Evaluation of basic surface segregation trends induced by short-range order in solid solutions

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Abstract

Short-range order (SRO) effects on surface segregation in solid solutions are considered on the basis of general thermodynamical conditions for surface–bulk equilibrium, combined with a qualitative estimation of SRO-related perturbations in the total free energy as a function of concentration. The SRO effects originate from the preferential attraction of solute atoms to growing compositional fluctuations in the bulk or at the surface, governed by solute–solvent interatomic forces. In comparison to results of Bragg–Williams-type approximations, concentration-dependent suppression or enhancement of segregation levels are predicted.

Keywords: Alloys; Equilibrium thermodynamics and statistical mechanics; Surface segregation

Numerous experimental and theoretical studies have been devoted to equilibrium surface segregation in binary alloys [1]. The most common statistical–mechanical approach to the problem is based on the classical mean-field theory, which is equivalent to the Bragg–Williams (BW) approximation, assuming random distribution of atoms at identical lattice sites. Recently, we reported the observation of distinct surface segregation phenomena in a Ni–9%Al solid solution [2], characterized by low Al enrichment levels which increase with temperature, in contrast to predictions of BW-type theories. The free-energy cumulant expansion approach, adapted for surface segregation, revealed that short-range order (SRO) plays a dominant role in the Ni–Al segregation behavior [2]. Some previous studies used quasi-

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chemical or cluster-variation approximate approaches [3–5], including electronic structure calculations for Cu-Ni(001) [6], in order to evaluate SRO effects on surface segregation. However, choosing a specific cluster approximation for certain alloy surface structures restricts the general applicability of the theory. In the present study, a more general approach has been chosen which does not rely on any statistical–mechanical approximation, and yet can help to gain insight into SRO effects on surface segregation. In particular, qualitative predictions of trends induced in segregation level are made for several distinct concentration ranges on the basis of equilibrium conditions and simple considerations concerning the relative shapes of surface and bulk free-energy wells.

From equilibrium thermodynamics, the in-depth concentration gradient in an alloy is formed in accordance with the tendency of a system to achieve minimum of the free-energy, F. Taking
into account conservation of the total number of constituent atoms in the alloy having bulk concentration \(c_b\), layer concentrations \(c_p\) (\(p = s, 1, 2, \ldots\)), and \(N_i\) sites per layer

\[ N_i \sum_p (c_p - c_b) = 0, \quad (1) \]

and using the Lagrangian multiplier technique, one obtains the following condition for the free-energy minimum

\[ \frac{\partial}{\partial c_p} \left[ F - \mu_b N_i \sum_p (c_p - c_b) \right] = 0, \quad \text{for all } p. \quad (2) \]

This equation identifies the "\(p\)-layer chemical potential" \(\mu_p = (1/N_i)(\partial F/\partial c_p)\) with the Lagrangian multiplier \(\mu_p\). Thus, \(\mu_p\) does not depend on \(p\) [7,8], and coincides at equilibrium with the bulk chemical potential.

In the following, it is convenient to use individual "\(p\)-layer free-energy wells" for the dependence of the free energy on the layer concentration. The equality \(\mu_p = \mu_b\) shows that at equilibrium, the slopes of all free-energy wells should be identical. Atoms of a given constituent pass from a layer with a greater chemical potential to a layer with a smaller chemical potential until this equality is achieved. Thus, any perturbation which changes the layer and bulk chemical potentials by the amounts \(\Delta \mu_p\) and \(\Delta \mu_b\), respectively, increases the layer concentration if \(\Delta \mu_b > \Delta \mu_p\), and decreases it in the case \(\Delta \mu_p > \Delta \mu_b\).

In the present context of a non-ideal solid-solution A–B, the most relevant factor affecting the chemical potential is the solvent–solute relative interaction, expressed within the Ising model by the parameter \(V = (V^{AA} + V^{BB} - 2V^{AB})/2\), with \(V^{IJ}\) denoting the \(I–J\) bond energy. The overall contribution to the free energy can be viewed as composed of two terms

\[ \Delta F_V = \Delta F_V^{BW} + \Delta F_V^{SRO}. \]

\(\Delta F_V^{BW}\) denotes the interaction effect in the BW-type approximation, while \(\Delta F_V^{SRO}\) is the SRO-related perturbation, which considers the non-randomness of the actual distribution of solute–solvent atoms in a solid solution. While interaction effects on segregation trends in the BW approximation are quite well understood (see, for example, the review by Sparnaay [9]), the basic physical mechanism of SRO-induced segregation effects needs some clarification. The dependence of \(\Delta F_V^{BW}\) and \(\Delta F_V^{SRO}\) on concentration has some similarities, but also significant differences. In the BW approximation, interactions do not affect the entropy of mixing [10], and hence \(\Delta F_V^{BW}\) coincides with the "mixing energy", which is positive or negative (endothermic or exothermic alloying). Being proportional to \(c(1-c)V\) [10], it vanishes in the two dilute limits and has an extremum at equiatomic composition. The same limits also hold for the SRO perturbations, but unlike \(\Delta F_V^{BW}\), \(\Delta F_V^{SRO}\) is always negative, since as a result of SRO-related changes in atom surroundings, the overall free energy is lowered, compared to the value predicted for a BW random alloy. Such ordered local regions (or "compositional fluctuations") always attract solute atoms (and repel solvent atoms), and thus, in the case of a demixing (mixing) tendency, clusters of like (unlike) atoms are able to grow (Fig. 1). As discussed above, this implies a decrease in the chemical potential of the atomic layers composing the fluctuations, as compared with the BW value for \(c < 1/2\) (\(\Delta \mu^{SRO} < 0\)) and its increase for \(c > 1/2\).

![Fig. 1. Illustration of short-range order effects in a binary solid solution. Driven by interatomic forces, solute atoms are attracted to local compositional fluctuations: (a) mixing tendency, (b) demixing tendency.](image-url)
(Δμ_{SRO} > 0; for c = 1/2, Δμ_{SRO} = 0). Unlike the BW case, the SRO driving force (Δμ_{SRO}) also vanishes in the dilute limits and at high temperatures, as a result of weakening and disappearance of compositional fluctuations. These features enable us to outline the corresponding short-range order free-energy wells given in Fig. 2. As indicated in Fig. 2, the BW driving forces increase or decrease solute concentration, depending on the mixing/demixing tendency, while the SRO driving force always tends to increase the solute concentration level.

Turning to the problem of surface–bulk equilibrium, in the present qualitative approach we ignore details of possible composition in-depth gradients, and assume equal interactions for the bulk and the surface layer. Then, the surface free-energy well should be shallower and less steep than that in the bulk, due to the reduced surface atomic coordination. Pure SRO effects on surface segregation (beyond the BW approximation) can be predicted from comparison of the SRO driving force directions in the bulk (Δμ_{SRO}^B) and at the surface (Δμ_{SRO}^S), and their relative strength. Such a comparison can be performed easily for specific concentration ranges by inspecting the corresponding surface and bulk SRO-related wells and assuming c_s < 1/2 without loss of generality (the condition c_b > 1/2 can be simply obtained by exchanging the notation of the constituent atoms): (1) Dilute solid solution. Δμ_{SRO}^B vanishes due to weak compositional fluctuations in the bulk of the dilute alloy. The stronger fluctuations at the non-dilute segregated surface lead, in principle, to segregation enhancement for c_s < 1/2 (Fig. 3a), or to its suppression for c_s > 1/2.

(2) Intermediate bulk concentration (non-

Fig. 2. Atomic interaction contributions to the solid solution free-energy as function of concentration: (a) Bragg–Williams approximation, (b) short-range order induced perturbations (the corresponding change in chemical potential is given by the dotted line). Arrows denote driving-force directions.

Fig. 3. Illustration of the competition between the attraction of solute atoms to surface compositional fluctuations and their attraction to bulk fluctuations in a binary solid-solution (right), and the corresponding free-energy wells (left): (a) dilute solid solution, (b) intermediate concentration range (the reduced coordination at the surface is responsible for segregation suppression). (c) Schematic diagram of the SRO enhancement (enh)/suppression (sup) effects on surface segregation (uniform interactions). (i), (ii) and (iii) are the three bulk concentration ranges discussed in the text (as 1, 2 and 3, respectively).
dilute, $c_b<1/2$). Since the bulk free-energy well is steeper in this range (see Fig. 3b), the bulk SRO driving force is stronger, $|\Delta \mu_b^{\text{SRO}}| > |\Delta \mu_s^{\text{SRO}}|$. Consequently, the tendency to increase the bulk solute concentration suppresses solute surface segregation. In the case $c_s>1/2$, the surface SRO driving force amplifies this suppression.

(3) Equiatomic solid solution. The SRO-induced attraction of solute atoms to the bulk vanishes for $c_b=1/2$, and so the surface SRO driving force can become dominant. Then, similarly to case (1), it can either enhance or diminish segregation levels.

Based on all these conclusions, a schematic diagram of SRO effects on surface segregation in binary alloys can be constructed (Fig. 3c). As mentioned previously, the above analysis assumes uniform solute–solvent interactions, whereas in transition-metal alloys, for example, the interactions can change at the surface. In case of enhancement [11], depending on its magnitude, the bulk free-energy well can be shallower and less steep than that of the surface (reversal of the corresponding graphs in Fig. 3). Therefore, instead of suppression, segregation enhancement is predicted for the intermediate composition range (case (2)). It should be emphasized that the magnitude of enhancement or suppression effects, as well as the exact boundaries between enhancement and suppression regions in the diagram, can be determined only on the basis of calculations for a specific binary solid solution and surface orientation using an appropriate statistical–mechanical approach. Numerical calculations based on equations of the free-energy cumulant expansion method, adapted for surface segregation [2], have revealed that in many binary alloys SRO-related perturbations are quite weak, and have minor effects on surface segregation at the temperatures required to achieve equilibration in reasonable annealing times. The subtle conditions for significant SRO effects on equilibrium surface segregation in solid solutions can be satisfied when the solute–solvent interactions are relatively strong and the segregation is weak, as in the case of Ni–9%Al [2] (belonging to the intermediate range, case (2)). In particular, the diminution of SRO-induced suppression of Al segregation with increasing temperature leads to the anomaly observed in its temperature dependence. Moreover, the suppression can, in principle, even reverse the segregation tendency (solute→solvent). Calculations made for a number of other alloys (e.g. V–Sn, Fe–Al or Cr–Ni) show that short-range order is expected to play a dominant role in their surface segregation.

References