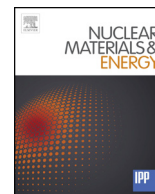




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Study on synergistic effects of H and He in α -Fe

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ABSTRACT

The synergistic effect of hydrogen and helium in α -Fe has been investigated using density functional theory calculation method. In perfect crystal of Fe, the presence of helium atom would decrease the dissolution energy of hydrogen atom near helium atom. This implies the existence of an attractive interaction between hydrogen and helium atoms. It is also revealed that the most stable places for both hydrogen and helium atoms are two tetrahedral sites (T-site) with a distance of 2.16 Å. Furthermore, a vacancy-helium complex (Va–He) would be an effective trapping site for hydrogen atom compared with mono-vacancy, a Va–He would be able to trap 8 hydrogen atoms.

1. Introduction

Ferritic steel has been used as a structural material for light water reactors [1] and also expected to be the first candidate material for fusion reactor component because of its corrosion and swelling resistance. In neutron irradiation environment, however, both hydrogen (H) and helium (He) can be generated in steels due to transmutation reactions. These gas atoms significantly influence microstructure evolution in irradiated materials and degrade the mechanical properties [2,3]. So far, the behaviors of H or He in α -Fe have been studied by both experimental and computational methods [4–17]. There are two different possible interstitial sites in α -Fe, one is tetrahedral site (T-site) and another is octahedral site (O-site). Previous studies showed that an individual H [9] or He [18] atom prefers to occupy the T-site in bulk α -Fe. And vacancy plays the role as a trapping site for both H and He in bulk α -Fe. Since H and He actually exist in irradiated steel at the same time, synergistic effect of H and He in α -Fe is a very important issue in order to understand microstructural evolution, especially at high irradiation doses. On the other hand, several studies of other transition metals, for instance in W [19,20] and Mo [21], have reported the synergistic interplay between H and He. H and He coexist in bulk at T-sites in W and Mo, respectively. And they have an attractive force between them. When monovacancy exists, He will occupy the center of vacancy, but H prefers to be the position near O-site. In this work, the synergistic effect of H and He in α -Fe has been studied using a density functional theory (DFT) calculation method.

2. Method

In this work, GPAW [22]: a real-space grid-based all-electron DFT code implemented in the projector augmented-wave formalism was used for calculations. The generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) was used for exchange–correlation [23]. K-points for sampling Brillouin zones and Grid space was set to $(3 \times 3 \times 3)$ [24] and 0.18 Å, respectively. With a bcc Fe cell with $(3 \times 3 \times 3)$, the lattice constant for bulk bcc Fe was calculated to be 2.84 Å. Both supercell size and atomic positions were relaxed to equilibrium, and energy minimization was continued until the forces on all atoms were converged to less than 5×10^{-2} eV/Å. Since the zero point energy (ZPE) of H has a significant effect on the dissolution energy of H [9,19], ZPE corrections were included in all calculation involving H atom. The ZPE of H was calculated by summing up the zero-point vibrational energies of H's normal modes. The ZPE of an H₂ molecule was calculated to be 0.28 eV. the ZPE of H in Fe with presence of H is about 0.22–0.23 eV, and the ZPE of H trapped in VaHe complex is about 0.18–0.22 eV.

3. Results and discussion

3.1. Coexistence of H and He in bcc Fe

In bcc Fe, T-site has been proved to be the most stable interstitial site for both H and He atom, compared with O-site [7,10]. Table 1 shows the calculated dissolution energy of single H and He in T-site and O-site, respectively. The calculated dissolution energy has good

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Table 1

The calculated dissolution energies (eV) of single H or He atom in Fe in comparison with the previous studies.

	H _{TIS}	H _{OIS}	He _{TIS}	He _{OIS}
Present work	0.19	0.23	4.47	4.68
[9]	0.23	0.26	–	–
[6]	–	–	4.49	4.68
[7]	0.20	0.45	4.91	5.11

agreement with previous studies [6,7,9]. It indicates that both H and He prefer to occupy T-sites since the dissolution energy at T-site is lower than that at O-site. In order to investigate the interaction between H and He in Fe, a single He and H was put at a T-site and a series of different interstitial site (including T-site and O-site), respectively. Then, each structure was relaxed. Results showed that He stayed in every case, while H did at a series of T-site as shown in Fig. 1(a). The dissolution energy (E_d) of H at different positions, as shown in Fig. 1(b), are calculated by

$$E_d(H) = E_{(Fe,H,He)} - E_{(Fe,He)} - E_H, \quad (1)$$

Where $E_{(Fe,H,He)}$ is the total energy of Fe cell with interstitial He and H atoms, and $E_{(Fe,He)}$ is the total energy of Fe cell with a single interstitial He atom. The third term E_H is one-half of the energy of a H_2 molecule.

In Fig. 1(b), the dot line represents the dissolution energy of single H in Fe without He, It can be found that in all cases except A the E_d of H in

Fe with He was lower than this value. It suggests that an attractive interaction exists between He and the closest H. The configuration D, which H and He are at two T-sites with the distance of 2.161 Å, is the most stable since it has the lowest H dissolution energy. It is notable that the most stable structure of H and He in Fe, W [19] and Mo [20] are different each other. This is probably due to the difference in lattice constant.

The E_d of single H with He changes as a function of H–He distance. The similar results were found in W [19]. The direct influence from He is the expansion in volume of the space near He, meaning that the T-sites near He would gain external volume. As a result, the charge density in these T-sites decreases. The charge densities of T-sites from A to F are shown in Fig. 2(a). The dot line represents the charge density of T-site in Fe without He. It can be seen that the closer to the He atom T-site is, the lower charge density it has. It is known that H in metal prefers to stay at place which has low charge density [25,26]. In another words, the decrease in charge density results in the decrease in E_d of H. It is the reason why the E_d of H in T-sites of F, E and D become lower and lower. Dissolution energy of H in T-sites of A, B and C doesn't continue decreasing, although they have a lower charge density. This would be due to a strong repulsive interaction between H and He, when H and He were too close to each other. Fig. 2(b) shows the binding energy of an H–He pair in vacuum. In this figure the negative value represents the repulsive interaction. It is clear that the repulsive interaction between H and He becomes quite strong when the H–He distance is shorter than 2.25 Å.

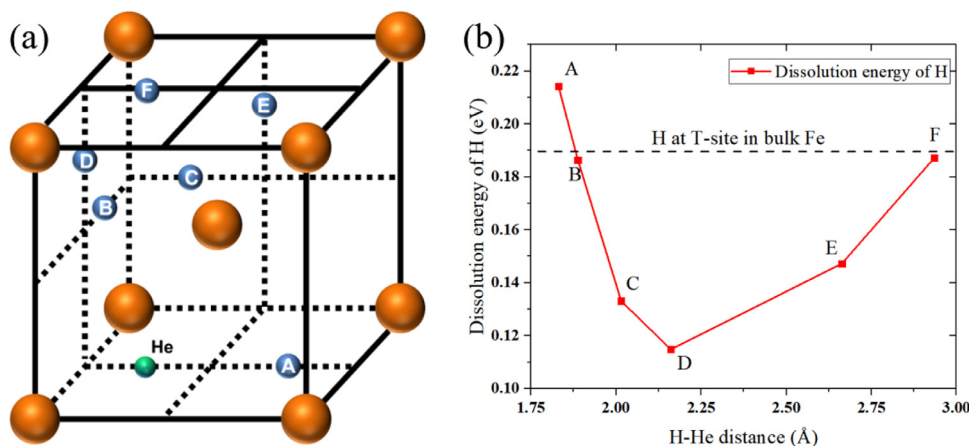


Fig. 1. (a) The configuration of H and He in Perfect Fe. (b) The dissolution energy (E_d) of H as a function of the distance between H and He.

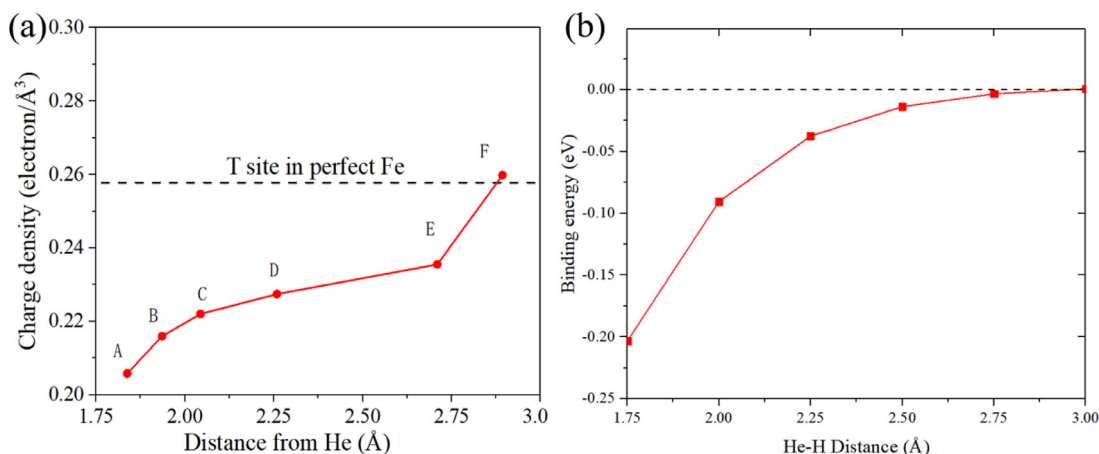


Fig. 2. (a) The charge density of different T sites. (b) The binding energy of an H–He pair in vacuum.

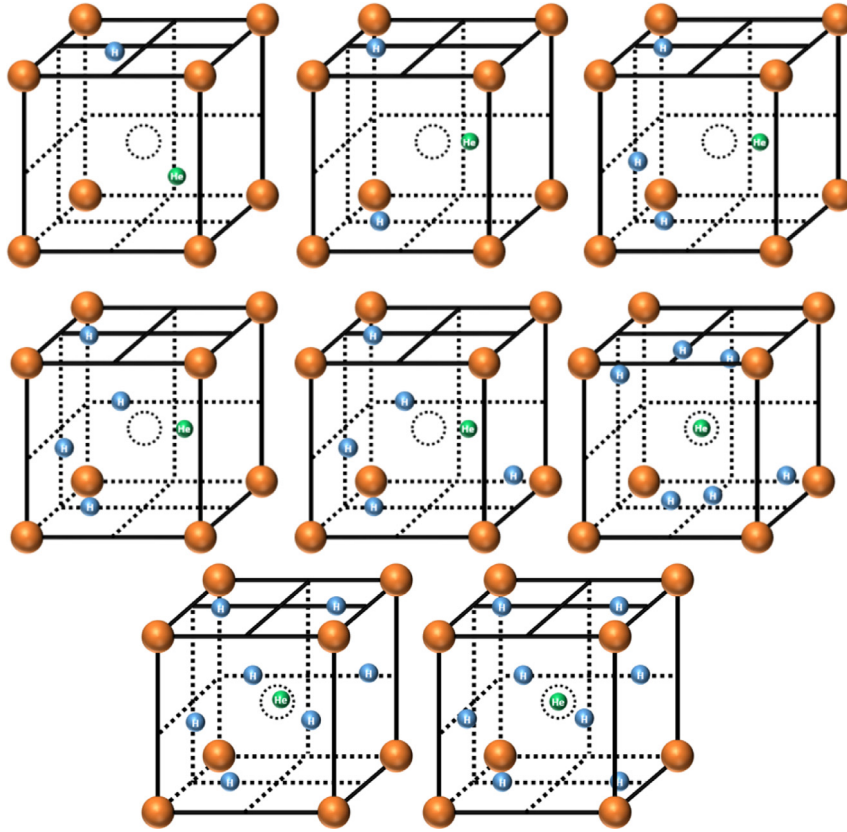


Fig. 3. Configuration of Va-He- H_n cluster in Fe. Yellow, blue and green balls represent Fe, H and He atoms respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.2. Coexistence of H and He with monovacancy in bcc Fe

Previous studies have demonstrated that vacancy is a kind of trapping site for both H and He in Fe [9,10,27]. With the presence of monovacancy, H prefers to stay at a position which is slightly offset from an O-site around vacancy [9], while He prefers to stay at just the center of vacancy [10]. In this study, the synergistic behavior of H and He with vacancy is studied. As shown in Fig. 4, H is stable at a near T-site position, while He is stable at an off-center position. The site preference of He would be different from that in W [19] and Mo [20]. In W and Mo, He would stay at the center of vacancy even though H stays close to He. The difference is mainly due to the strong repulsive interaction between H and He in Fe compared to that in W and Mo. The vacancy volume in Fe would be smaller than that in W and Mo, because the lattice constant of Fe (2.84 Å) is smaller compared with that of W (3.16 Å) and Mo (3.15 Å). The dissolution energy (E_d) of H and He in Vacancy-He (Va-He) complex was estimated to be -0.40 eV, which indicates that the dissolution of H in Va-He would be exothermic reaction. Therefore, H would be easily trapped by Va-He. In order to clarify the trapping of H by Va-He complex, a series of Va-He- H_n clusters in Fe was investigated. Several configurations were calculated for each, and the most stable system was presented in Fig. 3.

The E_d of H in the most stable Va-He- H_n clusters was calculated in two ways. The E_d of the Nth H atom solution in Va-He- H_{n-1} clusters to form Va-He- H_n is calculated by

$$E_{d(H)} = E_{(Fe,Va,He,Hn)} - E_{(Fe,Va,He,Hn-1)} - E_{H}, \quad (2)$$

Where $E_{(Fe,Va,He,Hn)}$ is the total energy of Fe with vacancy, He and n H atoms, and $E_{(Fe,Va,He,Hn-1)}$ is the total energy of perfect Fe with vacancy, He and $n - 1$ H atoms. And the average E_d of H in each cluster is calculated by

$$\bar{E}_{d(H)} = \frac{1}{n} [E_{(Fe,Va,He,Hn)} - E_{(Fe,Va,He)} - nE_H], \quad (3)$$

Where $E_{(Fe,Va,He)}$ is the total energy of Fe with vacancy, He but no H atoms.

As seen in Fig. 4, the average E_d of H increases with increasing the number of H atoms. This suggests that the bigger the cluster size is, the harder it forms. But the E_d of the Nth H strongly depends on the number of H. For example, the E_d of 3rd and 7th H is the local maximum, while

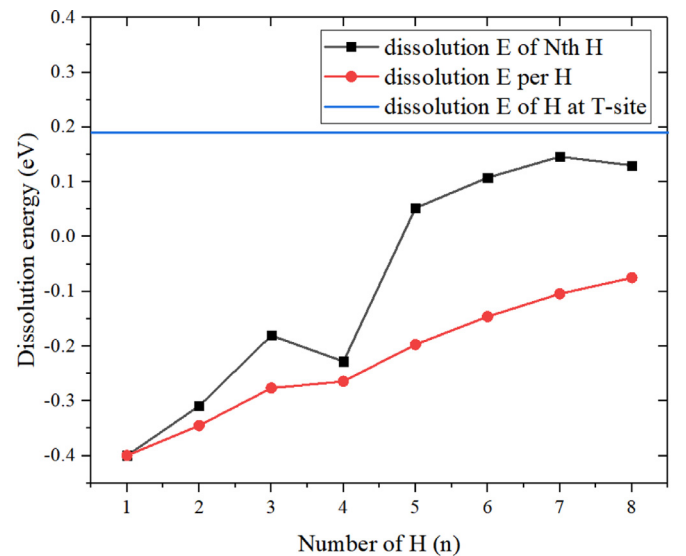


Fig. 4. The E_d of H in each different Va-He- H_n clusters. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

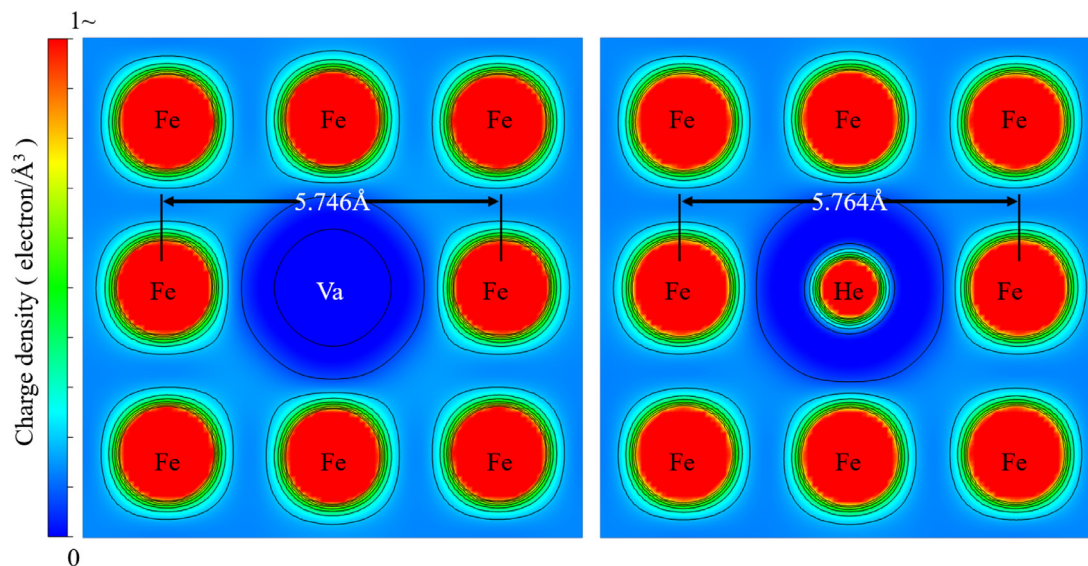


Fig. 5. Charge density plots of monovacancy and VaHe complex in α -Fe.

the E_d of 4th and 8th H is the local minimum. A cluster with a symmetric structure would have the local minimal value in E_d of Nth H, like Va-He-H₄ and Va-He-H₈. While, the cluster with an asymmetric structure would have the local maximal value in E_d of Nth H, like Va-He-H₃ and Va-He-H₇. When the number of H is up to 8, the E_d of H would still be lower than that of H at T-site in Fe (blue line in Fig. 4). However, when 9 H atoms are put into the structure, one or more H atoms always get out of vacancy. It implies that Va-He-H₈ cannot trap H atom any more. Thus, a Va-He-H₉ can hardly form and the maximal number of H trapped in one Va-He complex is 8. Va-He shows stronger ability in trapping H than monovacancy, as the previous study shows the maximal number of H atoms trapped in monovacancy would be 6 [27]. The charge density of monovacancy and Va-He complex are presented in Fig. 5. The Va-He complex provides an isosurface with low charge density, which H energetically prefers to stay. It is clear that Va-He complex has a bigger volume than monovacancy. This can be one of the reasons why Va-He complex can accommodate more H atoms than monovacancy.

4. Conclusion

The synergistic interaction of H and He in bcc Fe is studied by density functional theory calculation method.

In Fe without vacancy, H and He coexist by staying at different T-sites. The most stable configuration is two T-sites with the distance of 1.94 Å. There is an attractive interaction between H and He in Fe, which is originated from the redistribution of charge density caused by He, and this could drive H segregation towards He.

In Fe with monovacancy, the Va-He complex can trap more H atoms than monovacancy. The maximum number of H trapped in Va-He complex would be 8.

Declaration of interests

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

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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