Journal of Nuclear Materials 492 (2017) 134–141

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

First-principles study of noble gas atoms in bcc Fe

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HIGHLIGHTS

- Interstitial noble gas atoms tend to stay together with each other by self-trapping.
- H/He prefers to locate interstitial sites nearby Ne atom than other interstitials.
- Noble gas atoms like Ne can act as a trapping site for H/He impurities in bcc Fe.

ARTICLE INFO

Article history:
Received 23 January 2017
Received in revised form
17 May 2017
Accepted 17 May 2017
Available online 19 May 2017

Keywords:
Noble gas
Fe
Interaction
Irradiation
First principles

ABSTRACT

We investigate the energetics and clustering trend of noble gas atoms (He, Ne, and Ar) in bcc Fe, and their interactions with vacancy or H/He impurities using first-principles calculations. We determine the formation energy of single and double noble gas atoms inside Fe host lattice as well as the resulted volume changes. The Ne/Ar formation energy is two and three times that of He. The attraction between Ne/Ar and vacancy is stronger than He-vacancy, indicating higher dissolution energy of Ne/Ar. The interstitial Ne-Ne/Ar-Ar pairs have stronger attractions (−1.91 eV/−1.40 eV) than He-He (−0.37 eV), forming stable <110> configurations. Such strong attraction means that He/Ne/Ar tend to aggregate, which can be well explained by the lower electron density induced by interstitial noble gas atoms and its strong repulsion with Fe atoms. Moreover, H/He energetically prefers to occupy the tetrahedral sites nearby Ne/Ar atom. The attraction energies of He-Ne/He-Ar pairs (−1.01 eV/-0.85 eV) are much stronger than those of H-Ne/H-Ar (−0.22 eV/−0.10 eV) and their charge density differences are discussed. The distinct attraction strengths by various noble gas atoms provide a preliminary explanation for the difference in irradiation effects on Fe solid by He, Ne, Ar, and He+H/Ne+He. These findings improve our understanding about the behavior of noble gas atoms and gas bubble formation in iron under irradiation.

1. Introduction

High-strength Fe-based alloys of bcc phase have been widely used in nuclear reactors [1–3]. Large amounts of He and H impurities are produced in the neutron-irradiated Fe solid and alloys via (n, α) transmutation reactions, which play an important role in microstructure evolution and degradation of mechanical properties, known as the irradiation damage effect [4–7]. Thus, understanding the effect of He atoms in metals and alloys is crucial for development of materials resistant to irradiation under fusion and fission environments. Experimentally, multi-beam irradiations by He/Ne/Ar ions have been intensively carried out to investigate He embrittlement and irradiation damage in metals and alloys [8–15]. Previous TEM experiments [8,11,13] observed formation of noble gas bubbles of He, Ne, or Ar in pure Ni, W metals and Fe alloys. He atoms can be deeply trapped in vacancies and grain boundaries, leading to bubble formation [16,17]. The volume change associated with void swelling is quite large (over 10%) [18]. Until now, experimental data on defect energies of the noble gas atoms in bcc Fe solid and its alloys, especially the formation/binding energy of noble gas atoms and their binding energies with vacancy/H/He, are generally scarce.

Density functional theory (DFT) calculations have been extensively performed to investigate the defect formation energy, diffusion and clustering of He atoms in bcc Fe [19–28]. Fu and

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http://dx.doi.org/10.1016/j.jnucmat.2017.05.022
0022-3115/

Willaime examined the stability of He and He-vacancy clusters, their results showed that He migration barrier is very small (about 0.06 eV) and the strength of He-He attraction in α-Fe lattice is 0.43 eV [19]. Seletskaia reported that magnetic interactions influence the behavior of He in bcc Fe [20] and revealed that strong hybridization between He and the surrounding Fe atoms results in high defect formation energy. Sakuraya et al. investigated the effects of H, He, C, and N impurities in α-Fe [24] and found the magnetic moment of Fe slightly increases after He insertion. Our recent studies demonstrated that interstitial He greatly reduces the vacancy formation energy in bcc Fe [22] and interstitial He-He has strong attraction in bcc Fe, Cr, Mo and W metals, suggesting that He clustering may occur by self-trapping [29]. Kong revealed He clustering in W host lattice by self-trapping [30]. However, the effects of other noble gas atoms and their impact on H/He behaviors in bcc Fe have received much less attention in terms of atomic simulations.

Owing to the accumulation of He and other noble gas atoms in pure Fe, steels, and other metals, accurate determination of defect formation energies and their interaction strengths are important for developing predictive models for the quantification of irradiation damage. In this paper, we investigate the energetics and clustering trend of noble gas atoms (He, Ne, and Ar), as well as their interactions with vacancy and H/He impurities in bcc Fe solid using first-principles calculations. Firstly, we determine the occupying site, volume changes and formation energy of single and dual noble gas atoms in Section 3.1. We then calculate binding energy between a noble gas atom and a vacancy in Section 3.2. We further calculate binding energy between two noble gas atoms (Ne/Ar and H/He) and discuss their electronic structures in Section 3.3 and 3.4. We find that interstitial noble gas atoms tend to stay together with each other and are able to attract He/H impurities. The present results provide vital insights into the behavior of noble gas atoms and gas bubble formation in iron under irradiation.

2. Computational methods and models

All calculations were performed using spin-polarized density functional theory and the plane-wave pseudopotential approach [31,32], as implemented in the Vienna Ab initio Simulation Package (VASP 5.3.5) [33,34]. We adopted the generalized gradient approximation (GGA) with the Perdew and Wang (PW91) functional [35] for the exchange-correlation interaction and the projector-augmented wave (PAW) potentials [36,37] for the ion-electron interaction. A 128-atom bcc supercell (4 × 4 × 4 unit cells) of Fe was used and the cutoff energy of plane-wave basis was set as 350 eV. For accurately describing the interaction between two noble atoms and the defect formation energy, single-point-energy calculations were carried out with a higher energy cutoff of 500 eV. During relaxations, the Brillouin zone integration was achieved using a Methfessel-Pazton smearing width of 0.1 eV. The Brillouin zones were sampled with 3 × 3 × 3 **k** points by Monkhorst-Pack scheme [38]. The atomic positions were fully relaxed at constant volume until the force on each atom is less than 0.005 eV/Å. The climbing image nudged elastic-band (CI-NEB) method [39,40] was used to determine the diffusion barriers of noble gas atom in bcc Fe solid. Five images between the initial and final configurations were considered and all images were relaxed until the force on each atom is less than 0.01 eV/Å.

Formation energy of an interstitial and substitutional impurity X (X = H, He, Ne, Ar) in Fe host solid can be defined by Refs. [19,41]:

$$E^{\mathrm{f}}(\mathrm{X}_{\mathrm{interstitial}}) = E(1\mathrm{X},\ N\mathrm{Fe}) - E[N\mathrm{Fe}] - E(\mathrm{X}_{\mathrm{isolated}}), \quad (1)$$

and

$$E^{\mathrm{f}}(\mathrm{X}_{\mathrm{substitutional}}) = E(1\mathrm{X},\ N\mathrm{Fe}) - (\mathrm{N}-1)E[N\mathrm{Fe}]/N - E(\mathrm{X}_{\mathrm{isolated}}), \quad (2)$$

respectively. Here $E(1\mathrm{X}, N\mathrm{Fe})$ and $E[N\mathrm{Fe}]$ are the energies of supercell with and without a X atom, respectively; $E(\mathrm{X}_{\mathrm{isolated}})$ is the energy of an isolated noble X atom in vacuum, while $E(\mathrm{H}_{\mathrm{isolated}})$ is half of the energy of a H_2 molecules in vacuum (−3.40 eV from our calculations). By definition, a positive energy denotes endothermic process, while a negative energy denotes exothermic.

Binding energy between two defects, i.e., A and B, can be defined by:

$$E^{\mathrm{b}}(\mathrm{A},\mathrm{B}) = E^{\mathrm{f}}(\mathrm{A}+\mathrm{B}) - E^{\mathrm{f}}(\mathrm{far\ A}+\mathrm{B}). \quad (3)$$

Here E^{f}(A+B) is the formation of energy for coexistence of A and B defects, E^{f}(far A+B) is the formation of energy for A and B defects far away from each other. Obviously, a negative binding energy means attractive interaction between two defects, while a positive one means repulsive interaction.

Using the present computational scheme, we first determine the bulk properties of bcc Fe and the intrinsic defect formation energies of monovacancy, divacancy and self-interstitials (SIA) in Fe host lattice in comparison with the available experimental data and theoretical results, as summarized in Table 1. The calculated lattice constants (a), bulk modulus (B) and magnetic moment μ_B of bulk Fe solid are 2.83 Å, 177 GPa and 2.16 μ_B, respectively, in good agreement with the experimental values (2.87 Å, 168 GPa and 2.22 μ_B) [42] and previous DFT results (2.83 Å, 174 GPa and 2.20 μ_B [43]; 2.88 Å 180 GPa and 2.31 μ_B [44]), respectively. The calculated monovacancy formation energy of 2.16 eV coincides with the experimental data of 2.0 ± 0.2 eV [42,45] and previous DFT values of 2.14 eV [46] and 2.12 eV [47]. The divacancy formation energy (Vac_2) as first (1nn) and second (2nn) nearest neighbor are 4.12 eV and 4.10 eV, respectively, in line with previous theoretical results (4.13 eV and 4.04 eV [47], 4.08 eV and 4.01 eV [19,44]). For self-interstitials, the <110> configuration is most stable with the formation energy of 3.85 eV relative to both <100> and <111> configurations, which accords with other DFT results of 3.93 eV [47]

Table 1
The lattice constants (a), bulk modulus (B), magnetic moment μ_B, and formation energies (eV) of intrinsic defects (mono-/di-vacancy and self-interstitial) and H defects in bcc Fe in comparison with the available experimental and theoretical results [19,42–48,50,52,53].

Type	This work	Theor.	Exp.
a (Å)	2.83	2.83[a], 2.88[b]	2.87[c]
B (GPa)	177	174[a], 180[b], 160[d]	168[c]
μ_B	2.16	2.20[a], 2.32[d]	2.22[c]
E^{f} (Vac)	2.16	2.14[e], 2.12[f],2.17[g]	2.0 ± 0.2[c]
E^{f}_{1nn} (Vac_2)	4.12	4.13[f], 4.08[h]	
E^{f}_{2nn} (Vac_2)	4.10	4.04[f], 4.01[h]	
$E^{\mathrm{f}}_{<100>}$(SIA)	4.96	4.97[f], 4.64[b]	
$E^{\mathrm{f}}_{<110>}$(SIA)	3.85	3.93[f], 3.64[b]	
$E^{\mathrm{f}}_{<111>}$(SIA)	4.53	4.58[f], 4.34[b]	
$E^{\mathrm{f}}(\mathrm{H_{T\text{-}site}})$	0.30	0.27[i]	
$E^{\mathrm{f}}(\mathrm{H_{O\text{-}site}})$	0.46	0.45[i]	
$E^{\mathrm{d}}(\mathrm{H_{O\text{-}T}})$	0.16	0.13[g]	
E^{b}(H-vacancy)	−0.62	−0.58[g]	

[a] DFT calculations (PAW-GGA-VASP) from Ref. [43].
[b] DFT calculations (PBE-GGA-SIESTA) from Refs. [19,44].
[c] The experimental values from Refs. [42,45].
[d] DFT calculations (PW91-GGA-VASP) from Ref. [53].
[e] DFT calculations (PW91-GGA-VASP) from Ref. [46].
[f] DFT calculations (PBE-GGA-VASP) from Ref. [47].
[g] DFT calculations (PAW-GGA-VASP) from Ref. [48].
[h] DFT calculations (PBE-GGA-PLATO) from Refs. [50,52].
[i] DFT calculations (PBE-GGA-GPAW) from Ref. [24].