PHYSICAL REVIEW B **80**, 153403 (2009)

Tuning the surface chemistry of Fe-Cr by V doping

E. Airiskallio, E. Nurmi, I. J. Väyrynen, and K. Kokko*
Department of Physics and Astronomy, University of Turku, FI-20014 Turku, Finland
and Turku University Centre for Materials and Surfaces (MatSurf), FI-20014 Turku, Finland

M. Ropo
Department of Information Technology, Åbo Akademi, FI-20500 Turku, Finland

M. P. J. Punkkinen
Department of Physics and Astronomy, University of Turku, FI-20014 Turku, Finland
and Applied Materials Physics, Department of Materials Science and Engineering,
Royal Institute of Technology, SE-10044 Stockholm, Sweden

B. Johansson
Applied Materials Physics, Department of Materials Science and Engineering,
Royal Institute of Technology, SE-10044 Stockholm, Sweden
and Department of Physics and Materials Science, Uppsala University, SE-75121 Uppsala, Sweden

L. Vitos
Applied Materials Physics, Department of Materials Science and Engineering,
Royal Institute of Technology, SE-10044 Stockholm, Sweden;
Department of Physics and Materials Science, Uppsala University, SE-75121 Uppsala, Sweden;
and Research Institute for Solid State Physics and Optics, P.O. Box 49, Budapest H-1525, Hungary

(Received 17 June 2009; revised manuscript received 4 September 2009; published 5 October 2009)

The reversal of the magnitudes of the bulk and surface chemical-potential differences induces the outburst of Cr on the otherwise pure Fe surface of Fe-Cr alloys. This threshold value for the Cr content is about 10 at. %. It is found that vanadium addition to Fe-Cr shifts the Cr threshold to a substantially lower value suggesting V having a positive effect on the corrosion resistance of low Cr steels. The obtained shift in the Cr threshold is shown to be connected to the change in volume of the alloy.

DOI: 10.1103/PhysRevB.80.153403 PACS number(s): 68.47.De, 68.35.Dv, 68.35.bd, 71.15.Nc

I. INTRODUCTION

The superb properties of stainless steel, such as resistance to corrosion, high strength, ductility, low maintenance, and relatively low cost, make it an ideal base material for a host of commercial applications. For example stainless steels are used in cookware, cutlery, hardware, surgical instruments, major appliances, industrial equipment, as an automotive and aerospace structural alloy, and construction material in large buildings.

Stainless steel differs from corrodible carbon steel mainly by the amount of chromium in the bulk. Stainless steels have sufficient amount of chromium present so that a thin and transparent film of chromium oxide rapidly forms to the open surface of the metal, which prevents further surface corrosion and blocks corrosion from spreading into the internal structure of the material. More importantly, this oxide layer quickly reforms when the surface is scratched. This phenomenon is called "passivation" and is seen also in other metals, such as aluminum and titanium.

High oxidation resistance in air at ambient temperature is normally achieved with chromium additions in steels. The observed steep increase of the corrosion resistance of the ferritic stainless steels starts when the Cr content in bulk reaches the level of about 10 at. %.[1] The observed bulk threshold of Cr correlates surprisingly well with the calculated reversal point of the magnitudes of the bulk and surface chemical-potential differences. This reversal of the chemical potentials is the cause for the outburst of Cr on the otherwise pure Fe surface of Fe-Cr alloys.[2]

Vanadium is a common component, for instance, in tool steels. Vanadium addition to Fe-Cr increases the hardness, tensile strength, wear resistance, and impact resistance.[3,4] However, little has been published on the corrosion properties of the Fe-Cr-V alloys and on the role of vanadium in the passivation process. It is known that the addition of vanadium to an Fe18Cr alloy increases the rate of repassivation of surface defects and therefore enhances the resistance of the passive scale in acidic Cl^- environments.[5] This also decreases the dissolution of the alloy thus improving the corrosion resistance of the alloy. It is also known that vanadium additions increase the pitting corrosion resistance of ferritic 18% Cr stainless steels.[6] In Fe25Cr about 6 wt. % V more than doubles the amount of Cr in the passive film compared to the Cr content in the bulk.[7] Vanadium addition is also observed to increase the rate of the repassivation of a surface defect in Fe18Cr.[5] Energy dispersive x-ray spectroscopy measurements show that the Cr content in Cr oxide layer is higher in 4.5 wt. % Cr, 0.20 wt. % V alloy than in 12.5 wt. % Cr, 0.0 wt. % V alloy. However, the observed effect cannot be related solely to V since the investigated alloys differed also with respect to W and Mo contents.[8] All in all, it seems that there is no a single dominant explaining effect related to vanadium in increasing the corrosion resistance of steels. The beneficial effects of vanadium doping are, for instance, the decreased rate of formation of metastably growing pits and the reduced probability of metastably growing pits attaining stability.

In this Brief Report we investigate the role of V on the Cr threshold. We show that vanadium addition to Fe-Cr shifts the Cr threshold to a substantially lower value. Our finding suggests that V is a possible candidate for improving the corrosion resistance of low Cr steels. The rest of the Brief Report is divided into two main sections and conclusions. The theoretical tool is briefly reviewed in Sec. II and the results are presented and discussed in Sec. III.

II. METHOD

The calculations are based on the density-functional theory[9,10] and performed using the exact muffin-tin orbitals (EMTOs) method.[11,12] The EMTO method is an improved screened Korringa-Kohn-Rostoker method,[13] where the one-electron potential is represented by large overlapping muffin-tin potential spheres. By using overlapping spheres, one describes more accurately the crystal potential, when compared to the conventional non overlapping muffin-tin approach.[14–16]

The EMTO basis set included *s*, *p*, *d*, and *f* orbitals. The one-electron equations were solved within the scalar-relativistic and soft-core approximation. The generalized-gradient approximation[17] was used for the exchange-correlation functional. The EMTO Green's function was calculated self-consistently for 32 complex energy points distributed exponentially on a semicircular contour, which included states within 1 Ry below the Fermi level. In the one-center expansion of the full charge density, we adopted an l-cutoff of 8 and the total energy was calculated using the full charge density technique.[11,15] For each alloy the calculated equilibrium lattice constant was used. The convergence of the total energy with respect to the number of **k** vectors was tested. It was found that 1240 uniformly distributed **k** vectors within the irreducible wedge of the Brillouin zone was enough for the present purposes.

The Fe-rich Fe-Cr alloys adopt the body-centered-cubic (bcc) phase of α-Fe. A number of previous works demonstrate that below the magnetic transition temperature (900–1050 K) the energetics of Fe-Cr alloys with less than 10% Cr are well described using the substitutionally disordered ferromagnetic bcc phase.[18,19] Furthermore, according to the common phase diagrams, at ambient conditions more than 20% V can be dissolved in bcc Fe. Therefore, the present Fe-Cr-V system was also modeled by substitutionally disordered ferromagnetic bcc alloys.

Since in the present investigation we map a large concentration region with Cr and V contents approaching zero, the conventional supercell method would require enormously large supercells. Here, we resolve this difficulty by employing the coherent potential approximation (CPA).[20] Within the CPA, the alloy components are embedded in an effective medium, which is constructed in such a way that it represents, on the average, the scattering properties of the alloy. The EMTO approach in combination with CPA has been applied successfully in the theoretical study of various structural and electronic properties of alloys and compounds[11] demonstrating the accuracy and efficiency needed for the present investigation.

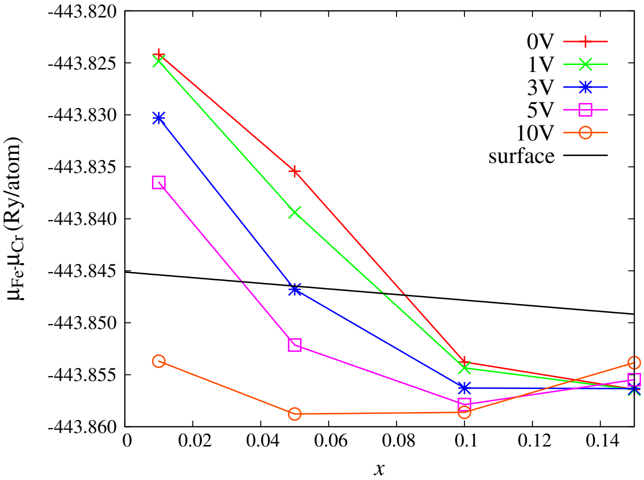

FIG. 1. (Color online) Effective chemical potentials $(\mu_{Fe}-\mu_{Cr})$ of $Fe_{1-x-y}Cr_xV_y$ for bulk (symbols) and surface (black solid line) as a function of x and for V concentrations $y=0,0.01,0.03,0.05,0.10$. The threshold value of the Cr outburst to the surface corresponds to the intersection point of the bulk and surface curves. Cr prefers surface sites when the bulk curve is below the surface curve.

III. RESULTS AND DISCUSSION

In our previous, work it was demonstrated that the chemical composition of the close-packed surfaces of Fe-Cr alloys follows closely the characteristic threshold behavior of the corrosion resistance of ferritic stainless steels.[2] In dilute $Fe_{1-x}Cr_x$ alloys ($x \lesssim 0.05$) the surfaces are exclusively covered by Fe, whereas the Cr-containing surfaces become favorable when the bulk Cr concentration exceeds 10 at. %. The discovered threshold of the concentration of bulk Cr was found to be a consequence of the reversal of the magnitudes of the bulk and surface effective chemical potentials $(\mu_{Fe}-\mu_{Cr})$, which in turn originates from the peculiar electronic and magnetic structure of Fe-rich Fe-Cr alloys.

In the present work we investigate to what extent this threshold value of bulk Cr is affected by V doping of Fe-Cr. We calculated bulk effective chemical potentials $(\mu_{Fe}-\mu_{Cr})^{bulk}$ for Fe-Cr-V alloys containing 1, 3, 5, and 10 at. % V. According to our calculations (not shown) the surface and the first subsurface atomic layers of Fe-Cr-V are depleted of V. This is in line with the predicted moderate antisegregation of V at the Fe surface.[21,22] Due to the surface depletion, the V doping does not affect the surface chemical potentials. Therefore, in the following we approximate the surface effective chemical potential of Fe-Cr-V, $(\mu_{Fe}-\mu_{Cr})^{surf}$, by that of the Fe-Cr alloys.[2]

Figure 1 clearly shows that increasing of the vanadium content in the bulk lowers the $(\mu_{Fe}-\mu_{Cr})^{bulk}$ curve at small

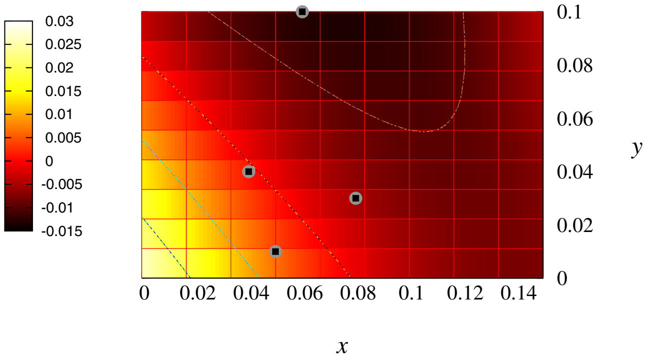

FIG. 2. (Color online) The difference of the effective chemical potentials $(\mu_{\mathrm{Fe}}-\mu_{\mathrm{Cr}})^{\mathrm{bulk}}-(\mu_{\mathrm{Fe}}-\mu_{\mathrm{Cr}})^{\mathrm{surface}}$ (Ry/atom) of $\mathrm{Fe}_{1-x-y}\mathrm{Cr}_x\mathrm{V}_y$ as a function of atomic fractions x and y. The threshold value of the Cr concentration corresponds to the zero level equipotential curve. The equipotential curves are from top to bottom: −0.01, 0.00, 0.01, and 0.02 Ry/atom. For reference, Cr and V contents of some powder metallurgy tool steels are included in the figure (square centered circles) to show that the predicted lowering of the Cr threshold, due to V addition, falls well into the tool steel concentration region.

Cr concentrations. Because the $(\mu_{\mathrm{Fe}}-\mu_{\mathrm{Cr}})^{\mathrm{surf}}$ is independent of the vanadium concentration the threshold value of the Cr outburst to the surface is accordingly shifted to lower bulk Cr concentrations.

The effect of the local lattice relaxation on the effective chemical potentials was estimated by calculating the total energies for vanadium impurities in pure iron and chromium. According to our VASP (Ref. 23) calculations for a 16 atom unit cell the difference in total energy between the relaxed and unrelaxed configurations is 0.00 mRy/atom and 0.04 mRy/atom for V in Fe and V in Cr, respectively. Corresponding to the obtained energy change the nearest-neighbor distance for the V impurity changes too, that being 0.002 and 0.010 Å for V in Fe and V in Cr. Comparing these results with the effective chemical potentials shown in Fig. 1 one sees that the effect of local relaxation is negligible compared to the relevant energy scale of the present investigation. Especially, the relative error due to the local relaxation on the estimated Cr threshold values is about 2/1000.

The obtained decrease of the bulk Cr threshold with increasing V content can be related to the increase of the volume of the alloy due to V addition. As a verification, we performed similar type of calculations for several dopant atoms (Al, Ti, Co, Mn, and Ni) in Fe-Cr. Our results (not shown) demonstrate a clear correlation between the threshold value and the volume of the alloy. Among these dopants, the V solute is found to produce the largest volume effect and the most significant decrease in the threshold value. Interestingly, the volume effect due to V is such that V atoms act like Cr atoms. This kind of behavior is evident if the Cr threshold (x^{T}) is plotted against V content (y). Then approximately $x^{\mathrm{T}}\approx 0.08-y$, which corresponds to the zero value of $(\mu_{\mathrm{Fe}}-\mu_{\mathrm{Cr}})^{\mathrm{bulk}}-(\mu_{\mathrm{Fe}}-\mu_{\mathrm{Cr}})^{\mathrm{surface}}$. This can be seen also in Fig. 2 where the zero level equipotential curve is confined to the almost zero curvature region and therefore it is approximately a straight line.

TABLE I. The volume misfit parameter of $\mathrm{Fe}_{1-x-y}\mathrm{Cr}_x\mathrm{V}_y$. The Cr and V contents are given in atomic fractions.

Cr	V			
	0.01	0.03	0.05	0.10
0.01	0.241	0.218	0.194	0.136
0.05	0.138	0.133	0.127	0.115
0.10	0.079	0.079	0.078	0.077
0.15	0.074	0.076	0.079	0.085

The observed trend in the relation between the Cr threshold value and the volume of the alloy can be understood by considering the total energy of the alloy. The connection between the threshold value and the volume can be elucidated as follows:

(1) the increased (decreased) volume is related to the decreased (increased) bonding between the atoms, and consequently to the increased (decreased) total energy of the alloy;

(2) the increasing (decreasing) total energy of dilute Fe-Cr alloys decreases (increases) the magnitude of the negative slope of the mixing enthalpy of $\mathrm{Fe}_{1-x}\mathrm{Cr}_x$ at $x\approx 0$. This is due to the characteristic shape of the mixing enthalpy of $\mathrm{Fe}_{1-x}\mathrm{Cr}_x$ alloys at small x.[2]

(3) The relation between the effective chemical potential of bulk Fe-Cr and the slope of the mixing enthalpy (ΔH) of the alloy[24]

$$(\mu_{\mathrm{Fe}}-\mu_{\mathrm{Cr}})^{\mathrm{bulk}}\approx-\frac{\partial\Delta H}{\partial x}+\text{constant} \tag{1}$$

shows that the effective chemical potential at $x\approx 0$ consequently decreases (increases).

(4) Finally, the decrease (increase) in $(\mu_{\mathrm{Fe}}-\mu_{\mathrm{Cr}})^{\mathrm{bulk}}$ at small x shifts the threshold value to the lower (higher) Cr contents.

We also calculated the volume misfit parameter $[V(x,y)]^{-1}\partial V(x,y)/\partial y$ for $\mathrm{Fe}_{1-x-y}\mathrm{Cr}_x\mathrm{V}_y$ alloys (Table I). It is largest for small Cr contents in accordance with Fig. 1 where the largest changes in the chemical potentials appear at small Cr additions.

The predicted V induced shift in the bulk Cr threshold, related to the surface Cr outburst of Fe-Cr alloys, is expected to be an accessible discovery among commercial tool steels. Their chemical compositions cover the concentration zone at. % Cr and $\mathrm{V}\lesssim 10$ where the sharp threshold should be clearly discernible (zero level equipotential curve in Fig. 2).

IV. CONCLUSIONS

Using density-functional theory, we investigated the surface chemistry of Fe-Cr-V random alloys and showed that V doping plays a significant role in the surface composition of this system. The employed computational method provides an efficient and straightforward tool to scan the bulk and surface effects of different dopants at any doping level.

We have demonstrated that although vanadium preferably occupies bulk sites compared to surface sites in Fe-Cr, it significantly affects the surface properties of Fe-Cr alloys. Especially, the threshold value of bulk Cr for the outburst of surface Cr is decreased substantially with V doping. This result and conclusion are valid for random Fe-Cr-V alloys, i.e., both Cr and V partitioned in the solid-solution phase (without precipitations). Assuming that the stainless property of Fe-Cr is governed by the presence of Cr near the alloy surface, our findings suggest that the corrosion resistance of the Fe-rich Fe-Cr alloys can be tuned (improved) by adding a small amount of substitutional V to bcc Fe-Cr.

ACKNOWLEDGMENTS

The computer resources of the Finnish IT Center for Science (CSC) and Mgrid project are acknowledged. Financial support from the Academy of Finland (Grant No. 116317) and Outokumpu Foundation are acknowledged. The Swedish Research Council (L.V. and B.J.), the Hungarian Research Fund (Grant No. T048827) (L.V.), National Graduate School in Materials Physics (E.N.), and the Carl Tryggers Foundation (M.P.) are also acknowledged.

---

*kalevi.kokko@utu.fi

[1] G. Wranglén, *An Introduction to Corrosion and Protection of Metals* (Chapman and Hall, New York, 1985).

[2] M. Ropo, K. Kokko, M. P. J. Punkkinen, S. Hogmark, J. Kollár, B. Johansson, and L. Vitos, Phys. Rev. B **76**, 220401(R) (2007).

[3] F. Unkić, A. Pre1oščan, and V. Đukić, Materiali in Tehnologije **37**, 19 (2003).

[4] S. C. Tjong, ISIJ Int. **31**, 738 (1991).

[5] H. C. Brookes, J. W. Bayles, and F. J. Graham, J. Appl. Electrochem. **20**, 223 (1990).

[6] M. H. Ras and P. C. Pistorius, Corros. Sci. **44**, 2479 (2002).

[7] C. Hubschmid, D. Landolt, and H. J. Mathieu, Fresenius' J. Anal. Chem. **353**, 234 (1995).

[8] D. Chaliampalias, G. Vourlias, E. Pavlidou, G. Stergioudis, and K. Chrissafis, Appl. Surf. Sci. **255**, 6244 (2009).

[9] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[10] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[11] L. Vitos, *Computational Quantum Mechanics for Materials Engineers: The EMTO Method and Applications*, Engineering Materials and Processes Series (Springer-Verlag, London, 2007).

[12] L. Vitos, I. A. Abrikosov, and B. Johansson, Phys. Rev. Lett. **87**, 156401 (2001).

[13] O. K. Andersen, O. Jepsen, and G. Krier, in *Lectures on Methods of Electronic Structure Calculations*, edited by V. Kumar, O. K. Andersen, and A. Mookerjee (World Scientific, Singapore, 1994), p. 63.

[14] O. K. Andersen, C. Arcangeli, R. W. Tank, T. Saha-Dasgupta, G. Krier, O. Jepsen, and I. Dasgupta, *Tight-Binding Approach to Computational Materials Science*, edited by P. E. A. Turchi, A. Gonis, and L. Colombo, MRS Symposia Proceedings No 491 (Materials Research Society, Pittsburgh, 1998), p. 3.

[15] L. Vitos, Phys. Rev. B **64**, 014107 (2001).

[16] L. Vitos, H. L. Skriver, B. Johansson, and J. Kollár, Comput. Mater. Sci. **18**, 24 (2000).

[17] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[18] P. Olsson, I. A. Abrikosov, and J. Wallenius, Phys. Rev. B **73**, 104416 (2006).

[19] P. Olsson, I. A. Abrikosov, L. Vitos, and J. Wallenius, J. Nucl. Mater. **321**, 84 (2003).

[20] P. Soven, Phys. Rev. **156**, 809 (1967); B. L. Gyorffy, Phys. Rev. B **5**, 2382 (1972).

[21] B. Nonas, K. Wildberger, R. Zeller, and P. H. Dederichs, Phys. Rev. Lett. **80**, 4574 (1998).

[22] A. V. Ruban, H. L. Skriver, and J. K. Nørskov, Phys. Rev. B **59**, 15990 (1999).

[23] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993).

[24] M. Ropo, K. Kokko, L. Vitos, J. Kollár, and B. Johansson, Surf. Sci. **600**, 904 (2006).