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Ab initio study of the geometric dependence of AgPd surface segregation

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The role of surface orientation and surface relaxation on the segregation profile of AgPd random alloys is investigated. The calculations are performed using the full charge density exact muffin-tin orbitals method in combination with the coherent potential approximation. The equilibrium concentration profiles for the first three close-packed surfaces are established as a function of bulk composition and temperature. In AgPd alloys the surface relaxation is significant only on the (100) and (110) facets. For these facets our study shows that the top layer relaxation has negligible effect on the segregation profile. The present results obtained for ideal surface geometries are compared to former theoretical and experimental data. Strong Ag segregation to the top surface layer is found for all surfaces and all bulk concentrations. At the same time, the behavior of the subsurface layer in Pd rich alloys depends significantly on the surface orientation.

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I. INTRODUCTION

Surface phenomena are important in many different areas of modern technology, for example, in catalysts, maintenance-free self-cleaning surfaces, and corrosion protection of metals. Tuning the surface properties assumes an atomic level understanding of the chemistry and physics of the surfaces. Surface segregation is one method of producing the desired surface properties for a specific application. Despite advanced laboratory equipment, experimental data on multilayer segregation remains scarce. In this situation a modern theoretical approach might be used which has already been shown to represent an efficient tool for obtaining accurate data on segregation.

During the last decade, there have been several successful surface segregation studies based on either the first-principles theory[1–4] or on semiempirical techniques.[5,6] On the other hand, even the most elaborate *ab initio* methods have been used to investigate ideal crystal structures near the surface, and only a few semiempirical approaches addressed the impact of surface geometry on the concentration profile. For instance, Lundberg investigated this effect in PdNi alloy using the embedded-atom method.[5] To our knowledge, no first-principles investigation of this problem has so far been presented.

In this paper we address this question using *ab initio* calculations combined with thermodynamics.[1,4,7] Calculations are based on the exact muffin-tin orbitals (EMTO) method[8,9] and the coherent potential approximation (CPA).[10] We study the role of surface geometry on the surface segregation of $\mathrm{Ag}_c\mathrm{Pd}_{1-c}$ alloys. Calculations are carried out for the first three low-index fcc surfaces, namely the (111), (100), and (110) facets. It is well established that the layer relaxation is negligible on the close packed (111) facet, but it becomes important on (100) and (110) facets.[11,12] Therefore, we study the effect of geometry on the segregation profile only for the (100) and (110) facets. We demonstrate that even on the relatively loosely packed (110) surface, the changes in the segregation profile due to the inward relaxation are within the scope of the *ab initio* method. The concentration profiles obtained for the ideal surfaces are used to reveal the effect of surface orientation on surface segregation.

The remainder of the paper is divided into three sections. In Sec. II, a brief description of the calculation method is given. The results are presented and discussed in Sec. III and the conclusions are drawn in Sec. IV.

II. METHOD

A. Computational method

In our calculations the bulk and surface part of the system are separated into two distinct subsystems which were calculated separately. These subsystems are allowed to exchange atoms. The bulk subsystem (B) acts as a reservoir for the surface system. The surface subsystem (S) is approximated by a repeated slab geometry. As independent variables we use the concentrations $c_A^{S,\alpha}$ and c_A^B, where A refers to Ag or Pd and α is used to specify an atomic layer parallel to the surface. For the sake of simplicity, we introduce notations $c^\alpha \equiv c_{\mathrm{Ag}}^{S,\alpha} = 1 - c_{\mathrm{Pd}}^{S,\alpha}$ and $c \equiv c_{\mathrm{Ag}}^B = 1 - c_{\mathrm{Pd}}^B$.

The surface segregation profile is obtained from minimizing the grand potential of surface

$$\Omega^S = U - TS - \Delta\mu^B \sum_\alpha n_s^\alpha (c^\alpha - c), \tag{1}$$

where U, T, S, and $\Delta\mu^B$ are the internal energy, temperature, entropy, and effective chemical potential of the bulk. In our calculations we consider only the configurational part of the entropy which led to the following form of Eq. (1):

$$\Omega^S(\{c^\alpha\}) = U^S(\{c^\alpha\}) + 2k_B T \sum_\alpha [c^\alpha \ln c^\alpha + (1-c^\alpha)\ln(1-c^\alpha)] - 2\{\Delta\mu_0^B(c) + k_B T[\ln c - \ln(1-c)]\}\sum_\alpha (c^\alpha - c), \tag{2}$$

where k_B is the Boltzmann constant, $\Delta\mu_0^B$ is the zero-temperature effective chemical potential of the bulk and the internal energy $U^S(\{c^\alpha\})$ is obtained from *ab initio* surface slab calculations. The factor 2 in Eq. (2) is from two surfaces of the slab.

The bulk and surface calculations were performed using the full charge density exact muffin-tin orbitals (FCD-

TABLE I. The number of atomic and vacuum layers and the number of k points in the IBZ used in calculations for different surface subsystems.

	Orientation		
Number of	(110)	(100)	(111)[a]
Atomic layers	10	8	8
Vacuum layers	6	4	4
k points	315	231	241

[a]Reference 7.

EMTO) method.[8,9,13,14] The problem of disorder was treated using the coherent potential approximation (CPA).[10] The renormalization of the effective medium in the single-site CPA was treated with screened impurity model.[15] This kind of renormalization is required in the calculations of effective potential in the single-site CPA as demonstrated by Ruban and Skriver.[16] The exchange-correlation potential was treated within the local density approximation using the Perdew and Wang parametrization[17] of the result of Ceperley and Alder.[18] The zero-temperature effective chemical potentials in the bulk were calculated from the concentration derivatives of the bulk internal energy per atom.[7] We were not considering the possible ordered low temperature phases;[19] on the contrary, our focus was on the disordered phases of AgPd. The atomic positions were kept fixed, except during the relaxation study, where the distance between the first two layers was changed.

B. Numerical details

The one-electron equations were solved within the scalar-relativistic and soft-core approximations. In the EMTO basis set we included s, p, d, and f orbitals. The Green's function was calculated for 16 complex energy points distributed exponentially on a semicircular contour. In order to minimize numerical errors the effective chemical potentials in the bulk and the internal energies of surfaces were calculated using identical Brillouin zone sampling parallel to the surfaces for each orientation separately. The number of atomic and vacuum layers as well as the number of $\vec{k}$ points used for different surface orientations are given in Table I. The thickness of the metal plus vacuum slab is sufficient to decouple the surfaces from each other. The concentration of the first two layers were variables and the concentration of the rest of the atomic slab was kept fixed to the bulk value c.

III. RESULTS AND DISCUSSION

A. Effect of the layer relaxation

It is well known that for the close-packed surfaces of late transition metals surface relaxation is negligible.[12,20] Therefore, we are interested in more open (110) and (100) surfaces. Recently surface relaxation of pure Ag and Pd were studied by Kádas *et al.*[11] For the (100) surface the results were for Ag 1.08% and for Pd 0.75% inward relaxation. For the (110) surface the results were for Ag 2.70% and for Pd 2.73% inward.

In the following we focus only on how the surface relaxation affects the surface segregation profile. Our results are shown in Fig. 1. We investigate relaxations up to the displacement of 4% inward for both surfaces. The effect on the surface concentration is found to be minimal. We obtain only a small ($\leq 2\%$) percentage decrease in the Ag concentration.

However, for the subsurface layer the effect is larger. The maximum reduction in the Ag concentration of the second layer obtained for the (100) surface was 9%, corresponding to 4% inward displacement of the surface layer, notably more than for pure Ag and Pd metals. The effect on the (110) surface is similar to the (100) case. The maximum decrease in Ag concentration is 7%. The obtained effects are small, producing only negligible effects and, therefore relaxation is not taken into account in the rest of the paper.

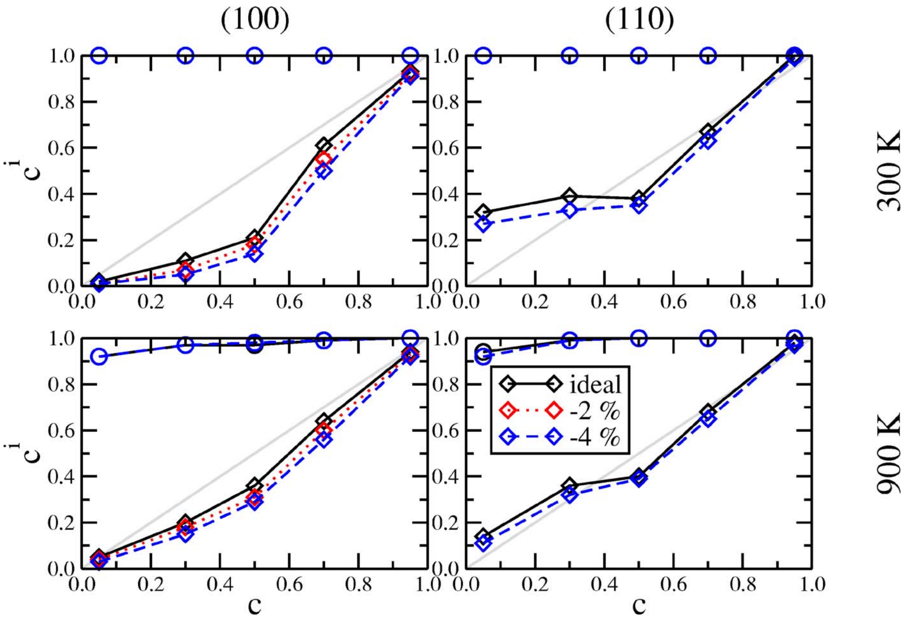

FIG. 1. (Color online) Effect of the inward surface relaxation on the segregation profile as a function of surface orientation, temperature, and bulk Ag concentration (c). Circles present Ag concentration of the first surface layer (c^1) and diamonds Ag concentration of the second surface layer (c^2). The solid gray line is the line for homogeneous alloy. Lines are added to guide the eye.

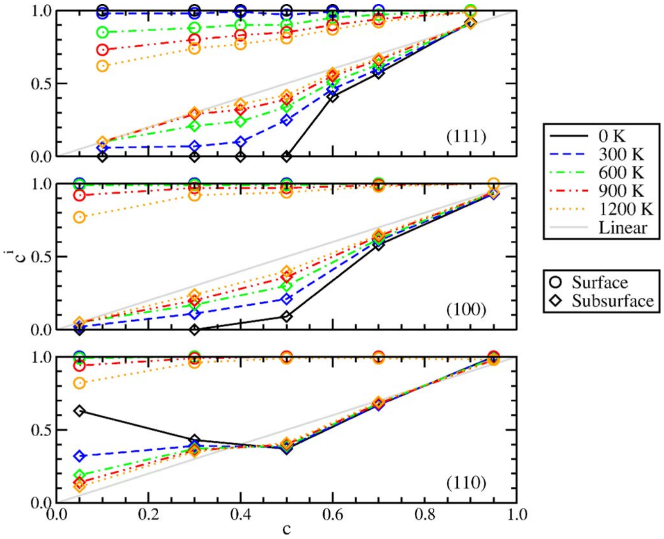

FIG. 2. (Color online) The surface segregation profile of AgPd alloys as a function of surface orientation, temperature, and bulk Ag concentration, c. Circles present Ag concentration of the first surface layer (c^1) and diamonds Ag concentration of the second surface layer (c^2). Color code for temperature is the same for both layers. The solid gray line is the line for homogeneous alloy. Lines are added to guide the eye.

B. Segregation profiles

The segregation profile up to the second surface layer is determined for the fcc(100) and fcc(110) surfaces of the Ag_cPd_{1-c} alloys for $c=0.05$, 0.30, 0.50, 0.70, and 0.95 and for $T=0$, 300, 600, 900, and 1200 K. The surface profile of the (110), (100), and (111) (Ref. 7) surfaces are shown in Fig. 2 as a function of c, T, and surface orientation.

For all, (111), (100), and (110) surface orientations we find that the first surface layer is composed of pure Ag for all investigated bulk concentrations at 0 K (Fig. 2). For more open surfaces, (100) and (110), this strong silver concentration is very stable as the temperature is increased. Only at the lowest Ag bulk concentrations is there a noticeable decrease of surface Ag concentration as the temperature rises above 900 K. The temperature effect for the (111) surface is already seen at 600 K. From Fig. 2 we see how the Ag surface concentration is stabilized by the surface orientation. For all these surfaces the temperature effect is largest with the Pd rich alloys. This is due to the entropy term that drives the alloy layers towards the bulk concentration as the temperature increases, leading to more homogeneous systems.

The Ag concentration of the second layer at 0 K depends strongly on the bulk concentration and the surface orientation. For the (100) and (111) surfaces there is Pd segregation to the subsurface layer for all alloy concentrations. The Ag concentrations of the second layer at 0 K is zero for $c<0.5$ [$c\leq 0.5$ for (111) surface]. It rapidly increases with increasing c for $c>0.5$. The reason for this rapid increase of the Ag concentration in the second layer for alloys with $c\geq 0.5$ is the behavior of the effective chemical potential of the bulk[7] which decreases rapidly at $c\geq 0.5$.

The behavior of the subsurface layer of the (110) surface differs drastically from that of the (100) and (111) surfaces. For $c=0.5$ there is only mild Pd segregation compared to the (100) and (111) surfaces, where we find strong Pd segregation. Contrary to the (100) and (111) surface the (110) surface shows Ag segregation to the second layer for $c<0.5$ and $c=0.95$. This segregation gets stronger when the Ag concentration is decreased from $c=0.3$ to $c=0.05$. The concentration profile of the second layer shows similar independence of the temperature as the first layer except in $Ag_{0.05}Pd_{0.95}$ alloy, where we discover the very strong temperature dependence on the second layer concentration. The temperature stability of the second layer for alloy concentrations $c\geq 0.3$ is due to the fact that the concentration of the second layer is almost the same as the bulk concentration of the alloy.

TABLE II. Theoretical and experimental surface segregation profile for fcc(100) surface.

	At. % Ag				
Bulk	1	2	T(K)	References	Method
30	97	20	900	[a]	Theory
30	95	10	800	21	Theory
30	70		900	22	Theory
33	100		770	23	Experiment
50	97	36	900	[a]	Theory
50	97	18	800	21	Theory
50	88		900	22	Theory
55	61.4		673-873	24	Experiment
70	99	65	900	[a]	Theory
70	100	54	800	21	Theory
70	96		900	22	Theory

[a] This work.

In Table II we compare our result for the (100) surface with the available theoretical and experimental data. We found two independent theoretical works and two experimental measurements on the surface segregation of AgPd random alloys. Rousset *et al.*[21] used equivalent medium approximation (EMA) with a modified tight-binding scheme to investigate segregation profiles of Ag_cPd_{1-c} alloys. Their result for the first layer agrees well with our results, but for the second layer they predict somewhat lower Ag concentrations than our EMTO results. Abrikosov and Skriver[22] investigated the segregation of the first surface layer with the LMTO-CPA method combined with a thermodynamical model. Their results show lower Ag concentration to the surface compared to our predictions, especially at $c=0.3$, where their result is significantly lower than ours. This might be due to the atomic sphere approximation and *spd* basis set used in their LMTO-CPA calculations.

Wouda *et al.* used a scanning tunnelling microscope to investigate the top layer of the $Ag_{33}Pd_{67}$ alloy. The surface of the alloy was observed to be pure Ag at 770 K. Reniers *et al.*[24] investigated the $Ag_{55}Pd_{45}$ alloy with Auger electron microscopy (AES). Their result is significantly lower than ours.

For the (110) surface we found only one investigation related to our work. Massobrio *et al.*[25] investigated the structure and energetics of Pd on the Ag (110) surface using the embedded atom model. They mention that Pd prefers to reside inside the substrate more than on top of it.

IV. CONCLUSION

We studied the surface segregation profile of AgPd alloys as a function of temperature, surface relaxation, surface orientation, and alloy concentration by *ab initio* calculations combined with thermodynamics.[7] We found that the surface relaxation did not change the concentrations of the surface layer and it has a minor impact on the subsurface layer. However, the impact of the surface relaxation on the segregation profile might be stronger in the alloys with more open structures than in the investigated close-packed fcc structure.

Our calculations predicted strong Ag segregation to the surface layer for all investigated surfaces and alloy concentrations. Ag segregation is stable against temperature for (110) and (100) alloys. Only at the Pd rich end of the alloys did we see some deviation from the Ag surface. The close-packed (111) surface was not as stable as the more open (100) and (110) surfaces.

The behavior of the subsurface layer depends on the orientation of the surface. For (100) and (111) surfaces at 0 K the Ag concentration of the second layer was found to be zero for $c<0.5$ and it increases rapidly when the alloy concentration is increased. Still the Pd segregation was seen in all alloys. As the surface becomes more open, the concentration of the subsurface layer changes. For the (110) surface there was Ag segregation to the second layer for $c\leqslant 0.3$ and $c=0.95$ alloys and mild Pd segregation was found for $c=0.5$ and $c=0.7$ alloys. The Ag segregation to the subsurface layer for $\mathrm{Ag}_{0.05}\mathrm{Pd}_{0.95}$ was especially strong.

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