Ordering tendency inside a surface segregation: Application to Pt-Ni alloys

Mats Hillert and John Rundgren

Royal Institute of Technology, S-10044 Stockholm, Sweden

The composition profile inside a surface, showing segregation in a binary alloy, has been calculated from the simple nearest-neighbor-interaction model. For alloy systems with an ordering region an oscillation in composition is predicted even far away from the ordering region. This result is in general agreement with experimental observation.

I. INTRODUCTION

It has recently[1] been reported that Pt-Ni alloys, which have been annealed at 900 °C and quenched to room temperature, show a high Pt content in the first atomic plane on (111) surfaces and that the next atomic plane shows a deficit. The third plane shows a slightly increased Pt content. For an alloy with 78 at. % Pt the first plane contained 99 at. % Pt, the second plane about 30 at. % Pt and the third plane about 87 at. % Pt. It is worth noting that in this case there is thus a net deficit of Pt in the surface layer, corresponding to a deficit of 18 at. % in one atomic plane.

Presumably, there is some factor which makes it preferable for Pt atoms to be situated at the very surface. The present work was undertaken in order to test if the fact that the second atomic plane shows a deficit of Pt can be related to the fact that the Pt-Ni system has an ordering transformation below 645 °C. A simple model calculation was carried out based on the nearest-neighbor-interaction model. It was assumed that the special factor operating at the surface only affects the atoms in the first atomic plane. The results of that calculation will now be reported.

II. THE NEAREST-NEIGHBOR-INTERACTION MODEL

The nearest-neighbor-interaction model for alloys was first proposed by Gorsky[2] and further developed by Bragg and Williams.[3] It has been the basis for many theories developed later on. The simplest theories use the so-called zeroth approximation,[4] which assumes random mixing of the various components. In the case of ordering this assumption is applied to the sublattices. A common feature of these theories is that they concern solutions which are essentially homogeneous in composition. An exception was Becker's[4] treatment of the interfacial energy between the phases on the two sides of a miscibility gap. He assumed that the composition of each phase was homogeneous all the way to the interface, producing a sharp discontinuity in composition at the interface. His treatment of interfaces was later improved by Ono,[5] who allowed the composition to vary monotonically from one phase to the other. Finally, Hillert[6,7] generalized the treatment and was thus able to model nucleation, spinodal decomposition, and ordering transformation.

As a special case Hillert gave an equation which relates the composition of three successive atomic planes if the system contains some large region where all the planes have a common composition, x_∞.

$$x_{p+1} = \frac{Z}{z}x_\infty + \frac{kT}{2zv}\ln\frac{1-x_\infty}{x_\infty} - \left(\frac{Z}{z}-2\right)x_p$$
$$+ \frac{kT}{2zv}\ln\frac{x_p}{1-x_p} - x_{p-1} \ . \tag{1}$$

Z is the coordination number, which is 12 for the fcc structure of Pt and Ni. z is the number of nearest neighbors of an atom which are situated in the next atomic plane. For (111) planes in fcc, $z = 3$, for (100) planes, $z = 4$. v is the interaction energy and is related to the enthalpies of the bonds by

$$2v = 2H_{AB} - H_{AA} - H_{BB} \ . \tag{2}$$

Hillert's method was applied to segregation in solid/liquid interfaces by Nason and Tiller[8] and to free surfaces by Williams and Nason.[9] The original relation, Eq. (1), still appears in recent developments[10] of segregation but for the topmost planes of atoms it is modified due to the presence of the free surface. This is natural since the $p-1$ plane does not exist if the p plane is the topmost plane. By simply introducing the enthalpies of the broken bonds, H_{Av} and H_{Bv}, at the surface one obtains

$$x_{p+1} = \frac{Z}{z}x_\infty + \frac{kT}{2zv}\ln\frac{1-x_\infty}{x_\infty} - \left(\frac{Z}{z}-2\right)x_p + \frac{kT}{2zv}\ln\frac{x_p}{1-x_p}$$
$$- \frac{1}{2} + [(\tfrac{1}{2}H_{AA} - H_{Av}) - (\tfrac{1}{2}H_{BB} - H_{Bv})]/2v \ . \tag{3}$$

By assuming that a free atom in the gas phase has Z broken bonds and further assuming that they have the same energy as the broken bonds in the surface, it is possible to evaluate $\frac{1}{2}H_{AA} - H_{Av}$ and $\frac{1}{2}H_{BB} - H_{Bv}$ from the enthalpy of sublimation for pure A and B, respectively, by dividing by Z. Sometimes H_{Av} and H_{Bv} are not introduced and do not appear in Eq. (3), an error which is compensated by the erroneous identification of $\frac{1}{2}H_{AA}$ and $\frac{1}{2}H_{BB}$ with the enthalpies of sublimation divided by Z.[9,10]

The effect of the surface may reach deeper into the crystal and a relaxation model has been discussed by Wil-

liams and Nason[9] which extends to the second plane of atoms.

III. METHOD OF CALCULATION

The main purpose of the present work was to examine whether an oscillation in composition inside the topmost plane of atoms could be explained by the nearest-neighbor-interaction model. An explanation of the composition of the topmost plane itself was not attempted. Instead, that composition was taken as experimental information. As a consequence, it is not necessary to use Eq. (3). The whole calculation can be carried out using Hillert's original relation, Eq. (1).

After selecting the composition of the topmost plane, in accordance with experimental information, the composition of the second plane was estimated and the compositions of the subsequent planes could be calculated one by one in succession. The estimation of the composition of the second plane was changed and by trial and error it was possible to find a solution where the composition gradually approached the average composition of the alloy. That solution was accepted as a model description of the state of equilibrium.

If one also wanted to calculate the composition of the topmost plane, one would start by guessing its composition, then one would calculate the composition of the second plane from Eq. (3), and finally proceed with Eq. (1) as before. It is worth noting that Williams and Nason[9] and Ng et al.[10] have only considered four planes of atoms, which is an unnecessary limitation because Eq. (1) is a recurrence formula.

IV. SURFACE-SEGREGATION CALCULATIONS

A. Interaction energy in Pt-Ni alloys

The equiatomic Pt-Ni alloy is known to transform to the AuCu ordered structure at low temperatures.[11] The interaction energy v is thus negative, and its value can be evaluated from the critical temperature of ordering which is 645 °C.[4] The ordered AuCu structure is composed of (100) planes alternatively rich in one component or the other. For such planes $z = 4$ and it can be shown that $kT/2v$ should be equal to -1 at the critical temperature for ordering.

B. The (100) surface

The first calculation was carried out for the equiatomic alloy at the critical temperature by using $kT/2v = -1$. It was assumed that the special surface effect caused the Pt content of the first atomic plane on a (100) surface to be 90 at. %. The result of the calculation is presented in Fig. 1(a). It is shown that the high surface content gives rise to an oscillation in composition of the same kind as in an ordered alloy but in the present case the oscillation is damped. This is necessary, of course, because the alloy is only on the border of the ordering region in the phase diagram.[11]

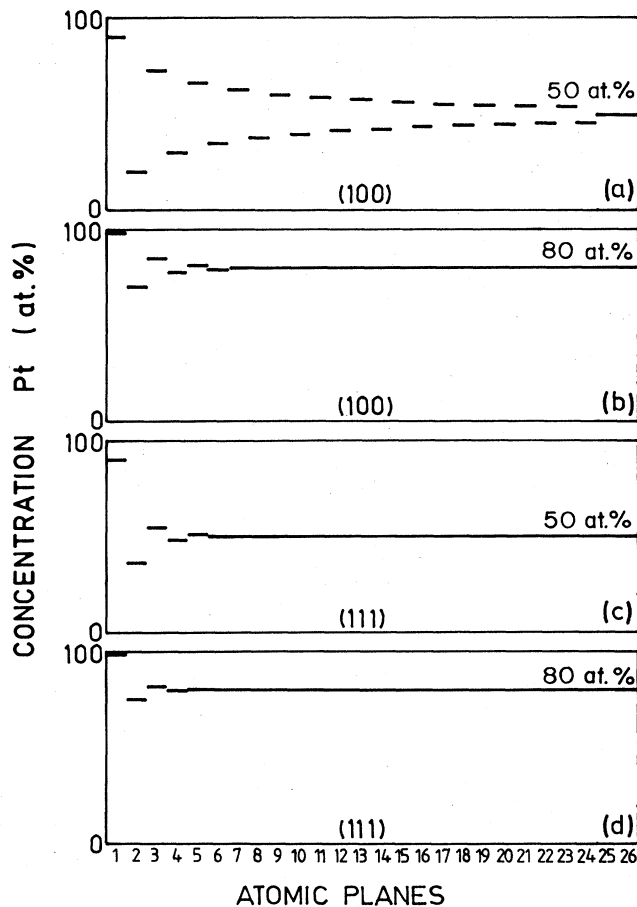A similar calculation for an alloy with 80 at. % Pt was carried out at the same temperature under the assumption

FIG. 1. Variation in composition inside the surface of two Ni-Pt alloys at $kT/2v = -1$, calculated for four cases. (a) (100) surface in a 50 at. % Pt alloy, assuming a Pt content of 90% in the first atomic plane. (b) (100) surface in an 80 at. % Pt alloy, assuming a Pt content of 99% in the first atomic plane. (c) (111) surface in a 50 at. % Pt alloy, assuming a Pt content of 90% in the first atomic plane. (d) (111) surface in an 80 at. % Pt alloy, assuming a Pt content of 99% in the first atomic plane.

of a surface content of 99 at. % Pt [see Fig. 1(b)]. An oscillation in composition is again found but the damping is now much stronger and only a few atomic planes are affected appreciably. This is natural since the alloy is far away from the ordering region in the phase diagram.

C. The (111) surface

The experimental results[1] on the oscillatory variation in composition close to the surface concern the (111) surface. Ordering of the type giving oscillations in the composition of (111) planes is possible but cannot be explained by the simple nearest-neighbor-interaction model because an atom in a (111) plane has as many neighbors in its own plane as in the two neighboring planes, z being 3. It was thus of considerable interest to examine whether the simple model could explain oscillatory variations in composition close to a (100) surface. Indeed, this was the case as

TABLE I. Composition oscillations in Pt-Ni alloys at 900 °C.

x_∞	Face	x_1	x_2	x_3	x_4	x_5	$\sum_i (x_i - x_\infty)$	Remark
0.50	(100)	0.88	0.287	0.624	0.427	0.543	0.25	This work
0.50	(111)	0.88	0.390	0.532	0.491	0.503	0.29	This work
0.50	(111)	0.88	0.09	0.65			0.12	Ref. 1
0.78	(100)	0.99	0.687	0.816	0.765	0.786	0.14	This work
0.78	(111)	0.99	0.728	0.792	0.777	0.781	0.17	This work
0.78	(111)	0.99	0.30	0.87			−0.18	Ref. 1

demonstrated in Figs. 1(c) and 1(d), which were calculated with the same value of $kT/2v = -1$ and with surface contents of 0.9 and 0.99, respectively.

A comparison of the results obtained for the two surfaces in the 80 at. % Pt alloy shows very similar results although the damping is stronger for the (111) surface. The difference in damping is even more dramatic for the equiatomic alloy, Figs 1(a) and 1(c), but this is mainly due to the fact that Fig. 1(a) holds for a system at the critical point for ordering.

V. DISCUSSION AND COMPARISON WITH EXPERIMENT

It is evident that the nearest-neighbor-interaction model predicts oscillations in composition inside the topmost plane of atoms when the interaction energy is negative. This result is obtained even for conditions from the ordering region in the phase diagram. The effect is stronger for the crystallographic plane which is active in ordering but the effect can be quite appreciable for other planes as well.

The oscillations are strongly damped and it is usually sufficient to consider four or five planes close to the surface. The limitation of the treatment to four planes, found in some papers,[9,10] is thus acceptable although unnecessary, because the calculation can easily be extended to any number of planes. It is only close to the ordering region that it is essential to consider a large number of planes.

The Pt-Ni system has an ordering region and, thus, a negative interaction energy. The experimental observation[1] of an oscillation is thus explained qualitatively. A quantitative comparison is given in Table I, which gives the results of calculations carried out for the experimental alloys at the experimental temperature. For the equiatomic alloy it is evident that the calculations predict a stronger damping than observed experimentally and, as a

consequence, the predicted net segregation, represented by $\sum_i (x_i - x_\infty)$, is larger than the experimental one. It is worth noting that the net segregation would be at a maximum of 0.40 if the first plane has 90 at. % Pt and the damping is so strong that all the subsequent planes have close to 50 at. % Pt.

For the 78 at. % Pt alloy the predicted damping is also stronger than that observed experimentally. In this case, the experimentally observed net segregation is negative despite the fact that the primary factor might be a tendency towards enrichment of Pt to the surface. This surprising result was not reproduced by the model calculations.

VI. CONCLUSIONS

The oscillation in composition observed experimentally[1] inside a Pt-enriched (111) surface on Pt-Ni alloys can be explained qualitatively by the simple nearest-neighbor-interaction model despite the fact that the Pt-Ni system does not show any tendency of ordering in the [111] direction. The system does show an ordering tendency in the [100] direction, and for a (100) surface the model predicts a slightly stronger oscillation.

The model predicts that the net segregation to the surface is lower than the segregation represented by the enrichment in the first atomic plane. However, a negative net segregation, which has been reported from one experiment, cannot be predicted by the simple model.

ACKNOWLEDGMENT

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