

Anomalous surface segregation profiles in ferritic Fe-Cr stainless steel

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The iron-chromium alloy and its derivatives are widely used for their remarkable resistance to corrosion, which only occurs in a narrow concentration range around 9 to 13 atomic percent chromium. Although known to be due to chromium enrichment of a few atoms thick layer at the surfaces, the understanding of its complex atomistic origin has been a remaining challenge. We report an investigation of the thermodynamics of such surfaces at the atomic scale by means of Monte Carlo simulations. We use a Hamiltonian which provides a parametrization of previous *ab initio* results and successfully describes the alloy's unusual thermodynamics. We report a strong enrichment in Cr of the surfaces for low bulk concentrations, with a narrow optimum around 12 atomic percent chromium, beyond which the surface composition decreases drastically. This behavior is explained by a synergy between (i) the complex phase separation in the bulk alloy, (ii) local phase transitions that tune the layers closest to the surface to an iron-rich state and inhibit the bulk phase separation in this region, and (iii) its compensation by a strong and nonlinear enrichment in Cr of the next few layers. Implications with respect to the design of prospective nanomaterials are briefly discussed.

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The iron-chromium alloy and its derivatives are inexpensive, have satisfactory mechanical properties, and above all exhibit a remarkable resistance to corrosion: It is the most widely used class of alloy in the world. Its outstanding corrosion resistance is known for a century¹ to only occur in a narrow range of concentrations, around 10 atomic percent of chromium (at. % Cr).² Their excellent properties make them candidate materials for future fusion nuclear reactors,^{3,4} one of the reasons that induced a considerable amount of work on the various aspects of the Fe-Cr alloy both experimentally^{5,6} and theoretically.⁷

Corrosion resistance of stainless steels is due to the passivation of the material by an inert, chromium rich layer at the interface between the alloy and the environment, i.e., at the surfaces. Passivation is a phenomena inherent to how much Cr is located at the surfaces, which is a nonlinear function of the bulk concentration.⁸ In austenitic Fe-Cr, which only exists at high temperatures above $\approx 800^\circ\text{C}$ and for less than ≈ 10 at. % Cr, the more chromium in the bulk, the more chromium in the surface, and thus the more stainless the alloy. In ferritic Fe-Cr alloys, the picture is more complex. Without additive elements, the Cr content at which the alloy is passivated is narrow, from 9 to 13 at. % Cr, beyond which occurs an increase in the corrosion rate and a strong decrease in mechanical properties.

This important property of stainless steels has been extensively studied, but its complex origin at the atomic scale has remained a missing understanding, subject to controversial findings: How chromium causes passivation, i.e., how it interacts and reacts with chemical elements coming from the environment like dioxygen, is out of the scope of this study. The reader is referred to Greeley *et al.*⁹ for a review of surface chemistry of metal surfaces at the atomic and electronic scale. Surface reaction requires nevertheless that Cr is present in large enough quantity on the surface to form a few atoms thick protective layer, e.g., of chromium(III) oxide Cr_2O_3 . How chromium atoms enrich the surfaces remains

unclear. Venus and Heinrich¹⁰ showed by angle-resolved Auger electron spectroscopy that Cr atoms deposited on a whisker of Fe (100) migrates from the surface to the first few layers, in contradiction with the expected tendency. This surface alloying has been clearly identified to be linked to anomalies in the magnetic properties of the Cr/Fe system, specifically the change in surface magnetization at low Cr coverage and the strong interactions between surface Cr atoms.^{11,12} Ropo *et al.* showed by first principles that a pure Fe-Cr surface behaves like stainless steels with respect to Cr enrichment.¹³ They also put in evidence a competition between the relative stabilities of the surfaces and the complex thermodynamics of the bulk alloy. Later, *ab initio* calculations revealed that unexpected interactions between subsurface Cr atoms and surface Fe atoms¹⁴ are at the origin of an anomalous^{15,16} segregation behavior of Cr in Fe in the dilute regime.

At temperatures of industrial and technological interest, i.e., between 300 and 600 K, the body-centered cubic (bcc) solid solution of Fe-Cr shows a miscibility gap from 9–13 to 94–99 at. % Cr.⁶ Inside, a phase separation occurs into an iron-rich bcc solid solution α and chromium-rich bcc precipitates α' as one would expect for a binary alloy that seemed to have a segregation tendency, i.e., that mix solely for entropic reasons. However, both theoretical and experimental studies subverted this simple picture, showing favorable dissolution energy of chromium in iron up to an anomalously high ≈ 7 at. % Cr^{17–19} due to a competition between repulsive Cr-Cr interactions and attractive Fe-Cr interactions.^{20–23} The increased chromium content leads to more frustrated magnetic interactions in between Cr atoms that make the dissolution exothermic at low concentrations, then endothermic. Several theoretical models^{7,24–28} have successfully reproduced the sign change of the mixing energy.

Here the iron-chromium ferritic stainless steel is modeled by the Hamiltonian proposed recently in Ref. 28. It is specifically designed to reproduce both (i) the whole experimental α - α' phase diagram at all temperatures and compositions,

TABLE I. Parameters of the local concentration and temperature dependent pair potential from Ref. 28. Experimental cohesive energies from Ref. 30 are given in eV per atom.

α	β (eV)	γ (eV)	δ (eV)	θ (K)	$E_{\text{coh.}}(\text{Fe})$	$E_{\text{coh.}}(\text{Cr})$
0.070	-2.288	4.439	-2.480	1400	4.28	4.10

and (ii) the change of sign of the mixing energies. It is also compatible with large-scaled simulations, because of its conceptual simplicity and its rigid bcc lattice nature: The internal energy $\Delta H_{\text{mix}} = -\Omega c_b (1 - c_b)$ is a function of the bulk concentration in chromium c_b and of the order energy Ω described in terms of local concentration and temperature dependent pair interactions:

$$\Omega = \sum_i \frac{z^{(i)}}{2} (\epsilon_{AA}^{(i)} + \epsilon_{BB}^{(i)} - 2\epsilon_{AB}^{(i)}), \quad (1)$$

where $z^{(i)}$ is the coordination number of shell i and $\epsilon_{jj'}^{(i)}$ is the pair interaction between atoms of type j and j' on i th neighbor sites. Influenced by the strategy of Caro *et al.*,²⁴ the order energy is advantageously expressed as a simple concentration and temperature dependent Redlich-Kister²⁹ expansion:

$$\Omega(x, T) = (x - \alpha)(\beta x^2 + \gamma x + \delta) \left(1 - \frac{T}{\theta}\right), \quad (2)$$

where x is the local concentration and T is the temperature. Discrete mixing energies have been calculated *ab initio* in the whole range of concentrations and interpolated by Eq. (2), whose coefficients α , β , γ , and δ are given in Table I. Coefficient θ , also given in Table I, is the critical temperature of the miscibility gap.

Homoatomic pair interaction energies in Eq. (1) are given by the experimental cohesive energy of the pure elements, given in Table I, according to $E_{\text{coh}}(j) = -\sum_i z^{(i)} \epsilon_{jj}^{(i)}$. The expressions of the heteroatomic interactions $\epsilon_{AB}^{(i)}(x, T)$ are then easily deduced from Eqs. (1) and (2). They are consequently simple parametric functions of the temperature T and local concentration x . This last quantity x around a pair including an atom on site i and an atom on another site j is naturally defined as

$$x = \frac{\sum_{n=0}^r \sum_{k=1}^{z^{(n)}} p_{ik}^{(n)} + \sum_{n=0}^r \sum_{k=1}^{z^{(n)}} p_{jk}^{(n)}}{2 \sum_{n=0}^r z^{(n)}}, \quad (3)$$

where $p_{ik}^{(n)} = 1$ when the k th site of the n th coordination shell of site i is a Cr atom, and 0 if it is a Fe atom or an empty site, i.e., a site outside the surface. The interaction range is restricted to second nearest neighbors with $\epsilon_{ij}^{(2)} = \epsilon_{ij}^{(1)}/2$, which has been found optimal. It is worth emphasizing that the resulting bulk phase diagram is in very good agreement with the most recent experimental reviews.^{5,6} While this model does not capture the extraordinarily complex electronic structure of the bcc Fe-Cr alloys, it captures both the local nature of the interactions and the associated energetics, without empirical parameters.

This paper focuses on the most stable surface of bcc iron, which has the orientation (100).³¹ It is modeled by a stack of 100 layers of 400 atoms each, in periodic boundary conditions. Interactions between periodic images in direction

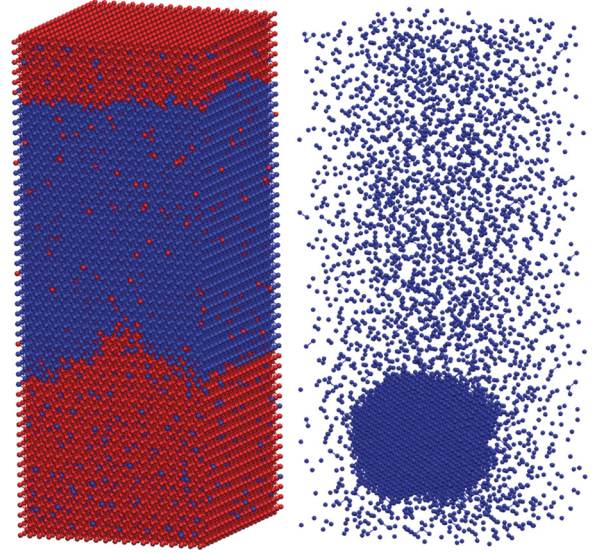


FIG. 1. (Color online) Snapshots of the simulation cell containing the (100) Fe-Cr surface at 300 K for bulk concentrations $c_b = 0.5$ (left) and $c_b = 0.15$ (right). The top and bottom surface layers are at the top and bottom of the figure. Fe atoms are shown in red and Cr atoms in blue. For $c_b = 0.15$, only Cr atoms are shown. In both cases, the bulk phase separation α - α' occurs.

$\langle 100 \rangle$ are prevented by a slab of vacuum. Special attention has been given to the choice of the size of the system in order (i) not to artificially hide the surface effects by a too large volume/surface ratio, and (ii) not to restrain the formation of precipitates by too small systems, i.e., to give the system the ability to precipitate and have the precipitates to interact with the surfaces. It induces that the bulk solubility limit near the surfaces can be slightly different from that of a pure bulk system. A perspective view of the supercell is shown in Fig. 1(a).

As stated above, the model does not capture the effect of the surface on the electronic structure of atoms in its vicinity, such as expected stronger bonds. It captures the effect of the reduced coordination in terms of energetics: Eq. (3) implies that the more reduced the coordination, the more the local energetics are dependent on the remaining bonds. The various surface orientations only differ in the number of surface-induced dangling bonds, and thus in the strength of the surface effects described below. Conclusions are thus transferable to other orientations. Importantly, the effectiveness of our Hamiltonian allows us to deal with a number of atoms that makes it possible to finely tune the bulk and layer concentrations. Here, one atom accounts for the bulk concentration by less than 10^{-4} at. % and the layer concentration by 5×10^{-3} at. %. This point is crucial as recent *ab initio* calculations have been limited to few layers and few atoms per layer, imposing large bulk and even larger planar concentrations. Our Hamiltonian is sampled by Monte Carlo simulations using the Metropolis algorithm in the canonical and pseudo-grand-canonical ensembles.³² The equilibrium state is considered reached after 10^4 accepted permutations per site.

We define the planar concentration $c_p = \sum_{i=1}^{N_p} q_i / N_p$ as the chromium content of each layer p parallel to the surface, with N_p the number of atoms per layer (400 here) and $q_i = 1$

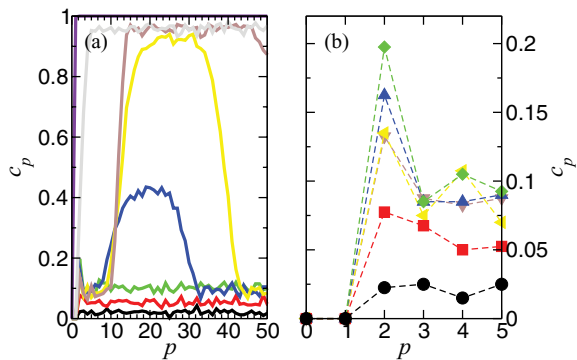


FIG. 2. (Color online) (a) and (b) Concentration profiles of a Fe-Cr surface at 300 K. Index $p = 0$ indicates the top surface layer. Various bulk concentrations c_b are indicated: 0.02 (black); 0.05 (red); 0.10 (green); 0.15 (blue); 0.30 (yellow); 0.50 (brown); 0.90 (gray); and 0.98 (violet). (b) Only the first six layers are shown. Note the change in scale.

if site $i \subset p$ contains a Cr atom, $q_i = 0$ otherwise. p ranges from 0 for the top surface layer to 99 for the bottom surface layer.

In Fig. 2 we plot the concentration profile $c_p(p)$ of Fe-Cr at 300 K ($\approx 1/3 T_c$) and various bulk concentrations c_b ranging from 0.02 to 0.98. Special attention is given to the temperature range that is of industrial and technological importance, i.e., for c_b below 0.3. The concentration profiles are highly nonlinear functions of the bulk concentration.

In order to get insight to these concentration profiles, semi-grand-canonical Monte Carlo simulations have been performed, where the total number of sites and the difference in chemical potential $\Delta\mu$ between pure bcc-iron and pure bcc-chromium are kept fixed, while the bulk concentration is free.³² The evolution of the surface and bulk concentrations with respect to $\Delta\mu$ at 300 K are plotted in Fig. 3. Three hysteresis loops are found, which are indicated in the figure by asterisks. They bring out three phase transitions. The first and stronger one, indicated by the black asterisk in Fig. 3(a), is evidence of the well-known bulk phase separation α - α' happening in

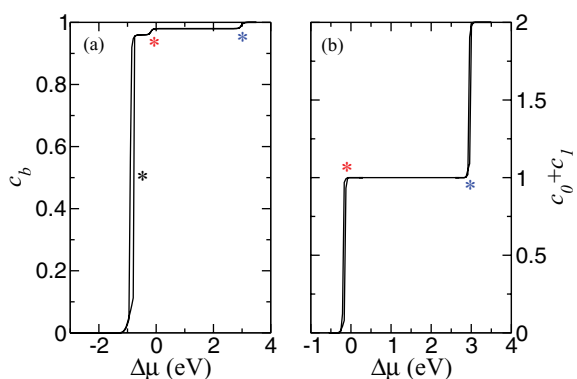


FIG. 3. (Color online) (a) Evolution of the bulk concentration with the chemical potential $\Delta\mu$ at 300 K. (b) Evolution of the sum of the concentrations of the top surface and subsurface layers versus the same chemical potential. In both figures, the black asterisk indicates the bulk phase separation, the red and blue asterisks show the transitions in the subsurface and surface layers, respectively.

bcc Fe-Cr alloys and discussed in the introduction. Note that the bulk solubility limit at low chromium concentration is slightly affected by the presence of the surface. It causes the large variations in the density profiles in Fig. 2 more than 10 layers away from the surface for $c_b \gtrsim 0.12$. Two Snapshots of systems that undergo phase separation at $c_b = 0.15$ and $c_b = 0.5$ are shown in Fig. 1. At higher differences in chemical potential, as indicated in Fig. 3(b), two less visible phase transitions occur. Each transition is localized in a single layer. The first one corresponds to the subsurface layer transiting from pure Fe to pure Cr [indicated by the red asterisk in Fig. 3(a)], followed by an accompanying transition in the surface layer [blue asterisk in Figs. 3(a) and 3(b)]. The change in concentration of the two first layers is abrupt and discontinuous. It also gives insight to the emptiness in Cr of these layers. First, the difference in surface chemical potential of the two elements, which is proportional to the difference in surface energies of Fe and Cr, implies that Fe recover the layers where bonds are dangling. Indeed, surface energies of Fe are always lower than that of Cr for a given orientation. They range from 2.2 to 3.4 J/m² and 3.2 to 4.2 J/m² for iron and chromium, respectively.^{33–35} Second, and in relation, the chemical potential of surface atoms is highly modified by the surface, which explains why the alloy do not phase separate at the same concentration than in the bulk. One could see them as two new alloying elements only present in the surfaces.

As shown in Figs. 2(b) and 4(a), the concentration of the third layer c_2 increases quickly with c_b , contrary to that of the first two layers discussed above: c_2 gets from 0 to 0.2 when c_b goes from 0 to 0.1, which represents a relative increase in c_2 of about 100% at $c_b \approx 0.1$. Importantly, c_2 is at this point greater than the bulk solubility limit, so that phase separation would occur in the absence of the surface: Its presence changes here the very nature of the Fe and Cr atoms, particularly their complex magnetic interactions as shown experimentally¹¹ and theoretically,¹⁴ and consequently the perturbed alloy's thermodynamics. For higher bulk concentrations, c_2 decreases sharply and becomes even depleted in Cr with respect to the bulk at $c_b \gtrsim 0.13$.

Finally, and most importantly, we plot in Fig. 4(b) the surface concentration $\bar{c}_s$ defined as the average concentration of all layers in direct contact with the surface, i.e., $\bar{c}_s = \sum_{i=1}^{i_{\max}} c_i / i_{\max}$ with $i_{\max} = 4$ for orientation (100), as a function of c_b at 300, 450, and 600 K. The same behaviour is found at all temperatures. Two regimes are clearly identified: (i) For bulk concentrations under 0.12, the surface concentration increases with c_b , up to a narrow maximum between 0.09 and 0.12. As soon as $c_b = 0.07$, surface composition exceeds the bulk solubility limit, where phase separation would occur in the bulk alloy. (ii) For larger bulk compositions, there is a discontinuity in $\bar{c}_s$, which is reduced to a flat regime $\bar{c}_s \approx 0.05$, equivalent to that of a α - α' phase-separated bulk. Indeed, α' precipitation occurs as expected and discussed above to explain the large variations in the density profiles of Fig. 2, and illustrated in Fig. 1.

Between 300 and 600 K the profiles shown in Fig. 4 are almost temperature independent. It reflects a subtle compensation between the temperature dependence of the order energy, more specifically of the energy associated with magnetism,

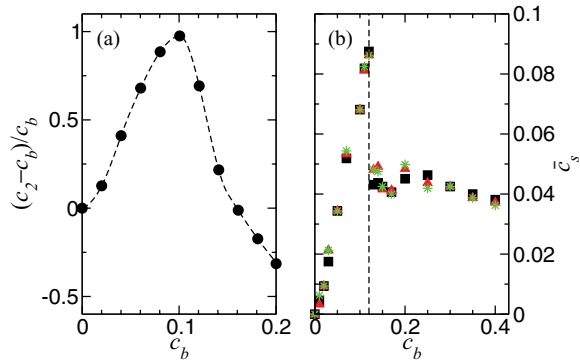


FIG. 4. (Color online) (a) Relative evolution of the concentration of the third layer c_2 versus the bulk concentration c_b at 300 K. (b) Average surface concentration $\bar{c}_s = (c_0 + c_1 + c_2 + c_3)/4$ as a function of c_b at 300 K (black squares), 450 K (red triangles), and 600 K (green stars). A black shaded line indicates the optimal concentration $c_b^{\text{opt}} \approx 0.12$ at which ferritic Fe-Cr steel is the most corrosion resistant.

and the entropic effects. It was identified in the bulk as the cause of the anomalously steep solubility limit of the Fe-Cr alloy at low temperatures, and identified by Williams as an effect of magnetism.^{28,36}

An atomistic explanation of the thermodynamic origin of the narrow optimum in corrosion resistance of stainless steels emerges from the above results. The difference in surface

chemical potential between Fe and Cr induces a strong Cr depletion in the first layers, where atoms have dangling, because the surface energies of Fe are always lower than that of Cr. The subsurface layers balance this local depletion by a strong enrichment in Cr. These combined effects lead to three distinct regimes. (i) At low bulk concentrations the ordering energy drives chromium into solution, far away from the surface: The resistance to corrosion is low and increases with Cr concentration. (ii) In a narrow range of bulk concentrations between 0.07 and 0.12 enough Cr is present to strongly enrich the surface in average but not to exceed the α - α' solubility limit.³⁷ The Cr content in the surface is maximum. (iii) At higher bulk concentrations the bulk solubility limit is exceeded and most of available chromium bulk precipitates in the α' phase, depleting the surfaces: Stainlessness is lost.

In light of the above results, in order to improve the stainlessness of the Fe-Cr system and its derivative alloys, one may consider adding alloying elements that increase the solubility of Cr in Fe, without altering the anomalous thermodynamics of the Fe-Cr surfaces. The sharp decrease in the surface concentration would thus happen, nevertheless, but at higher bulk concentrations. Larger surface concentrations would be reached, inducing better protection against corrosion. One could also increase the quantity of chromium atoms at the surfaces without increasing the content in the bulk. This could for instance be done by the localized addition of chromium-rich nanoscale precipitates or dispersoids. Such strategy is already under investigation as it is also a promising route to strengthen these materials.^{3,38}

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