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Effect of interstitial impurities on grain boundary cohesive strength in vanadium

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ABSTRACT

We studied the embrittling and strengthening effects of non-metallic (C, N, O, S, Si, and B) and metallic (Fe and Mo) interstitial impurities at a $\sum 3\,(1\,1\,1)\,[1\,\bar{1}\,0]$ grain boundary (GB) in vanadium (V) using first-principles calculations. All impurities incorporated into the GB are exothermic reaction except for Mo along with outward expansion of the GB space. Upon optimization, the small C, N, and O impurities at the GB prefer the same interstitial site, while the S, Si, B, Fe and Mo impurities prefer another interstitial site. According to strengthening energy calculations, C, N, B, and Fe act as the GB cohesion, while O and S are strong embrittlers as well Si and Mo are weak embrittlers. The analysis of atomic and electronic structures indicate that the embrittling and strengthening behavior of the impurities mainly depends on the bonding behavior of the impurity with surrounding vanadium atoms, the impurity species and the atomic size.

1. Introduction

Impurities are frequently seen in structural materials for a wide variety of applications. Certain additives at the correct concentration can drastically improve the mechanical properties of the materials, while other impurities would cause a detrimental effect, leading to degradation of the various properties (like embrittlement). At present, vanadium-based alloys are regarded as the promising candidate structural materials for fusion reactors due to low neutron activation and excellent mechanical strength [1–3]. Under the severe environments of fusion reactors, the structural materials must remain excellent resistance to neutron irradiation as well as superior high-temperature mechanical properties in a long term. In typical V–(4–5)Cr–(4–5)Ti alloys and pure V from experiments [4–6], the main impurities include C, N, O, S, Si, B, Fe, and Mo, and their corresponding contents are in ranges of 25–200 wppm, 110–200 wppm, 210–400 wppm, 10–30 wppm, 200–1000 wppm, 5–10 wppm, 135–300 wppm, and 50 wppm, respectively. Therefore, investigating the physical mechanism of impurity effects is quite essential to improve the structural materials for fusion search.

From experimental observations, impurities are easy to segregate to the grain boundaries (GB) in pure V and V alloys and substantially affect their basic properties [3,4,7–9], such as GB embrittlement or occasionally can strengthen GB. Neutron irradiation experiments by Kameda et al. [7,8] demonstrated that the enrichment of C and O at grain boundaries is ascribed to not only segregation but also precipitation of carbides and oxides for various V alloys. S segregation has embrittling effect at GB while C segregation acts as GB toughening. Chen and co-workers [9,10] reported that O impurities cause GB weakening for V alloys and the ductility losses with increasing O concentration. In spite of the two decades of intensive studies, the effect of various impurities on GB cohesion in V alloys is still largely unclear. Few systematic theoretical studies have been reported in the literature. Therefore, it is important to study the effects of impurities in GB for developing and optimizing the advanced vanadium alloys.

So far, first-principles calculations have been devoted to investigating the effect of various impurities on GB in transition metals, including Fe [11–14], Ni [15,16], Al [17], Nb and Mo [18], and W [19]. For instance, interstitial C and B act as a strengthener at Fe GB [12], while N, O, and S act as an embrittler. Similarly, interstitial B is a strengthener at Ni GB [15]. In contrast, the behavior of various impurities in V GB is still unknown. In this work, we investigate the embrittling and strengthening effects of nonmetal (C, N, O, S, Si, and B) and metal (Fe, and Mo) interstitial impurities at a $\sum 3\,(1\,1\,1)$ GB in V using first-principles methods and the Rice–Wang model [13]. We first calculated the binding energy and strengthen energy for each kind of impurity incorporated at the

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GB and discussed GB structure changes with one impurity. Then, the electronic properties of relaxed atomic structures of impurity/V $\sum 3$ (1 1 1) [1 $\bar{1}$ 0] GB and the corresponding impurity/V (1 1 1) free surfaces (FS) were calculated to analyze the physical origin of embrittling or strengthening behavior of these impurities in the V GB.

2. Computational methods and models

All calculations were performed in the framework of density functional theory (DFT) and a plane wave pseudopotential approach [20,21], as implemented in the Vienna Ab initio Simulation Package (VASP) [22,23]. We adopted the generalized gradient approximation (GGA) with the Perdew and Wang (PW91) functional [24] for the exchange–correlation interaction and the projector-augmented wave (PAW) potentials [25,26] for the ion–electron interaction. A 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 [27]. All atomic positions were fully relaxed at constant volume with a convergence criterion of the force on each atom less than 0.005 eV/Å.

The selected $\sum 3$ GB represents a low-energy symmetric twin boundary in bcc V [28]. 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 slab model, as shown in Fig. 1. A 29-layer V slab (58 atoms) contains 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 atoms). To treat the periodic boundary condition, we separate the neighboring slabs along the [1 1 1] direction by a vacuum region of about 10 Å to avoid the interaction between slabs. The three dimension parameters 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 computed bulk value of bcc V (2.98 Å), in good agreement with the corresponding experimental value of 3.03 Å [29]. The effect of supercell size has been examined using larger slab with 116 atoms (7.42 Å × 8.56 Å × 35.76 Å). Our test results show that the embrittlement behaviors of all impurities investigated at the GB are unchanged and only values of impurity binding energy at the GB have some changes. Thus, the present 58-atom slab models are sufficiently to determine the embrittlement properties of interstitial impurity at the GB.

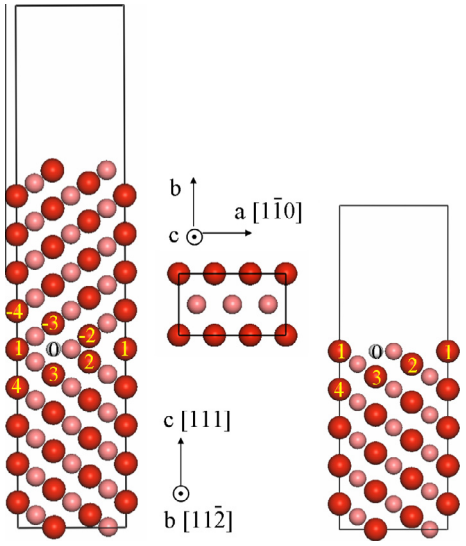

Fig. 1. Computational model of the GB and FS for V: (a) a $\sum 3$ (1 1 1) [1 $\bar{1}$ 0] GB and (b) a 13 layer FS (1 1 1). GB (0) indicates the interstitial site at the GB center. The atoms near the GB and FS are numbered by the atomic layer counted from the GB plane.

3. Results and discussion

3.1. Interaction and structure properties of impurities at GB

We first determined binding energies of various impurities at a V GB to investigate interaction strength between impurity and GB or FS. As shown in Fig. 1, the first layer and third layer are fully identical, and symmetrically equivalent with regard to the second one. We thus only placed impurities into interstitial site 0 at the first layer for GB and FS. The binding energy of an interstitial impurity (X = C, N, O, S, Si, B, Fe, and Mo) at the V $\sum 3$ (1 1 1) GB or on the V (1 1 1) FS is defined by [15]:

$$\Delta E_b = E(\mathrm{GB}) + E(\mathrm{X}) - E(\mathrm{X/GB}), \quad (1)$$

$$\Delta E_s = E(\mathrm{FS}) + E(\mathrm{X}) - E(\mathrm{X/FS}), \quad (2)$$

where E(GB) or E(FS) is the energy of the clean GB or FS; E(X/GB) or E(X/FS) is the energy of GB or FS with an interstitial impurity X; E(X) is the energy of a X atom. For O or N atom, $E(\mathrm{X}) = E(\mathrm{O_2})/2$ or $E(\mathrm{N_2})/2$, where $E(\mathrm{O_2})$ and $E(\mathrm{N_2})$ are the total energy of an isolated O_2 and N_2 molecules in vacuum (E(O) = −4.36 eV and E(N) = −8.3 eV from our calculations), respectively; E(C) = −8.04 eV/atom is the energy per C atom in graphite, in accordance with previous DFT results (−8.01 eV/atom) [30]. For S, Si, B, Fe, and Mo atoms, E(X) is the energy per atom in the bulk phase. By definition, positive binding energy indicates exothermic reaction, while negative value indicates endothermic reaction.

Table 1 summarizes calculated binding energies of various impurities (C, N, O, S, Si, B, Fe, and Mo) at the V GB. Apparently, incorporation of all impurities as interstitial at the GB is an exothermic process with positive binding energies except for Mo, namely, these impurities energetically prefer to stay at the GB. The sequences of interaction strength are O, N, C, S, Si, B, Fe, and Mo with binding energies of 4.80, 2.73, 2.21, 2.12, 1.47, 1.05, and −2.42 eV, respectively. The negative binding energy of −2.42 eV indicates Mo is unfavorable at the GB. Besides, stronger binding energy for nonmetal O, N, C, and S impurities mean that they are inevitable in realistic V materials and may further form compounds at the GB. Our theoretical result is consistent with available experimental data that the enrichment of C and O at GBs is ascribed to the segregation and the precipitation (carbides and oxides) [4,7,8].

To compare the change of GB structure after impurity segregation, Fig. 2 shows the relaxed GB structures within different interstitial impurities of C, N, O, S, Si, B, Fe, and Mo. Overall, all kinds of interstitial atom incorporated at the GB causes an outward expanding of the boundary space, although there are substantial differences in the amplitude of the displacements depending on the impurity species. It is worth mentioning that the eight impurities present two different trends of the favorable positions. Namely, C, N, and O atoms at site 0 are unstable and move toward [1 $\bar{1}$ 0] direction about 1.00–1.25 Å, while other six kinds of

Table 1
Calculated binding energies and strengthen energies $\triangle E$ (eV) of various impurities (C, N, O, S, Si, B, Fe, and Mo) at a V $\sum 3$ (1 1 1) GB.

Impurity	E^b (GB)	E^s (FS)	$\triangle E$	Effect
C	2.21	1.99	0.22	Strengthening
N	2.73	2.44	0.29	Strengthening
O	4.80	5.56	−0.76	Embrittling
S	2.12	3.52	−1.40	Embrittling
Si	1.47	1.62	−0.15	Embrittling
B	1.05	0.30	0.75	Strengthening
Fe	0.66	0.20	0.46	Strengthening
Mo	−2.42	−2.10	−0.32	Embrittling