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Surface Segregation in Alloys

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Calculations based on the regular solution theory of alloys suggest that segregation of the more volatile constituent to the surface of a bulk alloy or small alloy particle, a microcluster alloy, may occur for all alloy systems, regardless of temperature. If the bulk alloy should undergo phase separation, there is no nucleation barrier to this process at a surface and a microcluster should not be undercoolable as a homogeneous single phase material. Homogeneous single phase microclusters with unsegregated surfaces could be observed experimentally only if the annealing time given to the microcrystals is too short to allow diffusion to occur.

Similarly, on very highly dispersed materials where almost every atom is on the surface, segregation of one component is expected to sites with low coordination number such as ledges or kinks.

Dispersed heterogeneous catalysts are of great importance in the petroleum and chemical industries. These dispersed catalysts consist of microclusters of metal, often no larger than 50 Å in diameter, supported on a suitable substrate such as alumina. While many commercial microcluster catalysts are single metals, the catalytic properties of alloys are being increasingly examined. The motivation of the work is that the catalytic properties of alloys may be affected by both constituents and that, by using metals with unlike activity for the reactions of interest, new catalysts with new and desired properties can be produced.

It is not at all obvious what the microstructure of a highly dispersed binary alloy catalyst will be. One possibility, particularly if the constituents, which we will call A and B, are essentially immiscible in the bulk, is that separate microclusters of A and of B will form on the substrates (Fig. 1a). Sinfelt (*1*) has, however, shown that microclusters of Cu–Os and Cu–Ru can be produced with both constituents in one particle despite the insolubility of Cu in Ru or Os in the bulk. This work indicates that one must examine with care the possible microstructures of such mixed microclusters.

Another microstructure of these mixtures could involve a single phase mixed microcluster, A + B (Fig. 1b). Ollis (*2*) and Hoffman (*3*) have discussed the possibility of an initially single phase microcluster, Fig. 1b, phase separating into a microstructure such as in Fig. 1c. They both concluded that phase separation, as in Fig. 1c, would be suppressed in very small microclusters; Ollis reached this conclusion on thermodynamic grounds and Hoffman did so on kinetic arguments.

All discussion in this paper will be based on the regular solution model of an alloy (*4*), which was also used by Ollis and Hoffman in discussing microclusters and by Meijering (*5*) and Williams (*6*) in discussing segregation to interfaces. While this model is inadequate to describe the full complexity of real alloys and its validity for surfaces has not been established, it is widely used to illustrate metallurgical concepts and is the simplest model which

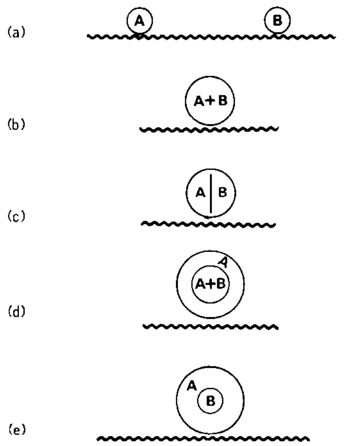

FIG. 1. Possible microstructure of a highly dispersed binary alloy on a substrate. (a) Separate microcrystals of A and B; (b) Single phase mixed microcrystal of A + B; (c) Phase separated microcrystal with both A and B on the surface; (d) Surface enriched microcrystal with A surrounding a single phase alloy of A + B; (e) Phase separated microcrystal with A surrounding B.

can exhibit a miscibility gap. Our attitude is that if the simple regular solution model predicts any interesting behavior for microclusters, we must at least consider the possibility of the existence of such behavior for real microcluster alloys. We also expect that this model will be as applicable to microcluster alloys as it is to the surface of bulk alloys as Friedel's work on alloys (7) indicates that bonding involves only nearest or next nearest neighbors and so thermodynamic calculations on alloys do not depend on the largeness of the sample.

In this paper we discuss segregation of one component of the microcluster to its surface. Our treatment is similar to that of Meijering (*5*) and Williams (*6*) who have proven that one component of a binary alloy can segregate to an interface. Our contribution is to extend this analysis to the possible structure of microcluster alloys.

There are two somewhat different possible microstructures with one component segregated to the surface: enrichment of one component in just the surface layer with a nearly homogeneous alloy at the center of the microcluster, Fig. 1d, and separation of the crystal into two concentric phases, one on the inside and one on the outside, Fig. 1e. We will prove that surface enrichment, Fig. 1d, occurs for simple alloys at equilibrium even if, in the bulk, the constituents are completely mis-

FIG. 2. Photographs of hard sphere models of microcrystals of 43 atoms showing a random atomic arrangement, left, and segregation of one component to the corners and edges, right.

cible and there is no phase separation. Accordingly we expect that all microcluster alloys may have their surfaces enriched in one component if they are annealed sufficiently long to attain their equilibrium microstructure. We also show that if the thermodynamic equilibrium state of the bulk alloy has two separated phases, the microcluster will also separate as in Fig. 1e; this phase separation will occur at nearly the same temperature as in the bulk and there will be no nucleation barrier to the separation.

In highly dispersed catalysts, where the microclusters are very small, it is impossible to distinguish between surface and bulk atoms as nearly every atom lies on the surface and does not have the full compliment of nearest neighbors. In this case, segregation of one component in an initially random mixture occurs not simply to the surface but rather to the surface sites of lowest coordination number, such as corners and edges, Fig. 2.

THEORY

We consider a microcluster as made up of n concentric shells of atoms, Fig. 3, with each atom in a given shell sitting on an equivalent site. The total free energy of the microcrystal, in regular solution theory (*4*), consists of the sum of the energies of all the nearest neighbor bonds [the term in square brackets in Eq. (1)] and an entropy term obtained assuming ideal mixing[1]:

$$F = \sum_i N_i \sum_j [(Z_{ij}/2)\,\{X_iX_jV_{\mathrm{AA}} + (1 - X_i)(1 - X_j)V_{\mathrm{BB}} + X_i(1 - X_j)V_{\mathrm{AB}} + X_j(1 - X_i)V_{\mathrm{AB}}\}] + RT \sum_i N_i\,\{X_i \ln X_i + (1 - X_i)\ln(1 - X_i)\}, \qquad (1)$$

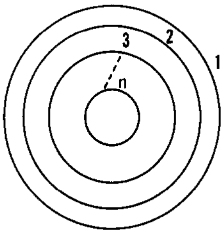

FIG. 3. A microcrystal as n concentric shells of atoms; each atom in a given shell sits on an equivalent site.

where N_i is the number of atoms in shell i, Z_{ij} is the number of nearest neighbors that an atom in shell i has in shell j,[2] X_i and X_j are the concentrations of A in shell i and j, $(1-X_i)$ is the concentration of B in shell i, V_{AA} is the (usually negative) energy of an A–A nearest neighbor bond, V_{BB} that of a B–B bond, and V_{AB} that of a A–B bond, R is the gas constant, and T the temperature.

At equilibrium, the chemical potential of the atoms at each type of site must be equal. Therefore

$$\frac{1}{N_i}\frac{\partial F}{\partial X_i} = \sum_{j=1}^{n} Z_{ij}[X_jV_{\mathrm{AA}} - (1 - X_j)V_{\mathrm{BB}}] + (1 - 2X_j)V_{\mathrm{AB}} + RT \ln \frac{X_i}{1 - X_i} = \lambda, \qquad (2)$$

where λ is a constant. It is possible to rearrange Eq. (2) into a somewhat simpler form

$$\lambda = \sum_{j=1}^{n} Z_{ij}\left\{-2X_jV + V + \frac{V_{\mathrm{AA}} - V_{\mathrm{BB}}}{2}\right\} + RT \ln \frac{X_i}{1 - X_i}, \qquad (3)$$

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[1] In writing down Eq. (1) for the free energy of a microcluster, we are really describing an ensemble of structurally identical microclusters and then calculating ensemble average properties.

[2] All of the information about the geometry of the system is in the coefficients Z_{ij}. If an atom in shell i has no neighbors in j, Z_{ij} is zero. For example, for a flat face centered cubic crystal with a (111) surface, $Z_{ii} = 6$, $Z_{i,i+1} = Z_{i,i-1} = 3$, and $Z_{ij} = 0$ otherwise.

where

$$V = (2V_{AB} - V_{AA} - V_{BB})/2 \qquad (4)$$

is a measure of the miscibility of the alloy constituents. If $V = 0$, a single phase alloy is formed in the bulk for all temperatures; if $V < 0$, the bulk alloy will tend to maximize the number of AB bonds and will therefore order at low temperatures; and if $V > 0$, the bulk alloy will tend to minimize the number of AB bonds and will therefore phase separate at low temperatures. If $V = 0$, Eq. (3) simplifies to

$$\lambda = \left(\frac{V_{AA} - V_{BB}}{2}\right) \sum_{j=1}^{n} Z_{ij} + RT \ln \frac{X_i}{1 - X_i}. \qquad (5a)$$

But the sum of the coordination numbers, Z_{ij}, is just the total number of neighbors, Z_i, that an atom of type i has and Eq. (5a) can be rewritten as

$$\lambda = \left(\frac{V_{AA} - V_{BB}}{2}\right) Z_i + RT \ln \frac{X_i}{1 - X_i}. \qquad (5b)$$

It is clear from Eq. (5b) that, in an alloy with no miscibility gap and no ordered phase (i.e., $V = 0$), the composition, X_i, of a site i is a function of only λ and the coordination of the site. Let us call X the composition of the alloy at a point where an atom has its full coordination of Z nearest neighbors. Solving Eq. (5b) for this site to obtain λ we get

$$\frac{X_i}{1 - X_i} = \frac{X}{1 - X}\, e^{\Delta Z(V_{AA} - V_{BB})/2RT}, \qquad (6)$$

where $\Delta Z_i = Z - Z_i$ is the deficiency in nearest neighbors of the site i. According to Eq. (6), if the AA bonds are weaker than the BB bonds, i.e., V_{AA} is less negative than V_{BB}, then the more volatile A atoms should segregate towards sites of low coordination number such as surfaces. Similarly on very highly dispersed materials where virtually every atom is on the surface, the more volatile constituent should segregate to ledges and kinks.

CALCULATIONS

We will now use Eq. (3) and (6) to explicitly discuss the likely microstructure of dispersed binary alloys. These equations are actually quite general and could be applied to a wide range of problems, such as free surfaces or greins boundaries, provided the coefficients Z_{ij} are suitably defined.

There is considerable uncertainty at present as to the structure of microclusters. It was previously thought that they would have bulk like structures; thus a Pt microcrystal should be face centered cubic. However, we have recently argued (*8*) based on work of Hoare and Pal (*9*) and others, that microcrystals have structures based on the icosahedron. This uncertainty in structure makes determination of the coefficients Z_{ij} in Eq. (3) and ΔZ_i in Eq. (6) impossible. Accordingly, we will limit our detailed calculations to some simple special cases and then make general qualitative statements about microclusters.

Bond Energies

The bond energies V_{AA}, V_{BB} and V_{AB} must be crudely estimated from the properties of pure metals and simple alloys (*4*). Assuming that a metal is bound by nearest neighbor bonds, V_{AA} can be estimated from the latent heat of sublimation, H_s,

$$V_{AA} = \frac{-2H_s}{Z}, \qquad (7)$$

where Z is the bulk coordination number. The bond energies in Table 1 were estimated using Eq. (8). V_{AB}, or V [Eq. (4)] can be estimated from the temperature, T_c, below which an alloy has a miscibility gap by

$$V = \frac{2RT_c}{Z} \qquad (8)$$

TABLE 1
ESTIMATED BOND ENERGIES, V_{AA}, FOR SOME FACE CENTERED CUBIC METALS

Metal	V_{AA} (kcal/mole)
Ni	−17
Cu	−13.5
Pd	−15
Ag	−11
Pt	−22.5
Au	−14

were estimated from Eq. (8). In alloys with miscibility gaps which can be described by regular solution theory, V is typically less than 0.5 kcal/mole.

Alloys Without a Miscibility Gap ($V = 0$)

If there is no miscibility gap, i.e., $V = 0$, the segregation of one component to the surface can be calculated from Eq. (6). Note that segregation occurs only to sites having a deficiency of nearest neighbors. We plot in Fig. 4 the concentration, X_i, on surface as a function of the bulk concentration, X, for various values of the parameter, P, which appears in Eq. (6).

$$P = \Delta Z_i(V_{AA} - V_{BB})/2RT. \tag{9}$$

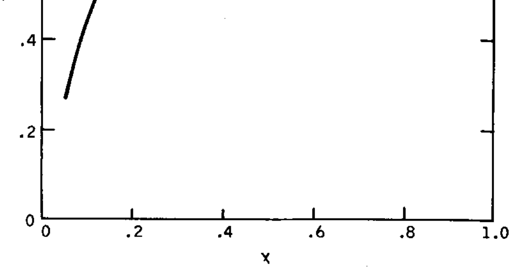

FIG. 4. The concentration, X_i, on the surface site as a function of the bulk concentration, X, for various values of the parameters P, Eq. (9). The values of the parameters shown correspond to the (100) surface of a CuNi at temperatures of ~1800, ~1200, and ~600°K (indicated in parentheses).

The values of the parameters shown would correspond to copper atoms segregated to the (100) surface of a copper–nickel alloy at temperatures of ~1800, ~1200 and ~600°K. It is quite apparent that the copper should be extensively segregated at low temperatures. This result that Cu may segregate to the surface of a CuNi alloy appears to be consistent with the interpretations of some published experiments on this alloy using gas adsorption (*10,11*), catalytic reactions (*12*) and work function measurement (*13*). However, the experimental situation is still rather unclear as other workers using Auger electron spectroscopy, which can directly determine composition, reported contradictory conclusions; Takasu (*14*) and Helms (*15*) reported segregation and Ertl (*16*) found no evidence for segregation.

Alloys with a Miscibility Gap ($V > 0$)

When there is a miscibility gap, the segregation of atoms towards the surface is not confined to the neighbor-deficient surface layer, but can extend into the interior of the crystal. We have solved Eq. (3), which is actually a system of simultaneous nonlinear equations, on a computer using appropriate boundary conditions for a face centered cubic film with a (111) surface using bond parameters appropriate to Au–Ni, which has a miscibility gap below 1100°K. The alloy is 50% Au, 50% Ni in the interior. At temperatures above the bulk phase separation temperature, 1100°K, the gold segregation to the surface is confined to a few planes very near the surface. Below the phase separation temperature, a thick gold rich region is expected near the surface with further enhancement of the gold concentration in the few planes closest to the surface, Fig. 5. These conclusions agree with the exper-

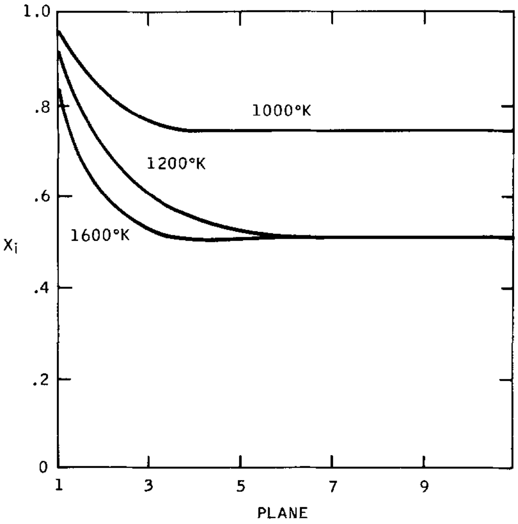

FIG. 5. Calculated composition, X_i, for various near surface planes (1 is the surface) of a 50% Au–50% Ni alloy with a (111) surface for various temperatures. The temperature of the miscibility gap is 1100°K.

imental results of Williams and Boudart (*17*), who have reported extensive segregation of Au to the surface of AuNi alloys.

We are particularly interested in this paper in microclusters, which are somewhat different from bulk crystals with surfaces. When a significant fraction of the atoms of a crystal are surface atoms, enrichment of the surface with one species involves significant depletion of the interior, which must be taken into account when looking at phase separation or segregation of a microcluster. In Fig. 6, we show the equilibrium composition of various planes of a thin film for different film thicknesses. The calculations are based on a 50% Au–50% Ni alloy (average composition) with a (111) surface and bulk phase separation near 1100°K. The results were again obtained by computer solution of Eq. (3). No surface segregation occurs on the two plane crystal, which is entirely surface atoms. All of the other crystals at equilibrium show surface segregation above 1100°K and phase separation as well as lower temperatures.

DISCUSSION

Our calculations indicate the following:

(1) A microcluster alloy of completely miscible constituents will have an equilibrium microstructure in which sites lacking a full shell of nearest neighbors are greatly enriched in the more volatile component of the alloys, Fig. 1d. At low temperatures, at equilibrium, even a very dilute alloy can have on its surface only its minor constituent, Fig. 4.

This phenomenon arises because the free energy of the system is lowered by putting the element with the smaller heat of sublimation (weaker bonds) at positions with fewer neighbors. Note that this result is not limited to surface enrichment. We would, by the same argument, expect edge sites on a microcrystal to be richer in the volatile component than surface sites, which are richer than the bulk. Similarly, corner sites should be still richer than edges. Thus, from Fig. 4, at 1200°K we would expect a (100) surface of a 5% Cu–95% Ni bulk or microcluster alloy to

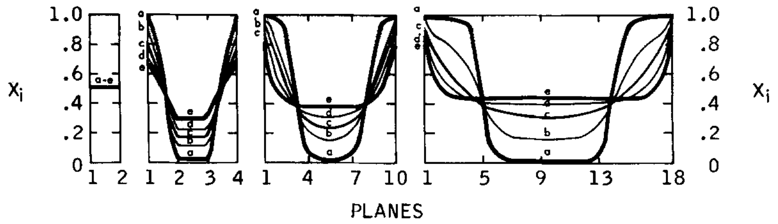

FIG. 6. Calculated composition, X_i, for the various planes of 50% Au–50% Ni (average composition) thin films with (111) surfaces. Data are shown for film thicknesses of 2–18 planes and various temperatures. Curve (a) 500°K, (b) 900°K, (c) 1100°K, (d) 1300°K, and (e) 1700°K. The temperature of the miscibility gap is 1100°K.

have a copper concentration of 50% and a corner on such a microcluster with only four nearest neighbors to be 95% copper.

In an alloy without any miscibility gap, the enrichment will be confined solely to the neighbor deficient sites and there will be no enrichment of the subsurface layers. Thus, the equilibrium microstructure should be thought of as an enriched surface layer on a completely homogeneous interior. We note that there is no nucleation barrier to form this surface segregated microstructure because moving even just one of the more weakly bonding atoms from the interior to the surface lowers the energy of the system.

(2) If the alloy shows phase separation in the bulk, the surface segregation extends beyond the surface plane, Figs. 5 and 6; however, this effect penetrates only one or two planes into the crystal at temperatures above the bulk separation temperature. Below the phase separation temperature, the microcluster alloy also appears to have a phase separated microstructure such as in Fig. 1e.

The surface segregation extends beyond the first plane in alloys with a miscibility gap because it is energetically favored for A atoms to be near A atoms and B near B. This gives rise to short range composition correlations. The segregated surface layer attracts like atoms to it in the planes below. When this alloy with a segregated surface is cooled further, there is no nucleation barrier to forming the phase separated microstructure as the separation occurs by growth of already enriched surface phase and moving even just one of the more weakly bonding atoms from the interior to the surface lowers the energy of the system. Note that, for very small microclusters with only a few bulk-like atoms such as the 4 plane film in Fig. 6, there is no clear difference between segregation and phase separation.

(3) In many catalytic systems, the material is so very highly dispersed that virtually every atom is a surface atom and it is not useful to think of segregation to the surface itself. However, a similar and important type of segregation will occur. Equations (3) and (6) show that the volatile component of an alloy can segregate to a site of lower coordination number; our derivation does not depend in any way on this site being a surface site. Therefore, even on very highly dispersed materials, we expect significant segregation of one component to special lower coordination number sites such as corners and edges, Fig. 2. Detailed concentrations for a microcluster can be calculated from Eq. (3) and (6) if the structural coefficients Z_{ij} can be estimated.

The microstructures of a phase separated microcrystal which we have proposed here, Figs. 1d and 1e, involve one phase near the surface and another near the center of the crystal. These microstructures are somewhat different from that studied by Ollis (*2*) and Hoffman (*3*), Fig. 1b. Their analyses are applicable to alloy constituents with nearly identical sublimation energies and a miscibility gap. In the notation of regular solution theory used in this paper, their analysis is applicable to alloys for which $V \gg | V_{AA} - V_{BB}|$, which is not the case in most simple alloys.

Throughout our remarks, we have been discussing the equilibrium microstructure of microcluster alloys. In many metallurgical problems, the observed microstructure is determined by kinetics considerations and not by thermodynamics, and therefore it is appropriate to wonder whether equilibrium microstructures are attained under typical experimental conditions. At 500°C a 50% CuNi or 50% AuNi might reach its equilibrium composition of its surface plane by diffusion in less than 10 sec; however the times required at 300°C could be as large as 10^3 sec in AuNi or 10^4 sec in CuNi.[3] These times could be significantly longer in alloys richer in Ni. The time required to produce the phase separated microstructure, Fig. 1e, would also be longer than that to produce the surface segregated microstructure, Fig. 1e.

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[3] These times were calculated from a diffusion distance of 10 Å and a diffusion coefficient for the alloy estimated from silver data (*18*) at the same reduced temperature T/T_m, where T_m is the melting temperature.