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Site segregation in size-mismatched nanoalloys: Application to Cu–Ag

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Abstract

In order to determine the energetic driving forces for surface segregation in bimetallic clusters, we use a combined approach coupling numerical simulations within an *N*-body interatomic potential and a lattice-gas model. This approach, which has been used successfully to study both the superficial segregation in semi-infinite alloys and the intergranular segregation, allows us to determine the relative contributions of the three elementary driving forces for the different sites of the cluster surface (vertices, edges and facets) in both dilute limits for the Cu–Ag system. We show that the segregation hierarchy based on broken-bond arguments (preferential segregation to the vertex sites, less to edge sites, and least to facet sites) is not at all universal. In particular, unusual hierarchies are predicted when the sizes of the constituents are strongly different. Furthermore, we compare the segregation driving forces for cubo-octahedral and icosahedral clusters. They are similar for the vertex sites and edge sites, whereas they differ significantly for the sites of the triangular facets. The segregation of the species with the largest atomic radius (Ag) is indeed largely enhanced in the icosahedral structure due to dilations of the orthoradial distances.

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1. Introduction

In a binary alloy, all defects (point defects, dislocations, stacking faults, surfaces and grain boundaries) modify the local concentrations in their vicinity. This is the so-called segregation phenomenon, which has been extensively studied for surfaces and grain boundaries [1]. This phenomenon is all the more important as the surface-to-volume ratio is large. This is typically the case for bimetallic clusters containing up to several thousands of atoms. These nanoparticles form the fundamental constituents of bimetallic catalysts, their technological applications being mainly controlled by their superficial properties [2]. This explains the increasing number of studies on superficial segregation in bimetallic clusters [3–21].

Theoretical predictions of the enrichment of the various sites of the cluster surface by one of the elements require an energetic model and a free-energy minimization using for instance the mean-field approximation [1] or Monte Carlo (MC) simulations [22]. Among the energetic models, the rigid-lattice approaches based on pairwise interactions allow one to determine simply the energetic driving forces for segregation but are too rough to lead to quantitative predictions. Conversely, ab initio surface segregation results are accurate but cannot be simply related to a few parameters which would enable one to understand the fundamental principles underlying segregation behaviour.

In this paper, we provide a combined approach for segregation in bimetallic clusters. Based upon a simplified description of the electronic structure while taking into

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account atomic relaxations, this approach allows us to analyse the energetic driving forces for segregation. For this purpose we derive an effective Ising model, whose energetic parameters are determined from the electronic structure. With this combined approach, already tested for interfacial segregation [1,23–25], we compare the segregation driving forces for clusters and for surfaces of semi-infinite alloys. Furthermore, we detail the hierarchy of these forces for the different sites of the cluster surface (vertices (V), edges (E) and facets (F)) in both infinitely dilute limits.

The Cu–Ag bimetallic system has been chosen due to the large number of studies previously performed on superficial segregation in this alloy [1]. Cu–Ag is used as a test case for systems with a strong tendency to phase separation [26] and characterized by a large difference in atom size ($r_{\mathrm{Ag}}/r_{\mathrm{Cu}} = 1.13$, where r_{I} is the atomic radius of metal I), the biggest atom (Ag) being the less cohesive ($E_{\mathrm{coh}}^{\mathrm{Ag}} - E_{\mathrm{coh}}^{\mathrm{Cu}} = 0.55$ eV).

The paper is structured as follows: in Section 2 we describe the model and the nanoparticles of interest; in Section 3 we compare the segregation enthalpies for the different surface sites of cubo-octahedral clusters with those of equivalent infinite surfaces. In Section 4 we report the variations of the segregation driving forces with the cluster shapes (cubo-octahedral or icosahedral) and with the size of the nanoparticles. Finally, the conclusions and perspectives are drawn in Section 5.

2. Model

2.1. Permutation and segregation enthalpies in a lattice-gas model

First, we define the energetic quantities that characterize segregation for both infinite surfaces and nanoparticles. Denote c_p the concentration for each p-type of site. Thus, for the surface of an $\mathrm{A}_c\mathrm{B}_{1-c}$ alloy, c_p corresponds to the concentration of the pth plane parallel to the surface (the surface layer being indexed by $p = 0$). For nanoparticles, c_p represents the concentration of the pth concentric shell ($p = 0$ corresponding to the outermost shell) with the possibility to distinguish the different sites (vertex, edge and facet) within each shell. For a lattice-gas model, minimizing the Gibbs free energy within the Bragg–Williams approximation leads to the basic equation for segregation [1,25]

$$\frac{c_p}{1-c_p} = \exp\left(-\frac{\Delta H_p^{\mathrm{perm}} - \Delta\mu}{k_{\mathrm{B}}T}\right), \tag{1}$$

where $\Delta H_p^{\mathrm{perm}}$ is the permutation energy corresponding to the energy balance due to the change of an atom of type B into an atom of type A on a site of the p-class. $\Delta\mu = \mu_{\mathrm{A}} - \mu_{\mathrm{B}}$ is the difference in chemical potentials that imposes the concentration. For the surface of an $\mathrm{A}_c\mathrm{B}_{1-c}$ alloy, Eq. (1) can be expressed with the more usual form [1,25]

$$\frac{c_p}{1-c_p} = \frac{c}{1-c}\exp\left(-\frac{\Delta H_p^{\mathrm{seg}}}{k_{\mathrm{B}}T}\right), \tag{2}$$

where the segregation energy $\Delta H_p^{\mathrm{seg}}$ is the energy change when an A atom in the bulk is exchanged with a B atom in the p-layer. This exchange can be split in two elementary permutations A → B in the bulk corresponding to $-\Delta H_{\mathrm{bulk}}^{\mathrm{perm}}$ and B → A in the p-layer corresponding to $\Delta H_p^{\mathrm{perm}}$, viz.

$$\Delta H_p^{\mathrm{seg}} = \Delta H_p^{\mathrm{perm}} - \Delta H_{\mathrm{bulk}}^{\mathrm{perm}}. \tag{3}$$

When considering an Ising model, $\Delta H_p^{\mathrm{perm}}$ can be expressed as a function of the pair interactions V_{AA}, V_{BB} and V_{AB} between atoms A–A, B–B and A–B in nearest-neighbour position. This leads to [25]

$$\Delta H_p^{\mathrm{perm}} = \Delta H_p^{\mathrm{perm,impurity}} + \Delta H_p^{\mathrm{perm,interaction}}. \tag{4}$$

$\Delta H_p^{\mathrm{perm,impurity}}$ is the permutation enthalpy in the infinitely dilute limit ($c \to 0$). This term is given by

$$\Delta H_p^{\mathrm{perm,impurity}} = Z_p(V_{\mathrm{AB}} - V_{\mathrm{BB}}), \tag{5a}$$

where Z_p is the coordination number of a site of the p-class. It is usual to express the term $(V_{\mathrm{AB}} - V_{\mathrm{BB}})$ with the help of a quantity related to pure metals, $\tau = 1/2(V_{\mathrm{AA}} - V_{\mathrm{BB}})$ and another one which drives the thermodynamic properties of the alloy, $V = 1/2(V_{\mathrm{AA}} + V_{\mathrm{BB}} - 2V_{\mathrm{AB}})$. In particular, the alloy pair interaction V characterizes the tendency of the system to form homoatomic pairs ($V < 0$) or heteroatomic pairs ($V > 0$). Hence

$$\Delta H_p^{\mathrm{perm,impurity}} = Z_p(\tau - V). \tag{5b}$$

$\Delta H_p^{\mathrm{perm,interaction}}$ corresponds to an alloying term that vanishes in the infinitely dilute limit

$$\Delta H_p^{\mathrm{perm,interaction}} = 2\sum_q Z_{pq}Vc_q, \tag{6}$$

where Z_{pq} is the mean coordination number between p-class sites and q-class sites.

The present study of the segregation driving forces being limited to the infinitely dilute limits, $\Delta H_p^{\mathrm{perm}}$ is simply equal to $\Delta H_p^{\mathrm{perm,impurity}}$. We note that $\Delta H_p^{\mathrm{perm,impurity}}$ is the sum of two terms, see Eq. (5b). The first one, which is proportional to the parameter τ relative to pure metals, is referred to as “site effect” as it equals the difference of the energies of the p-class sites between A and B $H_p^{\mathrm{A}} - H_p^{\mathrm{B}}$. The second term, proportional to the alloy pair interaction V, is referred to as “alloying effect”. Hence,

$$\Delta H_p^{\mathrm{perm,impurity}} = \Delta H_p^{\mathrm{perm,site}} + \Delta H_p^{\mathrm{perm,alloy}} \tag{7}$$

with

$$\Delta H_p^{\mathrm{perm,site}} = H_p^{\mathrm{A}} - H_p^{\mathrm{B}} = Z_p\tau, \tag{8a}$$

$$\Delta H_p^{\mathrm{perm,alloy}} = -Z_pV. \tag{8b}$$

When considering segregation enthalpies, Eqs. (7) and (8) become

$$\Delta H_p^{\mathrm{seg,impurity}} = \Delta H_p^{\mathrm{seg,site}} + \Delta H_p^{\mathrm{seg,alloy}}, \tag{9}$$

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