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Ab-initio approach to study hydrogen diffusion in 9Cr steels

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ABSTRACT

We calculate the equilibrium energies and migration barriers of Fe, Cr and H interstitial defects in α -FeX (X = Cr). We use the ab-initio electronic structure code, SIESTA, coupled to the monomer method to find activated states (or migration barriers), in order to study atomic defects diffusion. Ab-initio calculations reveal that in the presence of Cr the H migration barriers are higher than in pure α -Fe. On the other hand, our permeation tests on 9%Cr–91%Fe alloys reveal a permeation coefficient 10 times lower and a diffusion coefficient 200 times lower than in pure, annealed iron. Focusing on our experimental results, we explore very simple model of new H trapping sites and possible migration paths that can explain the experimental observations.

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1. Introduction

Recently, Hurtado Noreña et al. [1] have studied the hydrogen (H) diffusion effects on 9Cr steels, presently used in conventional supercritical thermal power plants and candidates for future Generation IV supercritical water cooled nuclear reactors. Based on the numerical resolution of Fick's equations in presence of trapping sites, and from the fit of electrochemical H detection curves, these authors provided quantitative information about the binding energy between H and trapping sites during diffusion process. In the present work, we calculate the equilibrium configurations and migration barriers of H in α -Fe_nX (X = Cr, $n = 54, 128$) using a very simple model to identify possible trapping sites for H diffusion in 9Cr ferritic–martensitic steels and 13Cr modified supermartensitic steels. The effect of c/a should be of interest for these steels in the “as quenched” state. However, the unusual condition is quenched and tempered where most of the carbon content precipitate as fine carbides which have the effect of anchoring the dislocations. This fact improves the mechanical properties in service and leads to $c/a \approx 1$ which justifies the use of a BCC (not BCT) [1] unit cell in our calculations. We have used a new theoretical approach based on ab-initio technique, employing the monomer method [2] adapted to SIESTA code [3] as in Ref. [4]. We start our calculation with (i) an α -Fe structure in presence of an adequate environment of Fe and Cr impurities; (ii) followed by the incorporation of a single interstitial H atom; finally, (iii) we calculate the migration

barriers of H through α -FeCr crystallite relevant to diffusion process. In the absence of H, we compare our calculations related to relaxed structures and migration barriers of α -Fe_nX (X = Cr) system, with those obtained firstly in Ref. [5] using the ab-initio VASP code and the Nudge Elastic Band Method (NEB) respectively.

2. Implementation and calculational details

The DFT calculations reported here were done with SIESTA [3] code. We employ the generalized gradient approximation (GGA) for exchange and correlation, a Mesh-CutOff parameter of 450 Ry, a smearing temperature of 0.15 eV (within a Fermi–Dirac scheme), and Brillouin zone sampling using a $7 \times 7 \times 7$ k-points mesh. A structure is considered relaxed when the forces are below 0.02 eV/Å. With this setup, we obtain a 0 K lattice parameter for BCC Fe of 2.885 Å. We use the DZP (polarized) default basis for Fe, Cr and H added to the perfect Fe lattice. All the calculations (with or without defects), were performed at constant volume. In order to analyze the interaction of H atom with $\langle 110 \rangle$ and $\langle 111 \rangle$ interstitial dumbbells we calculate the binding energy of different interstitial configurations as,

$$E_{bind}^I = E_f - E_i = [E(3) + E(4)] - [E(1) + E(2)], \quad (1)$$

where we consider the Fe crystallite containing (1) an isolated dumbbell defect, (2) an isolated H atom in a tetrahedral site (i.e., minimum energy of H in α -Fe), (3) with both defects simultaneously and $E(4)$ without defects. Note that in Eq. (1) the number of Fe atoms in E_f and E_i must be equal. The substitutional energy $E = E_{sub} + E_c(\text{Cr})$ of Cr in the α -Fe matrix is calculated from

$$E = E(n\text{Fe} + 1\text{Cr}) - \frac{n}{n+1} \times E((n+1)\text{Fe}), \quad (2)$$

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Table 1
Formation and binding energies of H, Fe and Cr-interstitial in α -Fe ($n = 54$). H_t , H_o and H_n means the tetra-, octa-hedral and new H sites respectively.

Defect	E_f [eV]	VASP [5]	Defect	E_{bind} [eV]
FeFe<1 1 0>	0	0	H ₀₁ FeFe<1 1 0>	0.444
FeFe<1 1 1>	0.752	0.842	H ₀₂ FeFe<1 1 0>	0.409
FeCr<1 1 0>	-0.048	-0.032	H ₁₁ FeFe<1 1 0>	0.412
FeCr<1 1 1>	0.397	0.460	H ₁₃ FeFe<1 1 0>	0.387
CrCr<1 1 0>	0.412	0.438	H ₀₁ FeCr<1 1 0>	0.170
CrCr<1 1 1>	0.532	0.580	H ₁₃ FeCr<1 1 0>	-0.025

with $E(n\text{Fe} + 1\text{Cr})$ the energy of the α -Fe supercell containing n Fe atoms and 1 Cr, $E((n+1)\text{Fe})$ is the energy of the α -Fe supercell with the same size as the former and $E_c(\text{Cr}) = -4.61$ eV/at. is the cohesive energy of BCC ferromagnetic Cr [6]. Static properties of defects are resumed in Table 1. Finally, we use the ab-initio electronic structure code, SIESTA, coupled to the monomer method [2,4] to find activated states (or migration barriers).

3. Experimental procedure

We performed hydrogen permeation tests on membranes taken from a 9%Cr–91%Fe alloy. The alloy was made by melting appropriate amounts of high purity metals, followed by casting, annealing and rolling up to a thickness of 0.5 mm. A final anneal was performed to remove the deformation produced during the slab process. The H permeation technique involved gas phase charging and electrochemical detection. Both input and exit sides of the permeation membrane were plated with a thin film (~ 10 nm) of Pd. The tests were performed in the range of temperature from 30 °C to 70 °C. Our experimental results at 30 °C show a permeation coefficient of 3×10^{-14} mol H cm⁻² s⁻¹ and a diffusion coefficient of 5×10^{-7} cm² s⁻¹, which are respectively 200 times and 10 times lower than the same parameters for pure and annealed iron.

4. Results and discussions

The addition of substitutional Cr in pure α -Fe breaks up the interstitial BCC symmetries, and the interaction of H during diffusion with Fe host changes. Consequently, saddle points shift and energies change. At this point, we define our first step to study H migration on FeCr alloys, i.e., where are these saddle points located in presence of a Cr environment? We start our ab-initio calculations with a substitutional Cr, and H located at any possible tetra- and octa-hedral (\sim T or O) sites, as found in pure α -Fe [4]. We compare our results with those in Ref. [5]. Finally, we study the new minimum configurations of H in the presence of Cr and Fe defects. It is known that the minimum energy configuration of both Fe or Cr interstitial in α -Fe, are FeFe<1 1 0> dumbbells or mixed FeCr<1 1 0> dumbbells. Then, our second step is to investigate the possible interstitial H sites in the presence of both kinds of dumbbells. Once the new minimum configuration sites are found, we calculate the H migration barriers to draw any possible H migration path, concluding our preliminary study of an adequate environment of Cr. As indicated in Section 3, a final anneal was performed to remove the deformation produced during the slab process. Although, the alloy is initially in a BCT phase, after a final annealing the phase changes to BCC. For this reason we employ the relation $c/a=1$ in the present ab-initio calculations. In Table 1, we summarize our results for both, FeCr and FeCrH system. In Fig. 1 the migration energies and final configurations reached from a starting minimum dumbbell

<1 1 0> configuration, are shown. We can see that the minimum energy corresponds to the mixed dumbbell FeCr<1 1 0>. The dumbbell can migrate via translation, τ , or roto-translation, $\omega\tau$. Although relaxed structures of H in FeCr are presented here, dumbbell migration in the presence of H interstitial atoms is out of the scope of the present work. In Fig. 2 we show the main T's, O's for the H interstitial sites. Π_0 and Π_1 correspond to the planes that contain the atoms in the vertex (black circles; Cr), and in the center (white circles) of the BCC conventional cell, respectively. As a remarkable result, we observe that the substitutional Cr atom generates a new interstitial site, $\bar{O}1$, instead of the central O1-site, after structure relaxation. In Ref. [4] we have explored the T1–T2 jump via the O1-site in the middle of the path. Because of the small difference between $\Delta E = E_{O1} - E_{T1} = 0.17$ eV, we had concluded that the O1-site resembles more a flat maximum than a well defined transition state [4]. It is then clear that the α -Fe lattice cannot retain H atoms efficiently, but in the presence of a substitutional Cr atom, things change. Now $\Delta E = E_{\bar{O}1} - E_{T1} = -0.94$ eV; $\Delta E = E_{\bar{O}1} - E_{T2} = -1.17$ eV and $\Delta E = E_{O2} - E_{T2} = 0.1$ eV. We conclude that the $\bar{O}1$ -site is a well defined minimum much more stable than T sites for hydrogen in presence of substitutional Cr. Results of H migration barriers between T1-sites and the new octahedral site are also showed. E_f [eV] and E_{bind} [eV] calculations were also realized for α -Fe_n ($n = 128$). Energies results are about of 5% lower than for $n=54$ Fe atoms. In the presence of Cr our main difficulty arises in the lack of information about minimum configurations. Depending on the distance $d(\text{H,Cr})$ the effect on the energy surface may be considerable. Octahedral sites are located either at the faces or at the edges of the unit cell cube. In the case of a pure BCC metal, all octahedral sites are equivalent. Now, assume that a foreign substitutional atom (such as Cr in the BCC Fe lattice) is located at a vertex of the unit cell cube. Different types of octahedral sites appear, which are well characterised by the distance from the Cr atom. The first neighbor octahedral sites are those located at the middle of the six unit cell cube edges that touch the Cr atom, and are located at a distance of $1/2a$ from the Cr atom. The second neighbor octahedral sites are those located at the middle of the 12 unit cell cube faces that touch the Cr atom. Now, we change the position of the foreign atom: the Cr atom is located at the center of the BCC unit cell. The six first neighbor octahedral sites are those located at the middle of the cube faces, while the 12 second neighbors are located at the middle of the cube edges. In Fig. 3 we show the H interstitial sites in the presence of a pure FeFe<1 1 0> dumbbell. As in the case of substitutional Cr, we found two new H minimum configurations named as I1 and $\bar{O}2$. Note that when an H is placed at T1 site, it relaxes towards T3. The tetrahedral T2 site after relaxation moves to an stable octahedral site O1, and the upper O2 site, relaxes towards $\bar{O}2$ at $\delta \sim a/8$ from O2 site. For mixed dumbbell, the H interstitial sites are summarized in Fig. 4. We remark that, interstitial H sites that were stable in α -Fe, leaves to be in the presence of defects.

5. Conclusions

The presence of Cr as a substitutional atom in the BCC Fe lattice causes the displacement of the stable T-sites of pure BCC iron to non-symmetrical locations; 2. Moreover, the presence of Cr makes O-sites much more stable than T sites for hydrogen, and new stable hydrogen sites appear; 3. the effect of a chromium substitutional atom extends beyond the first nearest neighbors. Experimental results with iron–chromium alloys at room temperature in general agree that the presence of Cr as a substitutional atom in the BCC Fe lattice causes a decrease of the diffusion coefficient in two or three orders of magnitude, and also causes a moderate decrease of the

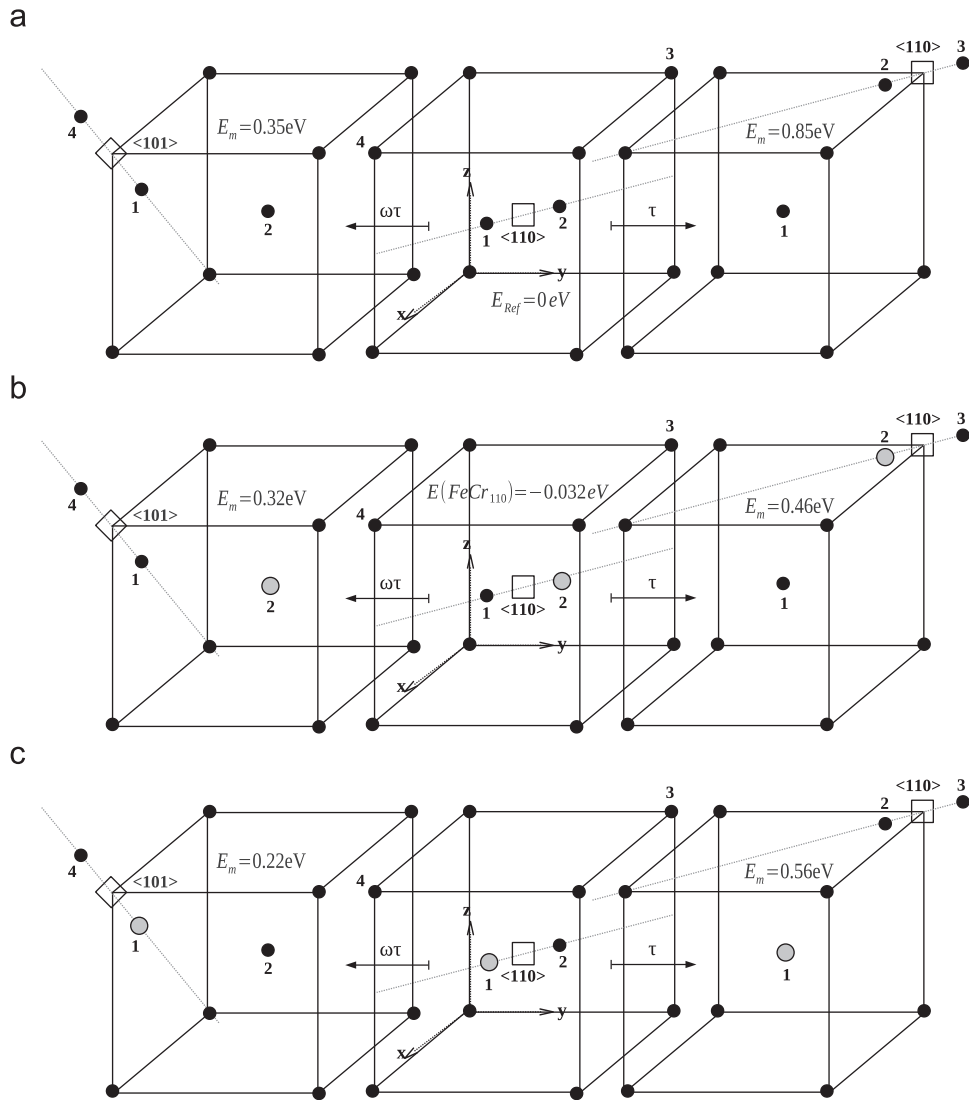


Fig. 1. Interstitial jumps of Fe/Cr (black/grey circles resp.) in α -Fe. Translation (τ) and roto-translation ($\omega\tau$) are showed at the right and left sides of the central dumbbell minimum configuration respectively. In (a) jumps of the Fe self-interstitial. In (b) and (c) mixed FeCr $\langle 110 \rangle$ dumbbells jumps. In the middle, the starting configuration.

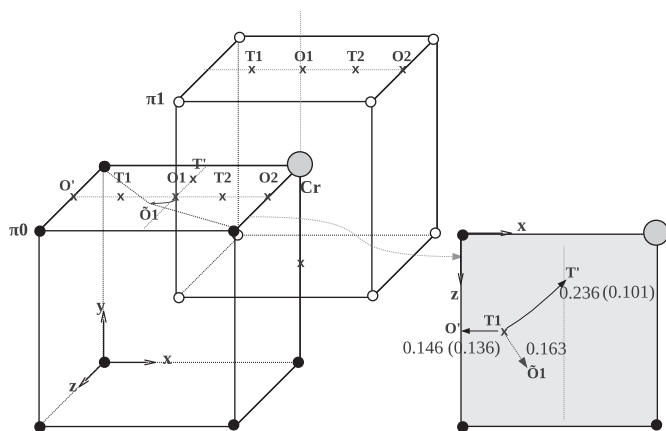


Fig. 2. Schematics jumps of H in α -FeCr, Cr substitutional. Black/white circles correspond to the planes that contain Fe atoms in the vertex/center of the BCC cell respectively. Note that: in the presence of Cr the central second order octahedral site O1, becomes a real minimum, $\hat{O}1$, with lowest energy than the T sites. Numbers represent the energy of the saddle point, and arrows the jump direction. In parentheses the barriers for pure α -Fe [4].

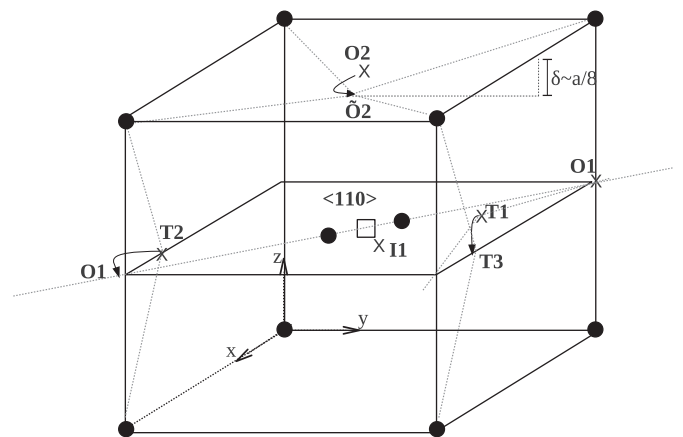


Fig. 3. Relaxed H interstitial configurations in the presence of a FeFe $\langle 110 \rangle$ dumbbell. Here, a new interstitial H relaxed configuration at I1. Note that, O2 and T1, T2 are displaced from the O and T sites in perfect α -Fe lattice respectively, and a is the red parameter. Energies in Table 2.

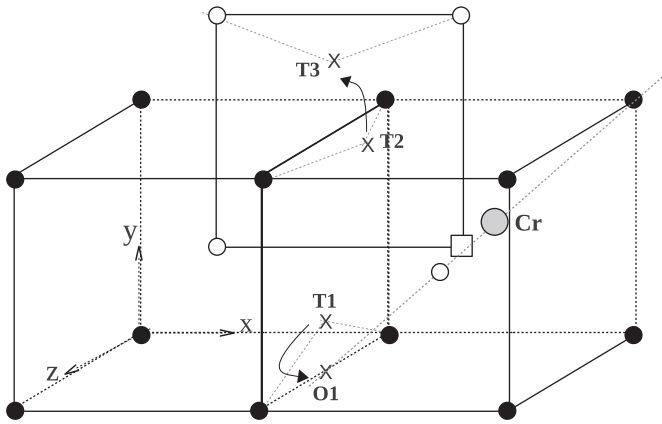


Fig. 4. H interstitial defect in the presence of FeCr $\langle 110 \rangle$ dumbbell. The symbol \times denotes the starting point for relaxation. Final configuration are displaced from \times after relaxation.

permeation coefficient. These results suggest that the presence of Cr causes an increase of the hydrogen solubility and a decrease of the hydrogen diffusion coefficient, may be related to the existence of

this new and real \tilde{O} -site. In a future work we pretend to study the H diffusion in presence of both, FeFe $\langle 110 \rangle$ and mixed FeCr $\langle 110 \rangle$ dumbbells. Also the dumbbells diffusion in presence of H. In other words we will identify the six Onsager coefficients J_{ij} ($i, j = \text{Fe, Cr, H}$) related to D_{ij} .

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