Equation 6 in Fig. 1 for three different cases: A_3B_1, AB, and A_1B_3, as a function of concentration c_B. We have chosen $\gamma_A = 1$, $\gamma_B = 2$, $A\gamma_A/RT = 1 f/RT = 5$ 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 from surface depletion of component A. The ideal solution model predicts surface segregation for all concentrations, whereas 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 [7, 8]. The system Ni-Al displays several intermetallic phases in the solid [9], and one has to make a choice of which one is to be modeled, which is obviously, 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 NiAl. Fig. 2 shows both, the experimental data, and our fit using Equation 6. The fit was performed using the Levenberg–Marquardt algorithm and resulted in following values of the fit parameters: $\gamma_{Al} = 0.738$ N/m, $\gamma_{Ni} = 1.725$ N/m, $\gamma_{Al}A/RT = 1.268$, $f/RT = 5.334$.

In summary, the proposed model helps to understand the effect of compound formation on the surface tension of a liquid alloy. It fits existing data surprisingly well.

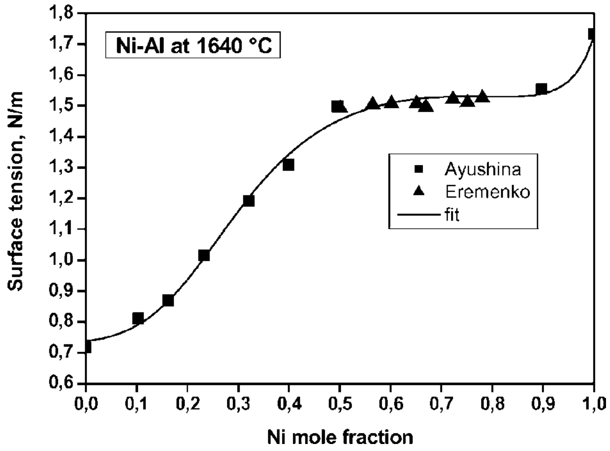

Figure 2 The surface tension of the Ni-Al system at 1640 °C. Squares are data from Eremenko [7], triangles are data from Ayushina [8], the full line is a fit with the present model, assuming NiAl clusters.

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