

CALCULATION OF CHEMISORPTION AND ABSORPTION INDUCED SURFACE SEGREGATION

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Using a pair bond type model for the interatomic interactions, we determine surface segregation on clean, H, O and CO covered surfaces of various alloys. Furthermore, we study surface segregation caused by bulk hydrogen absorption. Numerical results are presented for $\text{Pd}_x\text{Zr}_{1-x}\text{H}_y$. We find, that strong surface segregation may result from chemisorption of O and CO and from absorption of H in the bulk of an alloy.

1. Introduction

The surface composition of transition metal alloys has been studied intensively in recent years. Clearly, the catalytic activity and selectivity of such alloys [1] strongly depend on their surface composition. It has been observed, that chemisorption of atoms and molecules [2–5] and bulk absorption of hydrogen [6] can change the surface composition drastically, thereby influencing the heterogeneous reaction rate [7].

A detailed theoretical understanding of the effects of chemisorption and bulk absorption on surface segregation would require an electronic theory. So far, only a simple tight-binding electronic theory has been used to determine surface segregation for a few noble [8] and transition metal alloys [9,10]. An extension of such theories to segregation at the surface of transition metal alloys with chemisorbed species and bulk absorbed hydrogen is difficult. Therefore, in order to obtain a first physical understanding of the change in surface segregation due to chemisorption or due to H absorbed in the bulk, we use for the interactions between the atoms pair bond energies. Thus, we can easily describe the broken bonds due to the surface and the extra bonds due to chemisorbed or absorbed atoms. Such a bond-breaking model using interatomic bond energies has been successfully used to determine surface segregation in many transition metal alloys [11–14].

In section 2 we determine the change in surface segregation due to chemisorbed atoms like H and O and simple molecules like CO. In section 3 we determine the effect of bulk absorbed hydrogen on the surface segregation and

present results for $\text{Pd}_x\text{Zr}_{1-x}\text{H}_y$. In section 4 the obtained results are critically discussed and further applications are proposed. In section 5 we present a brief summary of our results.

2. Change of surface segregation due to chemisorption

In semiempirical theories, the major contribution to the driving force for segregation at the surface of alloys is the difference in the heats of vaporization or the surface energies of the constituents. However, there may be corrections due to relaxation of atoms in the surface layer and the strain energy arising from different atomic sizes of the constituents. For a monolayer regular solution model, the surface concentration x_s of A in the alloy A_xB_{1-x} is given by [13]

$$x_s/(1-x_s) = [x/(1-x)] \exp(Q_{\text{seg}}/RT), \quad (2.1)$$

where the heat of segregation Q_{seg} is the work involved in exchanging a surface A atom and a bulk B atom. An explicit expression for the heat of segregation in terms of the broken bonds can be easily given and will be used in section 3 (see eq. (3.1)). However, we prefer at the moment to use for Q_{seg} an expression derived by Miedema [11] for dilute alloys, which was successfully applied previously. Consider now a clean alloy surface (the average crystal plane), where one third of the bonds are broken. Clearly, the exchange of A (solute) and B (solvent) atoms will involve a heat of solution term to account for the modified environment of the exchanged atoms in the bulk and at the surface. Furthermore, due to the exchange of atoms at the surface, a second term will result describing the difference in the surface energies of the exchanged atoms. Thus we obtain the following expression [11] for the heat of segregation

$$Q_{\text{seg}} = \frac{1}{3} [f \Delta H_{\text{sol}}(A, B) - g(\gamma_A - \gamma_B) V_A^{2/3}]. \quad (2.2)$$

Here, the factor f takes into account the deviation from the average crystal plane due to atomic relaxation and has been given the value 0.71, g is a constant equal to 4.0×10^8 , and V_A is the molar volume of the solute. $\Delta H_{\text{sol}}(A, B)$ is the heat of solution of the solute in the solvent and $\gamma_{A(B)}$ is the surface energy of A(B). As we discuss in section 4, this expression also correctly describes the effect of the different atomic sizes of the alloy constituents on the segregation.

In the presence of adsorbates, eq. (2.1) should be modified as

$$x_s/(1-x_s) = [x/(1-x)] \exp(Q_{\text{seg}}^{\text{chem}}/RT), \quad (2.3)$$

where

$$Q_{\text{seg}}^{\text{chem}} = Q_{\text{seg}} + (E_A - E_B) \theta. \quad (2.4)$$

Here, $E_{A(B)}$ is the chemisorption energy of the adsorbate on A(B) and θ is the

Table 1

Values for the chemisorption binding energies of H, O, CO for various metals

Element	Chemisorption bond energy (kJ/mol)		
	H	O	CO
Ag		335 ^a	28 ^a
Au			38 ^b
Cu	239 ^a	299 ^a	63 ^a
Cr	263 ^b	423 ^b	
Fe	268 ^a	369 ^b	167 ^b
Ir	264 ^a	389 ^a	142 ^a
Ni	264 ^a	377 ^a	126 ^a
Pd	264 ^a	377 ^a	151 ^a
Pt	239 ^a	319 ^b	134 ^a
Rh	243 ^b	369 ^b	193 ^a
Zr			630 ^b

^a Ref. [15].^b Ref. [16].

adsorbate coverage ($\theta = 1$ means one monolayer).

From the most recent compilations [15,16] we have collected in table 1 experimental data for chemisorption bond energies of H, O and CO on metals, whose alloys have been studied in this work. The data for the surface energies and the heats of solution have been taken from the work of Miedema and coworkers [17]. Using eqs. (2.2) and (2.4), the heat of segregation has been

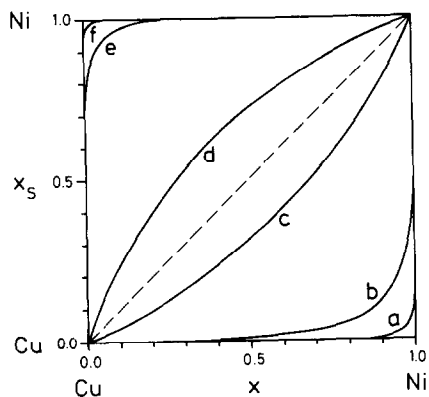


Fig. 1. Surface segregation for clean and covered surfaces of $\text{Ni}_x\text{Cu}_{1-x}$, calculated from eqs. (2.1) and (2.3) and using Q_{seg} values from table 2. Curve a refers to a clean surface at $T=600$ K. Curve b refers to a H covered surface ($\theta=1$) at $T=300$ K. Curves c and d refer to CO and O covered surface ($\theta=0.5$) at $T=600$ K. Finally, curves e and f refer to CO and O ($\theta=1$), respectively, at $T=600$ K.

Table 2

Heats of segregation Q_{seg} of the solute A for clean and monolayer covered surfaces of dilute alloys A_xB_{1-x} , calculated from eqs. (2.2) and (2.4); a positive (negative) value of Q_{seg} corresponds to segregation of solute (solvent); the magnitude of Q_{seg} is a measure of segregation strength: the experimental values in column 2 are taken from ref. [12], and references cited therein

Alloy A-B	Segregating element (expt.)	Q_{seg} (kJ/mol)	$Q_{\text{seg}}^{\text{chem}}(\text{H})$ (kJ/mol)	$Q_{\text{seg}}^{\text{chem}}(\text{O})$ (kJ/mol)	$Q_{\text{seg}}^{\text{chem}}(\text{CO})$ (kJ/mol)
Ag-Au	Ag	+14.5			+4.5
Ag-Cu	Ag	+38.8		+74.8	+3.8
Ag-Pd	Ag	+47.4		+5.4	-75.6
Ag-Rh	Ag	+103.0		+59.0	-62.0
Au-Cu	Au	+11.9			-13.1
Au-Ni	Au	+64.6			
Au-Pd	Au	+34.5			-78.5
Cr-Pt	none	-13.0	+11.0	+91.0	
Cu-Ni	Cu	+35.5	+10.5	-44.5	-27.5
Fe-Cr	Cr	-8.8	-3.8	-62.8	
Fe-Cu	Cu	-20.3	+8.7	+49.7	+83.7
Fe-Ni	Ni	-6.4	-2.4	-16.4	+34.6
Fe-Pt	none	-11.1	+17.9	+38.9	+21.9
Ni-Pd	Pd	-16.8	-16.8	-16.8	-41.8
Ni-Pt	none	+0.8	+25.8	+60.8	-7.2
Ni-Th	Th	-86.7			
Pd-Pt	Pd	+27.7	+52.7	+85.7	+44.7
Pt-Au	Au	-54.6			+41.4
Pt-Cu	Cu	-48.6	-48.6	-28.6	+22.4
Pt-Ir	Pt	+32.7	+7.7	-37.3	+24.7
Pt-Os	Pt	+55.3			
Pt-Rh	Pt	+10.1	+6.1	-39.9	-48.9
Sn-Au	Sn	+60.8			
Sn-Cu	Sn	+94.2			
Sn-Fe	Sn	+170.3			
Sn-Pt	Sn	+130.3			
Zr-Fe	Zr	+18.5			+481.5

calculated for a large number of alloys above phase separation and tabulated in table 2. Using these results, the surface composition of an alloy can be calculated easily from its bulk composition with the help of eq. (2.1). As an illustration, results for clean and covered surfaces of a $\text{Ni}_x\text{Cu}_{1-x}$ alloy are shown in fig. 1.

3. Surface segregation caused by hydrogen absorption in the bulk of a transition metal alloy

In this section we discuss surface segregation which is induced by bulk absorption of atoms. Recently, it has been observed [6] that hydrogen absorp-

tion in a $\text{Pd}_x\text{Zr}_{1-x}$ alloy caused a large segregation of Pd towards the surface, whereas in absence of hydrogen there was nearly no segregation.

One expects intuitively, that the observed surface segregation of Pd in $\text{Pd}_x\text{Zr}_{1-x}$ results from the large difference in the heat of solution of hydrogen in Pd or Zr. Note, the heat of solution is -0.5 kJ/mol for H in Pd and -76 kJ/mol for H in Zr [18].

In order to determine quantitatively the H induced surface enrichment with Pd in $\text{Pd}_x\text{Zr}_{1-x}$, we use again a bond model [13] for the interaction energies between Zr and Pd atoms in presence and in absence of hydrogen. For the case of a regular solution [19], the segregation behavior is described by eq. (2.1). For a non-dilute alloy, the heat of segregation Q_{seg} can be expressed in terms of pair bond energies which are first supposed to be the same in the bulk and at the surface. In Q_{seg} we express the difference of the Pd and Zr pair bond energies at the surface by the more appropriate difference in surface energies of the alloy constituents. The final expression for Q_{seg} is then [13]

$$Q_{\text{seg}} = \left[(\gamma_{\text{Zr}}\sigma_{\text{Zr}} - \gamma_{\text{Pd}}\sigma_{\text{Pd}}) - 2\omega Z_{\text{v}}(x - \frac{1}{2}) \right] + \left[2\omega Z_{\text{l}}(x_{\text{s}} - x) \right]. \quad (3.1)$$

The first term represents the difference in surface energies of Zr and Pd atoms; γ and σ are the surface tension and the surface area per atom. Z_{l} and Z_{v} are the lateral and vertical coordination of an atom, which we take from the equally close-packed fcc structure considering its (100) surface. Thus, $Z_{\text{l}} = Z_{\text{v}} = 4$ and the bulk coordination is $Z = Z_{\text{l}} + 2Z_{\text{v}}$. ω is the alloy parameter, which can be written in terms of Zr and Pd pair bond energies as

$$\omega = \epsilon_{\text{Pd,Zr}} - \frac{1}{2}(\epsilon_{\text{Pd,Pd}} + \epsilon_{\text{Zr,Zr}}).$$

Note, ω is related to the heat of mixing ΔH_{m} by

$$\omega = \Delta H_{\text{m}} / [Zx(1-x)].$$

In the bond picture, the surface energy of an atom has been related to its heat of vaporization as [13] $\gamma_i\sigma_i = 0.174 \Delta H^{\text{vap}}(i)$; $i = \text{Pd}, \text{Zr}$. Making use of this identity, the surface energy term in eq. (3.1) can be written as

$$\gamma_{\text{Zr}}\sigma_{\text{Zr}} - \gamma_{\text{Pd}}\sigma_{\text{Pd}} = 0.174 \Delta H^{\text{vap}}(\text{Pd}) \left[\left(\gamma_{\text{Zr}} V_{\text{Zr}}^{2/3} \right) / \left(\gamma_{\text{Pd}} V_{\text{Pd}}^{2/3} \right) - 1 \right]. \quad (3.2)$$

Using values given by Miedema [20] for γ and the molar volumes V , and an experimental value [21] for $\Delta H^{\text{vap}}(\text{Pd})$, this difference of surface energies will be 16.6 kJ/mol. From experimental data for the heat of mixing [22] of $\text{Pd}_{0.35}\text{Zr}_{0.65}$, we get $\omega = -21 \pm 9$ kJ/mol. Solving eqs. (2.1) and (3.1) self-consistently, the equilibrium surface composition has been calculated to be $\text{Pd}_{0.30}\text{Zr}_{0.70}$. Hence, no observable surface segregation will occur at the experimental temperature $T = 423$ K. This result does not change even if we take the large error in ω into account and use $\omega = -10$ kJ/mol. Thus, in absence of hydrogen, we expect no segregation in $\text{Pd}_{0.35}\text{Zr}_{0.65}$, which seems in accordance with experiment.

In the case of hydrogen absorption, eq. (3.1) must be modified. Then,

$$Q_{\text{seg}} = (\gamma_{\text{Zr}}\sigma_{\text{Zr}} - \gamma_{\text{Pd}}\sigma_{\text{Pd}}) - 2\omega^{\text{H}}Z_{\text{v}}(x - \frac{1}{2}) + 2\omega^{\text{H}}Z_{\text{f}}(x_{\text{s}} - x) + \Delta H'. \quad (3.3)$$

Here, ω^{H} is the alloy parameter modified due to the presence of H and $\Delta H'$ is the correction to the surface energies due to the absorbed hydrogen. $\Delta H'$ involves essentially the different binding of the absorbed H to the bulk Pd and Zr atoms. Clearly,

$$\Delta H' = \Delta E_{\text{s}}(\text{Zr}) - \Delta E_{\text{s}}(\text{Pd}),$$

where $\Delta E_{\text{s}}(\text{Zr})$ and $\Delta E_{\text{s}}(\text{Pd})$ denote the additional surface energy of a Zr atom and Pd atom, respectively, resulting from the presence of H. As the pair bond model need not be appropriate for the relatively long-ranged hydrogen–metal interactions, we determine the ΔE_{s} as follows. We study a (100) surface and assume a fcc lattice where hydrogen is in octahedral interstitial positions. We consider now the solution of H in pure Zr. The binding energy of a hydrogen atom in ZrH_y is, apart from an additive constant, the heat of mixing for Zr and metallic hydrogen [18] per hydrogen atom. For low hydrogen concentrations, this is the heat of solution $\Delta H_{\text{sol}}(\text{H}, \text{Zr})$ for H in Zr. Thus, upon hydrogen absorption, the total cohesive energy of Zr will increase. The additional binding energy of a bulk Zr atom due to absorbed H is

$$\Delta E_{\text{Zr,H}}^{\text{b}} = y \Delta H_{\text{sol}}(\text{H}, \text{Zr}).$$

Furthermore, we assume that this relation will hold also for the additional binding of Zr due to H in the alloy $\text{Pd}_x\text{Zr}_{1-x}$. Assuming then a random distribution of H, $\Delta E_{\text{Zr,H}}$ will linearly depend on the number of nearest neighbor octahedral sites available for hydrogen. In the bulk of the fcc structure, there are 6 such sites around an atom, whereas on the (100) surface there is only one. Therefore, the additional binding energy of a surface Zr atom due to H will be

$$\Delta E_{\text{Zr,H}}^{\text{s}} = \frac{1}{6}y \Delta H_{\text{sol}}(\text{H}, \text{Zr}).$$

Consequently, the additional surface energy due to bulk hydrogen absorption will be

$$\Delta E_{\text{s}} \equiv \Delta E_{\text{Zr,H}}^{\text{s}} - \Delta E_{\text{Zr,H}}^{\text{b}}.$$

This is

$$\Delta E_{\text{s}}(\text{Zr}) = -\frac{5}{6}y \Delta H_{\text{sol}}(\text{H}, \text{Zr}).$$

Thus, the additional difference $\Delta H'$ in the surface energies of Zr and Pd due to H absorption can be written as

$$\Delta H' = -\frac{5}{6}y[\Delta H_{\text{sol}}(\text{H}, \text{Zr}) - \Delta H_{\text{sol}}(\text{H}, \text{Pd})]. \quad (3.4)$$

Because of the large difference in the heats of solution of hydrogen in the alloy components, $\Delta H'$ is large and will induce Pd surface segregation even for low concentrations of absorbed hydrogen.

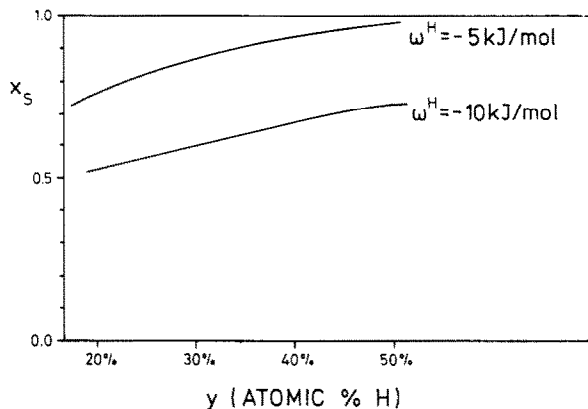


Fig. 2. Surface concentration x_s of Pd in $\text{Pd}_{0.35}\text{Zr}_{0.65}$ obtained from a self-consistent calculation using eqs. (2.1) and (3.3). The concentration of absorbed hydrogen is denoted by y . The alloy parameter ω^{H} is an input parameter.

In evaluating Q_{scg} one should note, that $\omega^{\text{H}} < \omega$. It has been discussed previously [23] that absorbed hydrogen will decrease the effective contact between bulk metal atoms, thereby decreasing the magnitude of the alloy interaction energy parameter ω . However, it is difficult to obtain reliable values for this effective ω^{H} in the presence of hydrogen. Therefore, for the numerical analysis, we will proceed by using ω^{H} as an input parameter. In order to obtain an idea for reasonable values of ω^{H} , the following remarks are made. First, we expect that ω^{H} should be smaller in glassy alloys than in the corresponding crystalline systems. Furthermore, as discussed previously [23], ω^{H} will be only a fraction of the alloy parameter ω in the absence of hydrogen. Note, that this fraction should generally depend on the hydrogen concentration. In view of the results presented in ref. [23], we expect ω^{H}/ω to be of the order of 0.25 to 0.5 for hydrogen concentrations between 20 and 50 at%.

Results for the equilibrium surface concentration x_s of Pd for different hydrogen concentrations and different values of the alloy parameter ω^{H} are presented in fig. 2. From these results it can be seen that, for hydrogen concentrations between 20–50%, one obtains for the surface concentrations x_s of Pd values between 0.6 and 0.9. This result compares well with the experimental results for glassy $\text{Pd}_{0.35}\text{Zr}_{0.65}$ with absorbed hydrogen [6]. The H concentrations were estimated to be of the order of 0.2.

4. Discussion

In this section, we critically discuss the approaches used for determining the chemisorption and absorption induced segregation and consider these problems as special cases of the more general interface problem.

First, we discuss eq. (2.2) describing the heat of segregation in a dilute alloy. As mentioned previously, strain energy effects may influence surface segregation in alloys. Tsai et al. [24] have proposed that these effects are important only if the solute is bigger in size than the solvent. In that case, the solute would segregate to the surface. That this feature is also incorporated in eq. (2.2) can be seen as follows. Consider the term $(\gamma_A - \gamma_B)$, which can also be written in terms of the heats of vaporization ΔH^{vap} as

$$\gamma_A \left(1 - \frac{V_A^{2/3} \Delta H^{\text{vap}}(\text{B})}{V_B^{2/3} \Delta H^{\text{vap}}(\text{A})} \right).$$

From this it can be seen that the surface is enriched with the constituent having lower heat of vaporization or the bigger atomic size. As can be seen from comparison of the second and third columns in table 2, we calculate correctly which atoms are segregating to the surface. This overall agreement with experiment suggests that eqs. (2.1) and (2.2) should also give qualitatively the correct results for alloys whose constituents differ appreciably in size. Although the validity of eqs. (2.2) and (2.4) is not clear in the case of concentrated alloys, we do not expect a qualitative change in the surface segregation behavior for concentrated alloys.

For a surface covered with chemisorbed species, the heat of segregation is modified by a term describing the new surface bonds to the adsorbates. However, eq. (2.4) needs further modification in the case of island formation of the chemisorbed atoms or molecules. Then, spatial fluctuations in the coverage occur which induce local variations in the surface segregation. With respect to the chemisorption induced surface segregation, note that the surface equilibrium concentration x_s , calculated from eqs. (2.1) and (2.3), will be achieved in the experiment after a time, depending on temperature and on the diffusion kinetics of the alloy. The observed $x_s(t)$ will change exponentially with time towards the equilibrium x_s . For Q_{scg} values very low in magnitude we expect no observable segregation. On the other hand, considerable segregation is expected to occur for high values of Q_{seg} even at relatively low temperatures. This is confirmed by experiment. Thus, chemisorption induced surface segregation should be observable at temperatures which are lower than the desorption temperature, but which are large enough so that surface segregation occurs within usual experimental observation times. This is not the case for chemisorbed hydrogen, which has a very low desorption temperature. As can also be seen from table 2, we do not expect a large change in the surface composition of an alloy upon chemisorption of hydrogen. This is in agreement with experiment [5,25]. For O and CO chemisorption we expect a significant change in surface segregation. This is evident from tables 1 and 2, and fig. 1. The influence of CO and O chemisorption on surface segregation is illustrated by the curves c and d. Note that the apparently large segregation corresponds to thermal equilibrium and can only be observed after a relatively long time as discussed before.

Though little experimental information is available on chemisorption induced segregation, our predictions agree with observations for O chemisorbed on Cu–Ni and Au–Ni and CO on Cu–Ni, Pt–Au, Ag–Pd, Au–Pd and Au–Ni alloy surfaces. In all these cases, one observes a reversal of the atoms which segregate to the surface. From experimental data on chemisorption energies of O and CO (table 1 and ref. [16]), both the magnitude and variation of chemisorption energy decrease as one goes from left to right of the transition metal series. This variation is quite small towards the noble metal end and that is why we do not expect any significant change in the segregation behaviour of noble metal — noble metal alloys. However, one will observe drastic effects for noble metal — transition metal alloys as discussed above. Furthermore, for transition metal alloys, whose constituents are not nearest neighbors in the periodic table, some significant changes can be expected as well. It can be seen from table 2 that for CO on Fe–Ni, Pt–Rh, Fe–Pt and O on Pt–Rh and Pt–Ir, we predict a reversal of the segregation expected for clean surfaces. However, for CO on Fe–Zr and O on Fe–Cr and Ni–Pt, the clean surface segregation is enhanced. No experimental results are available on these systems. For Sn, no chemisorption energy data could be found. However, from the above discussion we expect significant changes in segregation in Sn alloys. This is also supported by experimental data on CO covered Pt–Sn surfaces [5].

Note that for determining surface segregation in concentrated alloys, eqs. (2.1) and (3.1) need to be solved self-consistently. It can easily be seen that the last term in eq. (3.1) involving the difference of the surface and bulk concentration, couples this equation to eq. (2.1), whereby ω plays the role of a coupling constant. A negative (positive) ω will suppress (enhance) surface segregation whose nature and magnitude are primarily decided by the first term in eq. (3.1). It is the highly negative value of ω ($\omega = -21$ kJ/mol) which suppresses any surface segregation in pure $\text{Pd}_x\text{Zr}_{1-x}$.

It has already been mentioned in section 3 that, in the case of absorbed hydrogen, a pair bond type model for hydrogen binding might only be of limited validity due to the long-range interactions between H and the surrounding metal atoms. Therefore, we proceeded more generally, using total energy arguments (involving the experimentally accessible heat of solution of hydrogen) rather than pair bond energies. Two effects are responsible for the surface segregation in $\text{Pd}_x\text{Zr}_{1-x}$ induced by bulk hydrogen absorption. First, due to hydrogen absorption, the surface energies of Pd and Zr will be changed considerably. Secondly, the alloy parameter ω , which suppresses surface segregation in pure $\text{Pd}_x\text{Zr}_{1-x}$, decreases considerably due to H absorption. Note, the results presented in fig. 2 depend sensitively on ω^{H} . Further studies to determine ω^{H} would be very valuable. Note that bulk absorption and chemisorption induced surface segregation are special cases of the more general problems of segregation at interfaces or in ternary alloys. In the following we briefly discuss the problem of the interface between an alloy A_xB_{1-x} and a pure substance C, see fig. 3. The atomic segregation at the interface will be

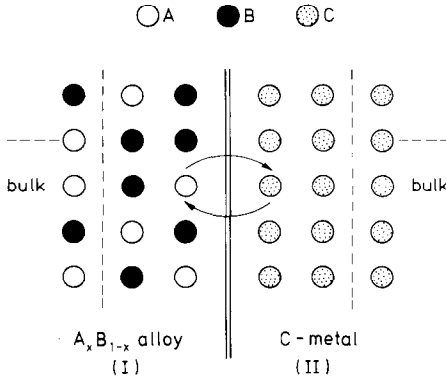


Fig. 3. Illustration of segregation at the interface of an A_xB_{1-x} alloy (I) and a metal C (II). Diffusion between I and II will occur, if the exchange of interlayer atoms (marked by arrows) is exothermic. At finite times, only the atomic layers close to the interface will experience a change in composition.

controlled by the exchange heats $Q_{\text{ex}}(A, C)$ and $Q_{\text{ex}}(B, C)$, describing the work involved in exchanging an A or B atom and a C atom across the interface. Within the pair bond model, $Q_{\text{ex}}(A, C)$ can be written as

$$Q_{\text{ex}}(A, C) = (1-x)(\epsilon_{AC} - \epsilon_{BC}) + (Z_l + 1)[(1+x)\omega_{AC} + (1-x)\omega_{BC} - (1-x)\omega_{AB}]. \quad (5.1)$$

A similar expression is obtained for $Q_{\text{ex}}(B, C)$. If both $Q_{\text{ex}}(A, C)$ and $Q_{\text{ex}}(B, C)$ are positive, there will be no atomic diffusion across the interface. We expect only interface segregation in the A_xB_{1-x} alloy, which depends on the metal C. This situation corresponds to the case of chemisorption induced segregation. In the opposite case of a negative heat of exchange, one expects exchange of atoms across the interface. Consider now the concentrations x_A , x_B and x_C in the atomic layers near the interface. Clearly, due to kinetic reasons, only the layers closest to the interface will be affected by diffusion. Consider a second possible case of a compound-forming tendency between A and C much stronger than between A and B, or B and C. Here, we expect a large interpenetration of A and C atoms, while B atoms will be pushed out of the interface. If only a finite layer of C atoms is present on AB, then it would be absorbed totally, pushing the B component to the surface. Such a case is very similar to the absorption induced segregation described in section 3.

5. Summary

Using a bond model for the interatomic interactions, we have studied chemisorption and absorption induced surface segregation. In the case of

chemisorption induced segregation, we observe large effects only for molecules, which strongly bind only to one type of the alloy atoms. For example, this is the case for oxygen or CO chemisorption on $\text{Cu}_{1-x}\text{Ni}_x$ alloys. While hydrogen chemisorbed on the surface will not effect much surface segregation, hydrogen absorbed in the bulk can change the surface alloy composition significantly. Obviously, this induced surface segregation is generally very important for the catalytic activity of (transition metal) alloy surfaces. For example, due to H absorption one may regenerate a surface "poisoned" catalyst. The case of surface segregation due to H absorption illustrates the essential features of surface segregation in ternary alloys. The chemisorption induced surface segregation illustrates the essential features of segregation at interfaces.

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