AGGLOMERATION VERSUS LOCALIZATION OF HYDROGEN IN BCC FE VACANIES

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ABSTRACT:
Severe embrittlement can be produced in many metals by small amounts of hydrogen. The interactions of hydrogen with lattice imperfections are important and often dominant in determining the influence of this impurity on the properties of solids.
The interaction between four-hydrogen atoms and a BCC Fe structure having a vacancy has been studied using a cluster model and a semiempirical method.
For a study of sequential absorption, the hydrogen atoms were positioned in their energy minima configurations, near to the tetrahedral sites neighbouring the vacancy. \( \text{VH}_2 \) and \( \text{VH}_3 \) complexes are energetically the most stables in BCC Fe. The studies about the stability of the hydrogen agglomeration gave as a result that the accumulation is unfavourable in complex vacancy-hydrogen with more than three atoms of hydrogen.

KEYWORDS: vacancy; iron; hydrogen; embrittlement.

INTRODUCTION
Iron embrittlement can be produced by very small amounts of hydrogen. Hydrogen-metal interactions have been shown to strongly control the mechanisms of hydrogen embrittlement and stress corrosion cracking of numerous metals and alloys [1-4]. Engineers have intent to solve technological problems such as protecting structure from hydrogen embrittlement [5-9], transporting of liquid hydrocarbons in the presence of hydrogen at high temperatures [10], storing hydrogen fuel at high densities without the danger of high pressures [11-13], and designing nuclear reactors [14]. However there is not a complete understanding for the hydrogen embrittlement mechanism [15].
Vacancy, an important defect widely present in materials, has strong interactions with other defects such as impurity. These interactions greatly affect the mechanical properties of the material. Hydrogen in bulk materials has been extensively studied by scientists and technologists [16-19]. However, the behaviour of hydrogen in a metal in the presence of other impurities has not been studied at a fundamental level.
Vacancy contributions to hydrogen embrittlement and hydrogen-induced degradation of mechanical properties have been interesting issues especially in steels [20].
Juan and Hoffman investigated the hydrogen on the Fe (110) surface and near the bulk bcc Fe vacancies [21]. The changes in the electronic structure of bcc Fe upon the introduction of H at a vacancy were addressed, and a comparison drawn with H adsorption at the Fe (110) surface. H in bulk Fe with vacancies prefers a tetrahedral site shifted toward the vacancy. The vacancies act as a strong trap for H. The Fe atom are initially more strongly bonded to each other as a consequence of vacancy formation; their Fe-Fe bond strength is then diminished as the new Fe-H bond is formed.
The hydrogen induced superabundant vacancies and the diffusion enhancement in fcc metals was studied by Fukai et al. Lattice contractions caused by the formation of extremely high concentrations of vacancies were observed in the fcc phases of Mn-H, Fe-H, Co-H, Ni-H and Pd-H systems at high temperatures (\( \leq 900 \) °C) and high \( \text{H}_2 \) pressures (\( \leq 5 \) GPa). From the observed lattice contraction process and concomitant diffusion enhancement, it is concluded that most vacancy-hydrogen clusters are introduced by diffusion from the surface but some of them are created instantly at internal sources [22].

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Tateyama et al. investigated the stability and binding properties of hydrogen-vacancy (VH_n) complexes in α-Fe by means of ab initio calculations based on the density functional theory (DFT) [23].

In a previous works, our group studied the Fe-H interaction [24] and the electronic structure and bonding of an H-H pair [25] in the vicinity of a bcc Fe bulk vacancy. Fe atoms surrounding the vacancy weaken their bond when hydrogen is present. This is due to the formation of H-Fe bonds. Hydrogen influences only its nearest Fe atoms. The H-H interaction was also analysed. For certain distances an H-H association is formed.

The interactions of hydrogen with lattice imperfections are important and often dominant in determining the influence of this impurity on the properties of solids. Nevertheless, in general, these interactions are far less understood at a fundamental level than the behaviour of hydrogen in perfect lattices. Experimental studies in iron are very difficult to perform due to the low solubility of H [26]. In this context, computational approach would be a suitable tool to address the problem. In recent years the increased computing power and progress in developing computational methods has made possible for researches to study materials at an atomistic level and establish a connection between models with actual material behaviour.

In this paper we use the atom superposition and electron delocalisation molecular orbital (ASED-MO) method to study the location of H in the region vacancy and the concept of density of states (DOS) and the crystal orbital overlap population (COOP) curves to analyse the Fe-H and H-Vacancy interactions.

**COMPUTATIONAL METHOD**

Our calculations were performed using the ASED-MO method [27-30]. The modification of the extended Hückel Molecular Orbital method (EHMO) was implemented with the YAeHMOP program [31]. Double zeta expansions of metal d orbitals were employed. The parameters are listed in Table 1.

The ASED-MO method is a semi-empirical method, which makes a reasonable prediction of molecular and electronic structure. The EHMO method in its original form is not able to optimise geometries correctly as it lacks repulsive electrostatic interactions. This deficiency can be overcome by introducing a two-body electrostatic correction term [32].

The ASED theory is based on a physical model of molecular and solid electronic charge density distribution functions [30-33].

The adiabatic total energy values were computed as the difference between the electronic energy (E) of the system when the impurity atom/fragment is at finite distance within the bulk and the same energy when that atom/fragment is far away from the solid surface. There are many types of energies concerning electronic structure calculations.

The “sequential hydrogen absorption energy” can be expressed as:

\[
\Delta E_{\text{abs,total}} = E(Fe_m H_n) - E(Fe_m H_{n-1}) - E(H) + E_{\text{repulsion}}
\]

where \(m\) is the size of the cluster and \(n\) is the number of hydrogens.

The stability of the agglomeration of hydrogen in Fe, that is the energy difference between the agglomeration of \(n\) hydrogen's and \(n\) single hydrogen atoms in Fe vacancies was also computed as:

\[
\Delta E_{\text{aggl,total}} = E(Fe_m H_n) - E(Fe_m) - n[E(Fe_m H_1) - E(Fe_m)] + E_{\text{repulsion}}
\]

The repulsive energy was computed taking into account all atom-atom interactions.

Although the ASED-MO method is quite approximate, the analysis of orbital interactions by this technique seems to be reasonably reliable. Our calculation method does not take into account exchange interaction and our results must be interpreted in their relative sense. The strength of ASED is in fact its transparency, not accuracy and the main objective of this work is to provide a qualitative picture of four-H atoms interacting within the Fe matrix.

To understand the Fe-Fe and Fe-H interactions we used the concept of density of states (DOS) and crystal orbital overlap population (COOP) curves. The DOS curve is a plot of the number of orbitals per unit volume per unit energy. The COOP curve is a plot of the overlap population weighted DOS vs. energy. The integration of the COOP curve up to the Fermi level \((E_f)\) gives the total overlap population of the bond specified and it is a measure of the bond strength.

**THE Fe-VACANCY CLUSTER MODEL**
\( \alpha \)-Iron has a bcc structure with a lattice parameter \( a \), of 2.861 Å and nearest neighbour distance of 2.470 Å [34].

### Table 1. Parameters for the ASED-MO calculations

<table>
<thead>
<tr>
<th>Atom</th>
<th>Orbital</th>
<th>Ionization potential (eV)</th>
<th>Slater exponent (au(^{-1}))</th>
<th>Linear coefficient</th>
<th>Electronegativity (Pauling)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1s</td>
<td>13.6</td>
<td>1.00</td>
<td></td>
<td>2.1</td>
</tr>
<tr>
<td>Fe</td>
<td>3d</td>
<td>9.00</td>
<td>5.35</td>
<td>0.5366</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>4s</td>
<td>7.87</td>
<td>1.70</td>
<td>0.6678</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4p</td>
<td>4.10</td>
<td></td>
<td>1.40</td>
<td></td>
</tr>
</tbody>
</table>

The cluster used to simulate solid \( \alpha \)-Fe has 86 atoms of Fe, distributed in seven layers ((110) planes) with a vacancy in the fourth layer, which it is set exactly at the centre of the cluster. The thickness of this slab is enough to approximate the electronic structure of 3D bulk Fe in the innermost layer.

The bcc lattice has two interstitial sites commonly called "tetrahedral" and "octahedral". We have computed the adiabatic to the energy of the system absorbing up to four hydrogen atoms in the Fe vacancy. The hydrogen's location is shown in Fig. 1. We computed the minimum energy position for the hydrogen atoms covering all the (110) plane. The plane contains the metal vacancy. After determining the most stable position for the H atoms in the zone near the vacancy, we analysed the H agglomeration and the Fe\(_n\)-H\(_n\) bond (Fe nearest neighbour to the H atom, \( n \) is the number of H) and the Fe\(_n\)-Fe\(_nn\) (Fe\(_m\) nearest neighbour to the Fe\(_n\) atom).

**RESULTS AND DISCUSSION**

Under a sequential absorption scheme located four hydrogens in the monovacancy region. The positions of lower energy result to be those near to tetrahedral interstitials.

The energy associated at each formed subsystem is presented in Table 2. The sequential absorption is possible. For such absorption the total energy difference is negative. The minimum Fe-H distances lay between 1.61 Å - 1.68 Å of its first neighbour Fe (see Table 3). Juan and Hoffmann found the Fe-H minimum distances of 1.64 Å and 1.75 Å respectively [21].

Let us discuss the stability of the agglomeration of hydrogen in Fe. The computed energy difference between the agglomeration of hydrogen and \( n \) single hydrogen atoms is presented in Table 2. It can be seen that VH\(_2\)
and VH₃ complexes are energetically stable. For n>3 the hydrogen prefer to be alone instead of agglomerating. We must emphasise that we are dealing with a monovacancy model, in a more realistic situation there would be additional vacancies that act as hydrogen traps. In this case, if enough vacancies were available, the H would have tendency to be located in another vacancy instead of crowding round. Fig. 2 shows the energy contour lines corresponding to the agglomeration energy for the Vacancy-H₂ complex. Also, the enhancement of vacancy formation by hydrogen trapping has been suggested by Fukai et al [35,36].

Table 2. Sequential hydrogen absorption energy (ΔE_{Abs}), agglomeration energy (ΔE_{Aggl}) and distances from Hᵣ to the tetrahedral and the octahedral sites near the vacancy.

<table>
<thead>
<tr>
<th>Distance (Å)</th>
<th>Energy (eV)</th>
<th>tetrahedral site</th>
<th>octahedral site</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₁</td>
<td>0.238</td>
<td>0.590</td>
<td>-6.152</td>
</tr>
<tr>
<td>H₉</td>
<td>0.213</td>
<td>0.580</td>
<td>-6.200</td>
</tr>
<tr>
<td>H₃</td>
<td>0.317</td>
<td>0.442</td>
<td>-6.209</td>
</tr>
<tr>
<td>H₄</td>
<td>0.565</td>
<td>1.011</td>
<td>-5.608</td>
</tr>
</tbody>
</table>

Tateyama et al. investigated the stability and binding properties of hydrogen-vacancy (VHᵣ) complexes in α-Fe [23]. They demonstrated that VH₂ is the major complex in α-Fe at ambient condition of hydrogen chemical potential. VH₂ formation energy is lower than the monovacancy formation without hydrogen by about 0.5 eV at ambient conditions. According to Boltzmann statistics at 300 K, this energy reduction leads to 10⁷ times increase of vacancy density by trapping two hydrogen atoms. Thus, enhancement of vacancy formation in presence of hydrogen is still very remarkable. The DOS of VH₂ indicates that a new state appears below the 4s band of the pure α-Fe. Partial electron density of these new states indicates Fe 3d - H 1s hybridisation. This hybridisation is responsible for the large H trapping energies for VH₂ (and VH) formation through the termination of broken Fe bonds. The new state has a bonding character mainly consisting of H 1s orbital and is doubly occupied by electrons. This indicates electron transfer to the region around the H atoms from the neighbour Fe. The resulting negatively charged H atoms repel each other. The repulsive interaction seems to become more dominant with increase in the number of trapped hydrogen atoms. This can explain the abrupt decrease of H trapping energies for VHᵣ (n ≥ 3). Consequently, the competition between hybridisation and Coulombic repulsion makes VH₂ the major complex at ambient condition. This view is supported by charge of H atoms positions depending on the number of H atoms in the vacancy. They found that the distances between H atoms and the corresponding octahedral sites in each VHᵣ do not alter between VH and VH₂, suggesting that the hybridisation effect prevails in these complexes. At n ≥ 3, the distance gradually decreases with n. This agrees with the explanation that the repulsion effect becomes effective in those complexes.

Our results show that the Fe-H interaction mainly involves Fe 3d and Fe 4s atomic orbitals. The contribution of p orbitals is much less important. There is an electron transfer to the H atoms from its nearest Fe neighbours. The charge and the electron densities are summarised in Table 3.

In our work, we observed that VH₂ and VH₃ are the major complexes in α-Fe. They have the lower energetic value than the other complexes (see Table 2). We also found that VH₁ and VH₂ are the complexes more neighbouring to the corresponding tetrahedral site (both positioned at 0.2 Å from it, see Table 2). This affirmation is not true in the case of the octahedral site. VH₃ is the complexes most neighbouring to it (0.4 Å).

Tateyama et al. analysed possible implications of the hydrogen-enhanced vacancy activities in the H embrittlement phenomena. The anisotropic vacancy clusterization induced by hydrogen can be directly linked with anisotropy observed in several fracture experiments. The {110} clusters are the first reasonable theoretical evidence of enhancement of fracture along these slip planes of bcc metals experimentally observed. In our work we can observe that the hydrogen's affect the states of its surrounding Fe atoms causing a rearrangement of their electronic densities. As a consequence, the OP between the iron atoms near the hydrogens decreases (see Table 3). These metal-metal bonds are then weakened. The Fe-H bonds are formed and the bonding is achieved at expense of the Fe-Fe nearest neighbours. Our results show how the decohesion of Fe-Fe bonds can contribute to the embrittlement process.

CONCLUSIONS
The interaction between four-hydrogen atoms and a $\alpha$-Fe structure having a vacancy has been studied. The most stable positions for the sequential H absorption atoms in the region near the vacancy were found. The

![Graph showing contour lines for Fe-H system](image)

**Figure 2.** Contour lines corresponding to the agglomeration energy (eV) for the Fe-H$_2$ system on the (110) plane, which contains the vacancy (V). The tetrahedral site positions are indicated (T).

**Table 3.** Atomic orbital occupations and net charges for the H$_n$ and their neighbouring Fe atoms. H-Fe and Fe-Fe distances and the corresponding overlap population values for these atoms.

<table>
<thead>
<tr>
<th>Atom</th>
<th>s</th>
<th>p</th>
<th>d</th>
<th>Charge</th>
<th>Bond</th>
<th>Distance (Å)</th>
<th>OP</th>
</tr>
</thead>
<tbody>
<tr>
<td>HII</td>
<td>1.127</td>
<td></td>
<td></td>
<td>-0.127</td>
<td>HII-FeII</td>
<td>1.675</td>
<td>0.193</td>
</tr>
<tr>
<td>HI</td>
<td>1.074</td>
<td></td>
<td></td>
<td>-0.074</td>
<td>HI-FeIII</td>
<td>1.612</td>
<td>0.262</td>
</tr>
<tr>
<td>HI  IV</td>
<td>1.152</td>
<td></td>
<td></td>
<td>-0.152</td>
<td>HI-FeIV</td>
<td>1.639</td>
<td>0.327</td>
</tr>
</tbody>
</table>

H atoms were found near to the tetrahedral sites neighbouring the vacancy. The stability of agglomeration of hydrogen in Fe was also studied. VH$_2$ and VH$_3$ are the major complexes in $\alpha$-Fe more stabilised than VH$_1$, in such a way that enough vacancies are present (or formed) the agglomeration for $n>3$ would be unfavourable. The Fe-H is formed and their binding is achieved at expense of their Fe-Fe first neighbours. The interactions mainly involve Fe 3d and Fe 4s atomic orbitals. The detrimental effect of H atoms on the Fe-Fe bonds can be associated with H embrittlement by decohesion mechanism $\alpha$-Fe.

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References: