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He–He and He–metal interactions in transition metals from first-principles

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ABSTRACT

We investigated the atomistic mechanism of He–He and He–metal interactions in bcc transition metals (V, Nb, Ta, Cr, Mo, W, and Fe) using first-principles methods. We calculated formation energy and binding energy of He–He pair as function of distance within the host lattices. The strengths of He–He attraction in Cr, Mo, W, and Fe (0.37–1.11 eV) are significantly stronger than those in V, Nb, and Ta (0.06–0.17 eV). Such strong attractions mean that He atoms would spontaneously aggregate inside perfect Cr, Mo, W, and Fe host lattices in absence of defects like vacancies. The most stable configuration of He–He pair is <100> dumbbell in groups VB metals, whereas it adopts close <110> configuration in Cr, Mo, and Fe, and close <111> configuration in W. Overall speaking, the He–He equilibrium distances of 1.51–1.55 Å in the group VIB metals are shorter than 1.65–1.70 Å in the group VB metals. Moreover, the presence of interstitial He significantly facilitates vacancy formation and this effect is more pronounced in the group VIB metals. The present calculations help understand the He-metal/He–He interaction mechanism and make a prediction that He is easier to form He cluster and bubbles in the groups VIB metals and Fe.

1. Introduction

Plasma-material interaction (PMI) is one of the major concerns in the International Thermonuclear Experimental Reactor (ITER) and the future fusion reactors [1–4] and is a key factor in the material selection and plasma-facing component (PFC) design. Under typical environment of a fusion reactor, large amounts of helium (He) impurities are produced by neutron transmutation reactions in the structural materials or come from the edge plasma in the plasma facing materials [5,6]. Experiments showed He impurities can be trapped in structural defects (such as vacancies, grain boundaries and voids), forming clusters and bubbles, and finally leading to embrittlement and swellings of the fusion materials [5,7–10]. To elucidate He effects on the mechanical and physical properties of the metal materials facing fusion plasma or under neutron irradiation, deep understanding of the fundamental mechanism of He–He and He–metal interactions is needed.

Previously, density functional theory (DFT) calculations have been extensively performed to study He behavior in bcc transition metals [11–20]. Seletskaia [14] systemically investigated the stable position of a single He impurity in bcc transition metals of V, Nb, Ta, Mo, and W. Fu and Willaime [11] studied the stability of He and He-vacancy clusters and found the strength of He–He attraction in Fe is 0.43 eV. Becquart and Domain [12] predicted that He–He attraction energy is 1.03 eV, which can result in formation of He bubbles even without vacancies. Recently, our group investigated the stability of He and He-vacancy clusters in V [16] and found weak attraction (0.02–0.21 eV) for He–He pair in V. Despite the above mentioned efforts, until now the physical mechanism of strong attraction of He–He in W and Fe has not been clearly elucidated. For fusion reactors, V, Ta, Cr, and Fe are the main low activation elements for structural materials. Thus, atomistic simulations of He–He/He–metal interactions in bcc transition metals not only are essential for understanding the microscopic mechanism of He aggregation and He bubble formation, but also help establish more

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accurate empirical potentials [21] to simulate the kinetic evolution of the microstructure of materials in larger length/time scale.

The purpose of this paper is to perform a systematical first-principles investigation of the He–He interactions and He effects on vacancy formation in bcc transition metals of group VB (V, Nb, Ta), group VIB (Cr, Mo, W) and VIII (Fe), including formation energy, binding energy, atomic configurations. We calculated binding energy of He–He pair as a function of distance in various metal host lattices and discussed the most stable configurations. We also analyzed geometry structures, charge densities and density of states to elucidate the attractive interactions of He–He in metals. Finally, we discussed the effects of interstitial He atoms on vacancy formation.

2. Computational methods

All calculations were performed using spin polarized DFT and plane-wave pseudopotential approach [22,23], as implemented in the Vienna Ab initio Simulation Package (VASP) [24,25]. We adopted the generalized gradient approximation (GGA) with PW91 functional [26] for the exchange–correlation interaction and the projector-augmented wave (PAW) potentials [27,28] for the ion–electron interaction. A bcc supercell of 128 atoms ($4 \times 4 \times 4$ unit cells) was used and the Brillouin zones were sampled with $3 \times 3 \times 3$ k points generated by the Monkhorst-Pack scheme [29]. The energy cutoff of planewave was chosen as 500 eV. Due to the ferromagnetism of bcc Fe, spin polarization was considered for all DFT calculations. The electronic configurations of transition metal atoms are $3d^4 4s^1$ for V, $4d^4\ 5s^1$ for Nb, $5d^3 6s^2$ for Ta, $3d^5 4s^1$ for Cr, $4d^5 5s^1$ for Mo, $5d^4 6s^2$ for W, and $3d^7 4s^1$ for Fe, respectively. The equilibrium configurations at constant supercell volume were fully relaxed with the convergence criterion of the force on each atom less than 0.005 eV/Å.

Within the present theoretical scheme, the cohesive energy of each metal is calculated by $E_{\mathrm{coh}} = \mathrm{E(perfect)} - \mathrm{N}E_{\mathrm{atom}}$, where E(perfect) is the energy of the supercell with perfect lattice (128 atoms), N = 128 is the number of atoms in the working supercell, E_{atom} is the energy of one metal atom in vacuum, here we considered spin polarization for a metal atom in the DFT calculations. We also calculated bulk modulus for the seven transition metals by fitting Birch–Murnaghan equation. The calculated equilibrium lattice constants (a), cohesive energy (E_{coh}) per atom, and bulk modulus (B) for seven bcc transition metals (V, Nb, Ta, Cr, Mo, W, and Fe) are compared with experimental data [30] in Table 1. Reasonable agreement is found between our DFT calculations and experiments. Calculated formation energies of single tetrahedral He in seven transition metals coincide well with previous DFT results (see Table 1). Besides, since He is a closed-shell atom, we discuss the effect of Van der Waals interaction of He–He and He–metal using dispersion corrected DFT method (DFT-D) [31]. It is shown that effect of Van der Waals interaction of He–He pair is quite small (−0.02 ~ −0.05 eV) on He–He binding energy, which is negligible for the He–He and He–metal interactions.

3. Results and discussion

3.1. He–He interactions in transition metals

As a light element, He is a typical interstitial impurity in metal lattices due to its smaller atomic radius relative to the metal atom. In the bcc solid of transition metals, a single He atom prefers to occupy at a tetrahedral interstitial site energetically rather than an octahedral interstitial site from previous experiments and calculations [14]. To discuss the He–He interactions in bcc transition metals, we calculated the binding energies of He–He pairs as function of distance by considering two He atoms at favorable tetrahedral sites as first (1nn) to 14 nn nearest neighboring sites (about 1–6 Å). The binding energy of He–He pair in a transition metal host is defined by:

$$E^b(\mathrm{He,He}) = E^f(2\mathrm{He}) - E^f(2\mathrm{farHe_T}), \tag{1}$$

$$E^f = E(m\mathrm{He}) - E(\mathrm{perfect}) - E(\mathrm{He}), \tag{2}$$

where E^f(2He) and E^f(2farHe$_{\mathrm{T}}$) are the formation energies of the supercell with a He–He pair and two separated He atoms, respectively. In Eq. (2), $E(m\mathrm{He})$ is the energy of the supercell with m He atoms (m = 1, 2); E(prefect) is the energy of the supercell with perfect lattice; E(He) is the energy of a He atom in vacuum. By definition, negative formation energy means exothermic process, and negative binding energy means attractive interaction.

The calculated binding energies of He–He pairs as function of distances in host lattices are plotted in Fig. 1. Generally speaking, He–He interactions show similar trend with their distance in host lattice for the seven metals considered: repulsion (less than 1.5 Å) → attraction → repulsion → no interaction (larger than 4.0 Å). As for the strength of attraction, we found a distinct group-specific trend: He–He pair exhibits weak attraction (less than 0.20 eV) in the group VB (V, Nb, Ta), while it is strong attraction (larger than 0.70 eV) in the group VIB metals (Cr, Mo, W). In all metals, 1nn configuration of He–He pair is unstable and would transform into 2nn configuration after relaxations. Both 3nn and 5nn He–He configurations in group VIB metals are unstable and tend to transform into 2nn configuration due to inter-helium attraction. As He–He distance exceeds 4.0 Å, the strength of He–He interaction drops to nearly zero and is negligible. Importantly, such a strong binding energy means that clustering of two single He impurities is quite probable and that the He clusters will be very stable. Namely, He in perfect Cr, Mo, W, and Fe solids can directly attract another He atoms in absence of other defects like vacancies. Previous first-principles calculations by Fu and Willaime [11] reported a He–He attractive energy of 0.43 eV in Fe, while Becquart and Domain [12] predicted that the strength of He–He attraction in W is 1.03 eV. All

Table 1
: Calculated equilibrium lattice constants a (Å), cohesive energies E_{coh} (eV), and bulk modulus B (GPa) for seven bcc transition metals (V, Nb, Ta, Cr, Mo, W, and Fe) in comparison with experimental data [30]. Single He formation energy at tetrahedral sites is compared with the present calculation and previous DFT results [11,14].

		V	Nb	Ta	Cr	Mo	W	Fe
a	This work	2.98	3.32	3.32	2.84	3.15	3.18	2.82
	Expt.	3.03	3.30	3.30	2.88	3.15	3.16	2.87
E_{coh}	This work	5.49	7.04	8.20	4.20	6.49	8.54	5.10
	Expt.	5.31	7.57	8.10	4.10	6.82	8.90	4.28
B	This work	173.5	170.4	191.7	185.3	256.2	298.7	177.5
	Expt.	161.9	170.2	200.0	190.1	272.5	323.2	168.3
$E^f(He_T)$	This work	2.95	3.09	3.42	5.42	5.33	6.24	4.66
	Other DFT	2.94	3.05	3.16	–	5.16	6.15	4.40