Diffusion and trapping of hydrogen in carbon steel at different temperatures

Javier Sanchez^{a,*}, Alvaro Ridruejo^b, Pedro L. de Andres^c

^a Instituto Eduardo Torroja de Ciencias de la Construcción-CSIC, Madrid, Spain

^b Universidad Politécnica de Madrid, Departamento de Ciencia de Materiales, Madrid, Spain

^c Instituto de Ciencia de Materiales de Madrid-CSIC, Madrid, Spain

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ABSTRACT

The presence of interstitial hydrogen in steel produces embrittlement, which poses a severe risk to the integrity of structural components. Although real steel, as a multi-phase material with crystal defects at several scales is too complex a system to be modelled utilizing ab-initio calculations, mechanisms of hydrogen (H) diffusion in metals have attracted interest and have been widely described in the literature. Here, we study from first-principles (DFT code CASTEP) the role of phonons on the diffusion of hydrogen at different temperatures in a bcc iron lattice (Fe₁₆H) via a calculation of Helmholtz's free energy, which has been fed into COMSOL for finite element calculations. The diffusion coefficient of hydrogen between 250 K and 700 K was obtained and, the increment in the diffusion barrier at the higher temperatures, traditionally attributed to a transition regime, is now explained by the contribution of phonons. The effect of different traps sites on hydrogen diffusion is studied by using the FEM model.

1. Introduction

The presence of interstitial hydrogen in steel produces a marked embrittlement that poses a severe risk to the integrity of structural components [1,2].

Some papers have dealt experimentally with the hydrogen diffusion coefficient within the iron lattice [3–5]. On the one hand, the experiments show a high dispersion due to different variables such as the test method, the purity of the material, grain size and texture, etc. On the other hand, present theoretical methods allow accurate calculations of activation energies, transition states and vibrational properties [6]. However, up to now the entropic term in the Helmholtz function had not been accurately introduced in such theoretical calculations.

The presence of microstructural heterogeneities such as dislocations, grain boundaries and other imperfections inherent to the material, give rise to so-called hydrogen traps [78]. These heterogeneities are called hydrogen traps because they are places where hydrogen can potentially be “trapped”. With a capture force proportional to the depth of the potential well, hydrogen traps are customarily classified as reversible or irreversible [4]. Following this classification, irreversible traps are those in which the activation energy is too high for hydrogen to escape at moderate temperature (e.g. room temperature and activation energy

greater than 60 kJ/mol), while reversible traps are not (activation energy less than 60 kJ/mol) [9–11]. As an example of irreversible traps, there are inconsistent precipitates and grain boundaries. On the other hand, the most common examples of reversible traps are dislocations, coherent precipitates and low angle grain boundaries [11].

Mechanisms of hydrogen diffusion in metals have been already described [12], but real steel is too complicated for ab-initio calculations [10,13]. Here, we intend to study the role of hydrogen in a bcc iron lattice (Fe₁₆H) using first-principles techniques. We have computed the phonon spectrum of iron with interstitial H atoms, and we have determined the effect of temperature on the diffusion of hydrogen. Our results have been gauged against other models [6] and experimental data [3]. The study is complemented with a finite element model which takes into account the effect of traps on the transport of hydrogen.

2. Methodology

First, an iron-only DFT model based on a $2 \times 2 \times 2$ bcc unit cell is employed to benchmark simulations against known experimental results for pristine iron [13–15]. Then, a single H atom is inserted into a high-symmetry site (either tetrahedral or octahedral), which are the preferential sites for accommodating interstitial H. The DFT code CASTEP was employed for all calculations. A $5 \times 5 \times 5$ Monkhorst-Pack grid was used

* Corresponding author.

E-mail address: javier.sanchez@csic.es (J. Sanchez).

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List of symbols

D	diffusion coefficient
H_{lattice}	hydrogen in the lattice
$H_{\text{trap},c}$	hydrogen in carbide traps
$H_{\text{trap},gb}$	hydrogen trapped in grain boundaries
k_1, k_2	kinetic constants
N_L	number of Fe atoms per unit volume
N_T	density of traps
T	temperature
V_M	molar volume of the lattice
W_B	trapping energy
a_L	activity of hydrogen in the lattice
a_T	activity of hydrogen in the traps
β	number of lattice interstices per Fe atom
θ_L	cover of hydrogen in the lattice
θ_T	cover of hydrogen in the traps

to sample wavefunctions in the Brillouin zone with a 1300 eV energy cutoff [16]. The exchange and correlation energy has been computed within the PBE generalized-gradient approximation [14]. Thresholds for converged geometry configurations are: 10^{-8} eV for internal electronic total energies, 10^{-3} eV/Å for the maximum residual force, 0.01 GPa for the residual stress and 10^{-4} Å for the maximum displacement of atoms in the last three iterations. For the calculation of phonons, the internal electronic total energy has been converged further to 10^{-10} eV. Standard statistical physics yields the entropic contribution of lattice vibrations to Helmholtz free energy which, in turn, leads to a simplified expression for the diffusion coefficient as a function of temperature, $D(T)$ [17].

Moving on to the upper scale, a finite element model (FEM) is used to study hydrogen trapping and diffusion. Hydrogen in traps (H_T) has been considered as a different chemical species than free hydrogen in the lattice (H_L), whose motion is spatially unrestricted and controlled by the defect-free diffusion coefficient, $D(T)$. Therefore, there is a chemical balance between both states:

$$\frac{\partial C_L}{\partial t} = \frac{\partial C_T}{\partial t} = k_1 \cdot \theta_L - k_2 \cdot \theta_T \quad (1)$$

Where k_1 and k_2 are the kinetic constants, and θ_L and θ_T are the coverage or degree of occupation of hydrogen in the lattice and the traps; which in turn define the activity (α) [1,18–20]:

$$\theta_L = \frac{C_L}{\beta \cdot N_L} \quad (2)$$

$$\theta_T = \frac{C_T}{\alpha \cdot N_T} \quad (3)$$

$$a_L = \frac{\theta_L}{1 - \theta_L} \quad (4)$$

$$a_T = \frac{\theta_T}{1 - \theta_T} \quad (5)$$

where N_L is the number of Fe atoms per unit volume, β is the number of lattice interstices per Fe atom, and N_T is the density of traps.

Taking into account the equation proposed by Oriani [21], it is possible to calculate the concentrations at equilibrium:

Table 1

Material properties of AERMET 100 [22].

Parameter	Value
Molar volume of the lattice (V_M) $\left[\frac{m^3}{mol}\right]$	7.116×10^{-6}
Partial molar volume of Hydrogen (V_H) $\left[\frac{m^3}{mol}\right]$	2×10^{-6}
Grain boundary binding energy ($W_B^{(GB)}$) $\left[\frac{kJ}{mol}\right]$	58.6
Grain boundary trapping site density ($\alpha^{(GB)} N_T^{(GB)}$) $\left[\frac{\text{sites}}{m^3}\right]$	8.464×10^{22}
Carbide binding energy ($W_B^{(C)}$) $\left[\frac{kJ}{mol}\right]$	11.5
Carbide trapping site density ($\alpha^{(C)} N_T^{(C)}$) $\left[\frac{\text{sites}}{m^3}\right]$	8.464×10^{26}

$$\frac{\theta_T}{1 - \theta_T} = \frac{\theta_L}{1 - \theta_L} \exp\left(\frac{W_B}{RT}\right) \quad (6)$$

where W_B is the trapping energy.

It is assumed that only hydrogen in the lattice is diffused according to Fick's law:

$$\frac{\partial C_L}{\partial t} = D \nabla^2 C_L \quad (7)$$

where D is the diffusion coefficient.

The above equations have been applied to the problem of hydrogen transport considering an initial concentration of interstitials of 6 ppm and a concentration of 0 ppm at the surface. A cylindrical geometry of 2 mm radius has been considered. In the study, two types of traps have been considered, and their parameters have been obtained assuming an AERMET 100 steel [22] (see Table 1).

3. Results and discussion

3.1. Diffusion coefficient of hydrogen inside the pristine iron lattice

The position of preferential sites for H in bcc lattice has been investigated with a DFT model. Fig. 1 shows orange and white spheres representing Fe and H atoms, respectively. The minimum of potential is found for H in tetrahedral sites for low occupation conditions [13–15], and a saddle-point appears between tetrahedral sites. Finally, the octahedral site is a local maximum.

Both for H in tetrahedral and octahedral sites, the static lattice distortion and the dynamic phonon dispersion are obtained. A high-frequency mode associated with the octahedral position has been found to cause a significant correction to the zero-point energy difference between both configurations. The calculation of Helmholtz free energies for both sites including the effect of phonons yields a variation with the temperature of diffusion barriers due to the entropic contribution (the electronic contribution is considered separately) [17]. The tetrahedral site gains stability compared to the octahedral one as temperature increases. Fig. 2 shows the variation of the diffusion barrier as a function of temperature.

Accordingly, the diffusion coefficient for Hydrogen in the iron lattice can be obtained from the following equation [17]:

$$D(T) = 0.312T \cdot \exp\left(\frac{-453}{T} \left(1 + (10^{-3}T)^2 + (10^{-3}T)^4\right)\right) 10^{-9} \left(\frac{m^2}{s}\right) \quad (8)$$

where the temperature T is expressed in Kelvin.

Fig. 3 shows the theoretical diffusion equation obtained by our ab-initio calculations (Eq. (7)), compared with one derived from an extensive compilation of experimental results [3]. There is a factor of almost 1/2 between the two equations that is attributed to the effect that traps have on the mobility of hydrogen. Such effect will be discussed in

Fig. 1. Potential field for H in the basal plane {100} of a bcc cell.

Fig. 2. Diffusion barrier for Hydrogen in iron lattice.

the next section, where traps are considered as discrete entities using a finite element model.

3.2. FEM desorption model

The FEM calculations have been made under the hypotheses that: i) hydrogen in the traps does not diffuse, ii) the kinetic constants between hydrogen in the lattice and in the traps, k_1 and k_2 , are $3.56 \cdot 10^{10} \text{ s}^{-1}$. These constants have been calculated in previous works and allow to reach chemical equilibrium in times lower than 0.1 s [23].

The results obtained in the FEM calculations are shown below. The behaviour at a certain temperature has been simulated at 173.15, 233.15, 273.15, 313.15 and 373.15 K. The total time in each of them is 1000 s. An initial uniform hydrogen concentration of 6 ppm ($47.2 \text{ mol}_H/\text{m}^3\hat{\text{E}}$) has been considered.

Fig. 4 shows the hydrogen concentration profile in the radial direction of the specimen. In these simulations an axial symmetry has been considered, i.e. there is no diffusion in the axial direction. The hydrogen profile for conditions of 313.15 K at different times is shown on the left. Green curves show the H in the lattice, blue curves show the H in carbide

traps and black curves show the H trapped in grain boundaries. The total concentration at the surface is not zero because the hydrogen in the irreversible traps, $H_{trap,gb}$, has not been released. On the other hand, for this temperature the concentration of hydrogen in the lattice is similar to that of the reversible traps, $H_{trap,c}$. On the right-hand side, a 3D representation of the total hydrogen concentration at $t = 60 \text{ s}$ can be seen.

The following figures show the evolution of the H concentration at a given fixed temperature (see Figs. 5–7). Two effects can be observed: (i) the effect of the diffusion coefficient, and (ii) the variation of the balance between H inside the lattice and inside the traps when the temperature changes. As shown above, as the temperature increases, the mobility of H in the lattice increases, making desorption more likely. Regarding the equilibrium constants, it is observed that for temperatures below 313.15 K, the concentration of H in the lattice, $H_{lattice}$, is lower than the corresponding in the carbides traps, $H_{trap,c}$. However, this behaviour is inverted for temperatures above 313.15 K. On the other hand, the hydrogen found in grain boundaries, $H_{trap,gb}$, remains trapped during the whole calculation time and only for temperatures of 373.15 K it is released in appreciable amounts.

Total concentration in ppm follows following equation:

$$H_{total}(t) = A + B^* \operatorname{erfc}(-C\sqrt{t}) \quad (9)$$

where A, B and C are constants, and t is the time in sec.

From the variation of total hydrogen concentration, it is possible to calculate the flux of hydrogen (or desorption rate) (see Fig. 8). For the first seconds, $t < 10 \text{ s}$, we can obtain the following approximation:

$$J_H(t) = -\frac{\partial H_{total}}{\partial t} = J_0/\sqrt{t} \quad (10)$$

Where J_0 is a constant.

Fig. 9 shows the evolution of J_0 in function of T in K, which follows an Arrhenius-type equation.

Fig. 3. Diffusion coefficient. Experimental (dashed) [3] and theoretical one [17] (solid).

Fig. 4. Hydrogen profile for $T = 313.15$ K. Left: lattice and traps hydrogen concentration. Right: 3D representation of total concentration of hydrogen at $t = 60$ s.

Fig. 5. Evolution of hydrogen concentration. Left: $T = 173.15$ K. Right: $T = 233.15$ K.

4. Conclusion

The present work provides a precise calculation of the hydrogen diffusion coefficient in the pristine iron lattice. The diffusion coefficient of hydrogen between 250 K and 700 K has been obtained. The increment in the diffusion barrier at higher temperatures, traditionally attributed to a transition between different regimes (Kiuchi and McLellan 1983), is now explained by the contribution of phonons.

The effect of hydrogen traps has been reproduced through a finite

element model where two levels of trapping have been taken into account. The model addresses the equilibrium and kinetic constants during hydrogen transport in the iron lattice at different temperatures.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Fig. 6. Evolution of hydrogen concentration. Left: $T = 273.15$ K. Right: $T = 313.15$ K.

Fig. 7. Evolution of hydrogen concentration for $T = 373.15$ K.

Fig. 8. Hydrogen desorption rate at several temperatures.

Fig. 9. J_0 as a function of temperature. The black solid curve marks the best fit.

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