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LETTER TO THE EDITORS

Comment on the Prediction of Segregation to Alloy Surfaces

Recently, Burton and Machlin (*1*) suggested that surface segregation is related to the equilibrium distribution, between liquid and solid, of a solute in an alloy. In particular, they proposed the following recipe: (a) If a dilute binary alloy has a melting curve in which the solute *does not* distribute from the solid to the liquid, then the solute *does not* segregate from the solid to the surface (they classify this as a melting curve type a); (b) if a dilute binary alloy has a melting curve in which the solute *does* distribute from the solid to the liquid, the solute *does* segregate from the solid to its surface, *provided* that the separation between the solidus and the liquidus is sufficiently *large* (melting curve type b). If this separation is *small*, the alloy surface will show no segregation (melting curve type b′). No quantitative rule was given to distinguish between melting curves b and b′. With this recipe, Burton and Machlin listed perfect agreement with 16 experimental alloy systems [Table III of Ref. (*1*)].

In attempting to reproduce Table III from Ref. (*1*), we choose to qualify the distinction between melting curve types b and b′ by calculating the segregation coefficients $k = C_L/C_S$ for the various alloy systems at solidus concentration C_S equal to 5 atom% of solute. We used two different publications of alloy phase diagrams (*2*, *3*) for estimating the segregation coefficients, but we favor the ASM publication (*3*) over the one (*2*) used by Burton and Machlin (*1*) because it is more current. In Table 1 we list our estimates for k. We specify the segregation coefficient $k_{bb'}$ that separates melting curve type b from melting curve curve type b′ by optimizing the number of successful predictions using the Burton–Machlin (*1*) scheme. Using the phase diagrams of Ref. (*2*), we find that $k_{bb'} \lesssim 1.6$, and the Burton–Machlin scheme fails for 2 out of 16 alloy systems [Pt(Fe), Pt(Ni)]. Using the more recent phase diagrams in Ref. (*3*), we find that $k_{bb'} \lesssim 1.6$, and the Burton–Machlin (*1*) scheme fails for 5 out of 16 alloy systems [Au(Ag), Fe(Cr), Pd(Au), Pt(Fe), Pt(Ni)]. On the basis of these results, we conclude that the Burton–Machlin scheme may not be useful in predicting segregation to alloy surfaces.

However, we wish to make an interesting observation. It is argued that one of the driving forces for segregation is elastic strain, and that segregation should occur whenever the size difference between the constituents is large, i.e., the driving force for segregation is the lowering of the elastic strain energy in the bulk which arises from lattice mismatch and which is proportional to $(\Delta v_{AB})^2$ = the square of the difference in atomic volumes of the two pure components, A and B (*4*). We note that this relation states that the elastic strain energy is independent of whether Δv_{AB} is greater than or less than zero! This is in contrast to current atomic calculations which show that there is no appreciable relaxation of atomic positions around a *vacancy* (*4*) because of the hard-core repulsion of the nearest neighbor interactions, while outward relaxation of the neighboring solvent atoms around an oversized solute atom may

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TABLE 1

Estimations of $K = C_L/C_S$ (5 atom%) with the Phase Diagrams of Hansen (*2*) and the ASM (*3*)

Solvent (solute)	Hansen (*2*)	Present work	Burton and Machlin (*1*)	ASM (*3*)	Present work	Burton and machlin (*1*)
Au(Ag)	1.6[a]	b	b	~1.0	b′	b
Cu(Au)	1.7	b	b	2.0	b	b
Fe(Cr)	2.3	b	b	~1.0	b′	b
Fe(Sn)	2.0[a]	b	b	2.0[a]	b	b
Fe(Zr)	2.0[a]	b	b	2.0	b	b
Ni(Au)	3.2[a]	b	b	3.0[a]	b	b
Ni(Cu)	2.0[a]	b	b	1.6	b	b
Pd(Ag)	2.0[a]	b	b	2.2	b	b
Pt(Au)	3.2[a]	b	b	3.0[b]	b	b
Pt(Sn)	2.0[a]	b	b	—	b	b
Zr(Fe)	3.0[a]	b	b	2.5	b	b
Ag(Au)	0.5[a]	a	a	~1.0[a]	a	a
Pd(Au)	~1.0[a]	b′	b′	2.2	b	b′
Pt(Cr)	~1.0[a]	b′	b′	~1.0[a]	a	b′
Pt(Fe)	2.7[a]	b	b′	2.5[a]	b	b′
Pt(Ni)	2.7[a]	b	b′	2.4[a]	b	b′

[a] Denotes appreciable uncertainty in either solidus line, liquidus line, or both.

[b] Note error in atomic percentage scale.

be appreciable. In other words, atomic calculations suggest that the elastic strain energy may be appreciably smaller for an undersized solute atom than for an oversized solute atom, even though $|\Delta v_{AB}|$ is the same. We extend this proposition by assuming that, if the solute atom is smaller than the solvent atom, the elastic energy driving force is too small to give rise to surface segregation in a dilute alloy. If the solute atom is larger than the solvent atom, the elastic energy driving force is large enough to give rise to surface segregation in a dilute alloy, i.e., if $\Delta v_{AB} < 0$, no surface segregation; if $\Delta v_{AB} > 0$, surface segregation. Using our recipe, we see from Table 2 that we are successful for 14 out of 16 alloy systems, while bond-breaking theory has 7 failures (*1*) and elastic strain energy theory has 7 failures (*1*).

TABLE 2

Does Segregation Occur?

Solvent (solute)	Experiment[a]	Bond breaking[a]	Elasticity theory[a]	Relaxation hypothesis
Au(Ag)	Y[b]	Y	N	Y
Cu(Au)	Y	N	Y	Y
Fe(Cr)	Y	N	N	Y
Fe(Sn)	Y	Y	Y	Y
Fe(Zr)	Y	N	Y	Y
Ni(Au)	Y	N	Y	Y
Ni(Cu)	Y	Y	N	Y
Pd(Ag)	Y	Y	N	Y
Pt(Au)	Y	Y	N	Y
Pt(Sn)	Y	Y	Y	Y
Zr(Fe)	Y	Y	Y	N
Ag(Au)	N	N	N	N
Pd(Au)	N	N	N	Y
Pt(Cr)	N	Y	N	N
Pt(Fe)	N	Y	Y	N
Pt(Ni)	N	Y	Y	N
No. wrong		7	7	2

[a] From Ref. (*1*).

[b] Y, yes; N, no.

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