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The chemical potential in surface segregation calculations: AgPd alloys

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Abstract

We put forward a technique for calculating the surface segregation profile in substitutional disordered alloys. The surface internal energy and the effective bulk and surface chemical potentials are calculated using the full charge density exact muffin-tin orbitals method, combined with the coherent potential approximation. The application of our approach is demonstrated to the close-packed surface of Ag_cPd_{1-c} random alloys with $0 < c < 1$. The surface concentration profile, surface energy and segregation energy are investigated as functions of bulk composition. The present results are compared with former theoretical and experimental data. It is found that at low temperature, Ag segregates to the surface layer for the entire bulk composition range. At 0 K, the subsurface layer contains 100% Pd for $c \lesssim 0.4$, and somewhat more than $(2c - 1)$ Ag in alloys with $c > 0.5$. The temperature dependence of the segregation profile is significant for Pd rich alloys and for alloys with intermediate concentrations. At temperatures $\gtrsim 600$ K, the subsurface layer is obtained to be almost bulk like.

Keywords: Density functional calculation; Surface segregation; Surface energy; Surface thermodynamics; Palladium; Silver; Alloys

1. Introduction

Surface phenomena play a decisive role in many different areas of our modern technology, e.g., in the development of catalysts, stainless steel products, maintenance-free self-cleaning surfaces, etc. Promoting or inhibiting certain surface phenomena requires a full control of the surface properties. Tuning these properties assumes an atomic-level understanding of the chemistry and physics of surfaces. Segregation at alloy surfaces is one way to produce materials having optimal properties for specific applications. However, despite of advanced laboratory equipments, the experimental data on multilayer segregation remains scarce. This can be ascribed, first of all, to the fundamental problem of resolving the chemistry of subsurface atomic layers. Today, modern theoretical approaches present an alternative possibility for obtaining accurate data on multilayer surface segregation.

The most widely used theoretical approach for surface segregation is based on Monte-Carlo (MC) technique [1–5]. In this approach, the equilibrium segregation profile is determined by changing the surface configuration repeatedly until energetically the most favorable solution is obtained. Because the total energy of a particular configuration is calculated from effective interactions, a MC method offers, in principle, a simple and fast algorithm for multilayer surface segregation studies. Unfortunately, its application is restricted to systems (i) with ideal undistorted

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underlying lattice, and (ii) where reliable effective interaction parameters can be constructed. An alternative approach is to combine thermodynamic models of surface segregation with ab initio total energy calculations. In this spirit, using the linear muffin-tin orbitals (LMTO) method [6] and the coherent potential approximation (CPA) [7], Abrikosov and Skriver [8] presented the first ab initio surface segregation study for CuNi, AgPd, and AuPt. However, these calculations were carried out within the atomic sphere approximation, which hindered their method to resolve the $\lesssim 0.1$ mRy per surface atom energy differences between different surface configurations.

Recently, a distinct step towards a more accurate surface segregation simulation was taken [9]. Using the full charge density exact muffin-tin orbital (FCD-EMTO) method [10,11], we investigated the surface segregation of $Ag_{0.5}Pd_{0.5}$ random alloy. In this calculation, an 8 atomic layers thick alloy film was used to model the close-packed surface of the face centered cubic (fcc) AgPd alloy. The average chemical composition of the film was fixed to 50%. The free energy was minimized as a function of concentrations of the two topmost atomic layers. In order to keep the average composition constant, we modified the composition of the central bulk-type atomic layers. The so obtained theoretical segregation profiles, calculated for temperatures between 0 and 1200 K, are in good agreement with available experimental data [9].

For bulk concentrations close to 50%, the effect of surface layers on the composition of the central layers is negligible, and the above procedure leads to correct surface segregation profile. However, for small ($\lesssim$30%) or large ($\gtrsim$70%) bulk concentrations, supercells containing a large number of bulk-type layers are needed in order to allow the surface profile to be formed. These large supercells make the constant-composition procedure [9] very cumbersome. In this paper, based on ab initio alloy theory [11], we put forward a new surface segregation model, which is suitable for any bulk composition. The model combines bulk and surface calculations, and presents a realistic picture of alloy surfaces with minimal computational cost. We demonstrate its application to the (111) surface of fcc Ag_cPd_{1-c} alloy with $0 < c < 1$. Because Pd and Ag form a continuous solid solution within the whole concentration range, this alloy presents an ideal system for testing new segregation models. Furthermore, by using AgPd as a test case, we can directly compare the present and our former approaches. We show that for intermediate bulk concentrations (~50%), the two models are equally efficient and lead to similar segregation profiles.

The rest of the paper is divided into two main sections, conclusion and appendix. Section 2 briefly presents the segregation model and the ab initio calculations. More details about the thermodynamics of the surface segregation are given in the appendix. The results are presented in Section 3. This includes a thorough discussion of the chemical potential, surface segregation and surface energy of AgPd solid solution.

2. Method

2.1. Segregation model

We consider a substitutional disordered binary alloy formed by X and Y atoms. Like in the direct exchange Monte-Carlo method [12], we start from distinct surface and bulk subsystems, as illustrated in Fig. 1. The surface region (S) is modelled by a repeated slab geometry, consisting of alloy films embedded in vacuum. The number of X and Y atoms, within an atomic layer α parallel to the surface, are $N_X^{S,\alpha}$ and $N_Y^{S,\alpha}$, respectively. The bulk region (B) is formed by N_X^B X and N_Y^B Y atoms, and it acts as an atomic reservoir for the surface layers (arrows in Fig. 1). During the optimization process of the surface concentration profile, atoms from the surface layers are interchanged with atoms from the bulk subsystem. In this process, the total number of atoms within each surface layer, $N^{S,\alpha} = N_X^{S,\alpha} + N_Y^{S,\alpha}$, and within the bulk, $N^B = N_X^B + N_Y^B$, are kept constant. The total number of X and Y atoms from the combined system, i.e., $N_A = \sum_\alpha N_A^{S,\alpha} + N_A^B$ with A = X and Y, are also conserved. The concentrations are defined as $c_A^{S,\alpha} = N_A^{S,\alpha}/N^{S,\alpha}$ and $c_A^B = N_A^B/N^B$, for A = X and Y. For the sake of simplicity, we introduce notations $c^\alpha \equiv c_X^{S,\alpha} = 1 - c_Y^{S,\alpha}$ and $c \equiv c_X^B = 1 - c_Y^B$. In practice, the atomic layers of the surface subsystem are divided into two groups: the concentrations in the first n^S surface layers are variables whereas the concentrations within the rest of the surface alloy film are fixed to the bulk concentrations. The thickness of the bulk-type central section and the vacuum regions are chosen sufficiently large to decouple the surfaces from each other. The bulk subsystem is considered to be infinite, i.e., $N^B >> N^{S,\alpha}$ for any α, and, therefore, the exchanged atoms

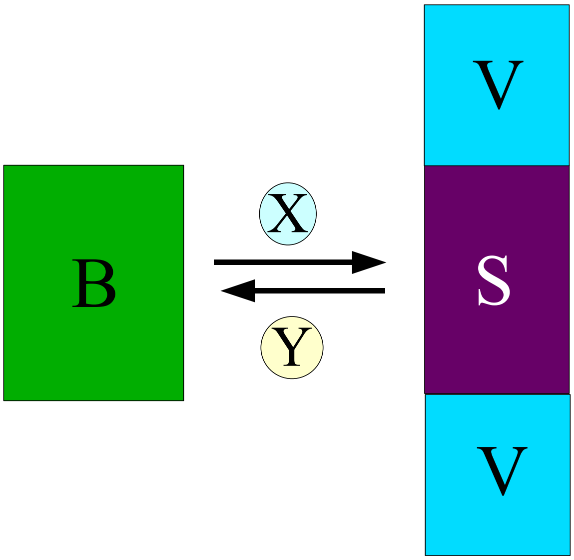

Fig. 1. Schematic plot of our model system. Green box (B) is the bulk subsystem, violet box (S) is the surface subsystem and light blue section (V) is the vacuum region. The X and Y represent a pair of atoms exchanged between the bulk and surface subsystem.