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BINDING ENERGY OF HYDROGEN TO MIXED AND SCREW DISLOCATION

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We have studied the effect of hydrogen on the cohesion of two types of dislocation in bcc iron at an atomistic level, using the atom superposition and electron delocalization molecular orbital (ASED-MO) method. The most stable positions for one hydrogen at each dislocation core were determined. It was found that the total energy of the cluster decreases when the hydrogen is located at the core. This effect is higher in a mixed dislocation in accordance with the experimental data. The computed results show that hydrogen is a strong embrittler and that a decrease in the Fe–Fe overlap population plays a dominant role in the decohesion of the crystal structure.

Keywords:

1. Introduction

Hydrogen in iron is an intensively studied system. Severe failure cases can be caused by hydrogen embrittlement of steels, appearing as surface blistering, hydrogen-induced cracking, stress corrosion cracking, classical, weld and stress cracking and hydrogen environment embrittlement.[1] To understand hydrogen embrittlement, the knowledge of fundamental properties of hydrogen in metals, such as diffusivity, solubility and trapping at dislocations, grain boundaries, voids, and so on, is essentially important. Hydrogen trapping by grain boundaries and dislocations in iron has been studied, measuring enhanced solubility, internal friction, permeability and hydrogen evolution in deformed iron. The binding energies obtained from these studies, however, range from 0.1 to 0.59 eV. The low solubility of H and its high mobility make direct observations

extremely difficult. Although theoretical work and simulations make the analysis of experimental results easier, the problem of hydrogen trapping has not been well understood.[2] One of the oldest proposed mechanisms for hydrogen embrittlement is the "decohesion mechanism" which associates this effect with a decreased metal bond strength in the presence of hydrogen.[3–5]

The H–Fe interaction has been the aim of previous studies our group. These have included electronic and energetic analysis of Fe structures containing vacancies, stacking faults, grain boundaries and dislocations.[6–13]

In this work a comparison between the energetics of H near mixed and screw dislocation is presented. An approximate computational method, the atom superposition and electron delocalization molecular orbital (ASED-MO), described in the Appendix, is employed to trace the relevant orbital interactions

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and discuss the electronic consequences of incorporating H in the Fe matrix.

2.   The Models

Plastic deformation in crystal occurs by the movement or sliding of one plane of atoms over another one so-called slip plane. The slip plane is normally the plane with the highest density of atoms and the direction of slip is the direction in the slip plane in which the atoms are most closely spaced.

Atoms arranged in a bcc structure most closely approach one another along the $<111>$ directions. The shortest distance between two atoms is $a(\sqrt{3}/2)$. Thus, the smallest possible Burgers vector of a perfect dislocation is $\mathbf{b} = (a/2)[111]$, where a is the lattice spacing. Any plane in bcc crystal that contains this Burgers vector is a potential slip plane. Experimentally, slip has been observed on the (110), (112) and the (123) planes. The (110) plane is the most nearly close-packed.[14] The (110) interlayer spacing is $a\sqrt{2}/2$. The stacking sequence of this type of plane is ABABAB, as shown in Fig. 1(a).

Starting from the perfect bcc crystal, two types of dislocations, mixed and screw, were built for the slip system $<111>\{110\}$.

To generate the mixed dislocation, two neighboring half planes of atoms were inserted into the lattice[9] [see Fig. 1(b)]. The Burgers circuits have been drawn in this figure. The dislocation line direction is along $[\bar{1}11]$. This orientation corresponds to an

angle $\theta = 72.52°$ with the Burgers vector, therefore, it is not a pure edge dislocation, but a mixed one. The dislocation structure presents a type of "channel" along the dislocation line. A single configuration is presented in Fig. 2. The neighbor Fe atoms on the slip plane, in $[1\bar{1}1]$ direction, belonging to these "channel like" are separated by a distance of $3.10\,\text{Å}$ (Fe_1 and Fe_2). In the perfect crystal, the minimum distance is $2.48\,\text{Å}$. This channel is relatively large and could trap impurities.

The second simulation model contains a screw dislocation [see Fig. 1(c)]. This dislocation is formed displacing the crystal on one side of the slip plane relative to the other side while the displacement terminates within the crystal. In the region surrounding the dislocation, the atoms remains in their correct array. However, along the dislocation line, the polyhedral coordination of atoms has become distorted by the displacement.[12] The atoms in the half portion of the crystal are linearly displaced in the $[1\bar{1}1]$ direction according to their distance from the original position and those belonging to lower layers in an opposite sense.

For mixed dislocation, we used a cluster formed by 85 atoms of Fe. For the screw dislocation, the cluster has 180 atoms. Pistonesi *et al.*[6] have evaluated the effects of cluster size on the cohesive energy calculations on the $3d$ band width and verified that the cohesive energies values converge for clusters containing more than 60 atoms. The lattice parameter for the bcc unit cell is $2.866\,\text{Å}$.[15]
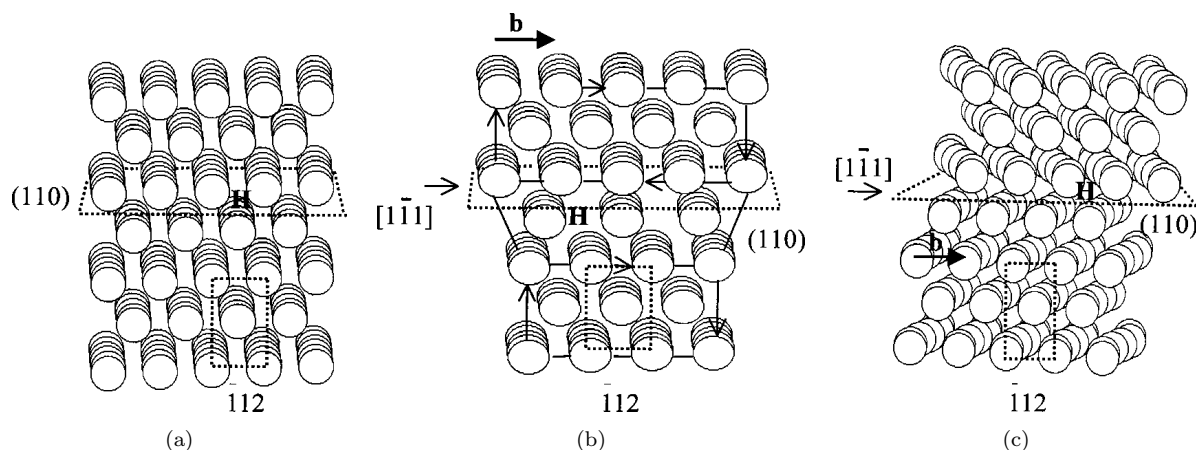

Fig. 1.   Iron cluster model. (a) Perfect crystal; (b) mixed dislocation; (c) screw dislocation. The slip plane and the 112 face are indicated by *dotted lines*.
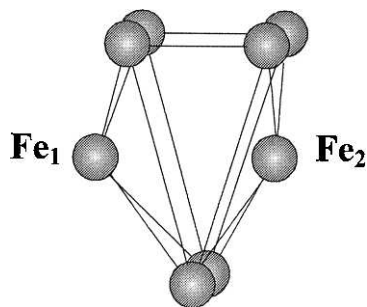
Fig. 2.   The interstitial configuration in the $(a/2)[1\bar{1}1]$ mixed dislocation core. Fe_1 and Fe_2 are in the slip direction.

The geometry was optimized in the defect region obtaining a relaxed structure at $0.01\,\text{Å}$ steps.

3.   Results and Discussion

In order to find the possible location of the H inside the cluster, we have evaluated the adiabatic total energy of the system.

Three types of calculations were carried out. In the first, the hydrogen atom moves from the vacuum to the Fe $(\bar{1}12)$ face of the crystal lattice and then goes into it following an optimized path [Fig 1(a)]. The H approaching the $(\bar{1}12)$ face of perfect bcc Fe shows an absolute minimum at $\sim 1\,\text{Å}$ from the surface. The calculated distance is similar to that reported by Moritz *et al.* on the Fe surface $(0.90\,\text{Å})$.[16] We can observe the presence of an activation energy barrier to diffuse into the bulk of $1.03\,\text{eV}$. After crossing the surface, the H path between the Fe layers presents a successive valley and barriers scheme. The minimum energy for H corresponds to an interstitial site with tetrahedral symmetry (see "T" in Fig. 3).

In the second calculation, the H moves to the $(\bar{1}12)$ face in the $[\bar{1}11]$ direction in a cluster containing a mixed dislocation and then, through the bulk [Fig.1(b)]. The corresponding energy curve is shown in Fig. 3. The activation barrier for H diffusion is only $0.11\,\text{eV}$ and when the H atom travels through the Fe layers to the center of the dislocation, a negligible barrier of $0.02\,\text{eV}$ is computed. The H that accesses this "channel" would reside near the center of this defect and remains associated with the dislocation.

In the third case, the H approaches from the $(\bar{1}12)$ surface to the bulk of a cluster with a screw dislocation [see Fig 1(c)]. The adiabatic total energy curve corresponding to the H–Fe interaction shows a very different behavior when compared with the two previous cases. It can be seen in Fig. 3 that, on the surface, the H–Fe system has two minimums at 0.30 and $1\,\text{Å}$. The activation diffusion barrier is somewhat lower than the first case $(0.63\,\text{eV})$. When H is in the bulk, another difference can be seen when compared with a path in perfect Fe. The region near screw dislocation is much more repulsive and is not a region of absolute minimum energy. These results allow us
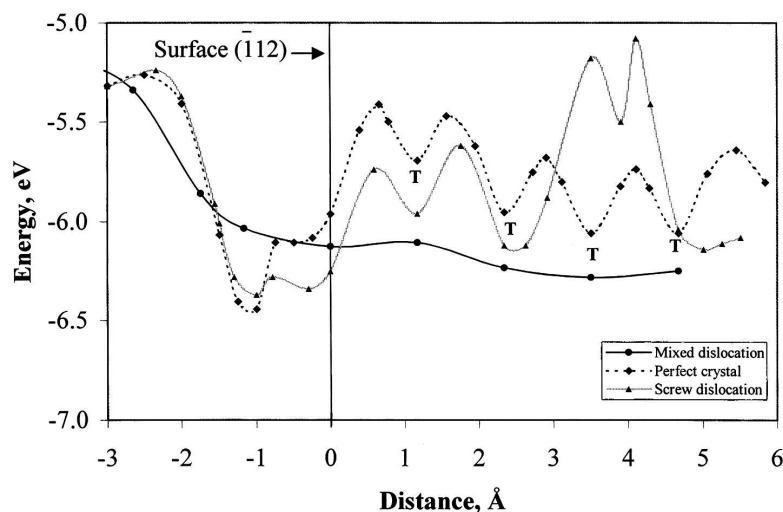

Fig. 3.   Total energy curve for the H–Fe in the cluster.

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to consider that H accumulation could be much less favorable near the screw dislocation than near the mixed dislocation.

When considering H trapping, it is usual to report binding energy (ΔE_B) defined as the difference between the energy of the H atom in the most favorable site of the perfect host metal and that of a H trapped at the lattice imperfection. Whereas for our mixed dislocation model, the binding energy is $\Delta E_B = 0.22\,\mathrm{eV}$, for the screw dislocation, it is a negligible $\Delta E_B = 0.06\,\mathrm{eV}$.

Hirth[17] reported experimental results for trapping of H in Fe according to the trap site. The E_B for H-screw dislocation core was 0.21 to 0.31 eV and 0.61 eV for the H-mixed dislocation core. This author also indicates that E_B varies from 0 to 0.21 eV according to the elastic medium theory by the relationship 0.21 ($\mathbf{b}/r$); that is, it varies with inverse distance r from dislocation ($\mathbf{b}$ is the Burgers vector). According to Myers *et al.*,[18] in the screw dislocation case, the H–Fe interaction energy is usually considered to be negligible. Besenbacher *et al.* reported experimental results for binding energies of H to vacancies in Fe of 0.63 eV.[19] The existence of an attractive interaction between interstitial H and the vacancy can be inferred from the open-volume character of the defect.[18]

The electronic structure of a bulk like Fe in the absence of H shows that the metal d states forms a band between -12 and $-7\,\mathrm{eV}$. The composition of Fe is $d^{6.78}s^{0.67}p^{0.14}$, which is close to $d^{7.02}s^{0.66}p^{0.32}$ obtained for bulk bcc Fe.[10] When we look at the dislocation core, its density of states (DOS) is similar to a bulk Fe atom,[11,12] however, its Fe atoms are less positively charged.

Figure 4(a) shows the projected DOS of an Fe atom, first neighbor to the screw dislocation. This curve is similar to that of the cluster with an H located in the dislocation core except for a small peak at $-15.8\,\mathrm{eV}$. This peak corresponds mainly to H-based states, which are stabilized after the H–Fe interaction. There is also an electron transfer to the H atom from its nearest Fe neighbors near the dislocation (see Table 1). The DOS and crystal orbital overlap population (COOP) plots for the mixed dislocation are sim ilar to that of the screw dislocation case.

Regarding the bonding, the COOP curves for the Fe–Fe bulk and atoms near dislocation core are similar. The bottom of the d, s or p band are bonding and the top antibonding. In Fig. 4(b) COOP curves are plotted for the same Fe–Fe pair inside the cluster, with and without an H in the dislocation region. We can see that when an H is located in the dislocated
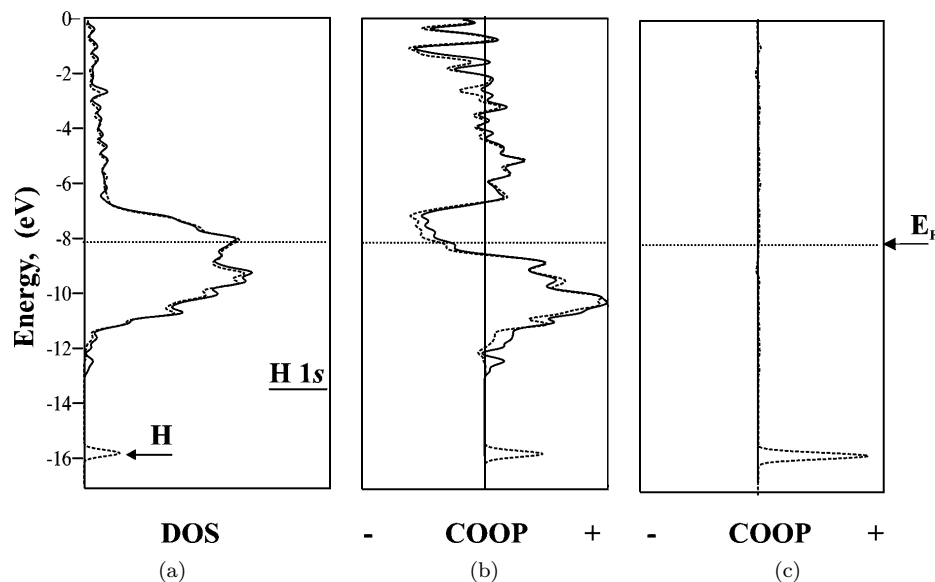

Fig. 4.   (a) Contribution to the DOS of Fe next to the screw dislocation. The bar indicates the H 1s energy before interaction. *Solid lines* denote the cluster without H, *dotted lines* denote the cluster with H. (b) COOP curves for Fe–Fe bond. (c) COOP curves for H–Fe bond.

Table 1.   Net charge and overlap populations (OP) for a cluster with a mixed dislocation and a cluster with a screw dislocation.

Structure	Mixed dislocation		Screw dislocation	
	Charge	OP	Charge	OP
Fe near dislocation	0.25^*	$-32\%^{(a)}$	0.26^*	$-19\%^{(a)}$
H	0.30	$0.32^{(b)}$	-0.27	$0.25^{(b)}$

*Relative to the same atom in a cluster without H.
$^{(a)}$Fe–Fe, relative to the same pair in a cluster without H.
$^{(b)}$Fe–H.

structure, the H–Fe interaction is always bonding [Fig. 4(c)].

The overlap population (OP) for different bonds in the cluster is a measure of the bond strength. The OP between Fe atoms nearest-neighbor to H atom reduces in both dislocations, but the effect in the mixed dislocation is higher. The OP in the mixed dislocation decreases 32% and in the screw dislocation only 19% (relative to OP of Fe–Fe without H). This bond weakening is a consequence of a strong H–Fe interaction. We can say that the H–Fe bonding is achieved at the expense of an Fe–Fe nearest-neighbors bond.[10]

Analysis of the bonding between H and Fe at the dislocation core confirms that the principal bonding comes from H $1s$ and Fe $4s$ interactions, which are almost the same as in the surface case.

4.   Conclusions

The energetics and electronic structure of H en bcc dislocated Fe have been studied by ASED-MO. Three cases were studied: interstitial H in a crystalline lattice, H located near a channel formed by the $(a/2)[1\bar{1}1]$ mixed dislocation and H in a screw dislocation.

The binding energy for the mixed dislocation is substantially higher than for the screw dislocation, which is consistent with results from the continuum mechanics and experimental data.

In both types of dislocations, it was found that H decreases the strength of the Fe–Fe bond close neighbors, but with different intensity: 32% for a mixed dislocation and 19% for a screw dislocation. A charge transference occurs from Fe nearest-neighbors to the H atom, which is found negatively charged. A H–Fe

bond is formed at the expense of Fe–Fe bonds and that can be the reason for the crystal decohesion.

Acknowledgments

Appendix

The calculations were carried out using the atom superposition and electron delocalization molecular orbital cluster method ASED-MO.[20] The ASED-MO is a semiempirical method, which makes a reasonable prediction of molecular and electronic structures. This theory is based on a physical model of molecular and solid electronic charge density distribution functions, whereby the latter is partitioned into a perfect following (with respect to the nucleus) atom part and an imperfect following bond charge part.[20,21] This method was described in a previous paper.[10]

The adiabatic total energy difference is defined as follows:

$$\Delta E_{\text{total}} = E(Fe_mH) - [E(Fe_m) + E(H)] + \Sigma E_{\text{repulsion}},$$

where E is the total energy of the system, m the size of the cluster and $E_{\text{repulsion}}$ is a repulsive pairwise electrostatic energy term. The parameters used in our calculations are described in Ref. 10.

Throughout this paper, two conceptual tools: density of states (DOS) and crystal orbital overlap population (COOP) curves are used to shed more light on the H–Fe interaction computed with the YAeHMOP program.[22] The DOS curve is a plot of the number of orbitals per unit volume per unit

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energy. The COOP curve is a plot of the overlap population weighed DOS versus energy. Integration of the COOP curve up to the E_F gives the total overlap population of the bond specified. Looking at the COOP, we analyze the extent to which specific states contribute to a bond between atoms or orbitals.[23]

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