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Theoretical evidence of the compositional threshold behavior of FeCr surfaces

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Using first-principles quantum-mechanical theory, we demonstrate that the surface chemistry of Fe-Cr alloys follows the peculiar threshold behavior characteristic of ferritic stainless steels. We find that in dilute alloys the surfaces are covered exclusively by Fe, whereas for bulk Cr concentration above ~10% the Cr-containing surfaces become favorable. The two distinctly dissimilar surface regimes appear as a consequence of two competing magnetic effects: the magnetically induced immiscibility in bulk Fe-Cr alloys and the stability of magnetic surfaces.

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In Fe-Cr alloys, a drastic decrease in the corrosion rate with chromium addition[1] occurs within a narrow concentration interval (9–13% Cr),[2] making the transition from the iron-type to the noncorrosive behavior quite abrupt. Alloys in the latter category form the basis of the so-called ferritic stainless steels. Phenomenological models have been introduced to describe the passivity of stainless steels,[3–9] and today there is a generally accepted mechanism based on the formation of a protective Cr-rich oxide surface film. On the other hand, despite the numerous experimental and theoretical investigations on alloy surfaces,[6–14] the observed threshold behavior in the Fe-Cr system has remained less well understood. There is experimental evidence for Cr-enriched alloy surfaces in the stainless regime at high temperatures.[7,11] From the theoretical side, all studies have focused on dilute alloys and most of them predicted the stability of Cr-free surfaces.[12–15] However, it seems very unlikely[16] that these pure Fe-terminated surfaces would facilitate the development of the passive oxide film and provide the self-healing property in the noncorrosive regime.

In the present work, we aim to resolve the above contradiction. We investigate the behavior of Fe-Cr surfaces as a function of bulk composition within an extended concentration range and try to reveal the mechanism that can stabilize Cr-containing surfaces in high-Cr alloys. Our ability to address this problem at a first-principles quantum-mechanical level has become possible through the exact muffin-tin orbital (EMTO) method[17] based on density functional theory[18] in combination with the generalized gradient approximation.[19] This approach has proved to be an accurate tool in the theoretical description of Fe-based random alloys.[20,21]

At ambient conditions, elemental Fe orders ferromagnetically while Cr has an incommensurable antiferromagnetic state, which can be approximated by a commensurable ($B2$ structure) antiferromagnetic state.[22,23] The Fe-Cr alloys, except the high-temperature Fe-rich γ phase and the σ phase observed around equimolar concentrations, adopt the body centered cubic (bcc) structure of α-Fe.[24] Here we focus on the technologically important $Fe_{1-c}Cr_c$ alloys with $c<0.25$. At normal operating temperatures, these bcc alloys are ferromagnetic with Curie temperatures around 900–1050 K.[24] For $c \lesssim 0.1$ and $T \gtrsim 600$ K, the Fe-Cr system is fully miscible, whereas nucleation or spinodal decomposition driven clustering occurs at higher Cr concentrations.[24] Nevertheless, it has been shown[25,26] that the energetics of $Fe_{1-c}Cr_c$ alloys with $c \lesssim 0.2$ are well described using the substitutionally disordered ferromagnetic bcc phase.

In the present magnetic systems, surface magnetism reduces the surface energy of open surfaces to the extent that the usual anisotropy of the surface energy is reversed.[22,27,28] In particular, the magnetic contribution to the surface energy of the (100) facet of pure Cr (Fe) is about −50% (−41%) compared to −2% (−16%) obtained for the close-packed (110) facet.[22] Accordingly, the most stable surfaces for pure Cr and for Fe-rich Fe-Cr alloys are the (100) crystal facet of the $B2$ lattice and the (100) crystal facet of the bcc lattice, respectively.

We modeled the Fe-Cr system by considering two distinct subsystems: one with surfaces (the so-called surface subsystem) and one without surfaces (the bulk subsystem). The two subsystems were allowed to exchange atoms with each other.[29,30] The bulk subsystem acted as a reservoir for the surface, enabling a change in the surface composition without finite change in the bulk composition. The surface subsystem for Fe-Cr alloys was described by periodically repeated atomic slabs formed of eight (100) atomic layers and separated by vacuum layers of thickness equivalent to four atomic layers. A similar slab geometry was adopted for modeling the pure Fe and Cr surfaces. In the case of alloys, the concentration in the top monolayer was allowed to relax and all the other layers had the bulk composition.[31] The substitutional disorder was taken into account using the coherent

potential approximation[32,33] (CPA) and assuming homogeneous solid solutions for the bulk and the surface layer. Going beyond this approximation would require Monte Carlo type of simulations,[34] which, however, is beyond the scope of the present work. The actual error introduced by our approximation may be established by comparing the present CPA mixing energies with the previous supercell results.[35] We estimate that the error bar in the equilibrium concentration profile is below ±1% in alloys with $c \lesssim 0.08$ and around ±2% for the rest.

The surface concentrations were obtained by minimizing for each temperature T the grand canonical potential of the surface subsystem. At $T=0$ K, this leads to the condition that the difference between the effective chemical potentials (ECPs) for the surface ($\Delta\mu_S$) and bulk ($\Delta\mu_B$) subsystems should be equal to the equilibrium segregation energy.[29,30] The latter vanishes for an equilibrium concentration profile, where all the alloy components have finite concentrations. The effective chemical potentials were calculated as the energy change when a Cr atom was exchanged with Fe. For calculations at $T>0$ K, the entropy was approximated by the configurational entropy $S_{\text{conf}}=-k_B[(1-c_i)\ln(1-c_i)+c\ln(c_i)]$, where c_i stands for the bulk or surface Cr concentration and k_B is the Boltzmann constant. We note that in Fe-rich alloys and for temperatures well below the magnetic transition temperature, the vibrational and magnetic entropy terms are expected to have negligible effect on the equilibrium concentration profile.[36] The accuracy of the above thermodynamic model in combination with the EMTO CPA method has been demonstrated in the case of Pd-Ag alloys.[29,30]

Figure 1 shows the bulk and surface effective chemical potentials calculated at $T=0$ K as a function of bulk composition. We find that the surface ECPs follow a monotonic trend, whereas $\Delta\mu_B$ exhibits an anomalous behavior with a marked minimum near 15% Cr. We will return to explain this anomalous behavior later. With the present convention, the chromium-containing surfaces become stable in alloys where we have $\Delta\mu_S > \Delta\mu_B$, i.e., where energetically it is more favorable to place a Cr atom at the surface layer than in the bulk. The corresponding equilibrium surface concentrations of Cr are given in Fig. 2 (circles). The profiles for $T=300$ (squares) and 600 K (triangles) were obtained by including terms due to the configurational entropy as described in Ref. 29. We point out that the entropy has only a minor effect on the concentration profile in low-Cr alloys, but significantly enhances the surface Cr content at large bulk Cr concentrations.

In Fig. 2, we observe a sharp change in the surface Cr content for alloys encompassing 8–12% Cr. Accordingly, at low temperatures there is practically no Cr present at the surface for $c \lesssim 0.08$. This means that thermodynamically the most stable surfaces are the Fe-terminated surfaces. For alloys with bulk Cr concentration above 8–9%, the Cr-containing surfaces start to become stable. The actual amount of Cr at the surface for $c \approx 0.1-0.2$ is close to, or slightly higher than, the Cr concentration in the corresponding bulk alloy, reaching a maximum of 20–27% (depending on temperature) for $c \approx 0.12-0.15$. The predicted stability of Cr-enriched surfaces in the stainless region is fully supported by experiments.[7,11] A quantitative comparison shows that the

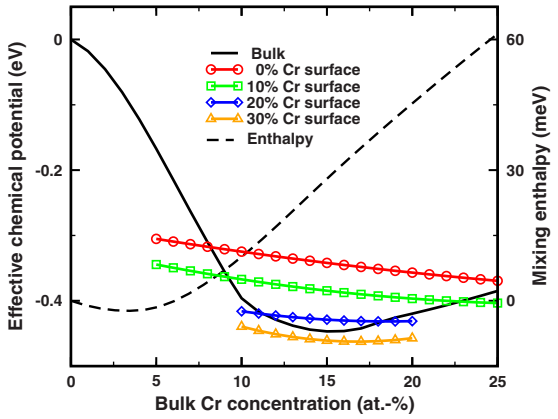

FIG. 1. (Color online) Theoretical surface and bulk properties of ferromagnetic $Fe_{1-c}Cr_c$ alloys as a function of bulk Cr concentration (in at. %). Left axis: Effective bulk (solid line) and surface (symbols, color) chemical potentials (in eV) calculated for $T=0$ K. The surface chemical potentials are shown for 0% (circles, red), 10% (squares, green), 20% (diamond, blue), and 30% (triangles, yellow) Cr in the surface layer. All curves are plotted relative to the bulk chemical potential for the dilute alloy. Right axis: The mixing enthalpy (in meV) of disordered Fe-Cr alloy (dashed line). The standard states are the ferromagnetic bcc Fe and antiferromagnetic $B2$ Cr. Note that the inflection point in the mixing energy around 15% Cr corresponds to the minimum of the bulk effective chemical potential.

present theoretical surface Cr content is below the observed values of 45% for $c=0.13$ and 69% for $c=0.25$.[11] However, it is important to note that these experiments were performed on samples heated to 973 K under ultrahigh vacuum. At this temperature, the Fe-Cr alloys are close to their magnetic transition, which is expected to have a substantial effect on the thermodynamics of bulk and surface alloys.[25]

The demonstrated transition in the surface Cr concentration in Fe-Cr alloys (Fig. 2) clearly shows the characteristics of the experimentally observed compositional threshold.[2] In

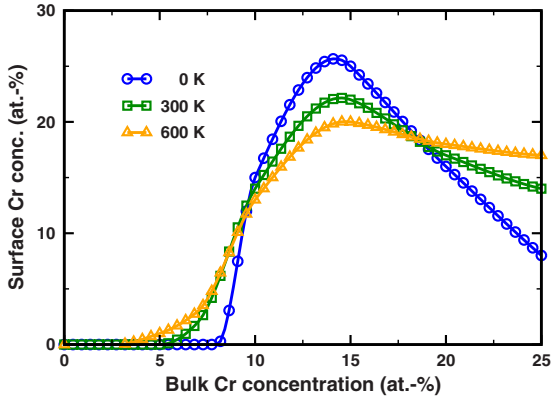

FIG. 2. (Color online) Theoretical surface concentration of chromium for ferromagnetic $Fe_{1-c}Cr_c$ alloys as a function of bulk Cr concentration (in at. %). The Cr concentration profiles, calculated for the thermodynamically stable (100) surface of the bcc lattice, are shown for 0 K (circles, blue), 300 (squares, green), and 600 K (triangles, yellow).

particular, we emphasize that the calculated transition interval (8–12% Cr) from Cr-free surfaces to surfaces with "bulk-like" composition is in excellent agreement with the concentration range within which the observed corrosion rate in Fe-Cr alloys drops from 0.1 mm per year (near ~9% Cr) to below the detectable limit (at ~13% Cr).[2] Note that the sharp increase in the surface Cr content around the theoretical threshold in Fig. 2 can be traced back to the particular stability of pure Fe-terminated surfaces in low-Cr alloys rather than to a considerable surface segregation of Cr in high-Cr alloys.

To arrive at a coherent and clear interpretation of our results summed up in Figs. 1 and 2, we examine the available theoretical data on surface and bulk Fe-Cr alloys. First, we make use of a simple version of the surface segregation model.[13] According to that model, in alloys with isostructural components the surface energy is an important driving force behind the segregation, namely, the alloy component with the lowest surface energy should segregate toward the surface of the alloy. We have calculated the surface energies of ferromagnetic Fe, antiferromagnetic Cr, and also ferromagnetic Fe covered by one monolayer of Cr. It turns out that, in spite of the large surface magnetic effects,[22,27,28] the surface energy of pure Cr is significantly (~30%) larger than the one calculated for pure Fe (1.41 eV per surface atom), thus preventing Cr atoms from going to the surface. Extending the segregation model to the case of an Fe-rich substrate, we find an even larger (~36%) surface energy difference between the pure Fe- and pure Cr-terminated surfaces. Thus, in contrast to Fig. 2 and experimental observations,[7,11] from standard surface energy considerations the Cr-containing surfaces should always be energetically less favorable compared to the Cr-free surfaces. As a matter of fact, this picture is in line with several theoretical investigations carried out on diluted Fe-Cr alloys.[10,12–14]

The insufficiency of the considerations above indicates that the bulk itself could play a key role in the stability of Cr-containing surfaces. Bulk Fe-Cr alloys have a broad and slightly skewed miscibility gap, allowing the solubility of a small amount of Cr in Fe but not vice versa.[24] In good agreement with other theoretical predictions,[25,35] we find that at low Cr concentrations the ferromagnetic solid solutions have slightly negative mixing enthalpies (Fig. 1, right axis) and therefore they are stable at all temperatures. It has been demonstrated[10,25,35,37,38] that the limited solubility of chromium in iron is connected to the complex magnetic interactions characteristic of solid solutions between antiferromagnetic (Cr) and ferromagnetic (Fe) species. These interactions originate from magnetic frustrations due to the strong antiparallel coupling between Cr and the Fe matrix and also between different Cr atoms.[10]

The energetically unfavorable magnetic interactions can be avoided or minimized by forming Cr-rich clusters[35] and simultaneously moving some of the Cr atoms to the alloy surface. The latter phenomenon becomes clear if one compares the bulk effective chemical potential and the mixing energy (Fig. 1). At low temperatures, apart from a constant shift and sign, the slope of the mixing enthalpy gives to a good approximation the value of the bulk effective chemical potential.[10] Similarly, the second-order concentration derivative (curvature) of the mixing enthalpy gives the slope of the bulk ECP. In particular, the large negative slope of the bulk ECP for Fe-Cr (Fig. 1, left axis) is related to the positive curvature of the mixing enthalpy of alloys with Cr content below ~15% (Fig. 1, right axis). When compared to the surface ECP, one can see that the crossover between the bulk and surface chemical potentials is indeed a consequence of the rapidly rising (convex) mixing enthalpy. On these grounds, we can conclude that the magnetism-driven solubility of Cr in Fe (Refs. 25, 35, and 37) is in fact the main factor responsible for the increasing stability of Cr-containing surfaces compared to Fe-terminated surfaces.

The decisive role of magnetic interactions in the bulk properties of Fe-Cr alloys has been proposed in several theoretical investigations,[10,25,35,37,38] but their impact on the surface chemical composition has not been revealed so far. Our results from Figs. 1 and 2, and the above arguments give clear evidence for the magnetic origin of the stability of Cr-enriched surfaces for bulk concentrations beyond the threshold. The presence of Cr-containing surfaces enables the formation of a protective surface layer in oxidizing environments. However, below the threshold a preferential formation of Fe-terminated surfaces ensues, which makes these alloys vulnerable to corrosion.

Finally, we point out that the strongly nonlinear change of the surface Cr content versus bulk composition is due to the delicate balance between bulk and surface effects. In particular, the lack of Cr at the surface of Fe-rich alloys is a direct consequence of the anomalous mixing of Fe and Cr at low Cr concentrations, which in its turn has a magnetic origin. This finding has important implication in modern materials science as it offers additional rich perspectives in the optimization of high-performance steel grades.

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