A review of the diffusion of hydrogen into and through γ-iron by density functional theory

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**A b s t r a c t**

The study of hydrogen embrittlement is very important for increasing the strength of steel and avoid the defect. The investigation of density functional theory (DFT) was applied through the (100), (110) and (111) surface for ϒ-iron, it was found that the hydrogen atoms absorb on the (100),(110) and (1110 surface energy were 4.06ev,3.92ev and 4.05ev respectively. For the bulk-like diffusion for the (100), (110) and (111) were 0.6ev,0.5ev and 0.7ev, respectively[1]. Based on the DFT calculation and experiment results, the surface of (111) is good for the hydrogen resistance, and (110) surface should avoid touching the hydrogen during the steel processing. A further experiment could be performed by using the ternary organic alloy to analyze the microstructure changing due to the hydrogen diffused into the steel as an impurity.

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**1.introduction**

The hydrogen is a really important factor that will influence the mechanical property of the steel, the hydrogen entered the steel through diffusion and resulting of increase the brittleness of the material, which should be avoided in the steel manufacturing, the process that hydrogen diffused into the steel either through the surface or bulk was called Hydrogen embrittlement (HE). There are two principal mechanisms that caused HE phenomenon, the HELP (Hydrogen Enhanced Localized Plasticity) and HEDE (Hydrogen Enhanced Decohesion) mechanisms [1]. In HELP, hydrogen lowers the activation energy for dislocation motion and increase the formation of highly-deformed localized regions in the microstructure, which allows the rapid initiation and propagation of a crack, it enhanced local plasticity but lead to brittle behavior for the entire material [2]. In HEDE, the hydrogen reduced the interatomic cohesive forces and makes atomic structure planes divided along grain boundaries. The hydrogen that dissolved into the material reduced the cohesive strength of the lattice and interfaces between atoms which kind of damage mechanism of the steel[3].

Density functional theory (DFT) is a new tool now that could investigate the structural, magnetic and electronic properties of molecules, materials property, and defects based on solving a series given model and functions. To use the DFT method simulate the hydrogen diffusion through the surface or bulk, it could tell which surface is easy for hydrogen to diffuse into and which is harder [1]. In this paper, the author simulated and modeled, the absorption of hydrogen through surfaces and the surface to the sub-surface, which is really important for understanding the hydrogen embrittle process.

**2. DFT computational method**

The Vienna ab initio simulation package (VASP) was used in DFT implement [1]. The electronic interactions were described by a plane-wave basis set and 3D periodic boundary conditions. The exchange and correlation effects were included by using generalized-gradient approximation (GGA), via the Perdew–Burke–Erzenhof (PBE) functional [1]. The interaction between the ionic core and valence electrons was described by the projector augmented-wave (PAW) approximation [1].

**3. modeling the material**

Several of the mesh grids were used to sample different hydrogen positions on the slab for each unit cell, the large numbers of the points meshed and tight in the grid of the slab, each of the points were used to describe the [1]. Then a single hydrogen atom was placed on the slab and the energy of each point was calculated by equation 1.

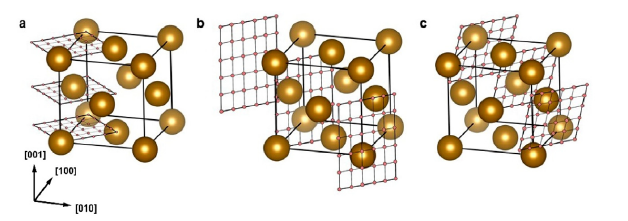


Figure 1 the mesh and grid to describe the potential energy of the surface

𝐸 = 𝐸slab+H − (𝐸slab + 𝐸H ) equation 1

where E slab + H is the energy of the slab with Hydrogen incorporated, E slab is the energy of the Hydrogen free slab and EH is the ground state energy of a single free H atom in a 10 ×10 ×10 Å3 unit cell. The energies were then calculated relative to the global minimum of the entire slab, which was set to zero energy [1]

**4.Extra in-situ testing through Bridgeman furnace**

The experiment that analyzing the hydrogen diffused into the steel during the manufacturing process could be designed, the interface structure between the liquid and solid-state of steel during the hydrogen diffusion could be observed and the function of how the hydrogen makes the steel brittle could be explained through the microstructure change.

For simulating the microstructure of metal-metal alloys like steel, or the microstructure change due to interstitial defect like hydrogen diffused into the steel is very hard since it is the material that lack of the transparency. Some organics that posted by Jackson-hunt [4] that could freeze like metals, there interface between the solid and liquid could form the lamellae or dendrites structure which same as the metals[5,6].

The Succinonitrile-camphor (SCN-CA) was the best choice to analyze the microstructure of metal-metal alloy like steel which was done by Takayuki in 1969[5] and analyzed by Huang [6]. To analyzing the interstitial defect like hydrogen into the steel by using the organic materials, the hydrogen could be pumped into the specimen (capillary that contains the SCN-CA alloy) which formed Succinonitrile-Hydrogen-camphor (SCN-H-CA) ternary system, since the hydrogen is in gas condition and will not resolute with solid, it will not influence the concentration of the SCN and CA for forming the eutectic reaction. This specimen could be observed by the in-situ method through the Bridgeman furnace[7], and it would be compared with the SCN-CA alloy about the microstructure difference. Since there none of the researchers has tried this method or build this ternary alloy system before, none of the results have been received or reported. But this method could be a way to observe microstructure changing due to the gas as the impurity diffused into an alloy, and it may explain how the atomic level varies response to the microstructure changing.

**5. Result**

5.1 the diffusion through the surface

For the calculation result of hydrogen adsorption on the surface (adhesion of atoms, ions or molecules from a gas, liquid or dissolved solid poured surface) [1]. For the (100) surface, the H atom prefers to stay at the fourfold 4f site at 4.06 eV. For the (110) surface, it stays at the short-bridge (sb) site, which is the short-site at 3.92eV, On the (111) surface, the H atom prefers to adsorb on the three-fold (3f) site and with the adsorption energy of 4.05 eV. However, the absorption energies are very close to each other between all three surfaces, it means hydrogen is almost equally to be adsorbed no matter which surface is exposed.

5.2 for the diffusion at sub-surface

The process that hydrogen diffusion from the surface to the subsurface was modeled by investigating the potential energy of the surface of the whole slab and calculate the energy barrier that needs to be overcome by hydrogen atom to penetrate the 𝛾-Fe slab and goes into the bulk [1]. They were ∼1.4 eV for the (100) surface, ∼1.2 eV for the (110) surface and ∼1.7 eV for the (111) surface [1]. The energy barrier for diffusion is highest on (111) surface based on the simulation which means the surface was most hard for penetration diffusion. And the (110) surface got the lowest energy barrier which means the hydrogen prefers to penetrate the surface and goes into the bulk through here.

For comparing the experiment values and DFT values, the total activation energy and the bulk-like activation energy were calculated by the experiment method. They were ∼1.4 eV for the (100) surface, ∼1.2 eV for the (110) surface and ∼1.7 eV for the (111) surface for the total actively energy [1]. For the bulk energy , ∼0.6ev for (100), 0.5ev for (110) and 0.7 eV for (111) surfaces [1]. These results indicated that it will require a large amount of energy to stick into the hydrogen on each given surface and less energy required to bulk diffusion. And it tells the same thing as the simulation that (111) surface has the highest energy barrier and (110) is the lowest which makes a good agreement between the DFT data and experimental results.

5.3 for the in-situ observation

Since there haven’t got any reports of pumping the hydrogen into the SCN-CA to make the ternary organic system, the change of the microstructure due to the hydrogen diffusion was unknown.

**6. conclusion and discussion**

In this paper, the density functional theory was applied to investigate hydrogen diffusion through the three major surfaces in 𝛾-Fe which were (100), (110) and (111), it helps to understand the process of hydrogen embrittlement in austenitic steels. The method of mesh grid which build a slab at each corner on the unit cell. The potential energy that hydrogen absorbed by the slab was calculated, they were 4.06 eV for the (100) surface, 3.92eV for the (110), and 4.05 eV (111) surface [1]. Based on the calculation result, the hydrogen would bind most tightly on (100) and (111) surface [1]. For the energy barrier of the hydrogen diffusion to the sub-surface and going to the deep bulk, they were ∼0.6 eV at (100) surface [1], ∼0.5 eV for the (110) surface and ∼0.7 eV for the (111) surface [1]. Based on the calculation for the energy barrier, the hydrogen was most hard to diffuse at (111) surface which means the steel will avoid the hydrogen embrittlement if the (111) surface is exposed in the manufacturing process. A further experiment could be performed by using the ternary organic alloy to analyze the microstructure changing due to the hydrogen diffused into the steel as an impurity, it may help to relate the knowledge about the microstructure changes with the changing of atomic scale.

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