Effect of hydrogen environment on the separation of Fe grain boundaries

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Abstract

A density-functional theory based empirical potential was used to explore the energies of different types of Fe grain boundaries and free surfaces in thermodynamic equilibrium with a hydrogen environment. The classical model for calculating the ideal work of separation with solute atoms is extended to account for every trapping site. This yields the lowest-energy structures at different hydrogen chemical potentials (or gas pressures). At hydrogen gas pressures lower than 1000 atm, the reduction of the reversible work of separation is less than 33% and it increases to 36% at a gas pressure of 5000 atm. Near the hydride formation limit, 5×10^4 atm, the reduction is 44%. Based on the magnitude of these reductions for complete decohesion, and accounting for experimental observations of the microstructure associated with hydrogen-induced intergranular fracture of Fe, it is posited that hydrogen-enhanced plasticity and attendant effects establish the local conditions responsible for the transition in fracture mode from transgranular to intergranular. The conclusion is reached that intergranular failure occurs by a reduction of the cohesive energy but with contributions from structural as well as compositional changes in the grain boundary that are driven by hydrogen-enhanced plasticity processes.

Keywords: hydrogen embrittlement, intergranular failure, iron.

1. Introduction

Hydrogen embrittlement, a catastrophic failure event, is characterized by a decrease in ductility and, in some systems, by a transition in failure mode from transgranular to intergranular [1-3]. This hydrogen-induced intergranular failure was often associated with the presence of other impurities on the grain boundaries, although it is now evident that the other impurities have an additive or synergistic effect but are not necessary for hydrogen to induce intergranular failure [4-7]. Although plasticity effects have always been evident on facet surfaces, the most common explanation for hydrogen-induced intergranular failure remains that hydrogen causes a reduction in the cohesive strength of the grain boundary such that it became the weakest link [8-10]. However, there have been no direct experimental measurements of the magnitude of the decrease of the grain boundary cohesive energy as a function of hydrogen coverage and of grain boundary type. By necessity, assessment of the potency of hydrogen to decrease the cohesive strength of the grain boundary sufficiently to induce intergranular failure has been made by Density Functional Theory (DFT) calculations or other atomistic simulations. For the hydrogen coverages explored, the result is always that hydrogen should cause intergranular failure of Fe. However, experimentally it is found that the predominant failure mode in the absence and presence of hydrogen is transgranular and by microvoid coalescence [5]. Hydrogen-induced intergranular fracture of α -iron is found for some cases that involve severe cathodic charging conditions [11-15].

The classic thermodynamic model developed by Hirth and Rice [16] and Rice and Wang [17] for intergranular fracture under constant solute concentration states that the reversible work of separation (or cohesive energy of the grain boundary (GB)) varies linearly with grain boundary

coverage, with the proportionality constant being the difference between the solute segregation energy on the GB and the free surface (FS). That is, if impurities energetically prefer the free surface compared to the grain boundary, the propensity for intergranular failure is higher. Based on this theory, Freeman and co-workers [9, 18, 19] assessed the embrittling / strengthening effect of different impurities on symmetric tilt grain boundaries of Fe by performing DFT calculations at 0 K and zero pressure. The embrittlement potency of a solute was defined as the difference, ΔE_{em} , in the segregation energies of solute atoms on the GB, E_{GB}^{seg} , and on the FS, E_{FS}^{seg} , i.e.,

$$\Delta E_{em} = E_{GB}^{seg} - E_{FS}^{seg}. \quad (1)$$

If $\Delta E_{em} > 0$, embrittlement of the GB occurs, and if $\Delta E_{em} < 0$, the GB is strengthened. For the body-centered cubic Fe-H system, the embrittlement potency was calculated to be +0.26 eV or 25.21 kJ/mol, which implies that the failure mode of Fe should be intergranular in the presence of hydrogen [20]. Solanki et al. applied molecular statics calculations to $\langle 100 \rangle$ tilt grain boundaries in Fe and found that the GB character affects the number and type of trapping sites for hydrogen and vacancies, and concluded that the hydrogen segregation energy in different trap sites was dependent on the local GB structure [21]. The occupancy of each site depends on the concentration of hydrogen in the GB and, hence, on the charging conditions. This conclusion is consistent with the concept that there is no unique segregation energy for a grain boundary as the energy changes from trapping site to site [17].

In this manuscript, the impact of the site occupancy of hydrogen atoms on grain boundary cohesive energy is explored as a function of hydrogen charging conditions. Specifically, this manuscript reports on the stable GB-H and FS-H structures that are in thermodynamic

equilibrium with the environment as a function of the hydrogen chemical potential. Through this approach, the magnitude of the reduction of grain boundary cohesive strength as a function of the hydrogen coverage, grain boundary type, and hydrogen gas pressure is assessed. The results are discussed in relation to the hydrogen embrittlement of Fe and the hydrogen-induced transition from transgranular to intergranular failure.

2. Theoretical background

Assuming the chemical potential of one Fe atom is $\mu_{Fe}(T, p)$, the total energy of a system containing n Fe atoms is $n\mu_{Fe}(T, p)$. The total energy of the Fe-H system containing n Fe atoms and m H atoms in one type of trapping site “ x ” is $E_{nFe-mH(x)}^{total}$; here the trapping site can be the tetrahedral (T-sites) or the octahedral (O-sites) sites of the lattice, dislocations, vacancies, grain boundaries or the free surface. With the assumption that E_{H_2} is the energy of an isolated H_2 molecule at 0 K and E_{def} the energy of other defects in the system, the dissolution energy, E_x^d , for a system with $m=1$ is:

$$E_x^d = E_{nFe-H(x)}^{total} - n\mu_{Fe}(T, p) - \frac{1}{2}E_{H_2} - E_{def} , \quad (2)$$

and the segregation energy, E_x^{seg} at site x is

$$E_x^{seg} = E_x^d - E_{T-site}^d . \quad (3)$$

Here E_{T-site}^d is the dissolution energy associated with hydrogen being trapped in the lattice tetrahedral site, which is the expected lattice site for hydrogen. For the empirical embedded atom method (EAM) potential used herein [22, 23], the minimum dissolution energy for each of the

different sites is shown in Table 1.

Thermodynamic analysis of the results of the static calculation is based on the Gibbs isotherm [17, 24, 25]. The change of either the GB or FS energy due to a change in the chemical potential μ_H depends on the excess of hydrogen, Γ_H ,

$$d\gamma_{GB/FS} = -\Gamma_H d\mu_H \text{ or } \Gamma_H = \left. \frac{\partial \gamma_{GB/FS}}{\partial \mu_H} \right|_{n,T,A}. \quad (4)$$

Here the subscript “GB/FS” denotes either the grain boundary or free surface and $\gamma_{GB/FS}$ is defined as the formation energy of either the GB or the FS. The original definition of Γ_H is the excess amount of hydrogen trapped at a GB or a FS in comparison to the defect-free crystal. For the Fe-H system with only H trapped at a GB and a FS, this excess of hydrogen is given by

$$\Gamma_H = \frac{m}{A}, \quad (5)$$

where m is the number of H atoms and A is the area of the GB/FS.

At a specific temperature (T) and pressure (p), for a model containing only one GB or one FS, the formation energy in the presence of hydrogen ($\gamma_{GB/FS}^H$) is:

$$\gamma_{GB/FS}^H = \left[E_{nFe-mH(GB/FS)}^{total} - n\mu_{Fe}(T,p) - m\mu_H(T,p) + \Delta G^{vib} \right] \frac{1}{A}, \quad (6)$$

where $E_{nFe-mH(GB/FS)}^{total}$ is the total energy of the relaxed structure of either the GB or FS containing m H atoms, and ΔG^{vib} is the vibrational contribution to the Gibbs free energy of the structure.

The range of chemical potentials explored in this study was established to enable comparison with potentials, or charging conditions, accessible experimentally. The upper limit, $\mu_H^{H(U)}(T, p)$, is defined as the chemical potential at which H atoms are saturated on the GB and are starting to be trapped on T-sites in the lattice. Thus, for this study it is defined as

$$\mu_H^{H(U)}(T, p) = E_{nFe-H(T-site)}^{total} - n\mu_{Fe}(T, p) , \quad (7)$$

where $E_{nFe-H(T-site)}^{total}$ is the total energy of the system with 1 H atom in a T-site. Equation (7) can be rewritten by using the dissolution energy defined in Eq.(2):

$$\mu_H^{H(U)}(T, p) = E_{T-site}^d + \frac{1}{2}E_{H_2} , \quad (8)$$

At the lower limit, the chemical potential is represented as $\mu_H^{H(L)}(T, p)$ and corresponds to the case in which the hydrogen coverage is limited such that the H atoms are restricted to occupy those sites on the grain boundary or free surface that are identified as having the lowest dissolution energy, $\min[E_{GB/FS}^d]$. Then,

$$\mu_H^{H(L)}(T, p) = \min[E_{GB/FS}^d] + \frac{1}{2}E_{H_2} . \quad (9)$$

Combining equations (8) and (9) gives the upper and lower bound of the hydrogen chemical potential:

$$\min[E_{GB/FS}^d] < [\mu_H(T, p) - \frac{1}{2}E_{H_2}] < E_{T-site}^d . \quad (10)$$

Using $\mu_H(0K, p^o) = E_{H_2}/2 = 0$ eV as a reference value for calculating the chemical potential and the dissolution energies in Table 1, according to Eqs. (8) and (9), $\mu_H^{H(U)}(T, p) = 0.28$ eV, and $\mu_H^{H(L)}(T, p)$ is -0.22 eV. The GB or FS formation energy with H interstitial atoms at the lower and upper bounds are then given by Eqs. (11) and (12), respectively.

$$\gamma_{GB/FS}^{H(L)} = \frac{1}{A} \{ E_{nFe-mH(GB/FS)}^{total} - n\mu_{Fe} - \min[E_{GB/FS}^d]m + \Delta G^{vib} \}, \quad (11)$$

$$\gamma_{GB/FS}^{H(U)} = \frac{1}{A} \{ E_{nFe-mH(GB/FS)}^{total} - n\mu_{Fe} - mE_{T-site}^d + \Delta G^{vib} \}. \quad (12)$$

By virtue of the definition of the segregation energy given in Eq.(3), the segregation energy of m hydrogen atoms to the grain boundary or free surface is:

$$mE_{GB/FS}^{seg} = E_{nFe-mH(GB/FS)}^{total} - n\mu_{Fe} - A\gamma_{GB/FS} - mE_{T-site}^d. \quad (13)$$

Then, with the use of the definition of Γ_H from Eq. (5), equations (11) and (12) can be rewritten as:

$$\gamma_{GB/FS}^{H(L)} = \gamma_{GB/FS} + \Gamma_H \{ E_{GB/FS}^{seg} + E_{T-site}^d - \min[E_{GB/FS}^d] + \overline{\Delta G^{vib}} \}, \quad (14)$$

$$\gamma_{GB/FS}^{H(U)} = \gamma_{GB/FS} + \Gamma_H \{ E_{GB/FS}^{seg} + \overline{\Delta G^{vib}} \}, \quad (15)$$

where $\overline{\Delta G^{vib}}$ denotes the Gibbs vibrational energy per unit area. According to Eqs. (14) and (15),

GB and FS energies decrease as μ_H increases if $\min[E_{GB/FS}^d] < E_{T-site}^d = 0.28$ eV.

In the classical decohesion model under constant solute coverage, a grain boundary of area A yields two free surfaces with total area $2A$ [16, 17]. The cohesive energy without hydrogen and with hydrogen can be expressed as:

$$\begin{aligned} 2\gamma_{int} &= 2\gamma_{FS} - \gamma_{GB} \\ 2\gamma_{int}^H &= 2\gamma_{FS}^H - \gamma_{GB}^H. \end{aligned} \quad (16)$$

With the same excess of H for $2\gamma_{FS}^H$ and γ_{GB}^H , and assuming separation occurs at a constant solute concentration, insertion of equations (14) and (15) into Eq. (16) yields the cohesive energies for the two cases:

$$2\gamma_{int}^{H(L)} = 2\gamma_{int} + \Gamma_H \{E_{FS}^{seg} - E_{GB}^{seg} + \min[E_{GB}^d] - \min[E_{FS}^d]\}, \quad (17)$$

$$2\gamma_{int}^{H(U)} = 2\gamma_{int} + \Gamma_H \{E_{FS}^{seg} - E_{GB}^{seg}\}. \quad (18)$$

Combining equations (18) and (1) gives

$$2\gamma_{int}^{H(U)} = 2\gamma_{int} - \Gamma_H \Delta E_{em}. \quad (19)$$

The parameter ΔE_{em} in Eq. (1) was originally derived from $\Delta E_{em} = (2\gamma_{int} - 2\gamma_{int}^H)/\Gamma_H$ [9, 18-20, 26]. Also Eq. (18) has the same form as that proposed by Rice and Wang (Eq. 28 in ref [17]) because the binding energy in their model is the macroscopic average of the segregation energies derived in this work. Thus, the classical model as expressed through the embrittlement potency criterion is in agreement with the case in which the hydrogen coverage on the grain boundary has reached the upper limit as defined herein. The excess of hydrogen for the two chemical potentials considered differ by $\Gamma_H \{\min[E_{GB}^d] - \min[E_{FS}^d]\}$. Since the excess of H on the GB is always

positive, if $\{min[E_{GB}^d] - min[E_{FS}^d]\} > 0$, the cohesive energy for the case in which the chemical potential is $\mu_{GB/FS}^{H(U)}$ is less than when it is $\mu_{GB/FS}^{H(L)}$.

In principle, the vibrational contribution to the Gibbs energy ($\overline{\Delta G^{vib}}$) per hydrogen atom for both GB and FS needs to be calculated. However, an accurate calculation of the absolute free energy is impractical due to insufficient sampling in finite length and time scale calculations. Herein it is assumed that the vibrational contributions to the FS and GB energy are of similar magnitude and as such can be neglected.

To connect the H chemical potential to conditions employed to introduce hydrogen thermally into the metal, the surrounding H_2 gas is treated as an ideal-gas-like reservoir whose potential obeys the thermodynamic expression [27]:

$$\mu_H(T, p) = \mu_H(T, p^o) + \frac{1}{2} kT \ln\left(\frac{p}{p^o}\right). \quad (20)$$

Here k denotes Boltzmann's constant, reference pressure $p^o = 1$ atm, and the $\mu_H(T, p^o)$ values can be found in the JANAF thermochemical tables [28]. Thus, the variation of cohesive energy can be plotted as a function of thermal charging conditions, hydrogen gas pressure and temperature, which provides a means to relate the calculated results to experimental hydrogen charging conditions. The GB, FS and cohesive energies were calculated directly from Eqs. (11), (12), (17) and (18), and then Eq. (20) was used to elucidate the physical meaning behind the plots of $\gamma_{GB/FS}$ versus hydrogen charging conditions expressed through $\mu_H(T, p)$. At a fixed temperature, by expressing the chemical potential in Eq. (4) in terms of Eq. (20), the relation of

$P\text{-}\gamma_{GB/FS}$ at specific H excess can be obtained. Equilibrium with the bulk and the GB/FS is not included as the simulation timeframe does not permit exchange between these systems.

3. Computational approach

3.1. Construction of GB and FS models

All calculations were performed using the parallel molecular dynamics code LAMMPS [29]. The EAM potential used in this work is Potential A tabulated by Ramasubramaniam et al. [22], which was updated by Song and Curtin to prohibit unphysical H–H interactions at a distance less than 0.21 nm [23]. Ramasubramaniam et al. have compared the trapping of H on Fe free surfaces to DFT data [22]. From Eq.(3), the lowest dissolution energies on GB and FS in Table (1) can be converted to segregation energies, -0.50 eV and -0.71 eV, respectively, which are comparable to experimental values of -0.61 eV and -0.73 eV [30]. Also, for the same atomic configuration of hydrogen in the grain boundary, the embrittlement potency of hydrogen on a $\Sigma 3(111)$ grain boundary obtained using this potential was +0.21 eV, which is similar to the DFT calculated value of +0.26 eV [20].

Fifty types of $\langle 100 \rangle$ symmetric tilt grain boundaries, with the interval of misorientation angle larger than 0.7 degrees, were constructed using three-dimensional Born-von Karman periodic boundary conditions that eliminated surface effects. This approach resulted in two identical grain boundaries in the simulation box, as shown in Figure 1. The macroscopic geometrical

degrees of freedom for describing the GB structure will be denoted henceforth as: rotation axis c , rotation angle θ , and boundary plane unit normal n . To prevent interactions between the two parallel boundaries and other finite-size effects, each of the grains has a length of 6 nm. As grain boundaries usually have rigid body translations [31], the grain boundaries are made by an atom deletion criteria [32, 33] along with multiple initial configurations with various in-plane rigid body translation vectors. Using the method developed by Rittner et al. [32], more than 3000 configurations were tested for each type of GB in order to properly determine the optimal minimum energy structures via non-linear conjugate gradient energy minimization. The GB energy is obtained by:

$$\gamma_{GB} = \frac{E_{nFe(GB)}^{total} - E_{nFe}^{total}}{2A}, \quad (21)$$

where $E_{nFe(GB)}^{total}$ is the total energy of a GB cell, E_{nFe}^{total} is the total energy of a perfect lattice containing the same number of Fe atoms as the GB model, and $2A$ is used because there are two grain boundaries in the bicrystal and each has an area A .

After creating an appropriate GB structure, two FS were created by separating one of the interior grain boundaries by 100 Å. The FS energy, after accounting for the second grain boundary, can be expressed as:

$$2\gamma_{FS} = \frac{E_{nFe(GB)}^{total} - E_{nFe}^{total}}{A} - \gamma_{GB}, \quad (22)$$

in which $E_{nFe(FS)}^{total}$ is the total energy of the separated cell. Here $2\gamma_{FS}$ is used as there are two surfaces and this is interpreted as the ideal Griffith work for the separation of a perfect crystal.

3.2. Mapping the trapping sites

To map the H dissolution energy in different trapping sites on each GB and FS, the possible trapping sites for H atoms in the GB and FS were calculated using a line-scan grid, as illustrated in Figure 1. The initial H positions located on the nodes of a three-dimensional grid with spacing of $(1/200) l_p$ (along p), d_n (along n), and $(1/4) l_c$ (along c), where l_p and l_c are the length in p and c directions, respectively, and d_n is the interplanar distance in the n direction. As the free volume of GB varies with the misorientation angle, the trapping distance of H atoms changes as well. To include all the possible trapping types, it is important to cover the trapping distance with the grid nodes, thus the range of the grid is increased until the convergence of dissolution energy is found. For example, for the $\Sigma 5(120)$ GB, $200 \times 30 \times 4$ (grid points $p \times n \times c$) initial GB-H and $200 \times 15 \times 4$ FS-H configurations were created and optimized using the conjugate gradient method with homogeneous relaxation of the bicrystal with respect to both the internal coordinates and the bicrystal dimensions.

3.3. Equilibrium GB-H and FS-H structure and their energies

According to the dissolution energy map, it is possible to create a series of Fe-H configurations with different hydrogen excesses. The interface energies of the GB and FS were then calculated from Eqs. (11) and (12), and Eqs. (17) and (18). The difference between the FS energy and GB energy gives the ideal work of separation. By connecting $(\mu_H^{H(L)}, \gamma_{GB/FS}^{H(L)})$ and $(\mu_H^{H(U)}, \gamma_{GB/FS}^{H(U)})$ for each hydrogen excess with a straight line, a plot of GB/FS energy as a function of the H chemical

potential is obtained, as described by Eq. (4). Note that the atomic configurations following the straight lines are obtainable only when the chemical potential of H is sufficient, and do not represent an equilibrium configuration under a specific environment condition. The equilibrium state at a specific chemical potential can be obtained by comparing all possible configurations. The accuracy of the resultant state is dependent on the number of input Fe-H configurations. However, as only a finite number of possible sites were considered, there remains the possibility that other favourable states may exist. All of the grain boundary and free surface energies were calculated using this approach. The $\Sigma 5(120)$ GB was chosen as an example for showing the analysis process.

The approach used to introduce hydrogen was to add it to the lowest energy sites first until the maximum excess of hydrogen on the surface was achieved, i.e., 87.74 nm^{-2} or 48 H atoms. This excess of hydrogen corresponds to a saturated FS and assumes that any short-range H-H interactions induced by increasing the number of H atoms are addressed by the modified potential [23]. To verify that the potential described the interactions appropriately, especially over the hydrogen excess range used experimentally, hydrogen atoms were added to the grain boundary to the level at which the H-H short-range interaction can be neglected; for the cell size used this corresponded to an excess of 24 H atoms. For the two different H excesses, the results were identical over the range of interest for comparing to experimental charging conditions. The data for the second case is provided in the appendix.

4. Results

4.1. GB, FS and cohesive energies in the absence of H

The calculated energies of 50 types of GB and FS are shown in Figure 2. The $\langle 100 \rangle$ symmetric tilt grain boundaries have energies ranging from 600 to 1200 mJ/m². As indicated by the dashed lines in Figure 2, there are four singular grain boundaries with local energy minima in the high-angle range; these grain boundaries are $\Sigma 13(150)$, $\Sigma 5(130)$, $\Sigma 5(120)$ and $\Sigma 13(230)$. The corresponding FS energies ($2\gamma_{FS}$) varied from 3800 to 4300 mJ/m², and depended on the orientation of the lattice. At 0 and 90 degrees, there is no GB in the simulation box and the cohesive energy equals the FS energy, associating $2\gamma_{FS}$ with the ideal work of separation of the lattice. In comparing the ideal work of separation of grain boundaries to that of the lattice, it is found that it is nearly 1000 mJ/m² lower for the grain boundaries. Of course, the failure mode of Fe in the absence of hydrogen is by microvoid coalescence, indicating that plasticity processes, microvoid nucleation growth and coalescence occurs at a lower energy.

4.2. Hydrogen trapping map

Four typical trapping maps obtained using the line-scan method are shown in Figure 3; all cells are viewed along a direction parallel to the tilt axis $\langle 100 \rangle$. The smaller circles indicate possible hydrogen trapping sites, and these are colored according to the dissolution energy. Note that the projections include no information about trapping along $\langle 100 \rangle$, and consequently some sites that actually reside in different layers appear to overlap. Different grain boundaries possess different structural units, thus the dissolution energy distribution of each GB type is unique. Taking the $\Sigma 5(120)$ case as an example, the hydrogen trapping maps and the dissolution energy distribution

curves for this GB and FS are presented in Figure 4. The lowest dissolution energy for this GB is -0.22 eV and the site with this energy is located in the middle of the GB plane. The FS configuration has the lowest dissolution energy of -0.43 eV on the top surface layer. The plateau in the dissolution energy distribution curves indicates the dissolution energy in the interior. It is noted that due to the insufficient number of scanning grid points and the use of a fixed scanning direction, the converged value of the dissolution energy is lower than the O-site dissolution energy, which is the highest dissolution energy in the interior (0.35 eV); see Table 1. The highest dissolution energy in the FS region is for the O-site, but in the GB region it is much higher. Therefore, as a very high H chemical potential would be required to fill such sites, they have the lowest probability of being filled and for the purpose of discussion are classified as *improbable*. Sites with energy lower than that of the O-site will be referred to as *probable*. This distinction is important as the density of *improbable* traps will depend on the GB misorientation, which will have ramifications on the embrittlement potency of each grain boundary and the required hydrogen coverage. In an actual failure it is likely that the density of each trap site will vary with increasing strain and as dislocations interact with the grain boundary.

The highest and lowest dissolution energies as well as the GB and FS energy curves are shown in Figure 5a and Figure 5b, respectively. The horizontal bold dashed line delineates the boundary between *probable* and *improbable* trapping sites with those above the line being *improbable* and those below *probable*. The density of *probable* sites on the FS and in the GB, and their dissolution energy distributions determine their capability to accommodate H under different H concentrations or charging conditions. Only the high-angle singular grain boundaries (indicated by vertical dash lines) have a dissolution energy comparable to that of the O-site; all other grain

boundaries have *improbable* trapping sites. For the FS, all sites appear to be *probable*, and the lowest and the highest dissolution energy are almost constant, independent of misorientation angle.

The maximum excess (or the density of *probable* sites), calculated by dividing the total number of *probable* sites by the area, was used to evaluate the trapping ability of a GB and FS, as marked by pentagons in Figure 5c and Figure 5d, respectively. In Figure 5c and Figure 5d, the value for the maximum excesses are on the right axis, and the energies of GB or FS on the left axis. The trapping ability of a GB is in the range of 80~230 nm⁻² and for a FS it is 40~110 nm⁻². The trapping ability is strongly depending on the GB/FS type. It is found that the low-angle grain boundaries and their free surfaces have higher maximum excesses of H than high-angle boundaries. For both GB and FS, the trapping ability of H has a tendency to decrease as the misorientation angle approaches 45 degrees.

4.3. GB and FS configurations with H and their cohesive energies

To assess the influence of H on the cohesive energy of the grain boundary the H atoms were added one by one to the available low energy trapping sites until the maximum value was attained. This resulted in a series of configurations for different H excesses. The GB/FS energies for a H excess up to the maximum value of 87.74 nm⁻² for a $\Sigma 5(120)$ GB are plotted as a function of H chemical potential in Figure 6a. In this figure, the horizontal line labelled $2\gamma_{FS}^{H-free}$ is the surface case in the absence of hydrogen and the corresponding line for the grain boundary is the horizontal dashed line labelled γ_{GB}^{H-free} . The cohesive energy of the grain boundary in the

hydrogen-free case is given by the difference of $2\gamma_{FS}^{H-free}$ and γ_{GB}^{H-free} . The energy of the two free surfaces in the presence of hydrogen is shown as the dashed-dotted lines and labelled 2FS. The GB energies with different hydrogen excesses are represented by the dotted lines and labelled GB. The numerals above the 2FS dash-dot lines indicate the number of hydrogen atoms added; the number of lines shown for the 2FS differs from that of the GB because it was assumed that the 2 free surfaces have the same number of hydrogen atoms. Comparison of the lines of all configurations results in the two bold lines, with the triangles marking the lowest 2FS energy and the circles marking the lowest GB energy; the distance between these lines represents the cohesive energy of the grain boundary in the presence of hydrogen.

At a hydrogen gas pressure lower than 10^4 atm (~ 0.08 eV), the excess of hydrogen on the 2FS, as determined from the gradient of the line marked by triangles in Fig 6a, is almost constant at 16 nm^{-2} . In contrast, the bold line for the GB indicates that at pressures lower than 10^4 atm the H excess is in the range of $1\sim 5 \text{ nm}^{-2}$. That is, the grain boundaries are unsaturated at pressures less than 10^4 atm. The difference arises because the average H dissolution energy of a GB is much higher than that of a FS, and there are more *probable* traps in the FS than on the GB. At a chemical potential around 0.1 eV, $\sim 10^{10}$ atm., the slope of the 2FS line transitions to a higher value, which may be due to the H-H short-range interaction produced by large numbers of H atoms.

The GB cohesive energy, determined as the distance between the lines delineated by triangles (surface) and circles (grain boundary) in Fig. 6a, is plotted as a function of hydrogen gas pressure at 300 K in Fig. 6b. Here the upper limit of the gas pressure was set at 5000 atm as this is a

reasonable upper bound for comparison to experimental hydrogen charging conditions. Initially, the grain boundary cohesive energy decreases rapidly to a gas pressure around 500 atm and then it decreases at a slower rate. The cohesive energy at 1 atm hydrogen pressure is 80% of $2\gamma_{int}^{H-free}$ which is marked by the horizontal dash line; 70% at 2000 atm, and 64% at 5000 atm. The maximum reduction in the cohesive energy occurs for the upper limit of the chemical potential $\mu_H^{H(U)} = 0.28 \text{ eV}$, this is indicated in Fig. 6a and is marked by a horizontal solid line in Fig. 6b. The grain boundary cohesive energy is now 17% of the hydrogen-free case. As noted in Fig. 6a, this condition would be achieved for an effective hydrogen gas charging pressure greater than 10^{16} atm. It is worth noting that, for hydrogen gas pressures greater than 5×10^4 atm, an iron hydride phase may form, which changes the possible failure mode completely [34].

The variation of the cohesive energy at 300 K for five different grain boundaries, under three different chemical potentials (-0.22 eV, -0.12 eV, and 0.28 eV), are summarized in Table 2. The Γ_H^{GB} and Γ_H^{FS} are the excesses of hydrogen in the lowest energy atomic configurations at corresponding H chemical potentials. Only for a chemical potential of 0.28 eV do the $\Sigma 3(111)$ and $\Sigma 5(120)$ cases yield the assumption in the classical model: $\Gamma_H^{FS} = \Gamma_H^{GB}/2$ [17]. For chemical potentials of -0.22 eV and -0.12 eV, the GB always has less excess than the FS. This is because most of the GB traps cannot be filled in these low chemical potential conditions. For all grain boundaries listed in Table 2 at the chemical potential of -0.12 eV, which corresponds to a hydrogen gas pressure of 1000 atm, the magnitude of the reduction of the cohesive energy is no more than 33% of the H-free case. For the $\Sigma 5(130)$ and $\Sigma 3(112)$ grain boundaries, respectively, this decrease was 12% and 20% of the H-free case. In other words, for the same chemical potential, the magnitude of the reduction in the cohesive energy of the grain boundary is

dependent on the grain boundary type; this finding has important implications for determining the fracture pathway associated with intergranular failure.

4.4. Discussion

Previous DFT calculations, based on the classic theory of Hirth and Rice [16, 17], found that the tendency for hydrogen-induced intergranular fracture can be predicted by comparing the segregation energy of H to the FS and the GB [9, 18-20]. However, as noted by Rice and Wang [17], the concept of the segregation energy is a macroscopic average based on the Langmuir-McLean law, and there is no unique value as the energy is dependent on the trap site. As shown herein, the segregation energy criterion reflects the condition in which the grain boundary trapping sites are saturated. Although the embrittlement potency is a convenient tool for qualitative analysis, it cannot be applied directly to calculate how much the cohesive energy was reduced at a specific pressure of hydrogen gas, particularly those used in experiments. However, to assess the relationship between the cohesive strength of the grain boundary and the hydrogen coverage, it is necessary to determine this dependency. Furthermore, it is essential that this assessment be conducted as a function of GB type as the impact on various boundaries may differ even for the same hydrogen excess. The calculation method in this study used a more general application of the classical model by accounting for every possible trapping site. Instead of focusing on the lowest energy sites, the full map of both *probable* and *improbable* trapping sites was investigated, and the corresponding cohesive energy of the GB was calculated for different excesses of hydrogen. In an attempt to link these results to experimental parameters, the

hydrogen excesses were related through the hydrogen chemical potential to the hydrogen gas charging pressure.

By mapping the dissolution energy of H in the GB and FS, it was found that the cohesive energy was dependent on the energy of the lowest energy sites, the distribution of those sites and the type of GB/FS types. Therefore, given the complexity of GB/FS atomic structures, it is necessary to evaluate all possible trapping sites for the ideal initial structures. The most important difference between H trapping at the free surface and at grain boundaries is that all trapping sites on the FS are *probable*, whereas in most types of GB there are more *improbable* than *probable* sites. Those *improbable* sites cannot be filled with H even under severe hydrogen charging conditions. The *probable* trapping sites in the FS have lower levels of dissolution energies than the ones in the GB, thus the saturation of those sites can be readily achieved even at a low hydrogen chemical potential. In contrast, for the grain boundaries, saturation is unlikely as there are fewer *probable* sites and the average dissolution energy is higher. Therefore, at low gas pressures (low H chemical potential) only a fraction of the *probable* sites can be filled and the GB is always unsaturated. Only at extremely high gas pressures or low temperatures can all the *probable* sites be filled. However, the condition to fill all available sites may be only attainable theoretically.

To assess how these results compare to experimental observations of hydrogen-induced failure of Fe, it is worth noting that the failure mode in the presence of hydrogen, with a few exceptions, is ductile transgranular not intergranular. The exceptions occur under cathodic charging conditions in which high concentrations of hydrogen can be pumped into the system [35, 36]. To assess

the conditions under which cathodic charging results in intergranular failure in terms of the present results, the findings of Kimura and Kimura are considered [14] . They reported 100% intergranular fracture of Fe charged during the tensile test at a cathodic current density of 20 A/m². Assuming the relationship between the hydrogen concentration introduced by gas phase charging $\{C(wppm) = 42.7\sqrt{p_{H_2}(atm)}\exp\left(-\frac{3280}{T}\right)\}$ [37] and for cathodic charging $\{C(wppm) = 0.017\sqrt{i(A/m^2)}\}$ [36, 38] can be equated, it can be shown that $p_{H_2} \approx [500i(A/m^2)](atm)$. That is, to have the same hydrogen chemical potential as at 500 atm hydrogen gas pressure, 1 A/m² cathodic current density must be applied; this assumes that the charging condition induces no other changes in the microstructure and simply introduces hydrogen. The relative hydrogen pressure used in the work of Kimura and Kimura would be approximately 1×10^4 atm. From Figure 6, the reduction of the work of separation for this hydrogen charging pressure is approximately 37%. Based on this calculation, the following questions must be considered:

- Is this hydrogen-induced reduction in the grain boundary cohesive energy of sufficient magnitude to cause intergranular failure such that any and all other possible factors can be discounted?
- Can the level of hydrogen needed to achieve a 37% reduction at any and all grain boundaries be reached through diffusional processes alone?
- Can the critical level of hydrogen at each grain boundary be attained during the failure process, which is actually a dynamic process?

Although the answers to these questions remain elusive today, recent observations of the microstructure beneath hydrogen-induced intergranular facets in Fe [11] and Ni [39] indicate that hydrogen-enhanced plasticity effects and the impact of these on slip transfer across grain boundaries plays a role, and perhaps even a deterministic one, in establishing the conditions that ultimately cause intergranular fracture by decohesion. A key experimental observation was that the observed microstructure was further evolved and more complex than would be anticipated for the failure strain. Furthermore, the accelerated development of the evolved microstructure was not confined to a near facet region but extended significant distances from it. This latter observation suggests the microstructure is not determined solely by plasticity processes associated with crack propagation along the grain boundary but does suggest that the pre-failure deformation may be important. Although slip initiation is a heterogeneous process, it is transferred across grain boundaries, and it is pertinent to question the role of this process when combined with the hydrogen-enhanced plasticity on enabling intergranular failure. The act of transferring slip is known to cause disruptions in the structure of the grain boundaries locally; these may be of sufficient magnitude to produce a discontinuity in the grain boundary [40, 41]. These discontinuities could be the origin of the markings found on intergranular facets. If the dislocations incident on the grain boundaries are transporting hydrogen, as they must for the hydrogen-enhanced localized plasticity mechanism to operate continuously [3], the act of slip transfer will deposit hydrogen on the grain boundaries. This hydrogen accumulation occurs as the slip transfer process does not involve necessarily the same number of accommodated and emitted dislocations [40, 42-45], not all sites of incident dislocations become sites of dislocation ejection, and the stronger trapping of hydrogen at the grain boundary will modify the flow of hydrogen into and out of the grain boundary. Furthermore, with an increase in the structural

disorder associated with slip transmission, the grain boundary will be able to accommodate more hydrogen as additional low energy sites are generated; this dynamic effect on type of site available in the grain boundary is not considered in the current simulations. Finally, as the rate of impingement of dislocations on grain boundaries will be enhanced in the presence of hydrogen, it is possible that the grain boundary will not be able to accommodate all of them and they will accumulate in the vicinity of the grain boundary. The dislocation accumulation will change the local stresses on the grain boundary. All of these effects will be greatest in regions of high local stresses because of the higher local hydrogen concentration, which will maximize the combined effects to a specific volume of the material. The proposed mechanism provides a natural explanation for the plasticity, which has always been recognized but never explained, and an explanation for the “slip” traces on the facets. It also provides a mechanism for attaining high levels of hydrogen on grain boundaries, especially ones in regions of high dislocation activity. Under this scenario the average reduction of the grain boundary cohesive energy as assessed by the hydrogen charging conditions is likely an underestimate of the hydrogen concentration needed on the grain boundaries that ultimately fail by a decohesion process.

The concept that intergranular failure induced by environments is attributable to factors other than the species segregated to the grain boundary reducing the cohesive strength has been proposed to explain liquid metal embrittlement. For example, Luo et al. reported that the cause of failure of Ni due to the presence of Bi was the formation of a bilayer interfacial phase in Ni with Bi atoms [46]. Furthermore, Martin et al. reported that the presence of liquid Pb on Fe grain boundaries did not reduce the cohesive energy sufficiently to cause intergranular failure by itself and concluded that an additional driving force had to exist [47]. Based on the observed

microstructure beneath intergranular facets, they concluded that the additional driving force was provided by the evolution of the microstructure, namely the interaction of dislocations with the grain boundaries and the local stress state.

5. Conclusions

The reduction of the GB cohesive energy under H chemical potentials representative of the range of charging conditions employed experimentally has been explored using molecular dynamics computer simulations. Under charging conditions for which hydrogen-induced intergranular fracture has been observed, the reduction in the GB cohesive energy due to hydrogen is 37%. Coupling the results of this calculation with experimental observations of the observed microstructural state beneath intergranular facets leads to the posit that hydrogen-enhanced localized plasticity effects on slip transfer across grain boundaries establishes the conditions for grain boundary failure by decohesion. The posited mechanism explains the observed plasticity, provides a mechanism to enhance the concentration of hydrogen on the grain boundary that is dependent on plasticity processes, increases the disorder on the grain boundary, and changes the local stress imposed on the grain boundary. The ultimate failure of the grain boundary is attributed to decohesion which is caused by contributions from changes in the structure and composition of the grain boundary that are driven by the hydrogen-enhanced plasticity.

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Appendix

The $\Sigma 5(120)$ GB was filled with H atoms until the excess reached 43.87 nm^{-2} (24 H atoms on GB); this limit prohibits the formation of unacceptable H-H interactions that may not be well described by the empirical potential. The GB/FS energies at different excesses are plotted as a function of H chemical potential in Figure A1. The distance between the “GB” line and the “2FS” line is the GB cohesive energy. At gas pressures lower than 10^9 atm , the cohesive energy is the same as in Figure 6a, which indicates that the H-H short-range interaction has no influence on the H-GB and H-FS atomic structures and energies up to these pressures. At pressures higher than 10^9 atm , the GB cohesive energy in Figure 6a decreases to a level that is an order of magnitude lower than in the Figure A1. However, the required hydrogen pressure is significantly higher than that used experimentally. This comparison indicates that the empirical potential applied in this study appropriately described the H-H interaction within the experimentally accessible range of hydrogen excesses.

References

- [1] W.H. Johnson. On some remarkable changes produced in iron and steel by the action of hydrogen and acids, *Proc. R. Soc. London* 23 (1875) 168-179.
- [2] J.P. Hirth. Effects of hydrogen on the properties of iron and steel, *Metall. Trans. A* 11A (1980) 861-890.
- [3] H.K. Birnbaum, P. Sofronis. Hydrogen-enhanced localized plasticity - a mechanism for hydrogen-related fracture, *Mater. Sci. Eng. A* 176 (1994) 191-202.
- [4] X.Y. Liu, J. Kameda, J.W. Anderegg, S. Takaki, K. Abiko, C.J. McMahon Jr. Hydrogen-induced cracking in a very-high-purity high-strength steel, *Mater. Sci. Eng. A* 492 (2008) 218-220.
- [5] C.J. McMahon Jr. Hydrogen-induced intergranular fracture of steels, *Eng. Fract. Mech.* 68 (2001) 773-788.
- [6] C.J. McMahon Jr. Brittle fracture of grain boundaries, *Interface Sci.* 12 (2004) 141-146.
- [7] J. Kameda, C.J. McMahon, Jr. Solute segregation and hydrogen-induced intergranular fracture in an alloy steel, *Metall. Trans. A* 14A (1983) 903-911.
- [8] S.F. Pugh. An introduction to grain boundary fracture in metals, IOM Communications Ltd, London, 1991.
- [9] R. Wu, A.J. Freeman, G.B. Olson. First principles determination of the effects of phosphorus and boron on iron grain boundary cohesion, *Science* 265 (1994) 376-380.
- [10] M. Yamaguchi, M. Shiga, H. Kaburaki. Grain boundary decohesion by impurity segregation in a nickel-sulfur system, *Science* 307 (2005) 393-397.
- [11] S. Wang, M.L. Martin, P. Sofronis, S. Ohnuki, N. Hashimoto, I.M. Robertson. Hydrogen-induced intergranular failure of iron, *Acta Mater.* 69 (2014) 275-282.

- [12] K.S. Shin, M. Meshii. Effect of sulfur segregation and hydrogen charging on intergranular fracture of iron, *Acta Metall.* 31 (1983) 1559-1566.
- [13] R.H. Jones. Analysis of hydrogen induced subcritical intergranular crack growth in iron and nickel, *Acta Metall. Mater.* 38 (1990) 1703-1718.
- [14] A. Kimura, H. Kimura. Effect of carbon on the hydrogen induced grain boundary fracture in iron, *J. Jpn. Inst. Met.* 47 (1983) 807-813.
- [15] S. Moriya, H. Matsui, H. Kimura. The effect of hydrogen on the mechanical properties of high purity iron II. Effect of quenched-in hydrogen below room temperature, *Mater. Sci. Eng.* 40 (1979) 217-225.
- [16] J.P. Hirth, J.R. Rice. On the thermodynamics of adsorption at interfaces as it influences decohesion, *Metall. Trans. A* 11 (1980) 1501-1511.
- [17] J.R. Rice, J.-S. Wang. Embrittlement of interfaces by solute segregation, *Mater. Sci. Eng. A* 107 (1989) 23-40.
- [18] W.T. Geng, A.J. Freeman, G.B. Olson. Influence of alloying additions on grain boundary cohesion of transition metals: First-principles determination and its phenomenological extension, *Phys. Rev. B* 63 (2001) 165415.
- [19] W.T. Geng, A.J. Freeman, R. Wu, C.B. Geller, J.E. Raynolds. Embrittling and strengthening effects of hydrogen, boron, and phosphorus on a $\Sigma 5$ nickel grain boundary, *Phys. Rev. B* 60 (1999) 7149-7155.
- [20] L. Zhong, R. Wu, A.J. Freeman, G.B. Olson. Charge transfer mechanism of hydrogen-induced intergranular embrittlement of iron, *Phys. Rev. B* 62 (2000) 13938-13941.
- [21] K.N. Solanki, M.A. Tschopp, M.A. Bhatia, N.R. Rhodes. Atomistic investigation of the role of grain boundary structure on hydrogen segregation and embrittlement in α -Fe,

- Metall. Trans. A 44 (2013) 1365-1375.
- [22] A. Ramasubramaniam, M. Itakura, E.A. Carter. Interatomic potentials for hydrogen in a-iron based on density functional theory, Phys. Rev. B 81 (2010).
 - [23] J. Song, W.A. Curtin. Atomic mechanism and prediction of hydrogen embrittlement in iron, Nat. Mater. 12 (2013) 145-151.
 - [24] R. Kirchheim. Reducing grain boundary, dislocation line and vacancy formation energies by solute segregation. I. Theoretical background, Acta Mater. 55 (2007) 5129-5138.
 - [25] R. Kirchheim. Reducing grain boundary, dislocation line and vacancy formation energies by solute segregation: II. Experimental evidence and consequences, Acta Mater. 55 (2007) 5139-5148.
 - [26] M. Dadfarnia, P. Novak, D.C. Ahn, J.B. Liu, P. Sofronis, D.D. Johnson, I.M. Robertson. Recent advances in the study of structural materials compatibility with hydrogen, Adv. Mater. 22 (2010) 1128-1135.
 - [27] K. Reuter, M. Scheffler. Composition, structure, and stability of RuO₂ (110) as a function of oxygen pressure, Phys. Rev. B 65 (2001) 035406.
 - [28] D.R. Stull, H. Prophet. JANAF thermochemical tables. DTIC Document, 1971.
 - [29] S. Plimpton. Fast parallel algorithms for short-range molecular dynamics, J. Comput. Phys. 117 (1995) 1-19.
 - [30] J.P. Hirth, C. B. Hydrogen adsorption at dislocations and cracks in Fe, Acta Metall. 26 (1978) 1795-1803.
 - [31] V. Vitek, D.A. Smith, R.C. Pond. Structure of tilt grain boundaries in b.c.c. metals, Philos. Mag. A 41 (1980) 649-663.
 - [32] J.D. Rittner, D.N. Seidman. <110> symmetric tilt grain-boundary structures in fcc metals

- with low stacking-fault energies, *Phys. Rev. B* 54 (1996) 6999-7015.
- [33] M.A. Tschopp, D.L. McDowell. Structures and energies of $\Sigma 3$ asymmetric tilt grain boundaries in copper and aluminium, *Philos. Mag.* 87 (2007) 3147-3173.
 - [34] J.V. Badding, R.J. Hemley, H.K. Mao. High-pressure chemistry of hydrogen in metals: In situ study of iron hydride, *Science* 253 (1991) 421-424.
 - [35] R.A. Oriani. The diffusion and trapping of hydrogen in steel, *Acta Metall.* 18 (1970) 147-157.
 - [36] T.P. Perng, J.K. Wu. A brief review note on mechanisms of hydrogen entry into metals, *Mater. Lett.* 57 (2003) 3437-3438.
 - [37] M.H. Armbruster. The solubility of hydrogen at low pressure in iron, nickel and certain steels at 400 to 600°, *J. Am. Chem. Soc.* 65 (1943) 1043-1054.
 - [38] J.K. Wu. Electrochemical method for studying hydrogen in iron, nickel and palladium, *Int. J. Hydrogen Energy* 17 (1992) 917-921.
 - [39] M.L. Martin, B.P. Somerday, R.O. Ritchie, P. Sofronis, I.M. Robertson. Hydrogen-induced intergranular failure in nickel revisited, *Acta Mater.* 60 (2012) 2739-2745.
 - [40] J. Kacher, B. Eftink, B. Cui, I.M. Robertson. Dislocation interactions with grain boundary interactions, *Curr. Opin. Solid State Mater. Sci.* 18 (2014) 227-243.
 - [41] I.M. Robertson, P. Sofronis, A. Nagao, M.L. Martin, S. Wang, D.W. Gross, K.E. Nygren. Hydrogen embrittlement understood, *Metall. Trans. A* 46a (2015) 2323-2341.
 - [42] J. Kacher, I.M. Robertson. In situ and tomographic analysis of dislocation/grain boundary interactions in titanium, *Philos. Mag.* 94 (2014) 814-829.
 - [43] T.C. Lee, I.M. Robertson, H.K. Birnbaum. In situ transmission electron microscope deformation study of the slip transfer mechanisms in metals, *Metall. Trans. A* 21 A (1990)

2437-2447.

- [44] T.C. Lee, I.M. Robertson, H.K. Birnbaum. TEM in situ deformation study of the interaction of lattice dislocations with grain boundaries in metals, *Philos. Mag. A* 62 (1990) 131-153.
- [45] J. Kacher, I.M. Robertson. Quasi-four-dimensional analysis of dislocation interactions with grain boundaries in 304 stainless steel, *Acta Mater.* 60 (2012) 6657-6672.
- [46] J. Luo, H. Cheng, K.M. Asl, C.J. Kiely, M.P. Harmer. The role of a bilayer interfacial phase on liquid metal embrittlement, *Science* 333 (2011) 1730.
- [47] M.L. Martin, T. Auger, D.D. Johnson, I.M. Robertson. Liquid-metal-induced fracture mode of martensitic T91 steels, *J. Nucl. Mater.* 426 (2012) 71-77.

Figure captions

Figure 1 Schematic of computation cell with typical dimensions and hydrogen line-scan grid.

Figure 2 Grain boundary energies (circles), free surface energies ($2\gamma_{FS}$, diamonds) and cohesive energies (triangles) of 50 types of symmetric tilt grain boundaries. The vertical dashed lines indicate singular boundaries. (color online)

Figure 3 Hydrogen trapping energy maps of four singular types of GB/FS, the viewing direction for all cells is along $\langle 100 \rangle$. The larger spheres are Fe atoms (brown), and the smaller ones indicate possible trapping site of H. (color online)

Figure 4 Dissolution energy for hydrogen trapped at (a) $\Sigma 5$ (120) GB and (b) (120) FS. The atom plots are shown as insets, the open circle marks 0 point in the horizontal axis of the energy-coordinate plots and the arrows indicate the scan direction (n-axis). (color online)

Figure 5 Summary of dissolution energy map for 50 types of GB and FS. (a) minima and maxima of H dissolution energy in GB, with squares denoting the dissolution energy (right axis) and circles denoting GB energy (left axis); (b) minima and maxima of H dissolution energy FS, with triangles denoting the dissolution energy (right axis) and diamonds denoting FS energy (left axis); (c) maximum excess (trapping ability) of H in GB, with pentagons denoting the excess of H (right axis) and circles denoting GB energy (left axis); (d) maximum excess of H in FS, with pentagons denoting the excess of H (right axis) and diamonds denoting FS energy (left axis). The

horizontal bold dashed lines in (a) and (b) represent the dissolution energy of H at O-site in normal lattice. (color online).

Figure 6 Energies of one Σ 5 (120) GB and two (120) free surfaces plotted as a function of hydrogen chemical potential, maximum H excess is set to 87.74 nm^{-2} . (a) Free surfaces and grain boundary energies as a function of H chemical potential (pressure). The horizontal solid line marked with “ $2\gamma_{FS}^{H-free}$ ” indicates the 2FS energy without H, horizontal dash line marked with “ γ_{GB}^{H-free} ” indicates the GB energy without H, and the difference between these two lines $2\gamma_{int}^{H-free}$ is the corresponding reversible work of separation for H-free case. The double arrowheads labelled by $2\gamma_{int}^{H(L)}$ and $2\gamma_{int}^{H(U)}$ indicate the cohesive energy at chemical potentials of -0.22 eV and 0.28 eV, respectively; and the slopes of straight lines equal to excesses of H, for instance, in FS lines (dash-dot lines), the marked 2, 4, 6, 8 correspond to number of H in trapping sites of corresponding 2FS configuration. The upper x-axis gives the equivalent hydrogen charging pressure; note the scale is logarithmic. (b) Cohesive energies as a function of hydrogen gas pressure at 300K, the dash horizontal line indicates the cohesive energy without hydrogen, the solid horizontal line indicates the cohesive energy $2\gamma_{int}^{H(U)}$. (color online)

Figure A1. Energies of one Σ 5 (120) GB and two (120) free surfaces plotted as a function of hydrogen chemical potential, maximum H excess is set to 43.87 nm^{-2} (24 H atoms on GB). The horizontal solid line labelled “ $2\gamma_{FS}^{H-free}$ ” indicates the 2FS energy without H, horizontal dash line labelled “ γ_{GB}^{H-free} ” indicates the GB energy without H, and the difference between them $2\gamma_{int}^{H-free}$ is the corresponding reversible work of separation for H-free case. The double

arrowheads marked as $2\gamma_{int}^{H(L)}$ and $2\gamma_{int}^{H(U)}$ indicate cohesive energy of the grain boundary at the lower (-0.22 eV) and upper (0.28 eV) chemical potentials considered. The upper x-axis gives the equivalent hydrogen charging pressure at 300K; note the scale is logarithmic. (color online)

Table captions

Table 1. The dissolution energy of H in different trapping sites of Fe from EAM potential [22]. The GB and FS columns only show the minimum dissolution energy by comparing all investigated $\langle 100 \rangle$ tilt boundaries, and minimum GB energy and FS energy are from $\Sigma 5(120)$; for edge and screw dislocations, the H atom is trapped in the dislocation core region (termed as edge core and screw core).

Table 2. The hydrogen environment effect on the degradation of grain boundaries at 300K. The H environment is represented by the chemical potentials of H atoms, and the -0.12 eV corresponds to 1000 atm gas pressure. The $2\gamma_{int}^H$ is the cohesive energy for the lowest energy configuration. The Γ_H^{GB} and Γ_H^{FS} are the excesses of hydrogen in the energetic preferred atomic configurations on the grain boundary and free surface, respectively.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6a

Figure 6b

b

Figure A1

Table 1 The dissolution energy of H in different trapping sites of Fe from EAM potential [22]. The GB and FS columns only show the minimum dissolution energy by comparing all investigated <100> tilt boundaries, and minimum GB energy and FS energy are from $\Sigma 5(120)$; for edge and screw dislocations, the H atom is trapped in the dislocation core region (termed as edge core and screw core).

Sites	T-site	O-site	GB	FS	Vacancy	Edge core	Screw core
E_x^d (eV)	0.28	0.35	-0.22	-0.43	-0.28	-0.10	0.02

Table 2 The hydrogen environment effect on the degradation of grain boundaries. The H environment is represented by the chemical potentials of H atoms and temperature, and the -0.12 eV corresponds to 1000 atm gas pressure. The $2\gamma_{int}^H$ is the cohesive energy for the lowest energy configuration, which was obtained using the same approach as presented in Figure 6. The Γ_H^{GB} and Γ_H^{FS} are the excesses of hydrogen in the energetic preferred atomic configurations on the grain boundary and free surface, respectively.

GB-type	μ_H at 300 K (eV)	Γ_H^{GB} (nm ⁻²)	Γ_H^{FS} (nm ⁻²)	$2\gamma_{int}^H$ (mJ/m ²)	$\frac{2\gamma_{int}^{H-free} - 2\gamma_{int}^H}{2\gamma_{int}^{H-free}}$
$\Sigma 5(120)$ <100>	-0.22	5.48	14.62	2522.80	18.20%
	-0.12	5.48	16.45	2079.79	32.12%
	0.28	74.95	38.39	535.09	82.51%
$\Sigma 5(130)$ <100>	-0.22	1.29	14.22	2179.29	9.12%
	-0.12	7.75	14.22	2776.04	12.33%
	0.28	23.27	38.78	2359.18	25.50%
$\Sigma 13(230)$ <100>	-0.22	1.13	14.74	2501.83	16.34%
	-0.12	3.40	14.74	2071.14	30.74%
	0.28	66.88	44.21	241.29	91.93%
$\Sigma 3(111)$ <110>	-0.22	1.18	9.44	2873.15	10.84%
	-0.12	4.72	14.16	2557.31	20.64%
	0.28	87.31	43.66	525.25	83.70%

	-0.22	0.83	10.85	3521.28	11.09%
$\Sigma 3(112)$				3148.94	
$\langle 110 \rangle$	-0.12	0.83	13.35		20.49%
	0.28	20.02	20.02	2142.37	45.90%