Effect of helium and vacancies in a vanadium grain boundary by first-principles

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ABSTRACT

We present the preferential site, segregation and embrittlement behavior of helium (He) and vacancies in a vanadium (V) $\sum 3$ (1 1 1) [1 1̄ 0] grain boundary (GB) by first-principles calculations. Energetically, He prefers to occupy interstitials rather than substitutional sites at the GB, and segregate to the GB with a driving force of 0.16 eV. Vacancy formation in GB is considerably easier than in bulk regardless of He presence or no for V metal, similar to the behavior of vacancy in Fe and W metals. He acts as a strong embrittler at the V GB with embrittlement energy of 2.80 eV, similar to He behaviors at the GBs of Fe and Ni metals. He segregation weakens bond strength between surrounding V atoms, leading to degradation of GB strength. The present results provide a useful reference for He effects on the mechanical properties of the GB.

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1. Introduction

Under 14 MeV neutrons irradiation in the fusion reactors, large amounts of helium (He) impurities are produced continually in structural materials along with irradiation damage [1]. Because of its insolubility, He tends to form complex clusters and promotes bubble nucleation or segregates to grain boundaries and causes embrittlement [2–4], consequently degrading the properties of engineering alloys. Vanadium (V) based alloys are considered as the promising first wall structural material in fusion reactors owing to excellent resistance to neutron irradiation and superior high-temperature mechanical properties [5,6]. He embrittlement is significant problem for V based alloys under fusion reactor operation. Therefore, it is important to understand the relative roles of He impurities in grain boundaries (GB) of pure V and V alloys for fusion research.

First-principles calculations have been devoted to investigate the segregation and embrittlement properties of He at GB in transition metals, such as Fe [7,8], W [9], and Ni [10]. Both Rice–Wang thermodynamic theory and first-principles calculations revealed the embrittling or strengthening effect of He impurities. The results showed that He act as a embrittler at GB for Fe, W, and Ni metals in agreement with experimental observations. However, the behavior of He in V GB has hardly been explored by first-principles simulations.

In this work, we present the effect of He and vacancies in the V $\sum 3$ (1 1 1) GB using both first-principles methods and Rice–Wang model, including the preferential site, segregation energy, and embrittlement energy. Firstly, we determine the formation energy of He and vacancy at different positions in the GB. We analyze charge density distributions and atomic structures, and further discuss the relationships between bonding behavior of He with surrounding V atoms and GB embrittlement. The present simulations provide a useful reference for the effect of He on the mechanical properties of the V GB.

2. Computational methods and models

All first-principles calculations were performed using density-functional theory and a plane-wave pseudopotential approach [11,12], as implemented in the Vienna Ab initio Simulation Package (VASP) code [13,14]. We adopted the generalized gradient approximation (GGA) with the Perdew and Wang (PW91) functional [15] for the exchange–correlation interaction and the projector-augmented wave (PAW) potentials [16,17] for the ion–electron interaction. The cutoff energy of 500 eV was used for the plane wave basis. The Brillouin zones were sampled with

$4 \times 6 \times 1$ k points by Monkhorst–Pack scheme [18]. All atomic positions were fully relaxed at constant volume with a convergence criterion of the force on each atom less than 0.01 eV/Å.

The selected $\sum 3$ grain boundary represents low energy symmetric twin boundary in bcc vanadium [19]. We modeled the $\sum 3$ (1 1 1) [1 $\bar{1}$ 0] GB and $\sum 3$ (1 1 1) free surface (FS) of V by a single free slab, as shown in Fig. 1. For the GB system, a 29-layer V slab (58-atom) containing two identical grains (15 atomic layers each) was adopted to simulate the clean GB. For the FS system, the V(1 1 1) substrate was simulated by a 15-layer slab (30-atom). We separated the neighboring slabs in [1 1 1] direction by a vacuum region of about 10 Å to minimize the interaction between periodic slabs. The three dimensions for the V GB supercell are 7.42 Å × 4.28 Å × 35.76 Å. The two-dimensional lattice constant for stress-free systems was chosen to be the equilibrium value optimized for the bcc V lattice (2.98 Å), which is in good agreement with the experimental value of 3.03 Å [20].

3. Results and discussion

3.1. Formation energy of He in a vanadium GB

To find the favorable site for He in GB, we firstly investigate He formation energy at different interstitial and substitutional sites, as shown in Fig. 1. We consider different sites of He at the first layer for GB and FS because these three layers are symmetrically equivalent. A single He atom is placed at different interstitial sites from I_1 to I_6, and different substitutional sites from site 1 to site 4,
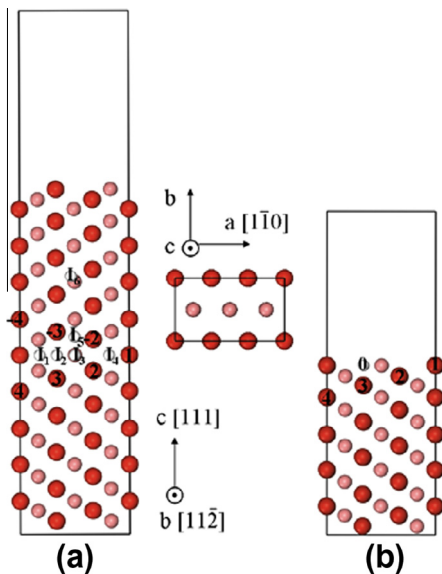
Fig. 1. Computational models of GB and FS: (a) the V $\sum 3$ (1 1 1) [1 $\bar{1}$ 0] GB and (b) the 13 layer V FS (1 1 1). Sites from I_1 to I_6 indicate different interstitial sites for GB and site 0 for FS. The atoms near the GB and FS are numbered by the atomic layer counted from the GB plane.

respectively. The formation energy E^f of He in the V $\sum 3$ (1 1 1) GB or on the V(1 1 1) FS is obtained by:

$$E^f = E(\text{He/GB}) - E(\text{GB}) - E(\text{He}), \qquad (1)$$

$$E^f = E(\text{He/FS}) - E(\text{FS}) - E(\text{He}), \qquad (2)$$

where $E(\text{GB})$ or $E(\text{FS})$ is the energy of clean GB or FS, $E(\text{He/GB})$ or $E(\text{He/FS})$ is the energy of GB or FS with a interstitial He atom; $E(\text{He})$ is the energy of a He atom in vacuum (10 Å × 10 Å × 10 Å supercell). When the He atom replaces a V atom, the formation energy of He is obtained by:

$$E^f(\text{substitutional}) = E(\text{He/GB}) - E(\text{GB}) + E(V_{\text{atom}}) - E(\text{He}), \qquad (3)$$

$$E^f(\text{substitutional}) = E(\text{He/FS}) - E(\text{FS}) + E(V_{\text{atom}}) - E(\text{He}), \qquad (4)$$

where $E(V_{\text{atom}})$ is the energy of a lattice V atom in bulk. By definition, positive formation energy indicates endothermic reaction and negative formation energy indicates exothermic reaction.

Table 1 shows the calculated formation energies of He at different interstitial and substitutional sites in the GB. Apparently, He prefers to occupy interstitial sites in the GB rather than substitutional sites. For interstitial sites, we found that the site I_2 for He is the most stable with the lowest formation energy of 2.79 eV, and other interstitial sites in the GB are unstable. He at the sites I_1, I_3, and I_5 are unstable and would move into the site I_2 by about 1.00 Å, while site I_4 He would move into an interstitial site of the middle layer (equivalent to site I_2). For He at substitutional sites, the sites 2–4 for He with a range of 3.22–3.69 eV are more stable than the substitutional site of He in bulk with 4.39 eV. Site 2 for He is the most stable one with formation energy of 3.22 eV, while site 1 is the least favorable. Besides, previous DFT studies showed that He prefers to occupy a tetrahedral interstitial site ($E^f = 2.95$ eV) in pure V [21], while the most stable site for a He atom is close to an octahedral site near one vacancy (with $E^f = 2.00$ eV) in the bulk containing a vacancy [22], which is more stable than He at a vacancy center by 0.22 eV. The main reason comes from the fact that a octahedral He near a vacancy causes less distortion on the LDOS of the nearby host V atoms than He at vacancy center [22]. In general, the sequence of He preferential site for V is bulk vacancy, GB interstitial, bulk tetrahedral, GB substitutional and bulk substitutional sites. The present results indicate that GB defects provide trapping locations for He impurities in V, similar to vacancy defects.

Because of its insolubility, He insertion will affect GB structure, and then we analyze interatomic distances of He at stable sites of GB before and after relaxations. In Table 2, two noticeable changes are the expansion of the He–V_3 bond (about 0.26 Å) and the expansion of V_3–V_3 bonds (about 0.52 Å). The changes of He–V_1, He–V_2 He–V_4, V_1–V_2, V_2–V_3, and V_3–V_4 bond is quite small (less than 0.1 Å). This finding means that He in V GB weakens the GB strength.

Table 1
Formation energies and segregation energies (eV) of He in the V $\sum 3$ (1 1 1) GB and on FS for interstitial and substitutional sites in comparison with He at tetrahedral interstitial (T), vacancy (Va) and substitutional (S) sites in bulk V.

	GB(I_1)	GB(I_2)	GB(I_3)	GB(I_4)	GB(I_5)	GB(I_6)	FS(0)	Bulk (T)	Bulk (Va)
E^f	–	2.79	–	–	–	3.49	−0.01	2.95 [21]	2.00 [22]
E^{seg}	–	−0.16	–	–	–	0.54			
	GB(1)	GB(2)	GB(3)	GB(4)	Bulk(S)				
E^f	4.50	3.22	3.69	3.58	4.35 [22]				
E^{seg}	1.55	0.27	0.74	0.63					