

Cr segregation at the Fe-Cr surface: A first-principles GGA investigation

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The segregation of Cr at the Fe-Cr alloy surface is essential in the formation of a thin, corrosion-resistant oxide film. Recent angle-resolved x-ray photoelectron spectroscopy measurements indicated Cr segregation at a high temperature in vacuum. However, two independent *ab initio* density functional theory calculations within the local density approximation (LDA) suggested no segregation. We have calculated the segregation energy for Cr at the Fe-Cr(001) surface using the all-electron full-potential linearized augmented plane wave method within the generalized gradient approximation (GGA). Our GGA results support the previous LDA investigations. The disagreement between experiment and theory remains unresolved.

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The oxidation of Fe-Cr alloys and stainless steels has been under intensive investigation for both dry (O_2) and aqueous environments as the thin, Cr-enriched oxides film is far more corrosion resistant than the otherwise Fe oxides.¹ In a dry environment, it is well established that the composition and also the structure of the oxides film change with the heat treatment and the oxygen partial pressure.¹ It has been known for decades that the Cr concentration in this thin film is higher than that in the bulk due to the higher reactivity of Cr with oxygen than Fe.^{2,3,4} The stable oxides on an Fe-Cr alloy surface should be those of Cr, provided that the supply of oxygen from the gas phase is not sufficient, or, equally put, the supply of Cr from the alloy is sufficient. As a matter of fact, various experimental works have shown that a low oxygen partial pressure favors the formation of a chromium-rich oxide film on stainless steels.^{5,6,7} Due to the insufficient supply of Cr at temperatures below 600 °C, steels tend to form an unprotective Fe-rich oxide film.⁸

Since the kinetics during the initial oxidization of Fe-Cr alloys depends on the composition and structure of not only the oxide films but also the substrate underneath, it is of much importance as well to have a detailed knowledge of the Cr concentration profile in the Fe-Cr surface prior to the oxidation. By x-ray photoelectron spectroscopy (XPS), Lince *et al.*⁹ studied the interaction of oxygen with the $Fe_{0.84}Cr_{0.16}(001)$ surface. They found that the Cr percentage at the surface of this alloy prior to the exposure of oxygen depends on annealing conditions, indicating a temperature dependence of the Cr segregation. A more recent angle-resolved XPS (AR-XPS) investigation on high purity Fe-Cr alloy by Suzuki *et al.*¹⁰ also demonstrated that Cr segregates to the surface of high-purity Fe-13.5% and -24.9% Cr alloys at high temperature in ultrahigh vacuum. They estimated the segregation zone to be less than 10 Å thick and the mean concentration of Cr in this segregation zone a few times as high as in the bulk. However, the surface orientation in Ref. 10 is not specified and the picture of Cr distribution near the surface is not clear. Based on the pair bonding arguments,¹¹ it is tempting to attribute the driving force for Cr segregation to the observed smaller surface energy of Cr compared with Fe.^{12,13}

In the dilute limit for Cr in Fe, however, two recent independent *ab initio* investigations suggest that the Cr segrega-

tion is unlikely to occur. Nonas *et al.*¹⁴ calculated the energetics of 3d impurities in the Fe(001) surface by using full-potential Korringa-Kohn-Rostoker (FP-KKR) Green's function method within the local density approximation (LDA). Their results show that Cr has a slightly negative segregation energy (-0.05 eV) at zero temperature. This energy, however, is too small to overcome the entropy term in a practical environment (room and higher temperature). In a systematic study of surface segregation energies of single transition metal impurities in transition metal hosts by Green's-function linear-muffin-tin-orbital (LMTO) calculations, Ruban *et al.*¹⁵ found that the segregation energy of Cr in Fe(001) is positive ($+0.2$ eV), i.e., Cr does not tend to segregate. Together, experimental and theoretical works suggest that Cr segregates to the Fe-Cr alloy surface at moderate bulk concentrations such as those of stainless steel, but not in the dilute limit. However, since Cr and Fe atoms have equal sizes and their alloys form solid solutions, very similar to the Ni-Cu systems,¹⁶ it is not unreasonable to expect that the occurrence of Cr segregation should not depend on the bulk concentration. Hence, there seems to be a contradiction between experiment and theory, although they studied different Cr concentrations.

On the other hand, the quantitative discrepancy between the FP-KKR and LMTO calculations poses some uncertainty in the conclusion on Cr segregation in the dilute cases. In Ref. 15, the authors attributed this discrepancy to the atomic sphere approximation (ASA) in their approach. We note, nevertheless, in Ref. 14, that a full charge density including all nonspherical terms was only evaluated and used in the calculation of the total energies, whereas the atomic potentials and potentials in the vacuum region used to solve the Kohn-Sham equation were still approximated by spherical potentials. Moreover, both calculations were performed within the LDA, which is known to yield a poor description of the ground state of Fe (Ref. 17) and Cr.¹⁸ It therefore appears still desirable to carry out a full potential generalized gradient approximation (GGA) investigation on the issue of Cr segregation at low bulk concentrations. Meanwhile, of equal theoretical significance is the Cr segregation behavior in the high concentration limit, which is identical to the issue of Fe segregation in the dilute limit. If Fe segregates to the Fe-Cr alloy surface in the dilute Fe limit, the Fe percentage

in the surface would be of a finite magnitude and a substrate with Fe could help stabilize Cr_3O_4 ,¹⁹ which does not form on pure Cr surfaces.^{20,21,22}

With these motivations, we carried out an *ab initio* study on the Cr segregation in the Fe-Cr surface at both low and high concentration limits. Our calculations were performed by using the all-electron full-potential linearized augmented plane wave (FLAPW) method.²³ The code we employed was the implementation of *WIEN97* (Ref. 24); and the GGA functional was that of Perdew, Burke, and Ernzerhof.²⁵ The FLAPW method is one of the most precise electronic band-structure methods, in which no shape approximations are made to the charge densities, potentials, and matrix elements. In a numerical implementation of any algorithm, one always has to replace infinite series and continuous integrations by finite sums, which leads to numerical errors. A very important aspect of the FLAPW method for solving the Kohn-Sham equations is the absence of uncontrolled numerical parameters.

The surface segregation energy is defined as the energy difference of a solute atom in the alloy surface and in the bulk. The Fe-Cr(001) free surfaces were simulated by repeated seven-layer slabs separated in z direction by a vacuum region of 20 a.u. For Cr (Fe) segregation in Fe (Cr), one Fe (Cr) atom in the outermost surface layer was replaced by a Cr (Fe) atom on each side of the slab. An inherent approximation in the slab model is its finite thickness. The choice of an appropriate thickness depends on the chemical or physical properties of interest and also on the specific system under investigation. It is known that for transition metals, a slab thickness of 10 Å is usually sufficient to obtain bulklike properties in the center of the slab and consequently true surface phenomena at the slab/vacuum interfaces, which, in the present work, means an eight-layer slab. Our test calculations on five-, seven-, and nine-layer clean Fe slabs show that a seven-layer slab is thick enough to minimize the interaction between the top and bottom surfaces and hence gives a reliable surface energy.

For different Cr concentrations in the Fe-Cr surface, we have performed calculations on four cases, namely, 1×1 , $c(2 \times 2)$, 2×2 , and $c(4 \times 4)$. The unit cell has five, 12, 26, and 54 Fe atoms and two Cr atoms, respectively. Since what we have studied were actually ordered, rather than random alloys, the ordering effect was neglected and only the results on the dilute limit have a clear physical meaning. The results on concentrated alloys, however, demonstrate how the interactions between solute atoms vary with their interatomic distances. The two-dimensional lattice constant, 5.44 a.u., was taken from our GGA bulk calculation on bcc Fe while the vertical atomic positions were determined by atomic force calculations. An energy cutoff of 14.5 Ry was employed for the augmented plane-wave basis to describe the wave functions in the interstitial region, and a 100-Ry cutoff was used for the star functions depicting the charge density and potential. The muffin-tin radius for Fe and Cr atoms was chosen as 2.1 a.u. Within the muffin-tin spheres, lattice harmonics with an angular momentum l up to 8 were adopted to expand the charge density, potential, and wave functions. Convergence is assumed when the average root-mean-square differences

TABLE I. The solution energy of Cr (in reference to bulk Cr) and the Cr-Cr nearest-neighbor distance (in scale of lattice constant a) in ordered Fe-Cr surface alloys. For explanation of Cr configuration, see text.

| Cr config. | 1×1 | $c(2 \times 2)$ | 2×2 | $c(4 \times 4)$ |
|----------------------------------|--------------|-----------------|--------------|-----------------|
| $d_{\text{Cr-Cr}}$ | a | $\sqrt{2}a$ | $2a$ | $2\sqrt{2}a$ |
| $E_{\text{sol}}(\text{Cr})$ (eV) | +0.31 | +0.04 | -0.11 | -0.15 |

between the input and output charge and spin densities are less than $1 \times 10^{-4} e/(\text{a.u.})^3$. The equilibrium atomic positions were determined according to the calculated atomic forces to be less than 0.003 Ry/a.u.. This tolerance results in an error to the atomic position of about 0.02 a.u., which results in a total energy error of about 0.02 eV.²⁶ The reciprocal space meshes of $13 \times 13 \times 1$, $9 \times 9 \times 1$, $6 \times 6 \times 1$, and $4 \times 4 \times 1$ were used for the (1×1) , $c(2 \times 2)$, (2×2) , and $c(4 \times 4)$ unit cells, respectively. Careful k -mesh tests on the (1×1) and $c(2 \times 2)$ systems show that the total energy error bar is within 0.01 eV.

With respect to bulk Cr, the solution energy of a Cr atom in an ordered Fe-Cr surface alloy is

$$E_{\text{sol}}(\text{Cr}) = (1/2)E_{\text{slab}}(\text{Cr on surface}) + E_{\text{bulk}}(\text{Fe}) - E_{\text{bulk}}(\text{Cr}) - (1/2)E_{\text{slab}}(\text{clean Fe surface}).$$

For each Cr concentration, we considered both ferromagnetic (FM) and antiferromagnetic (AFM) coupling between Fe and Cr, and we find that AFM is always lower in total energy and therefore more stable than FM coupling, in agreement with previous experimental²⁷ and theoretical results.^{28,29} Table I shows the calculated $E_{\text{sol}}(\text{Cr})$ for different Cr concentrations. It is seen that the interaction between Cr atoms decreases rapidly with the increasing Cr-Cr distance, and in a 2×2 configuration ($d_{\text{Cr-Cr}} = 10.88$ a.u.), the Cr-Cr interaction becomes practically negligible.

For bulk alloys $\text{Fe}_{1-x}\text{Cr}_x$, total energy calculations were performed for various Cr concentrations. The supercells contain two ($a \times a \times a$), four ($2a \times a \times a$), 16 ($2a \times 2a \times 2a$), and 32 ($4a \times 2a \times 2a$) atoms were employed, in which one Fe was replaced by one Cr, representing Cr concentrations of 50%, 25%, 6.25%, and 3.125%, respectively. Again, the lattice constant a was taken as that of the bulk Fe, in observance of the small lattice mismatch between Fe (5.44 a.u.) and Cr (5.39 a.u.). Internal freedoms were optimized according to the calculated atomic forces. Table II lists the calculated $E_{\text{sol}}(\text{Cr})$, which is defined as

TABLE II. The solution energy of Cr (in reference to bulk Cr) and the Cr-Cr nearest-neighbor distance (in scale of lattice constant a) in the ordered $\text{Fe}_{1-x}\text{Cr}_x$ alloys.

| x | 50% | 25% | 6.25% | 3.125% |
|----------------------------------|-------|-------|-------|--------|
| $d_{\text{Cr-Cr}}$ | a | a | $2a$ | $2a$ |
| $E_{\text{sol}}(\text{Cr})$ (eV) | +0.41 | +0.24 | -0.10 | -0.12 |

$$E_{\text{sol}}(\text{Cr}) = E_{\text{bulk}}(\text{Cr in Fe}) - E_{\text{bulk}}(\text{Fe}) \times (1-x)/x - E_{\text{bulk}}(\text{Cr}).$$

We see that when $x \leq 6.25\%$ ($d_{\text{Cr-Cr}} \geq 10.88$ a.u.) the interaction between solute atoms is negligible and therefore $E_{\text{sol}}(\text{Cr})$ can be taken as the solution energy of Cr as an isolated impurity in bulk Fe.

A quick comparison of surface and bulk situations tells us that in the dilute limit, the solution energy of Cr is slightly lower (-0.03 eV) in the surface of Fe than in the bulk Fe, suggesting an occurrence of Cr segregation at extremely low temperature. This result confirms the previous FP-KKR work.¹² In a realistic environment at the room and above temperature, however, the entropy term must be taken into account. The contribution to the segregation energy from the decrease of the entropy during segregation is³⁰

$$\Delta E_S = kT \times \ln[C_s(1-C_b)/C_b(1-C_s)],$$

where C_s and C_b represent the surface and bulk concentrations of Cr. If we take C_b as 6.25% and C_s as 25% (corresponding to the 2×2 case studied here), then $\Delta E_S \approx 2kT$, i.e., ~ 0.06 eV at 300 K and ~ 0.20 eV at 1000 K. This means that in a realistic environment, the entropy decrease will overcompensate the bonding energy increase during segregation and therefore the segregation will not occur.

In the study of Fe segregation in Cr, the two-dimensional lattice constant of the surface system, 5.39 a.u., was taken from our GGA bulk calculation on bcc Cr and the vertical atomic positions were also determined by atomic force calculations. Based on the knowledge of convergence from Cr-

TABLE III. The solution energy of Fe (in reference to bulk Fe) and the Fe-Fe nearest-neighbor distance (in scale of lattice constant a) in Cr bulk and Cr(001) surface.

| Fe in | Fe _{6.25%} Cr _{93.75%} | (2×2) Cr(001) |
|----------------------------------|--|---------------|
| $d_{\text{Fe-Fe}}$ | $2a$ | $2a$ |
| $E_{\text{sol}}(\text{Fe})$ (eV) | +0.46 | -0.15 |

in-Fe systems, we calculated only 2×2 configuration. The solution energy of an Fe atom (in reference to bulk Fe) in an ordered surface Fe-Cr alloy in dilute Fe case is -0.15 eV (Table III). To obtain $E_{\text{sol}}(\text{Fe})$ in bulk Cr, we calculated the total energy of a dilute Fe-Cr alloy, Fe_{6.25%}Cr_{93.75%}, with a Fe₁Cr₁₅ ($2a \times 2a \times 2a$) supercell. The lattice constant a was again taken as that of the bulk Cr. The calculated $E_{\text{sol}}(\text{Fe})$ in bulk Cr is $+0.46$ eV (Table III). Hence, the segregation energy of Fe is -0.61 eV, indicating that at low concentration limit, Fe does segregate to the alloy surface, in agreement with Ruban *et al.*'s result.¹³ The segregation of Fe toward the Cr surface can be readily understood from a recent first-principles result showing that the surface energy of Fe is substantially lower than that of Cr for a (100) surface.³¹ Our calculations therefore indicate that at a high concentration limit, Cr will not segregate to the Fe-Cr(001) surface.

To conclude, we have shown by highly precise *ab initio* DFT-GGA investigations that at both low and high concentration limits Cr will not segregate to the Fe-Cr(001) surface, confirming the previous DFT-LDA results. In view of the overwhelming success of DFT in surface science, this disagreement between experiment and theory is rather puzzling. Further experimental scrutiny is thus called for.

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