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Surface Segregation: A Comparison of Models and Results

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It is well established that the surface composition of a metal alloy may differ markedly from that of the bulk. Theoretical treatments of this phenomenon have been mostly based on models for regular or related solutions. Experimentalists have reported a large body of surface composition data, mostly from the electron spectroscopies. Comparison of these results with the predictions of the models is appropriate to indicate potentially fruitful directions for future work. Though general agreement between theory and experiment is good, quantitative correlation has been hampered by inadequate model calculations, clouded experimentation, and difficult-to-interpret experimental results. Extension of the quasichemical model and inclusion of strain effects improves correlations with previously reported data. Comparing the results of such improved calculations with the sampling capability of surface elemental analysis techniques shows that the relationship between the two is not simple and can be fully elucidated only in some instances.

Metal alloys have long been of interest to catalyst researchers; they are the subject of many experimental studies and a recent review (*1*). Practical catalyst users have also been interested in them as a route to more effective catalysts and a way to anticipate the effect of inevitable metal feedstock impurities. Traditional alloy studies have used chemisorption and chemical reactions; these have been strongly supplemented in the last decade by a variety of direct surface analytical techniques to produce an extensive literature. Theoretical models have been proposed to account for the relationship between surface and bulk composition and structure in metal alloys. These treatments have shed some light on earlier observations of catalytic activity, but are themselves the subject of considerable controversy. Our purpose here is to examine these treatments, to propose remedies for some of the problems which have been uncovered, and to speculate about our future progress as it may be useful to catalysis by alloys.

Let us begin by examining how the various models treat the surface segregation problem and testing their validity where possible. At the conceptual level, the surface segregation problem is not hard. Atoms at the surface of a metal are missing the bonds that would connect them to the next layer of atoms above if they were in the bulk. We may imagine that this surface was created by breaking the bonds across a plane in a metal crystal, so that the surface free energy consists of the energy to break the bonds and the entropy gained by the surface atoms. In an alloy crystal with atoms of two different elements, putting the atoms with the weaker bonds

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at the surface reduces the energy required to form it, creating a driving force for segregation. This saving is partly offset by the decreased randomness of the crystal when the atoms of one component are localized on the surface, and may be decreased further or increased by the concomitant change in the number of bonds between like and unlike atoms. Finally, atoms of different elements are usually not the same size so that strain energy may make a significant contribution as well. Thus the contributions to be considered include surface free energy (G_s), mixing enthalpy (H_m), mixing entropy (S_m), and strain energy (E_e). The models (*2–8, 62–66*) differ in their treatment of these contributions to obtain a free energy for the system and thereby calculate the surface composition.

1. SURFACE ENERGY

The simplest model for a free surface is a crystal in which atoms are bonded to nearest neighbors only, so that the surface consists of a layer of atoms from which the neighbors have been removed on one side. Then in the fcc structure with 12 nearest neighbors, the energy needed to remove three of them to create a (111) surface is one-fourth of the energy to break all the bonds:

$$H_s = 0.25 H_{at} \qquad (1)$$

where H_{at} is the atomization enthalpy. Table 1 shows values for surface enthalpy estimated this way agree wiell with experimental values for Group IB metals.

The surface enthalpy contribution to segregation is obtained (*3, 7*) as the difference enthalpies of the segretated and random surfaces. These in turn are obtained by simply summing the contributions from the atoms of each element on the surface; i.e., assuming that surface enthalpies mix ideally. Thus

$$\begin{aligned}\Delta H_s &= 0.25(H_{at}{}^{A} X_s + H_{at}{}^{B}(1 - x_s)) \\ &\quad -0.25(H_{at}{}^{A} x_b + H_{at}{}^{B}(1 - x_b)) \\ &= 0.25(H_{at}{}^{A} - H_{at}{}^{B})(X_s - X_b) \\ &= \Delta H_{at}(X_s - X_b) \qquad (2)\end{aligned}$$

where X_s and X_b are the segregated surface and bulk atom fractions respectively of element A and H_{at} the atomization enthalpy.

The bond breaking models offer no assessment of surface entropy and simply set the surface free energy change accompanying segregation equal to the surface enthalpy change given by Eq. (2). This is equivalent to assuming the surface entropies of metals of interest are all equal conditions of interest so that there is no significant change accompanying segregation. If the change in vibrational modes dominates the entropy change upon moving an atom to the surface, then the vibrational part of the specific heat should be nearly the same if the surface entropies are the same. This is indeed approximately true for copper and the precious metals (*31*), suggesting that ignoring the entropy is not unreasonable.

Table 2 presents values of the atomization enthalpy difference for several alloy

TABLE 1

Surface Thermodynamic Values[a]

Element	H_s (Calc)$^{(1)}$	H_s (Exptl)	G_s (Exptl)	H_s/G_s (Exptl)	Reference
Cu	2471	2350	1650	0.70	(*14*)
Ag	1631	1678	1140	0.68	(*15*)
Au	2122	2006	1400	0.70	(*16*)

[a] ergs/cm^2.

TABLE 2

Vaporization Enthalpy Differences[a]

Alloy system	Ag–Au	Ag–Pd	Au–Cu	Au–Ni	Cu–Ni	Cu–Pd	Cu–Pt	Ni–Pd	Ni–Pt
Hultgren *et al.* (1973) (*12*)	20,100	22,100	7,500	14,800	21,940	9,140	54,140	12,800	32,200
Hultgren *et al.* *et al.* (1963) (*18*)	19,200	16,230	6,440	15,370	21,810	3,470	54,110	18,340	32,300
Brewer (1965) (*19*)	18,900	22,600	6,200	15,500	21,700	9,900	54,100	11,800	32,400
Smithells (1962) (*20*)	24,900	—	9,000	—	—	—	53,100	—	—
Smithells (1967, 1976) (*21, 22*)	24,900	24,500	9,000	12,000	21,100	8,600	51,500	12,500	30,400
Kubachewski *et al.* (1967) (*23*)	22,600	22,100	9,800	12,100	21,900	9,400	49,500	12,500	27,600
Wagman *et al.* (1969) (*24*)	19,500	22,200	6,600	15,200	21,800	9,500	54,200	12,300	32,400

[a] cal/g-atom.

systems taken from seven different compilations. Although agreement is excellent for Cu–Ni, discrepancies of the order of 25% are not uncommon. Such uncertainties translate into uncertainties in the calculated surface composition at a worse than linear rate.

Alternatively the surface free energy can be approached through the surface tension; an element which would reduce the surface tension would be expected to segregate to the surface (*9*). Direct measurements of the surface tension of solids are notoriously difficult, so that it is attractive to obtain values from some other quantity which is more accessible to experiment. Such a relationship has been proposed (*4*, *17*) between surface tension and atomization enthalpy:

$$\sigma_{\rm m} = 0.16 H_{\rm at} \tag{3}$$

where surface energy $\sigma_{\rm m}$ is expressed on a molar, rather than area, basis. The surface entropy is included in the surface tension, but not in the atomization enthalpy, as noted earlier. Comparing Eqs. (1) and (3) and noting that $G_{\rm s} = \sigma_{\rm m}$ shows that this is equivalent to approximating the surface entropy by 0.09 $H_{\rm at}/T$. For this to be valid $H_{\rm s}/G_{\rm s}$ should be about 0.64; Table 1 shows that this is indeed true for the IB metals within the claimed 8% certainty. However, it suggests that the surface tension might have a strong temperature dependence, which is not in fact reported (*4*).

The surface tension of the alloy in its random and segregated states is obtained by assuming that the contribution of each element can be summed according to ideal mixing. Though reasonable for liquids, few experimental data are available to test this proposal for solid metal alloys. Further, if the elements comprising the alloy have appreciably different sizes, they will occupy different areas on the surface so that the total area of the alloy surface will be a function of composition and a strain term may appear in the surface tensions. Strain effects have not been treated in the

TABLE 3

Comparison of Mixing and Surface Contributions[a,b]

System	$\frac{3\overline{H}_{\rm m}}{4}$	$\frac{\Delta H}{4}$
Ag–Au	2553	5025
Ag–Pd	4624	5525
Au–Cu	2217	1875
Au–Ni	4623	3700
Cu–Ni	1434	5485
Cu–Pd	6099	2353
Cu–Pt	5133	13535
Ni–Pd	745	3200

[a] cal/g-atom.

[b] Data from Refs. (*12*) and (*13*).

context of surface tension, but rather as a separate elastic problem discussed below.

Overall, the surface tension approach suffers from a lack of good experimental data and the difficulty of generating it, especially for alloys. Where the surface tension is estimated from the atomization enthalpy, it differs from the bond-breaking approach in how the surface entropy is estimated. Given these uncertainties, it seems reasonable to use the bond-breaking model [Eq. (2)] to treat the surface energy contribution and add an entropy term if needed.

2. MIXING ENERGY

Mixing effects have been treated by regular solution theory, or directly by a Monte Carlo calculation. The simplest solution shows no heat of mixing since the ideal solution has no mixing enthalpy, where the energy of bonds between unlike atoms is just the average of the bond energy between like atoms. A real alloy can therefore be treated as ideal even when the mixing enthalpy is not zero if it is small compared to the bond-breaking contribution. To compare the two, imagine a dilute solution in which randomly

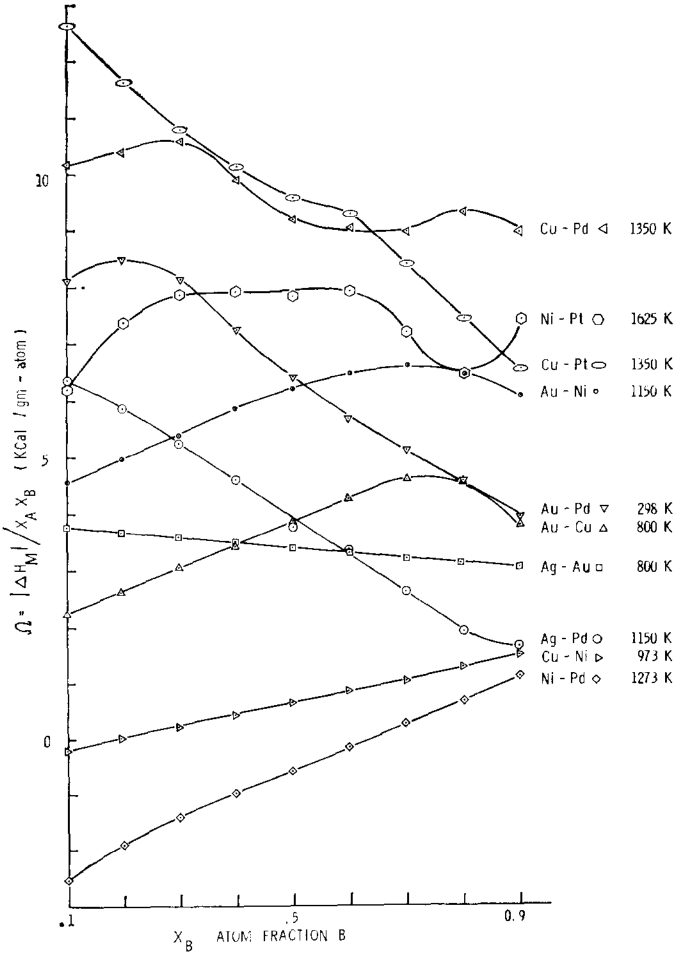

FIG. 1. Composition dependence of regular solution parameters.

distributed solute atoms are moved from the bulk to form a complete monolayer surface. Again considering the (111) surface of an fcc crystal, the atoms now in the surface have only three out of their original twelve unlike atom bonds remaining. Mixing enthalpy has been lost equal to three-fourths of the molar heat of mixing at the bulk concentration, while surface energy given by Eq. (2) has been gained. Table 3 compares these quantities for several alloy systems having complete solid solubility and shows that none of them can be treated as ideal.

Instead, the models treat the metal alloy as a regular solution characterized by three bond energies, one for each of the like atom pairs and one for the unlike. The like atom bond energies are obtained from the atomization enthalpy of the pure elements; the energy for the unlike atom bond is calculated from the experimental mixing enthalpy, H_m, from Ref. (*12*).

$$\Omega = \frac{H_m}{X_A X_B} = H_{AB} - \tfrac{1}{2}(H_{AA} + H_{BB}) \quad (4)$$

For a regular solution the bond energies are not a function of composition so that the quantity Ω should also be composition independent. Figure 1 shows the actual variation of Ω with composition for the alloy systems discussed earlier. Clearly only Ag–Au is close to regular. Evidently then a regular solution treatment cannot be expected to be successful for these alloy

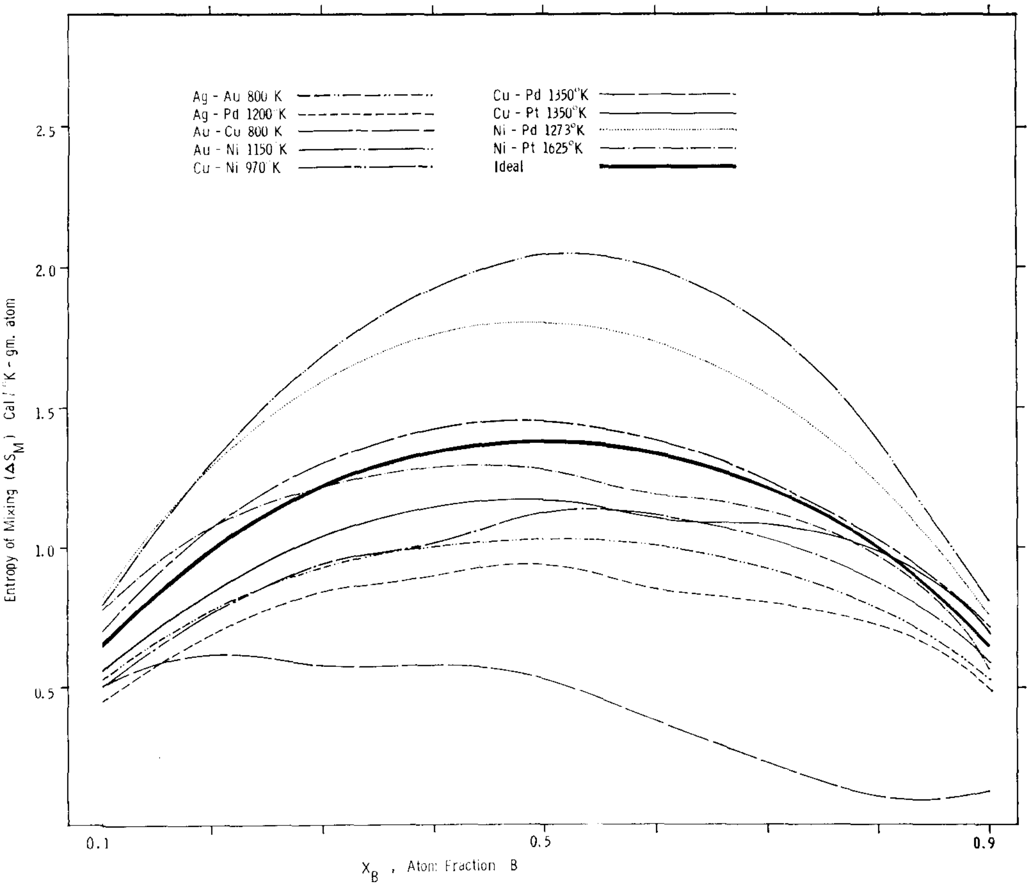

FIG. 2. Composition dependence of mixing entropy.

systems, nor can any other treatment (*11*) which assumes similarly derived constant bond energies. The most reasonable alternative seems to be using the experimentally determined dependence of the mixing enthalpy on composition.

The mixing entropy for both the ideal and regular solutions is treated as simple configurational; the familiar result is:

$$S_m = R(X_A \ln X_A + X_B \ln X_B). \quad (5)$$

Figure 2 compares the mixing entropy so calculated with experimental values (*12*) for the previously discussed alloy systems. Clearly the regular and ideal solution treatment of mixing entropy does not fit most of the alloy systems very well. A Monte Carlo treatment (*11, 62*) which can treat each alloy system individually or a still more sophisticated Kikuchi treatment (*64, 65*) is expected to agree better with experiment, if appropriate bond energies are used. The choice of bond energies is not clear for nonregular alloys and it seems more reasonable, therefore, to use the experimental values, where these are available, as with the mixing enthalpy.

3. SIZE EFFECTS

When an alloy is made from elements having different sized atoms, energy is required to change the size of a site in the solute lattice to accommodate a solvent atom in the bulk. But at the surface, a misfitting atom might be imagined to move outward to reduce lattice strain energy. It has been proposed (*25*) that the elastic energy expended to place a solute atom in the solvent lattice is entirely recovered if the solute atom is moved to the surface. This contribution can be quite large, amounting to nearly three times the atomization enthalpy difference contribution for the Au–Ni system (*25*). The strain energy can be calculated from either the radius misfit (*26*) or the volume misfit (*27*) between the solvent and solute elements. The first gives:

$$E_e = \frac{24\pi K_i G_m r^2 \dfrac{(r_i - r_m)^2}{r_i}}{3K_i + 4G_m} \quad (6)$$

where E_e is the energy required per atom to force a solute atom of radius r_i and bulk modulus K_i into a cavity of initial radius r_m in a crystal with shear modulus G_m. The radius r of the cavity after the solute atom is put in must be measured or obtained by some other calculation.

The second treatment uses the volumes of the elements in their own pure form instead of a final radius and is therefore somewhat more convenient:

$$E_e = \frac{2}{3} \frac{G_m K_i}{3K_i + 4G_m} \frac{(V_i - V_m)^2}{V_m} \quad (7)$$

where V_m and V_i are the atomic volume of the solvent and solute, respectively. A similar expression can be derived for atomic radii (*69*).

These elastic strain models (*60*) should be used cautiously, however, since they assume a dilute solution so that solute–solute effects can be neglected. While the bulk metal in a segregation experiment may indeed be described as a dilute solution, a surface which is almost fully covered by solute clearly cannot. Further, keeping lattice registry with the bulk requires that the solute atoms be strained to the same size as the solute and/or a defect structure be introduced near the surface to accommodate the misfit. While such an analysis is beyond the present scope, it is evident that the strain energy released for a concentrated surface will be less than what is estimated from these simple elastic calculations. Thus the elastic calculations give an upper bound on the magnitude of the strain contribution.

Inspection of Eq. (7) shows that elastic strain contribution is not affected by the sign of the misfit—whether the solute

TABLE 4

Strain Contribution to Segregation Energy Calculated from Eq. (7)[a]

System	E_e	$\frac{\Delta H}{4}$
Ag–Au	0.5	5025
Ag–Pd	<396	5525
Au–Cu	1570	1875
Au–Ni	10900	3700
Cu–Ni	236	5485
Cu–Pd	<612	2353
Cu–Pt	<529	13535
Ni–Pd	<1030	3200
Ni–Pt	<1220	8050

[a] cal/g-atom.

element is larger or smaller than the solvent. Thus this contribution can be expected to always favor segregation of the minority element in a binary alloy, opposing the bond-breaking contribution at one end of the phase diagram and reinforcing it at the other. Such a reversal of segregation has been observed experimentally in the strain-dominated Au–Ni system (*61*).

Table 4 compares strain energy per mole of solute calculated by Eq. (7) with data from Ref. (*18*) to the atomization enthalpy contribution for several systems. Sufficient elastic constant data were not available from some systems and values were calculated assuming that the nonvolume factors in Eq. (7) have a value less than 10^{11} dyn/cm^2; they are shown as "less than" in Table 4. It appears that the strain contribution may be significant for Au–Cu, Au–Ni, and Ni–Pd. It is not clear how to incorporate this contribution when a substantial concentration of the solute is expected at the surface, especially when it acts opposite to atomization enthalpy (e.g., Au–Cu). A more sophisticated approach (*28, 29*) considers the strain-induced change of interatomic potentials near the surface, but still does not address the problem of large-scale misfit on the surface.

Alternatively, the free energy problem can be solved (*57*) by considering d-electron interaction energies between the alloy elements. However, only nearest-neighbor interactions and ideal mixing entropy have been used (*57*). It is not easy to see how this approach voids the difficulties encountered by other similar atomistic models (*2, 7*) discussed above.

Using Gibbs' original concept of a dividing plane between two phases averts the problems of the atomistic models (*63*). This calculated surface concentration does not necessarily refer to the first monolayer of atoms, but rather to the total accumulation of solute in the region altered by the presence of the other phase nearby. It is therefore difficult to know how to compare it to first monolayer calculations from other models without assuming, say, that segregation is limited to the first monolayer.

The free energy problem may be avoided entirely by simply attempting to correlate observations of surface segregation with some other more readily observed phenomenon, such as melting behavior (*58, 68*). Such correlations are interesting, but unsatisfying in that they at best predict the direction but not the extent of segregation.

It seems then that a reasonable model to calculate surface segregation to a perfect (111) vacuum surface of an n-layer alloy slab can be based on competition between enthalpy gain at the surface and mixing energy change in the interior by maximizing

$$\Delta G = \sum^{n} H_{\mathrm{mix}}(X_{\mathrm{a}i}) - TS_{\mathrm{mix}}(X_{\mathrm{a}i}) - \frac{\Delta H_{\mathrm{at}}}{4} X_1 - n(H_{\mathrm{mix}}(X_{\mathrm{b}}) - TS_{\mathrm{mix}}(X_{\mathrm{b}})) + \frac{\Delta H_{\mathrm{at}}}{4} X_{\mathrm{b}} \quad (8)$$

where $X_{\mathrm{a}i} = \frac{1}{4}X_{i-1} + \frac{1}{2}X_i + \frac{1}{4}X_{i+1}$ to carry through the assumption of nearest-neighbor bonding. X_i is the concentration of the element having the lower atomization enthalpy in the ith layer. The entropy and enthalpy of mixing must be taken from experimental data obtained in the phase regime(s) which will actually appear during the course of segregation. Note that Eq. (8) contains no adjustable parameters. This "experimental" model, like all the others, suffers from disagreements in the experimental data used for the calculation and offers no way to deal with the strain problem described above. The results of the different models and comparison with observations are presented later.

A real catalyst is, of course, still more complex. A small metal alloy particle has sites at edges and corners where atoms are missing still more of their bonds than their neighbors on a flat surface. This increased loss of coordination can form the basis for quantitative treatment (*2, 3, 7*) of segregation to these sites based on the bond-breaking model, which shows that an atom expected to segregate to a flat surface is expected to segregate still more strongly to any site of still lower coordination. All the difficulties noted earlier for treating flat surfaces complicate this analysis as well. Similarly a small metal particle may not contain enough solute to reach the same surface concentration that would be found on a large slab. All models are able to deal with the effect of finite particle size by applying a conservation of mass constraint to solutions of the free energy problem.

The bonds of surface atoms, represented above as fully served in a vacuum environment, can take part in chemisorption if a gas is present. The bond-breaking models (*3, 7*) add the energy of this bond to the energy balance, its strength being deduced from the heat of adsorption. Strong chemisorption to one component of an alloy has in fact been shown (*25, 59*) to reverse the direction of surface segregation from that expected in vacuum. A similar effect can be anticipated for supported catalysts, where one component of the alloy may segregate to the interface and become effectively a "glue" attaching the particle to the support. Analysis of the particle–support interface may be further complicated by lattice mismatch between the metal particle and, typically, oxide support.

If the problems of constructing adequate models and obtaining sufficiently accurate thermochemical data can be overcome, we then need to measure surface compositions. Many investigators have used Auger electron spectroscopy (AES) and there are now over 100 such reports in the literature. The usual approach has measured the peak height of a low- and high-energy emission for each of the two elements in a segregated and unsegregated condition. The energy dependence of the electron escape depth is then used to obtain a value for surface composition.

The accuracy of the values depends on the accuracy of the escape depth. Compilations (*31, 32*) have presented data obtained mostly by the overlayer method. Recent improved measurements (*33*) using a continuous synchrotron radiation source report an accuracy of ±50% of their measured value. Since this uncertainty translates into an equivalent uncertainty in surface composition, it is difficult to see how AES can give sufficiently accurate values to test the predictions of theory.

Work function measurements have been used to characterize surface composition (*34, 35*), but the variation of work function with composition is not simple so that precise values for surface composition are difficult to obtain. The results of more recent efforts (*36–38*) to quantify this relationship seem encouraging, though they are limited to evaporated films.

Low-energy ion-scattering spectroscopy (ISS) is, in principle, sensitive to the first monolayer only (*41, 42, 70–72*). It has been applied to sputtered Cu–Ni surfaces (*40*) to show that the bulk and surface compositions are closely identical after such a treatment. It has also been applied to Ag–Au (*39*) and to Cu–Ni (*56, 70*) to show segrega-

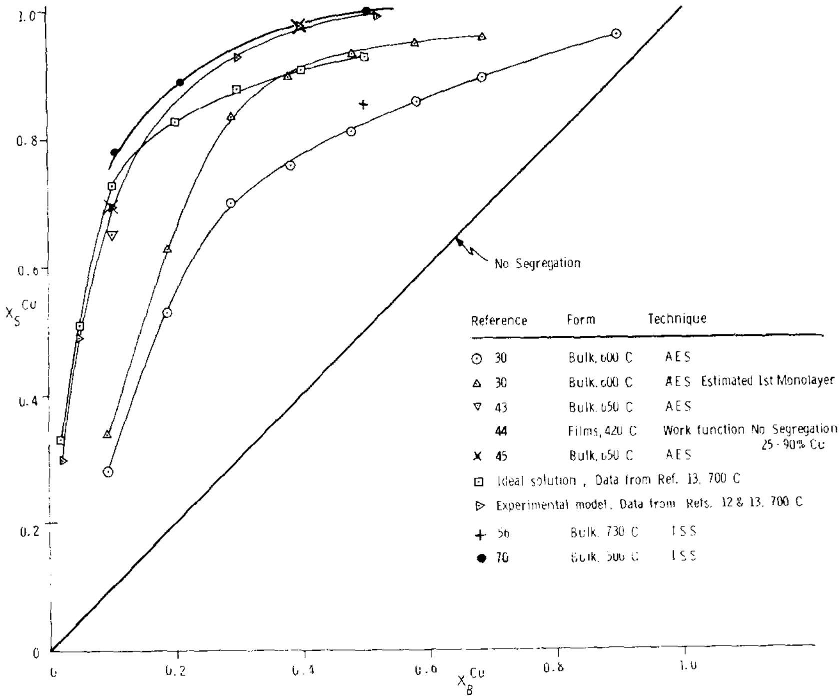

FIG. 3. Surface segregation in the copper–nickel system.

tion of Ag and Cu, respectively, to the surface. A first monolayer measurement by ISS can be used as an internal calibration for AES (*67*) to obtain depth profile information.

Figure 3 shows the results of several recent experimental studies (*30*, *43–45*, *56*, *70*) and calculations for Cu–Ni alloys. Several earlier studies (*46–49*) using higher energy Auger lines are omitted, since they are expected to be less surface sensitive. These latter studies found little evidence for any difference between the bulk and surface compositions. Figure 3 shows reasonable agreement between recent, more surface-sensitive findings and theoretical calculations. The agreement owes at least partly to the relatively small heat of mixing and strain effects (Tables 1 and 4) in the Cu–Ni system. The contrary finding by work function (*44*) might be due to the lower annealing temperature limiting the extent of surface equilibration.

Figure 4 shows results for the Ag–Au system. Clearly the encouraging signs of agreement found in the Cu–Ni system are absent here. The increased departure of the Ag–Au "bond" and the entropy of mixing from their ideal solution values (Table 3, Fig. 2) relative to Cu–Ni are incorporated differently by the various theories so that the surface compositions predicted for a given bulk composition range more widely. It can therefore be hoped that the Au–Ag system will provide a better test of the models.

The thin film studies (*38*, *44*) show no segregation for either this system or Cu–Ni. It is tempting to speculate that the silver segregated to some internal defect structure left from the deposition, but not removed by the 400–450°C annealing. Experiments where films were annealed to higher temperatures or examined by high-resolution transmission electron microscopy could explore this further.

The bulk alloy study (*50*, *51*) reports *in situ* slow strain rate fracture of the

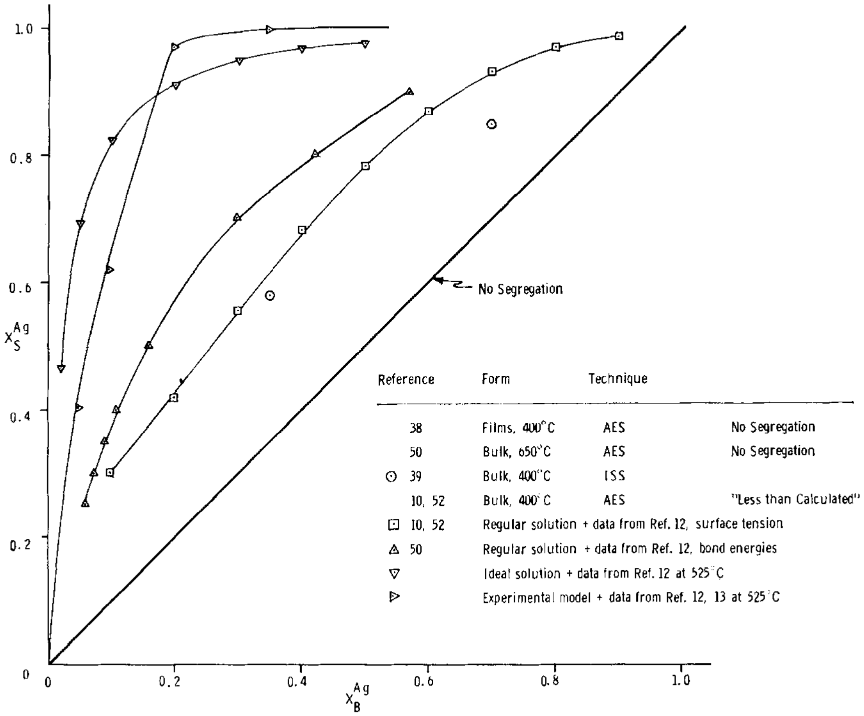

FIG. 4. Surface segregation in the silver–gold system.

alloy rods to give a "transgranular" fracture surface which was then examined. Such a fracture morphology is in contrast with most metallurgical experience (*53*), in which high-purity precious metals strained under these conditions fail by necking to chisel point with 100% reduction in area. If "transgranular" fracture implies faceting, it is a surprising result indeed. Strong ordering could impede slip and so promote a cleavage failure, but such ordering is not reported in the Au–Ag system (*54*). Alternatively, the alloy rods may have failed by reduction to a chisel point as described above and the extensive deformation involved would have given the sides of the rod a roughened appearance, possibly resembling facets. Since this area was the side of the original rod, any segregation would already have taken place when the rod was cooled from the melt so that no change would be expected during subsequent annealing. Thus this experiment may in fact provide evidence for surface segregation in the Ag–Au system, rather than against it. Clearly more experimental work is needed.

Variation of composition with depth beneath the surface further complicates experimental measurement of surface segregation. Auger measurements sum the contribution of several layers so that some assumption must be made about layer-to-layer variation. Commonly segregation is assumed limited to the first layer with the second and all succeeding layers having the same composition as the bulk (*2, 10, 25, 52*).

Model treatments of multilayer crystals, however, predict (*3, 7*) a large depth variation. Applying Eq. (8) to the (111) face of a 10-layer plus bulk Ag–Au crystal gives the result shown in Fig. 5. Though some of the detailed features in Fig. 5 may be consequences of the truncation procedure, depth variation is clearly significant and must be accounted for in experimental studies. Efforts to do this (*30*) have improved agreement between theory and experiment. The experimental model [Eq. (8)] predicts similar behavior for the Cu–Ni system, in contrast with the results (*62*) of Monte Carlo calculations. An UPS study (*73*) using variable photon energy to probe a range of near-surface depths found evidence for composition oscillations, supporting the use of Eq. (8).

Lastly, the rate of approach to equilibrium segregation needs to be considered. The investigators above who used bulk samples have sought to anneal at sufficient time and temperature for diffusion to attain an equilibrium distribution of solute. They have observed AES signals at high and low energy and taken constancy of the ratio as an indicator of this equilibrium. Whether this indeed represents true equilibrium or a kinetic limitation deserves some further exploration. A recent study (*55*) of diffusion from the surface in aluminum-rich aluminum–nickel alloys showed that diffusion is substantially impeded when the composition reaches a value corresponding to a specific ordered structure. Of course interaction energies in the Cu–Ni and Ag–Au systems are much less and intermetallic compounds are not found, but the force driving the segregation is less also. Short-range order may provide significant impediment to diffusion. Segregation experiments at temperatures high enough to ensure a substantial population of defects, even compositions corresponding favorable short-range ordering are desirable.

To summarize, we have examined the various theories of surface segregation. The bulk mixing part of the problem is not adequately treated by regular solution theory, but this difficulty is overcome by use of experimental mixing data. The surface part of the problem is reasonably treated as complete severing of one-quarter of the surface atom bonds. The treatments proposed for significant strain effects do not seem adequate, but it is possible to identify systems in which strain effects can be ignored.

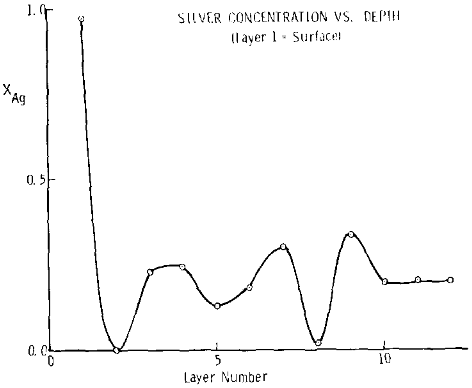

FIG. 5. Depth variation of segregation in the silver–gold system.

We have reviewed the thermodynamic data used in the various calculations and found major disagreements for some systems. The uncertainties arising from these disagreements are at least as great as the uncertainties arising from differences among the theories. The data of Refs. (*12*) and (*13*) seem best, but there is no assurance that they are free from error.

We have examined some of the major features of experimental measurements of surface segregation. There are large uncertainties inherent in the electron spectroscopies and the need for progress in measuring important electron spectroscopic parameters such as escape depth is evident. Other techniques just now being applied to surface segregation, such as ISS and work function, seem to hold promise for circumventing the problems of the electron spectroscopies. Further experience with them is needed to show how reliably they will be able to determine first monolayer compositions.

Finally we have noted that, as always, the most difficult part of the problem is good experimental work. Even with such simple-appearing systems as Cu–Ni and

Ag–Au there is no abundance of reliable data to test theoretical predictions. It is always easier to make mathematical models and write computer programs than it is to get unambiguous results in the laboratory. Without significant additional experimental information, it is unlikely that we will make much more progress toward understanding surface segregation behavior or designing catalyst alloys with specific surface compositions.

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REFERENCES

1. Sachtler, W. M. H., and Van Santen, R. A., *Adv. Catal.* **26**, 69 (1977).
2. Burton, J. J., Hyman, E., and Fedak, D., *J. Catal.* **37**, 106 (1975).
3. Kumar, D., Mookerjee, A., and Kumar, V., *J. Phys. F: Metal Phys.* **6**, 725 (1976).
4. Overbury, S. H., Bertrand, P. A., and Somorjai, G. A., *Chem. Rev.* **75**, 547 (1975).
5. Van Santen, R. A., and Sachtler, W. M. H., *J. Catal.* **33**, 202 (1974).
6. Sachtler, W. M. H., *Vide* **164**, 6F (1973).
7. Williams, F. L., and Nason, D., *Surf. Sci.* **45**, 33F (1974).
8. Van Santen, R. A., and Boersma, M. A. M., *J. Catal.* **34**, 13 (1974).
9. Defay, R., and Prigogine, I., "Surface Tension and Adsorption." Wiley, New York, 1966.
10. Overbury, S. H., and Somorjai, G. A., *Surf. Sci.* **55**, 209 (1976).
11. Sundaram, V. S., and Wynblatt, P., *Surf. Sci.* **52**, 569 (1975).
12. Hultgren, R., Desai, P. D., Hawkins, D. T., Gleiser, M., and Kelley, K. K., "Selected Values of Thermodynamic Properties of Binary Alloys." American Society for Metals, Metals Park, Ohio, 1973.
13. Hultgren, R., Desai, P. D., Hawkins, D. T., Gleiser, M., Kelley, K. K., and Wagman, 'D. D., "Selected Values of the Thermodynamic Properties of the Elements." American Society for Metals, Metals Park, Ohio, 1973.
14. Udin, H., Shaler, A. J., and Wulff, J., *J. Metals* **1**, 1936 (1949).
15. Buttner, F. H., Udin, H., and Wulff, J., *J. Metals* **3**, 1209 (1951).
16. Funk, E. R., Udin, H., and Wulff, J., *J. Metals* **3**, 1206 (1951).
17. Oriani, R. A., *J. Chem. Phys.* **18**, 575 (1950).
18. Hultgren, R., Orr, R. L., Anderson, P. D., and Kelley, K. K., "Selected Values of Thermodynamic Properties of Metals & Alloys." Wiley, New York, 1963.
19. Brewer, L., "High Strength Materials" (V. F. Zackey, Ed.), p. 12. Wiley, New York, 1965.
20. Smithells, C. J., "Metals Reference Book, 3rd Ed." Butterworths, London, 1962.
21. Smithells, C. J., "Metals Reference Book, 4th Ed." Butterworths, London, 1967.
22. Smithells, C. J., "Metals Reference Book, 5th Ed." Butterworths, London, 1976.
23. Kubachewski, O., Evans, E. L., and Alcock, C. B., "Metallurgical Thermochemistry, 4th Ed." Pergamon, New York, 1967.
24. Wagman, D. D., Evans, W. H., Parker, V. B., Halow, I., Bailey, S. M., and Schumm, R. H., "Selected Values of Chemical Thermodynamic Properties for Elements 35 through 53," National Bureau of Standards Technical Note 270–4 (1969).
25. Burton, J. J., Helms, C. R., and Polizotti, R. S., *J. Chem. Phys.* **65**, 1089 (1976).
26. McLean, D., "Grain Boundaries in Metals." Oxford, 1957.
27. Eshelby, J. D., *in* "Solid State Physics—Advances" Vol. 3, p. 79. (F. Seitz and D. Turnbull, Eds.), Academic Press, New York, 1956.
28. Jaeger, I., *Phys. Stat. Sol.* (*a*) **33**, 167 (1967).
29. Stuwe, H. P., and Jaeger, I., *Acta Met.* **24**, 605 (1976).
30. Watanabe, K., Hashibe, M., and Yamashira, T., *Surf. Sci.* **61**, 483 (1976).
31. Lindau, I., and Spicer, W. E., *J. Elect. Spectros.* **3**, 409 (1974).
32. Powell, C. J., *Surf. Sci.* **44**, 29 (1974).
33. Lindau, I., Pianetta, P., Yu, K. Y., and Spicer, W. E., *J. Elect. Spectros.* **8**, 487 (1976).
34. Bouwman, R., and Sachtler, W. M. H., *J. Catal.* **19**, 127 (1970).
35. Bouwman, R., and Sachtler, W. M. H., *Surf. Sci.* **24**, 350 (1971).
36. McDavid, J. M., Ph.D. thesis, Univ. Washington (1976).
37. Davidson, E. R., and Fain, S. C., *J. Vac. Sci. Tech.* **13**, 209 (1976).
38. Fain, S. C., and McDavid, J. M., *Phys. Rev.* **B9**, 5099 (1974).
39. Nelson, G. C., *Surf. Sci.* **59**, 310 (1976).
40. Swartzfager, D. G., *Surf. Sci.*, submitted.
41. Smith, D. P., *Surf. Sci.* **25**, 171 (1971).

42. Nelson, G. C., *J. Appl. Phys.*, submitted.
43. Helms, C. R., and Yu, K. Y., *J. Vac. Sci. Tech.* **12**, 276 (1975).
44. Franken, P. E. C., and Ponec, V., *J. Catal.* **42**, 398 (1976).
45. Yu, K. Y., Helms, C. R., and Spicer, W. E., *Sol. State Comm.* **18**, 1365 (1976).
46. Ertl, G., and Kuppers, J., *Surf. Sci.* **24**, 104 (1971).
47. Quinto, P. T., Sundaram, V. S., and Robertson, W. D., *Surf. Sci.* **28**, 504 (1971).
48. Nakayama, K., Ono, M., and Shimizu, H., *J. Vac. Sci. Tech.* **9**, 749 (1972).
49. Yakusu, Y., and Shimizu, M., *J. Catal.* **29**, 479 (1973).
50. Bouwman, R., Toneman, L. H., Boersma, M. A. M., and Van Santen, R. A., *Surf. Sci.* **59**, 72 (1976).
51. Van Santen, R. A., and Boersma, M. A. M., *J. Catal.* **34**, 13 (1974).
52. Somorjai, G. A., and Overbury, S. H., *Disc. Faraday Soc.* **60**, 279 (1975).
53. Reed-Hill, R. E., "Physical Metallurgy Principles." Van Nostrand, New York, 1964.
54. Elliott, R. P., "Constitution of Binary Alloys—First Suppl." McGraw–Hill, New York, 1965.
55. Hickl, A. J., and Heckel, R. W., *Met. Trans.* **6A**, 431 (1975).
56. Brongersma, H. H., and Buck, T. M., *Surf. Sci.* **53**, 649 (1975).
57. Kerker, G., Moran-Lopez, J. L., and Bennemann, K. H., *Phys. Rev. B* **15**, 638 (1977).
58. Burton, J. J., and Machlin, E. S., *Phys. Rev. Lett.* **37**, 1433 (1976).
59. Bouwman, R., and Sachtler, W., *J. Catal.* **19**, 127 (1970).
60. Wynblatt, P., and Ku, R. C., "Interfacial Segregation," ASM Materials Science Seminar, American Society for Metals, Metals Park, Ohio, 1977.
61. Wynblatt, P., and Ku, R. C., *Surf. Sci.* **65**, 511 (1977).
62. Donnelly, R. G., and King, T. S., *Surf. Sci.* **74**, 89 (1978).
63. Blakely, J. M., "Segregation to Surfaces: Dilute Metal Alloys of the Transition Metals," 3rd Intl. Summer Inst. in Surf. Science, U. Wisconsin, Milwaukee (1977). To be published in CRC Critical Reviews in the Solid State Sciences.
64. Moran-Lopez, J. L., and Falicov, L. M., *Phys. Rev. B* **18** (1978).
65. Moran-Lopez, J. L., and Falicov, L. M., *Phys. Rev. B* **18** (1978).
66. Jablonski, A., *Adv. Coll. Int. Sci.* **8**, 213 (1977).
67. Gallon, T. E., *Sur . Sci.* **17**, 486 (1969).
68. Tsai, N. H., Pound, G. M., and Abraham, F. F., *J. Catal.* **50**, 200 (1977).
69. Friedel, J., *Adv. Phys.* **3**, 446 (1954).
70. Brongersma, H. H., Sparnaay, M. J., and Buck T. M., *Surf. Sci.* **71**, 657 (1978).
71. Smith, D. P., *Surf. Sci.* **25**, 171 (1971).
72. Baun, W. L., *in* "Quantitative Surface Analysis of Materials" (N. S. McIntyre, Ed.), p. 150. ASTM, Philadelphia, 1978.
73. Ling, D. T., Miller, J. N., Lindau, I., Spicer, W. E., and Stefan, P. M., *Surf. Sci.* **74**, 612 (1978).