Vacancy trapping mechanism of multiple hydrogen/helium atoms in fcc-Fe: A first-principles study

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Abstract. Using first-principles calculations, we studied the dissolution and diffusion behaviors of H/He atom in perfect fcc-Fe and vacancy capture multiple H/He atoms mechanism in fcc-Fe. The calculation results show that H/He atom prefers to occupy octahedral site, and they diffused along octahedral site-tetrahedral site-octahedral site in perfect fcc-Fe. Inside vacancy, H atom prefers to occupy octahedral site, while He atom prefers to occupy the vacancy center. The exist of H/He atom would decrease the vacancy formation energy. According to capture energies, a vacancy can trap five H atoms in fcc-Fe, but more He atoms can be accommodated even when the number of He atoms reaches sixteen. Therefore, the result provides an important theoretical basis to research the mechanism of hydrogen and helium embrittlement.

1. Introduction
Face center cubic(fcc)-Fe has long been used as a fusion reactor material due to its high strength. In a fusion reactor environment, both helium and hydrogen can be generated by irradiation damage in the fcc-Fe. These H/He atoms significantly affect the microstructure evolution of irradiated materials and reduce the mechanical properties[1-2]. Therefore, understanding vacancy capture multiple H/He atoms mechanism in material is an important topic to study the hydrogen/helium embrittlement mechanism.

It was observed that multiple H/He atoms can be trapped in a monovacancy in experiments [3-4]. Although the experimental studies on the H/He effects in materials[5-7], it is hard to acquire the information about vacancy in metals and the energetics of H/He atom directly from experiments. Previous density functional theory (DFT) calculations have revealed the H/He atom behaviors in fcc-Fe. Sanchez[8] and Saravia[9] found that H atom tends to stay at octahedral site in perfect bcc-Fe, while H atom prefers to occupy octahedral site near the vacancy. He atom prefers to occupy the vacancy center and H likes to occupy a close octahedral site near the vacancy in body center cubic(bcc)-Fe[10]. Tateyama[11] predicted that multiple H/He atoms can be captured in a single vacancy space in bcc-Fe. Nonetheless, there is not too much research about vacancy trapping mechanism in fcc-Fe.

In this paper, using DFT calculations we researched the dissolution and diffusion behaviors of H/He atom, and understanding the vacancy capture multiple H/He atoms mechanism in fcc-Fe. Finally, we discuss the influence of vacancy defect on H and He behavior in fcc-Fe.
2. Computational methods and models

First-principles calculations are performed by Vienna Ab initio Simulation Package (VASP) [12-13]. We selected the generalized gradient approximation (GGA) functional for the exchange-correlation interaction and the perdue-burke-ernzerhof (PBE) potentials for the ion–electron interaction[14]. The calculations were performed using $2 \times 2 \times 2$ supercells, and the cutoff energy was fixed at 450 eV. The Brillouin zones were generated by the Monkhorst–Pack scheme[15], and the k points is $3 \times 3 \times 3$. The lattice constant of the bulk fcc-Fe was computed to be 0.349 nm, which is consistent with both previous DFT result(0.345 nm) [16] and the experimental value(0.364 nm) [17]. The vacancy formation energy is formulated as:

$$E_V = E_{Fe-V} - \frac{N_{Fe}}{N} E_{Fe}$$  \hspace{1cm} (1)

Where $E_{Fe-V}$ is the total energy of the supercell with a vacancy, and $N$ is the number of Fe atoms in a perfect crystal supercell.

The formation energy of an interstitial H/He atom near a vacancy is:

$$E_{int-V} = E_{Fe-int-V} - E_{Fe-V} - E_{int}$$  \hspace{1cm} (2)

Where $E_{Fe-int-V}$ is the total energy of the supercell with a vacancy and an interstitial H/He atom near the vacancy, the $E_{int}$ is the energy of an interstitial H/He atom.

To research the vacancy capture multiple H/He atoms mechanism, we calculated the capture energy for different number of H/He atoms. For the first H/He atom ($m = 1$) and multiple H/He atoms ($m > 1$) trapped in a single vacancy, the trapping energy can be calculated by[10]:

$$E_{trap} (1) = E_{int-V} - E_{int, V}$$

$$E_{trap} (m) = E_{int-V} - E_{int, V} - \left[ E_{int, V} - E_V \right]$$  \hspace{1cm} (4)

Here $E_{int, V}$ or $E_{int, (m-1), V}$ is the energy of the supercell with a vacancy, $m$ or $m-1$ H/He atoms; $E_{int, V}$ is the energy of the supercell with a vacancy and a octahedral H/He atom far away from the vacancy.

3. Results and discussion

3.1. Interstitial H/He in perfect fcc-Fe

To research the influence of vacancy defect on H and He behavior in fcc-Fe. we must studied which positions an individual H or He atom prefers to stay in perfect fcc-Fe. Octahedral site(O-site) and tetrahedral site(T-site) are typical interstitial sites in fcc lattice. We put a single H/He atom into the O-site and T-site and calculate the formation energy by the formula(1) (2). Table 1 shows the computed formation energy of H/He atom located in different sites.

|       | $E_O$ | $E_T$ | $E_{V-O}$ | $E_{V-T}$ | $E_{Vsub}$ | $E_V$ |
|-------|-------|-------|-----------|-----------|-----------|-------|
| H     | -2.02 | -1.86 | -3.34     | -2.88     | 0.11      | 1.25  |
| He    | 5.29  | 5.44  | 2.53      | 4.48      | 2.48      |       |

In fcc-Fe, the octahedral and tetrahedral site radii are 0.0457 and 0.0248 nm[18]. According to the space of the two sites, it can be inferred that H/He atom are more like to occupy the O-site. The formation energy of H atom in the T-site and O-site is -1.86 and -2.02 eV, and the formation energy of He atom in the T-site and O-site is 5.44 and 5.29 eV. It means that both H and He atom prefer to stay O-site in perfect fcc-Fe. The surrounding lattice expands slightly when H or He atom are in the T-site, indicating that the tetrahedral space is not enough accommodate H or He atom. The lattice has enough
space to hold more atoms because of the lattice distortion. Because O-site has larger volume, the lattice distortion did not occur. Therefore, H and He atom prefer to occupy O-site in perfect fcc-Fe.

3.2. H/He diffusion in perfect fcc-Fe

In order to study the diffusion mechanism of He/H atom in fcc-Fe, the climbing image nudged elastic band (CI-NEB) method is used to calculate the minimum energy path (MEP). Because H or He atom can occupy T-site or O-site, there are two possible diffusion paths in a perfect fcc-Fe: (1) octahedral site-octahedral site, (2) octahedral site-tetrahedral site-octahedral site. The distance between a O-site and T-site is 0.15 nm and two O-site is 0.25 nm. The diffusion energy barrier of H and He atom in fcc-Fe is shown in figure 1. The low diffusion energy barrier of He atom is 0.35 eV, and He atom diffuses from an O-site to its nearest O-site. This low diffusion barrier means that He atoms migrate rapidly in fcc-Fe at normal temperatures. It is also consistent with the previous results in bcc-Fe obtained by Fu[19], but the diffusion barrier is lower and the migration is faster in bcc-Fe. That is one of the reasons why fcc-Fe has better anti-hydrogen and helium embrittlement. For H atom, the diffusion barrier is 0.60 eV. In conclusion, the energy consumption which H or He atom diffuse between two O-site in fcc-Fe is relatively low. It means that the vacancy defect could captured H/He atom. It is also found that the migration of H or He atom between two O-site in fcc-Fe is not linear, but diffuse along octahedral site-tetrahedral site-octahedral site. So the diffusion path(2) is regarded as a part of diffusion path(1).

Figure 1. Diffusion energy barriers of H atom(a) and He atom(b) in fcc-Fe.

3.3. Interstitial H/He in vacancy fcc-Fe

The H or He atoms may occupy the following three positions: tetrahedral site, octahedral site and substitution site. The formation energies of three possible interstitial positions are shown in table 1. The O-site(-3.34 eV) for an interstitial H atom near a vacancy is energetically higher than T-site(-2.28 eV) near a vacancy. The formation energy of H atom near a vacancy is lower than which in perfect Fe, it means that the interstitial H atom promotes the formation of vacancy defect. This is similar to the study for He atom near a vacancy. The formation energy of He atom occupying O-site(2.53 eV) and T-site(4.48 eV) near a vacancy was lower than that of O-site(5.29 eV) and T-site(5.44 eV) in perfect fcc-Fe. In conclusion, the existence of an interstitial H or He atom contributes to the formation of vacancy defect in fcc-Fe and the influence is particularly evident for He. Because of the vacancy defect, the calculation results indicate that He atom prefers to occupy the vacancy center as its lowest energy (2.48 eV). It is also found from the relaxed structure, H atom neither occupies the center of vacancy nor O-site, but likes to occupy the middle position between O-site and vacancy. It is near the center of O-site and moves towards the vacancy center at 0.05 nm. The results agrees with experiments[17] that H atom is captured by a vacancy that moved 0.04 nm from the O-site to the center of the vacancy. Different from H, He atom which stay at both T-site and O-site near a vacancy is metastable, and He atom would enter the center of vacancy.
3.4. Interstitial H/He trapping in monovacancy

To investigate the vacancy capture multiple H/He atoms mechanism, we put multiple H/He atoms in the vacancy one by one to find out where H/He atoms prefer to occupy. For H atoms, they like to occupy the O-site near a monovacancy. H atoms and the vacancy are on the same lattice plane when the number of H atoms reached four, and all the O-site near the vacancy can be occupied by atoms when the number are six. Within the vacancy, He atoms tends to occupy the T-sites when the number of He atoms are less than seven and subsequently stay at the O-sites when the number of He atoms are more than seven. Figure 2 shows the capture energies of H/He atoms near a vacancy in fcc-Fe. The capture energies of H atoms shown in figure 2(a), we can see that it is more advantageous to capture five H atoms in a single vacancy space than to scatter these H atoms separately at isolated O-site. The capture energy of the sixth H atom is zero, it means that the stability of the sixth H atom is similar to that of the independent H atom in the O-site far from the vacancy. The capture energy is positive(0.67 eV) when the number of H atoms is seven. Meanwhile, the distance between H atom and H atom is 0.21-0.25 nm, which is longer than the bond between H\textsubscript{2} molecules by 0.074 nm. This also proves that H atoms do not spontaneously form H\textsubscript{2} molecules in fcc-Fe. The trapping energies versus the number of He atoms in vacancy fcc-Fe are illustrated in figure 2(b). The trapping energy increases with He incorporation and fluctuates from -3.82 to -1.20 eV. As a result, a monovacancy in fcc-Fe can trap five H atoms, but more He atoms can be accommodated even when the number of He atoms reaches sixteen. We also study the distances of atomic pairs in the vacancy to explain this phenomenon. The distance between He–He pairs trapped in a monovacancy is 0.15-0.17 nm and the lattice expansion is large, while the distance between H–H pairs is 0.20-0.26 nm and the lattice expansion is small. Therefore, we believe that the the larger vacancy space and the shorter He–He distances are the reasons why a single vacancy contains more atoms in fcc-Fe. Therefore, the trapping mechanism explains hydrogen/helium embrittlement inside vacancy defect in fcc-Fe.

![Figure 2](image_url)

Figure 2. The capture energies per atom as function of the numbers of H/He atoms in vacancy fcc-Fe.

4. Conclusions

First-principles calculations have been used to research the diffusion and dissolution behaviors of H/He atom and trapping energies of multiple H/He atoms inside vacancy space in fcc-Fe. H/He atom likes to occupy O-site in perfect fcc-Fe. They diffused along octahedral site-tetrahedral site-octahedral site in perfect fcc-Fe. The exist of H/He atom would reduce the vacancy formation energy. This implies H/He atom promote the formation of vacancy defect. According to capture energies, a vacancy can trap five H atoms in fcc-Fe, but more He atoms can be accommodated even when the number of He atoms reaches sixteen. We believe that the larger vacancy space and the shorter He–He distances are the reasons why a single vacancy contains more atoms in fcc-Fe. Therefore, to investigate the interaction between vacancy and H/He atom in fcc-Fe provides an important theoretical basis to research the mechanism of hydrogen and helium embrittlement.
Acknowledgments
This paper was supported by National Natural Science Foundation of China(Grant No. 11474358). The calculations were performed on LvLiang Cloud Computing Center.

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