

Phase Stability of Supported Bimetallic Catalysts

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Although in the bulk state copper is virtually immiscible with ruthenium or osmium, Sinfelt has found that silica-supported catalysts contain miscible bimetallic clusters of ruthenium-copper or osmium-copper. This miscibility on the scale of thin films (or clusters) may be explained by two phenomena, namely by the structural changes caused by the straining of the thin film (or cluster) by the substrate and/or the configurational changes occurring in small assemblies of atoms because of their smallness. A thermodynamic treatment is developed which permits the evaluation of the effect of the strain energy on the critical temperature of phase separation.

NOMENCLATURE		S	
a, a_1, a_2	lattice parameters of the substrate and the metals respectively	T	surface area of the interface temperature, °K
A, B	the two metals	u	potential energy of interaction between two atoms
c	constant in the expression of u	U	potential energy of interaction between one atom of the film and the substrate
C	ESh/n	W_{AA}, W_{BB}, W_{AB}	contribution of a pair of neighbors AA, BB, AB, respectively, to the energy
E	Young's modulus	x_1, x_2	molar fraction of the two metals
g_b	free energy per mole of a binary mixture of a bulk system	y	distance between a given metal atom and the metal-substrate interface
g'_b	free energy per mole of a binary film accounting also for the interaction with the substrate except the strain energy	z	lattice parameter during straining; also coordination number in the expression of α
g_s	strain energy per unit volume of strained film	α	$Nz(W_{AB} - 1/2W_{AA} - 1/2W_{BB})$
G	total free energy of the film	β	constant
h	film thickness	γ_{ss}, γ_{sg}	surface free energy at the solid-solid and solid-gas interface, respectively
m	exponent	μ_1, μ_2	chemical potentials of the pure metals in bulk
n	total number of atoms	μ'_1, μ'_2	chemical potential of the pure metals in the film ac-
N	Avogadro's number		
R	universal gas constant		
s	surface area of the section through the film normal to the solid-solid interface		

$\bar{\mu}'_1, \bar{\mu}'_2$

counting also for the interaction with the substrate (except the strain energy) average values of μ'_1 and μ'_2 over the thickness of the film stress

INTRODUCTION

Recently Sinfelt (1) has demonstrated that in silica-supported ruthenium-copper and osmium-copper catalysts, bimetallic completely miscible clusters of atoms exist on the carrier, although in the bulk state copper is virtually immiscible with ruthenium or osmium. The goal of the paper is to find some explanations for the difference in behavior of the two metals in the small clusters on the support and in the bulk state and to develop a quantitative thermodynamic treatment.

A higher miscibility at the scale of the film than in the bulk also has been reported for relatively thick alloy films of about 300–1000 Å, prepared by simultaneous evaporation of the components onto a substrate at 80°K (2–5). Of particular interest in the present context is the observation (5), which will be discussed later on, that an amorphous substrate produces an amorphous single phase deposit, whereas a metal substrate produces a single phase crystalline deposit with the same structure. The corresponding bulk alloys had a two phase structure.

POSSIBLE CAUSES OF THE HIGHER MISCIBILITY IN THE CLUSTERS

Theories have been developed for epitaxial overgrowth of a thin layer (or of a hemispherical nucleus) (6–9) on an infinite substrate for the simple case when both lattices are cubic and in parallel orientation. They predict that the misfit between lattices is accommodated partly by elastic strain and partly by dislocations at the solid-solid interface. If the misfit is smaller than a critical value (which depends upon the film thickness and upon the nature of the substrate and film and can be evaluated (6–8)), it is energetically favorable for the film (cluster) to be strained to coherency with respect to the substrate (the lattice

distances are the same for the thin layer and substrate at least in the planes parallel to the interface of the substrate). The thin layer (or the cluster) is pseudomorphic with respect to the substrate. The theory was tested experimentally. For instance, Jesser and Matthews (10) reported that if cobalt is deposited on a cold copper substrate, the structure and the lattice parameter of the cobalt remained that of the copper until the thickness of the film reached about 20 Å. At this thickness dislocations were generated. The straining of the film to exactly match its substrate was observed in many other situations (11–15). The bulk immiscibility of copper and osmium (or ruthenium) is caused by the strong crystallographic dissimilarity. Copper has a f.c.c. structure, whereas osmium and ruthenium, an h.c.p. structure. For sufficiently small clusters the structural modifications caused in the film by the substrate (in some conditions even a pseudomorphic structure with respect to the substrate) could allow perfect miscibility even though the two metals are immiscible in the bulk.

Stability computations (16–18) carried out for assemblies of relatively small number of atoms (<70) noninteracting with a substrate show that the stable configurations are never those of the bulk metals (f.c.c., h.c.p.), but are almost certainly among the "polytetrahedral" aggregates (i.e., figures of quite variable shape which can be constructed by packing approximately regular tetrahedra face to face). This would allow miscibility at the scale of clusters of two metals immiscible in the bulk.

Because of chemisorption, the chemical atmosphere can also affect the stable configurations of assemblies of small number of atoms and hence the miscibility at the scale of clusters of two metals immiscible or partially miscible in the bulk.

Structural changes caused by the interaction of the clusters (or thin films) with the substrate and/or configurational changes caused by the smallness of the clusters can explain Sinfelt's results. The thermodynamic considerations from the next sec-

tion will show that indeed the interaction with the substrate may have an effect on phase stability and that two metals partially miscible or immiscible in the bulk become completely miscible as a thin film on a substrate.

THERMODYNAMICS OF A BINARY METALLIC FILM ON A SUBSTRATE

The potential energy of a system composed of a binary metallic film and a substrate can be taken as the resultant of two body central forces with the appropriate pair potential. The positions of the atoms are found by minimizing this energy. The thermodynamic properties can be obtained, for instance, by computing the force-constant matrix for use in vibrational analysis and by writing the corresponding partition functions including, of course, translation and rotation. This kind of computation was used previously for the statistics and stability of small assemblies of less than 70 atoms (16-18) and it would be of interest to extend it to the present problem. Because of the interaction with the substrate, the computational difficulty becomes, however, prohibitively high.

A much more simple approach will therefore be used which, although less rigorous, has the advantage of providing some insight into the problem. The main element of the treatment is the assumption that the thickness of the film is small enough for the film to be strained to coherency with respect to the substrate. The interaction energy between substrate and film is decomposed into two terms: an interaction term between the substrate and the unstrained film, each of them being assumed a continuum, and a more structural term which accounts for the strain energy caused by the substrate when it forces a pseudomorphic structure in the film. The thermodynamic behavior of the binary film is described by the strictly regular solution model. The concentration in the thin film is not uniform, both because the film is under the action of the field caused by the substrate and because it has interfaces. Therefore, the problem should be treated using the methods of the

thermodynamics of nonuniform systems (19). For the sake of simplicity however, it is assumed that the concentration is nearly uniform and that only one atomic layer near each of the interfaces has a different composition.

The free energy per mole of a binary strictly regular solid solution has for a bulk system the form (20):

$$g_b = (1 - x_2)[\mu_1 + RT \ln(1 - x_2) + \alpha x_2^2] + x_2[\mu_2 + RT \ln x_2 + \alpha(1 - x_2)^2], \quad (1)$$

where x_2 is the molar fraction of one of the components, μ_1 and μ_2 are the chemical potential of the pure components, R is the gas constant, T is the temperature, and α is a constant (the interchange energy). The interchange energy α is given, in the nearest neighbors approximation, by the expression

$$\alpha = Nz(W_{AB} - \frac{1}{2}W_{AA} - \frac{1}{2}W_{BB}),$$

where W_{AA} , W_{BB} and W_{AB} are the contributions of each AA , BB , and AB pairs of neighbors to the energy.

The first interaction term between film and substrate is calculated as follows: the interaction potential between the atoms of the substrate and those of the overgrowth has often the simple form

$$u = -(c/r^m),$$

where r is the distance between the atoms and c and m are constants. For London dispersion forces $m = 6$. The potential energy of interaction between the substrate, assumed a continuum, and an atom of the film at a distance y from the solid-solid interface is given in this case by (21, 22)

$$U = -(\beta/y^{m-3}).$$

If between the atoms of the film only the nearest neighbor interactions are important, no change of the bulk chemical potential will be caused by the atoms of the film. For these conditions, the chemical potentials in the film, μ'_1 and μ'_2 , are related to the bulk chemical potentials, μ_1 and μ_2 , via

$$\mu'_1 = \mu_1 + NU_1 \quad (2a)$$

and

$$\mu'_2 = \mu_2 + NU_2. \quad (2b)$$

The second interaction term between film and substrate is the strain energy.

The free energy of a film of thickness h on a substrate G is composed of

$$G = ng'_b + S\gamma_{ss} + S\gamma_{sg} + Shg_s, \quad (3)$$

where n is the total number of atoms, S is the surface area of the interface, γ_{ss} is the surface free energy at the solid-solid interface, γ_{sg} is the solid-gas surface free energy, g_s is the strain energy induced by the substrate per unit volume of film for straining the film to coherency and g'_b is obtained from g_b replacing μ_1 and μ_2 by the average, over the thickness of the film, of μ'_1 and μ'_2 .

COMPUTATION OF THE STRAIN ENERGY

The evaluation of the strain energy will be made assuming that the film behaves as an elastic continuum and that each of the lattices can be characterized by a uni-dimensional model. The straining process induces a stress,

$$\sigma = [E(z - a')]/a',$$

where E is Young's modulus, a' is the lattice parameter of the unstrained binary solid solution, and z is its lattice parameter during straining. The strain energy for the coherency with the substrate is given by the work

$$\int_{a'}^a \sigma sdz,$$

where a is the lattice parameter of the substrate, and s is the surface area of the section through the film normal to the solid-solid interface. Therefore, the strain energy per unit volume of strained film is given by

$$g_s = \frac{1}{2}E[(a - a')^2/aa'].$$

If $a - a' \ll a$,

$$g_s \approx \frac{1}{2}E[(a - a')/a]^2. \quad (4)$$

For a bidimensional straining it is reason-

able to assume that g_s is twice as large, and hence

$$g_s \approx E[(a - a')/a]^2. \quad (5)$$

Equation (4) is similar to that obtained by Nabarro (23) and by Eshelby (24). As the thickness increases, the film is no longer pseudomorphic to the substrate and the misfit between film and substrate is accommodated partly by elastic strain and partly by dislocations at the interface. A number of equations are available for such situations (8, 9). Computations on their basis are similar to those given here, and therefore will not be included.

PHASE STABILITY OF A BINARY FILM ON A SUBSTRATE

The free energy per mole can be written as:

$$g = (1 - x_2)[\bar{\mu}'_1 + RT \ln(1 - x_2) + \alpha x_2^2] + x_2[\bar{\mu}'_2 + RT \ln x_2 + \alpha(1 - x_2)^2] + \frac{ESh}{n} \left(\frac{a - a'}{a} \right)^2 + g_1, \quad (6)$$

where g_1 includes the effects of the surface free energy for the solid-gas interface and the surface free energy for the solid-solid interface. Hoffman (25) has demonstrated that the critical solubility temperature is not strongly affected by the surface free energies, even for particles having a radius only three times larger than the lattice parameter. Thus, in the computation of the critical temperature, g_1 will be considered constant.

The system is stable (no phase separation occurs) if (26)

$$\partial^2 g / \partial x_2^2 > 0.$$

Phase separation occurs for temperatures lower than a critical temperature T_c which can be calculated from the equations:

$$\partial^2 g / \partial x_2^2 = \partial^3 g / \partial x_2^3 = 0.$$

Assuming that $C = (ESh)/n$ is a constant, and taking

$$a' = a_1 x_1 + a_2 x_2, \quad (7)$$

one obtains

$$RT_c \left[\frac{2x_{2,c} - 1}{x_{2,c}^2(1 - x_{2,c})^2} \right] = 0$$

and

$$RT_c \left\{ \frac{1}{x_{2,c}(1 - x_{2,c})} \right\} - 2\alpha + 2C \left(\frac{a_2 - a_1}{a} \right)^2 = 0.$$

Consequently, the critical molar fraction and the critical temperature result from

$$x_c = 1/2 \tag{8}$$

and

$$T_c = \frac{1}{2R} \left[\alpha - C \left(\frac{a_2 - a_1}{a} \right)^2 \right]. \tag{9}$$

Equation (9) shows that a partially miscible system can be transformed into a completely miscible system for all temperatures if

$$\alpha - C \left(\frac{a_2 - a_1}{a} \right)^2 \leq 0. \tag{10}$$

Among the assumptions used to deduce Eq. (9) two will be stressed once again: (1) the lattices of the substrate and of the metal of the film are cubic; and (2) the misfit between lattices is small enough. Only if the misfit is smaller than about 0.1 can the film be strained to exactly match the substrate and Eq. (5) is valid. If the misfit is larger than the critical value, dislocations develop at the solid-solid interface. The strain energy and the surface energy due to dislocations are in this case more weakly dependent upon $(a' - a)$ than in the pseudomorphic case (6). Equation (9) is however still useful since it gives a lower bound for T_c .

APPLICATION TO BIMETALLIC CLUSTERS

As mentioned in the Introduction, ruthenium and copper as well as osmium and copper form bimetallic clusters on an amorphous silica carrier. Because of the interaction with the amorphous substrate, a small cluster also has to have an amorphous structure (see below for some indirect experimental evidence). Of course, the model analyzed in the previous section

is too simplified to represent the present situation. However, the liquidlike distribution of atoms of the substrate causes the straining of the atoms in the cluster to occur with equal probability in any direction. This can change Eq. (5) only by a factor of order unity. Also dislocations probably will occur in a more difficult manner on an amorphous substrate and therefore, Eqs. (5) and (9) may be valid over a larger range than for the crystalline structure. The distance between two silicon atoms is about 5 Å, while the distance between silicon and oxygen atoms is about 2.7 Å. (See Table 1.)

Since Young's modulus is of the order of 10^{12} dynes/cm² and $n/S_H \approx 10^{-1}$ mole/cm³, one obtains

$$C \approx 10^{13} \text{ erg/mole} \approx 2.4 \times 10^5 \text{ cal/mole.}$$

Using $a_1 = 3.6147$ Å, and a_2 either 2.7353 Å or 2.7057 Å and taking for a the largest value, $a = 5$ Å (this makes the effect of the support smaller) one obtains

$$T_c - (\alpha/2R) \approx -1800^\circ\text{K.}$$

If for a_1 of copper, one takes the smallest distance, namely that between the atoms situated in the center and on the vertex of the same square ($a_1 = 2.556$ Å), and one assumes that the distance between two metal atoms is equal to that between the atoms of silicon and oxygen, one still obtains that $T_c - (\alpha/2R)$ is about -200°K for Cu-Ru and about -250°K for Cu-Os. The extension of Eq. (9) to the present more complex structures shows that the difference between the critical temperatures of the film on the substrate, T_c , and in the bulk, $(\alpha/2R)$, is large and hence that the straining to coherency with the substrate may be responsible for the com-

TABLE 1^a
LATTICE CONSTANTS

	a axis	c axis
Copper f.c.c.	3.6147 Å	
Osmium h.c.p.	2.7353 Å	4.3191 Å
Ruthenium h.c.p.	2.7057 Å	4.2816 Å

^a See Ref. 1(27).

plete miscibility at the scale of the clusters of two metals immiscible in the bulk.

Some experimental observations are available, concerning thin films of about 300–1000 Å thickness deposited onto a substrate at 80°K, which demonstrate that the substrate has an effect on miscibility and thus bring indirect support for a straining mechanism. Mader (5) deposited Cu–Ag films in thicknesses greater than 300 Å on an amorphous substrate at 80°K and obtained a single amorphous phase although the two metals form two phases in the bulk, for the same composition. Heating at higher temperatures (430°K), these films have crystallized into a single phase f.c.c. structure. Upon further heating at 500°K, the two phase structure of the bulk solid is obtained. When the Cu–Ag films were deposited, also at 80°K, on a freshly deposited silver layer, a single phase having a f.c.c. structure as the silver occurred. For very thin films (several tens of angstroms thick) these observations suggest that the straining might be able to impose on the binary film the structure of the substrate over a larger range of temperatures and thus to make completely miscible two metals partially or totally immiscible in the bulk.

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