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Quantitative Prediction of Surface Segregation

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An assessment has been made of the 32 available equilibrium measurements for surface segregation in substitutional pure binary alloy systems. These measurements have been analyzed in relation to the various terms proposed for the free energy of segregation. Three terms have been selected, the surface energies of the constituents, their enthalpy of mixing and a term related to the release of strain energy on segregation. A least squares fitting of the measurements to the three terms shows that some of the current theories are valid but that the importance of each term may not have been correctly emphasized. The assessment leads to a simple predictive relationship, valid for both dilute and concentrated alloy systems, which correlates with the experimental results over the range of free energies of segregation from −80 to 20 kJ/mol, with a standard deviation of less than 9 kJ/mol.

INTRODUCTION

The equilibrium segregation of major and minor constituents to interfaces in materials is of considerable and often dominating importance in their mechanical and kinetic behavior (*1*). Segregation to grain boundary interfaces in materials can cause failures of steel components, associated with the general phenomena of temper brittleness, creep embrittlement, and some forms of intergranular stress corrosion cracking. To understand these problems, general theories of grain boundary segregation, in binary and ternary systems, have been developed in recent years (*2, 3*). In binary systems the accuracy of general evaluations of the free energy of grain boundary segregation is very good and has a standard deviation of only 6 kJ/mol over the range −5 to −80 kJ/mol. The prediction requires simply the inverse of the atomic solid solubility, obtained from the equilibrium phase diagram (*4*). General evaluations for ternary systems are not available but Guttmann's theory (*5*), involving nearest neighbor bond terms in the regular solution approximation, can be used with high accuracy (*6*) in the description of metallurgical phenomena.

The equilibrium segregation to free surfaces, also important in metallurgical fracture phenomena, has not received as much attention and no general compilation exists, except for the early work, involving surface energy measurements, reviewed by Hondros and McLean (*7*). For many materials properties the segregating propensities of all constituents, especially the highly active trace impurities, are required. However, in other fields, such as catalysis, attention is focused on the segregation of one of the constituents of relatively concentrated substitutional binary metal systems. In this paper only this simpler problem of segregation in substitutional binary systems will be analyzed.

In the early work, Hondros and McLean (*7*) correlated the surface activity of solutes

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in dilute binary systems first with the atomic misfit of the respective atoms, measured by their difference in Goldschmidt atomic radii, and second with the inverse of the maximum of the solute solid solubility. The surface activities, all derived from surface energy measurements in the temperature range 1100 to 1800 K, exhibited scatters in both correlations equivalent to standard deviations of 22 kJ/mol in the free energies of segregation for energies ranging between −25 and −150 kJ/mol. The temperatures of interest in catalysis and in much metallurgical work, however, extend to greatly lower values. Since Hondros and McLean's analyses, many surface enrichment measurements have been made in this lower temperature range by Auger electron spectroscopy (AES). Also theories have been developed which should allow a correlation to be made with greater accuracy.

A number of assessments of the AES measurements have been made to support schemes for predicting which elements in binary systems will enrich the surface. In the first assessment, Burton and Machlin (*8*) tested the predictions of two theories, one in which the free energies were calculated from the nearest neighbor bond energies derived from sublimation enthalpies, and another which used McLean's (*9*) strain energy release term originally derived for grain boundary segregation. They found that the correlation for the free energies of surface segregation were poor for both theories, for the seven systems in which experimental results were available. They also found both theories poor in predicting which elements would enrich the surface. They then proposed that the enrichment or depletion at the surface would parallel enrichment or depletion of the liquid in equilibrium with the solid at the melting point—the segregant having lower symmetry, lower coordination, and no elastic strain term in both cases. Comparison with experimental results for 16 systems, to decide which elements segregate, showed excellent agreement with this hypothesis. Tsai *et al.* (*10*) later reassessed this correlation using more recent phase diagrams and found the correlation to be poor. They felt that a strain relaxation hypothesis, given by the square of the difference in atomic volumes of the two components of the alloy, should be more appropriate, but that it would be significant only for solute atoms larger than the solvent. This strain relaxation hypothesis gave 14 out of 16 correct predictions for systems which exhibit segregation. For many applications, however, it is not sufficient merely to be able to predict which systems will exhibit segregation; it is necessary to be able to estimate the degree of segregation at the free surface. None of these assessments gave such an estimate.

In the section that follows the terms contributing to the free energy of segregation will be outlined. These are then used to define a correlation with the 32 available surface analysis measurements of equilibrium surface segregation in pure binary systems, in the temperature range 500 to 1000 K, in order to provide the best general estimating procedure with a known estimating error.

THEORY

The basic theory describing surface segregation in both dilute and concentrated binary solutions, and which leads to a quantitative expression for the free energy of segregation, has been given by Williams and Nason (*11*). Using a layer-by-layer model of the surface, and by considering nearest neighbor bonding in the regular solution model, they show that, for the alloy BA, the fractional coverage of the A atoms in the first atom layer, $X_A{}^s$, is given by the Langmuir relation:

$$\frac{X_A{}^s}{1 - X_A{}^s} = \frac{X_A{}^b}{1 - X_A{}^b} \exp\left(\frac{-E}{RT}\right), \quad (1)$$

where $X_A{}^b$ is the bulk molar fraction of A and E is the free energy of segregation. The analysis given by Williams and Nason is expressed more simply by Wynblatt and Ku (*12*) as follows. The free energy of segregation is the energy decrease per mole when one atom of A is removed from the bulk and returned to the surface and an atom of B is transferred in the reverse direction. By summing over all nearest neighbor bonds, with energies (negative values) ϵ_{AA}, ϵ_{AB}, and ϵ_{BB} being assigned to AA, AB, and BB neighbors, respectively, the energy required to remove A from the bulk is:

$$-\left[Z_l\{X_A{}^b\epsilon_{AA} + (1 - X_A{}^b)\epsilon_{AB}\} + 2Z_v\{X_A{}^b\epsilon_{AA} + (1 - X_A{}^b)\epsilon_{AB}\}\right], \qquad (2)$$

where Z_l is the atomic coordination number in the layer and Z_v is the atomic coordination to one of the adjacent layers. The energy required to replace A at the surface is, similarly:

$$Z_l\{X_A{}^s\epsilon_{AA} + (1 - X_A{}^s)\epsilon_{AB}\} + Z_v\{X_A{}^b\epsilon_{AA} + (1 - X_{AB}{}^b)\epsilon_{AB}\}. \qquad (3)$$

By combining Eqs. (2) and (3) and their counterpart for the returning B atoms and using the alloy regular solution parameter:

$$\omega = \epsilon_{AB} - \tfrac{1}{2}(\epsilon_{AA} + \epsilon_{BB}), \qquad (4)$$

the free energy of segregation per atom becomes:

$$\frac{E}{N} = \tfrac{1}{2}Z_v(\epsilon_{BB} - \epsilon_{AA}) + 2\omega\{Z_l(X_A{}^b - X_A{}^s) + Z_v(X_A{}^b - \tfrac{1}{2})\} \qquad (5)$$

where N is Avogadro's number. In Williams and Nason's theory successive layers away from the surface are considered and for nonzero values of ω the composition of the second layer can also differ from that of the bulk. In the present work it is assumed that all of the composition variation occurs in the topmost atom layer. This simplifies the analysis and introduces errors that are negligible compared with the albeit small errors involved elsewhere.

Numerical evaluation of Eq. (5) can proceed in several ways. Following Wynblatt and Ku (*12*) the bond strengths ϵ_{AA} and ϵ_{BB} are best derived from the values of the molar surface energies of the two constituents. At absolute zero these energies may be expressed:

$$\gamma_A = -\tfrac{1}{2}Z_v\epsilon_{AA}N; \quad \gamma_B = -\tfrac{1}{2}Z_v\epsilon_{BB}N. \qquad (6)$$

The alloy parameter ω may be calculated (*13*) from tabulated values of the enthalpy of mixing, H^{m} (*14*):

$$\Omega = N\omega = \frac{H^{\mathrm{m}}}{ZX_A{}^bX_B{}^b}, \qquad (7)$$

where Z is the coordination number. Thus,

$$E = \gamma_A - \gamma_B + 2\Omega\{Z_l(X_A{}^b - X_A{}^s) + Z_v(X_A{}^b - \tfrac{1}{2})\}. \qquad (8)$$

Williams and Nason, in their original paper, evaluate ϵ_{AA} and ϵ_{BB} from the molar sublimation enthalpies:

$$H_A{}^{\mathrm{sub}} = -\tfrac{1}{2}Z\epsilon_{AA}N$$
$$H_B{}^{\mathrm{sub}} = -\tfrac{1}{2}Z\epsilon_{BB}N \qquad (9)$$

so that $(\gamma_A - \gamma_B)$, in Eq. (8), may be replaced by $(Z_v/Z)(H_A{}^{\mathrm{sub}} - H_B{}^{\mathrm{sub}})$. This is likely to be a poorer approximation as an uncertainty in Z_v is now involved and the effect of next nearest neighbors is not incorporated as effectively as in the surface energy term.

In addition to the terms cited above, Burton and Machlin (*8*) and Wynblatt and Ku (*12*) add a strain energy term:

$$\frac{-24\pi KGr_0r_1(r_0 - r_1)^2}{3Kr_1 + 4Gr_0} \qquad (10)$$

where K is the solute bulk modulus, G is the solvent shear modulus, and r_0 and r_1 are the appropriate radii for solvent and solute atoms in their pure states, respectively. Tsai *et al.* (*10*) accept this term but point out that current atomic calculations show there to be no appreciable relaxation of atomic positions about a vacancy, because of the hard core repulsion of nearest neighbor interactions. Thus, they only include relation (10) for solute atoms larger than the solvent atoms and otherwise ignore it.

From the above equations, a dilute solute of low surface energy or low enthalpy of sublimation enriches the surface of a binary alloy. Furthermore, a positive enthalpy of mixing (A–B bonds not preferred) and an excess sized solute atom also enhance the segregation.

COMPARISON OF THEORY AND EXPERIMENT

For the purposes of comparing the experimental measurements with the above theory, and in order to present the results for any given system in as straightforward a manner as possible, only the measurements for dilute alloys need be used. This does not mean that the final conclusions are not applicable to concentrated solutions. It is simply that a more accurate estimate can be made for E in the dilute case, than in the concentrated case, as E itself is segregation dependent, as described by Eq. (8). From a knowledge of the dilute behavior, Eq. (8) allows the behavior in more concentrated systems to be directly determined. From published measurements in binary systems, across the whole composition range, fairly accurate estimates of the surface enrichment factor, $\beta_A{}^s$, given by:

$$\beta_A{}^s = \frac{X_A{}^s}{1 - X_A{}^s} \cdot \frac{1 - X_A{}^b}{X_A{}^b} \qquad (11)$$

can be determined for A dilute in B and similarly for B dilute in A. These two conditions will be denoted as $B(A)$ and $A(B)$, respectively. Thus:

$$\ln \beta_A{}^s = -E/RT \qquad (12)$$

and, in the dilute case, E is reasonably constant.

In many publications surface compositions measured by AES and XPS are calculated directly from bulk element reference spectra (*15*). These compositions are averaged over the electron escape depths, typically one to six atom layers. In assessing the data it is assumed that all the enrichment is confined to the outermost layer and the necessary adjustments can then be made to bulk referenced spectra by using the recommended values of electron inelastic mean free paths (imfp's) from the compilation of Seah and Dench (*16*). This can increase the measured enrichment by a factor of up to 6 over that calculated ignoring the effect of the imfp.

In the above theory the approximations lead to $\gamma_A{}^s = (Z_v/Z)H_A{}^{\text{sub}}$ which, for $Z_v = 3$ and $Z = 12$ as are normally accepted for f.c.c. systems, is a factor 1.5 times that found in practice (*17*, *18*). Thus an unknown factor in the range 0.5 to 1.0 should precede the H^{sub} terms where they are used. A further problem that exists is that good surface energy values are available only for a limited range of elements and experimental inaccuracies are still high (*17*). Analysis shows that surface energies are more closely related to the melting temperature, T^{m} K, than to the sublimation enthalpy. Thus, here the surface energies are calculated from

$$\gamma_A{}^s = 37 T_A{}^{\text{m}} \text{ J/gat.} \qquad (13)$$

and, since T^{m} values are accurately known for nearly all elements, the correlation will be general. The coefficient, 37, varies with the source of the surface energy values but its precise value is not important here. Equations (8), (10), (12), and (13) may be combined to give:

$$\ln \beta_A{}^s = \{U(T_B{}^{\text{m}} - T_A{}^{\text{m}}) + V\Omega + W a_B(a_A - a_B)^2\}/RT \qquad (14)$$

where the coefficients U, V, and W, described below, are to be determined by comparison with experimental measurements. From Eqs. (13) and (8), U should be near 37 and V near unity. a_A and a_B are the atomic sizes of atoms A and B, respectively, and are calculated here in nanometers according to the relation:

$$\rho_A N a_A^3 = 10^{24} A_A \qquad (15)$$

where ρ_A is the bulk density (kg/m^3) and A_A the atomic weight of A. Strictly, of course, these atomic sizes are not those for relation (10). The sizes should be deduced from lattice parameter changes as the solute is introduced to the solvent. These are not always available and so the above simple relation is used. The coefficient W in Eq. (14) is difficult to estimate as part of this term must already appear in the enthalpy of mixing and the presence of the term itself must affect the other terms as discussed later. Also the value of W will depend on a_B and a_A through the atomic size dependence of the moduli K and G. However, in this term, the $(a_A - a_B)^2$ part is the important variable and these other effects will be ignored in this approximation. The first term in Eq. (14) may be replaced by Williams and Nason's $Y(H_B^{\mathrm{sub}} - H_A^{\mathrm{sub}})$ as an alternative.

Least squares fits are applied to the experimental $\ln \beta_A^s$ values (*20–37*) for Eq. (14), and its counterpart with sublimation enthalpies. Values of T_A^{m}, H_A^{sub}, and a_A are taken from standard compilations (*38*) and of H_A^{m} from Hultgren *et al.* (*14*). The only exception to these data is for the atom size of the nonmetallic element phosphorus, in iron, which Gale (*39*) shows to be very different from that in bulk phosphorus. The least squares analysis gives the coefficients U, V, W, and Y and the standard deviations for the scatter of experimental results about the best fit. Part of the scatter is caused by ignoring both the composition of layers other than the first and the entropy of segregation, part is due to experimental error and part because the theory is simply for nearest neighbor bonding in the regular solution approximation. Nevertheless the fits obtained are very good.

Analysis of many functions like Eq. (14) show that the scatter of results increases by a factor between 1.3 and 1.4 if the T^{m} term is replaced by H^{sub}. Thus, in agreement with Wynblatt and Ku (*12*), analysis in terms of surface energies (via T^{m}) is favored. The first analysis tests the validity of Eq. (8) so, in this case, the coefficient W in Eq. (14) is zero. The least squares description gives a relation in terms of T^{m}. If this is replaced by the surface energy term using Eq. (13), the description becomes:

$$\ln \beta_A^s = \{1.02(\gamma_B^s - \gamma_A^s) + 0.36\Omega\}/RT \pm 2.23. \qquad (16)$$

The result of a near unity coefficient for the surface energy term strongly supports the general approach leading to Eq. (8). Analyses can also be made using a recent compilation of actual surface energy values (*40*) directly instead of working via T^{m}. The above equation is again supported but the scatter of the experimental results around the best fit is double that obtained above. Thus, here and in later equations where the surface energy terms are written it should be noted that they are always derived from the T^{m} values via Eq. (13). Not too much importance should be attached to the precise value of the coefficient of Ω in Eq. (16) as this term is typically only 4% of the first term.

The strain term, shown in Eq. (14), may now be added, giving the least squares description:

$$\ln \beta_A^s = \{0.67(\gamma_B^s - \gamma_A^s) + 1.97\Omega + 43.3 \cdot 10^6 a_B(a_A - a_B)^2\}/RT \pm 1.44 \qquad (17)$$

where the coefficient of the strain term is in J(nm)$^{-3}$. The addition of the strain term has almost halved the scatter and numerically contributes as strongly as the surface energy term to the free energy of segregation.

The contribution of the strain release term could be written directly into Williams and Nason's approach and would involve changes in the coordination numbers and bond energies with site position. It would also require a modification in Ω as the enthalpy of mixing must contain strain terms. In this way the introduction of the explicit strain term causes a lowering of the surface energy coefficient.

The correlation of Eq. (17) with the 32 experimental results is very good, with the standard deviation of the prediction giving an error of less than 10 kJ/mol over a range of free energies of segregation from −80 to +20 kJ/mol. The quality of the correlation for the strain contribution is interesting. This correlation may be considered using the function:

$$\ln D = \ln \beta_A{}^s(\text{expt}) - \{0.67(\gamma_B{}^s - \gamma_A{}^s) + 1.97\Omega\}/RT. \quad (18)$$

The plot of this function against the difference in size of the solute and solvent atoms describes the strain contribution and is shown in Fig. 1. In agreement with the expressions of relation (10) and Eq. (14), the value of $\ln D$ increases with $(a_A - a_B)^2$ for $a_A > a_B$. However, in agreement with the hypothesis of Tsai *et al.*, this strain contribution disappears for $a_A < a_B$.

Thus, to include the hypothesis of Tsai *et al.*, the least squares analysis must now be repeated for Eq. (14) with the strain term only contributing for solute atoms larger than the solvent. Thus:

$$\ln \beta_A{}^s = \{0.64(\gamma_B{}^s - \gamma_A{}^s) + 1.86\Omega + M4.64\cdot 10^7 a_B(a_A - a_B)^2\}/RT \pm 1.29 \quad (19)$$

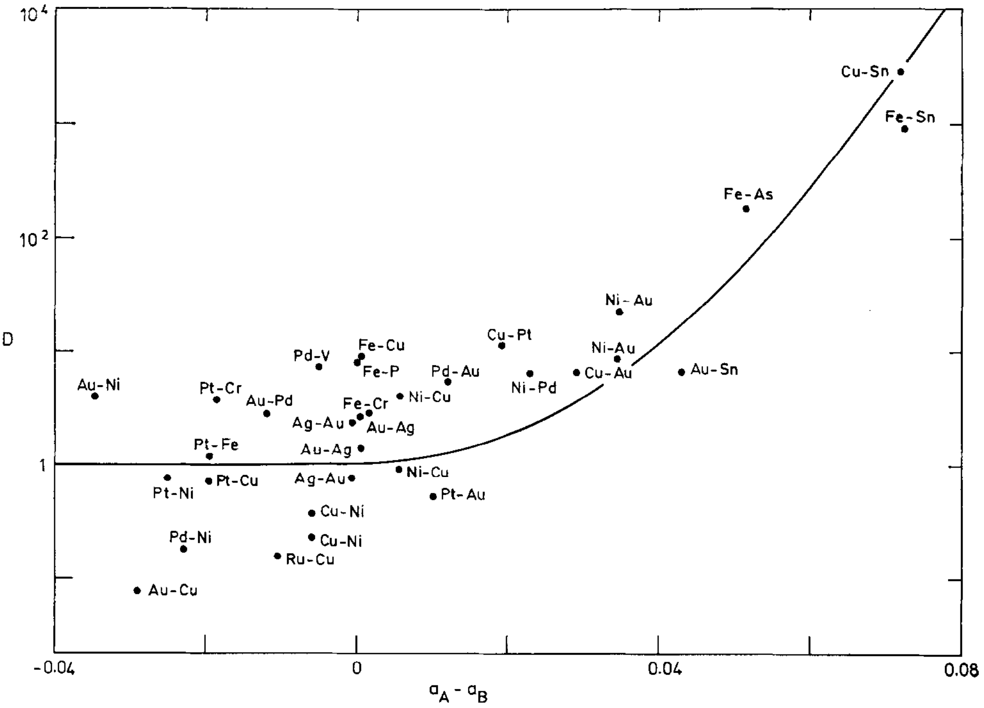

FIG. 1. The variation of D, from Eq. (18), with excess atom size of the solute. The solid line shows the hypothesis of Tsai *et al.* (*10*).

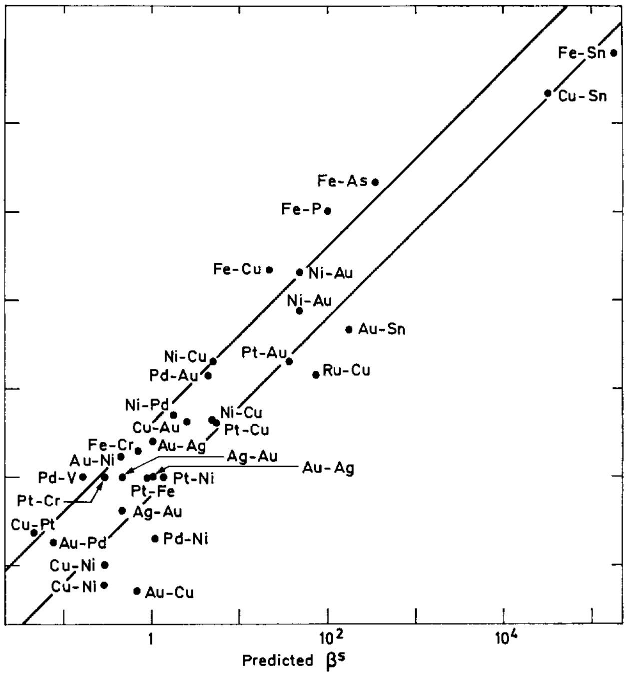

FIG. 2. The relationship of the predicted $\beta_A{}^s$, from Eq. (19), to the experimental measurements. The solid lines show the upper and lower quartiles of the results.

where $M = 1$ for $a_A > a_B$ and $M = 0$ for $a_A < a_B$. The correlation of the experimental results with this final prediction is shown in Fig. 2. Addition of the hypothesis of Tsai *et al.*, has significantly improved the correlation over that expressed in Eq. (17). The scatter of the experimental results about the final prediction has been reduced to a standard deviation of only 8.7 kJ/mol over the range of free energies of segregation from −80 to 20 kJ/mol.

CONCLUSIONS

Experimental measurements of the equilibrium surface enrichment of substitutional binary alloys are approximately described by Williams and Nason's theory with a standard deviation of the free energy of segregation of 15 kJ/mol. Introduction of the simplified strain energy term improves the description. The further constraint of the hypothesis of Tsai *et al.*, that the strain term should apply only for solutes larger than the solvent, is supported by the results and further improves the quality of the prediction to the final result shown by Eq. (19). For the purposes of predictive calculation the final Eq. (19) should be rewritten:

$$\ln \beta_A{}^s = \{24(T_B{}^m - T_A{}^m) + 1.86\Omega + M4.64\cdot 10^7 a_B(a_A - a_B)^2\}/RT \pm 1.29.$$

This relation, which has a standard deviation of only 8.7 kJ/mol over the range of free energies of segregation from −80 to 20 kJ/mol, is currently the most accurate relation for predicting equilibrium surface segregation in substitutional binary systems.

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