

Prediction of Segregation to Alloy Surfaces: A "Hume-Rothery" Size Correlation

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A single parameter γ (\equiv solute diameter/solvent diameter) appears to indicate whether strain (size difference) or quasi-chemical (solution) theories should be used to predict the *existence* of appreciable solute surface segregation from dilute binary metal alloys. For the 16 binary systems considered here, when $|1 - \gamma| > 0.1$, size-difference (strain) theories suffice, and if $0.95 \leq \gamma \leq 1.0$, solution theories should be used. This empirical result may be regarded as a "Hume-Rothery" rule for surfaces.

In binary solid solutions with copper or silver, Hume-Rothery, *et al.* (1) proposed in 1934 that solid solubility would be small if the atomic diameters of the two elements differed by greater than 13 to 14%. Subsequent consideration of other systems led to adoption of 15% as the criterion (2). Pairs of metals exceeding this value could exhibit terminal solid solutions of not more than 5 at.%; i.e., mixtures of higher *average* composition would be expected to separate into two *bulk* phases. This "Hume-Rothery rule" agrees with about 90% of all known binary systems as of 1963 (3).

The appropriate size measure for such comparisons is the distance of closest approach in each pure element phase, d , the ultimate rationale for this choice being that it provides "the best correlation between size and solubility" (2).

As the distortion energy arising from a solute atom at a free surface is less than that in a binary bulk phase, we may expect that strain-driven segregation from a bulk phase to a surface phase will occur with differences in d which are *less* than the "Hume-Rothery rule" for bulk limited

solubility. The total enthalpy of mixing in a binary system includes both elastic strain (size difference) and quasi-chemical (bond breaking) terms (4). Defining $\gamma = d_A/d_B$, where A and B are solvent and solute, respectively, the quasi-chemical terms will be most important for $\gamma \approx 1.0$. The strain energy contribution usually will be largest for γ far from 1.0. Accordingly, we expect there to be intervals of the parameter γ within which only the strain energy or only a solution (bond breaking) theory need be considered in order to predict the *existence* of appreciable surface segregation of the solute.

The data needed for the correlation sought here appear in a 1976 note (5) concerning bases for predicting the existence of surface solute segregation in dilute alloys (Table 1). These data include both recent (1976) and previously unreported results which allow a serious test of any segregation hypothesis.

Tsai *et al.* (13) suggested that an elastic energy criterion alone could suffice, specifically if "the solute atom is larger than the solvent atom, the elastic energy driving

TABLE 1
Comparison of the Predicted and Observed Segregation Behavior in Several Systems^a

Solvent (solute)	Does segregation occur? ^b		
	Experiment	Theory	
		Bond breaking	Size difference
Ag(Au) ^c	N	N	N
Au(Ag) ^d	Y	Y	N
Cu(Au) ^e	Y	N	Y
Fe(Cr) ^f	Y	N	N
Fe(Sn) ^g	Y	Y	Y
Fe(Zr) ^h	Y	N	Y
Ni(Au) ⁱ	Y	Y	Y
Ni(Cu) ^j	Y	Y	N
Pd(Au) ^k	N	N	N
Pd(Ag) ^l	Y	Y	N
Pt(Au) ^m	Y	Y	N
Pt(Cr) ⁿ	N	Y	N
Pt(Fe) ^o	N	Y	Y
Pt(Ni) ^p	N	Y	Y
Pt(Sn) ^q	Y	Y	Y
Zr(Fe) ^r	Y	Y	Y

^a Table II of (5), reprinted with permission.

^b The question asked is "Does segregation of the solute to the solvent surface occur?" and the answer is given as either Yes (Y) or No (N). Summary: Bond breaking is wrong 6 times out of 16. Size difference is wrong 7 times out of 16 (5)

^c G. A. Somorjai and S. H. Overbury, *Surface Sci.* **55**, 209 (1976), and G. C. Nelson, *J. Vac. Sci. Technol.* **13**, 512 (1976).

^d J. M. McDavid and S. C. Fain, *Surface Sci.* **32**, 161 (1975).

^e C. Leygraf, G. Hultquist, S. Ekelund, and J. C. Erickson, *Surface Sci.* **46**, 157 (1974).

^f M. P. Seah and C. Lea, *Phil. Mag.* **31**, 627 (1975).

^g R. S. Polizzotti and J. J. Burton, to be published.

^h J. J. Burton, C. R. Helms, and R. S. Polizzotti, *J. Vac. Sci. Technol.* **13**, 204 (1976), and *J. Chem. Phys.* **65**, 1089 (1976).

ⁱ C. R. Helms and K. Y. Yu, *J. Vac. Sci. Technol.* **12**, 276 (1975), and C. R. Helms, *J. Catal.* **36**, 114 (1975).

^j B. J. Wood and H. Wise, *Surface Sci.* **52**, 151 (1975).

^k J. A. Schwartz, R. S. Polizzotti, and J. J. Burton, to be published.

^l R. Bouwman, L. H. Toneman, and A. A. Holscher, *Surface Sci.* **35**, 8 (1973).

^m G. A. Somorjai and S. H. Overbury, *Surface Sci.* **55**, 209 (1976).

ⁿ J. J. Burton and R. S. Polizzotti, to be published.

force is large enough to give rise to surface segregation in a dilute alloy," and for the converse case, no segregation is expected. This presumption gives nearly 90% agreement with the earlier table. This correlation is unsatisfying because it does not clearly suggest the underlying cause which drives segregation. For example, this elastic argument proposes copper segregation from a nickel-rich alloy because Cu has a lattice parameter 3% larger than that for Ni. Yet Wynblatt and Ku (15) calculate an

alloy interaction contribution three times larger than the strain term for Cu/Ni and a surface tension difference about 15 times larger. Accordingly, solution theory (surface tension and alloy interaction terms) rather than strain should predict Cu/Ni behavior.

We now seek a plausible physically based correlation. In Table 2, the alloys of the first table are reordered according to the value of γ , calculated from appropriate d values (12). In a range where strain energy should be least, $0.95 \leq \gamma \leq 1.0$, the solution (bond breaking) model correctly predicts segregation or the lack thereof for five alloys [(\checkmark) correct, (X) incorrect], Fe(Cr) being the only apparent exception. Similarly, for situations suggesting considerable lattice strain, i.e., for $\gamma \leq 0.89$ or $\gamma \geq 1.11$, six of eight examples appear to be correct. Let us reexamine these three apparent exceptions.

TABLE 2^a

Solvent (solute)	Bond breaking	Size difference	$\gamma = \frac{d_{\text{solvent}}}{d_{\text{solute}}}$
Fe(Zr)	N(X)	Y(\checkmark)	0.78
Ni(Au)	Y(\checkmark)	Y(\checkmark)	0.86
Fe(Sn)	Y(\checkmark)	Y(\checkmark)	0.88 ^{b,c}
Cu(Au)	N(X)	Y(\checkmark)	0.89
Pd(Ag)	Y(\checkmark)	N(X)	0.95
Pd(Au)	N(\checkmark)	N(\checkmark)	0.96
Pt(Au)	Y(\checkmark)	N(X)	0.96
Ni(Cu)	Y(\checkmark)	N(X)	0.97
Pt(Sn)	Y(\checkmark)	Y(\checkmark)	0.99 ^b
Fe(Cr)	N(X)	N(X)	0.99 ^c
Ag(Au)	N(\checkmark)	N(\checkmark)	1.0
Au(Ag)	Y(\checkmark)	N(X)	1.0
Pt(Ni)	Y(X)	Y(X)	1.11
Pt(Cr)	Y(X)	N(\checkmark)	1.11
Pt(Fe)	Y(X)	Y(X)	1.12 ^c
Zr(Fe)	Y(\checkmark)	Y(\checkmark)	1.28

^a Correct results in "bond breaking" column and "size difference" column are noted in parentheses. (Correct (\checkmark), incorrect (X)).

^b Distance of closest approach of gray tin used = 2.810 Å, while for bulk white tin, $d = 3.022$ Å, in Pt₃Sn, d (Pt-Sn) = 2.81 Å (see van Santen and Sachtler, *J. Catal.* **33**, 202 (1974), and Hansen, M., "Constitution of Binary Alloys, McGraw-Hill, 1965). Hume-Rothery *et al.* (2, p. 125) argue that the diameter of the more ionized form of an element is the appropriate one; this would be gray tin.

^c Fe value of d assumed is 2.48 Å (bcc). The γ fcc form appears between 911 and 1392°C; inclusion of $d(\gamma) = 2.579$ Å in the Pt(Fe) and Zr(Fe) examples would change γ to 1.078 and 1.23, respectively.

1. The Fe(Cr) system referenced in (5) refers to segregation studies on $\text{Fe}_{0.84}\text{Cr}_{0.16}$ single crystals exposing (100) or (110) bcc faces (5). The authors of (5) reported clear segregation of Cr to Fe surfaces. Based upon a simple solution (bond breaking) argument, the same authors predict some segregation of Cr to an Fe surface; e.g., at 900 K, the equilibrium composition of the top layer is predicted to be 36% Cr and 51% Cr for the (110) and (100) surfaces of the $\text{Fe}_{0.84}\text{Cr}_{0.16}$ crystals used. Thus, the entry in Table 1 under "bond breaking" should read $Y(\checkmark)$, given that these experiments were regarded in (5) as exhibiting segregation.

2. Predicted heats of segregation for seven binary systems estimated from a bond breaking and from a strain energy approach were compared with reported experimental values in Ref. (5); these data are repeated in Table 3. The values of Q (experiment) and Q (calculation) are quite close for the size difference column in the case of Pt(Ni), Pt(Cr), and Pt(Au). The authors assumed that the "size-difference theory predicts segregation for size differences of greater than about 10%, which would imply a heat of segregation of about 4 kcal/mole in a typical system" (5). Given the approximate agreement between the experimental and calcu-

TABLE 3^a

Solvent (solute)	Experiment	Theory	
		Bond breaking	Size difference
Ni(Au) ^b	12	4	9
Zr(Fe) ^c	17	12	9
Fe(Zr) ^c	>30	-12	20
Pt(Ni) ^d	0	8	5
Pt(Fe) ^d	0	9	4
Pt(Cr) ^d	0	10	2
Pt(Au) ^e	>10	12	0

^a From (5), reprinted with permission.

^b J. J. Burton, C. R. Helms, and R. S. Polizzotti, *J. Vac. Sci. Technol.* 13, 204 (1976).

^c R. S. Polizzotti and J. J. Burton, to be published.

^d J. J. Burton and R. S. Polizzotti, to be published.

^e J. A. Schwarz, R. S. Polizzotti, and J. J. Burton to be published.

TABLE 4

Solvent (solute)	Bond breaking	Size difference
Fe(Zr)		$Y(\checkmark)$
Ni(Au)		$Y(\checkmark)$
Cu(Au)		$Y(\checkmark)$
Fe(Sn)		$Y(\checkmark)$
Pd(Ag)	$Y(\checkmark)$	} $\gamma < 0.9$
Pd(Au)	$N(\checkmark)$	
Pt(Au)	$Y(\checkmark)$	
Ni(Cu)	$Y(\checkmark)$	
Pt(Sn)	$Y(\checkmark)$	} $0.95 \leq \gamma \leq 1.0$
Fe(Cr)	$Y(\checkmark)$	
Ag(Au)	$N(\checkmark)$	
Au(Ag)	$Y(\checkmark)$	
Pt(Ni)		
Pt(Cr)		$N(\checkmark)$
Pt(Fe)		$N(\checkmark)$
Zr(Fe)		$Y(\checkmark)$

lated Q values for the size-difference approach, the *lack of segregation* observed in the systems Pt(Ni) and Pt(Fe) and the *segregation* observed with Ni(Au) and Zr(Fe) suggest that this assumption should be modified to read: "For $|1 - \gamma| > 0.1$, the size-difference theory predicts segregation for $Q_{SD} \geq 9$ kcal/mole, whereas alloys with $Q_{SD} \leq 5$ kcal/mole will not exhibit appreciable segregation from dilute solution." Note that we leave the original size-difference assumption unchanged. Application of this modified assumption to Table 2 would change the size-difference entries for Pt(Ni) and Pt(Fe) to $N(\checkmark)$ and $N(\checkmark)$.

Incorporating these changes for Fe(Cr), Pt(Fe), and Pt(Ni) results in Table 4.

This final table suggests that the parameter γ provides a simple guide which indicates whether a strain or a solution theory ought to be used to predict the existence of appreciable solute segregation to the surface of a binary alloy:

For $|1 - \gamma| > 0.1$, size-difference theories (strain) should be considered.

For $1.0 \geq \gamma \geq 0.95$, solution theories suffice.

For example, the most widely studied binary system, copper-nickel, is expected to be usefully approached with a solution theory (7). Similar solution analysis of

dilute Ni(Au) [$\gamma = 1.555$] or Au(Ni) [$\gamma = 0.866$] would appear inappropriate, since Table 4 suggests that strain considerations would dominate (the experimental demonstration of modest short-range ordering (8) in Au-Ni alloys was used earlier to argue that here " ΔH_m is probably composed principally of strain energy" (9)).

The size differences between first-row versus second- and third-row transition and group IB elements are significant, whereas within either family such differences are small. Table 4 suggests that dilute alloys formed from one of the elements (Cr, Fe, Co, Ni, Cu) and one among (Zr, Pd, Ag, Pt, Au) may be predominantly governed by strain. Binary dilute alloys with both elements from either group apparently may be approached with an appropriate solution theory¹.

The correlation proposed here may have difficulty with borderline cases of γ , for which strain and quasi-chemical contributions may be about equal. A unified segregation model, including pure component surface energies, alloy interactions, and solute strain energy has been examined by Wynblatt and Ku (14-16). Such complete theoretical approaches are needed when neither strain nor solution influences alone are dominant. Fortunately, such borderline situations in catalysis may be infrequent for the transition metal systems discussed in the preceding paragraph.

As further fundamental research with binary alloys is published, refinements to Table 4 may be expected. The requirements for experiments comparable to these data

¹ Related support for this approach derives from grain boundary studies. With a small lattice difference between cobalt and copper, the surface tension between dilute copper-cobalt solutions and cobalt rich precipitates therein appears reasonably estimated from a quasi-chemical theory (11).

are cited elsewhere (10); the two most demanding criteria are the following:

- (i) measurement at sufficiently high T that the surface and bulk are equilibrated;
- (ii) avoidance of selective evaporation of solute from surface.

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