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First-principles studying the properties of oxygen in vanadium: Thermodynamics and tensile/shear behavior

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ABSTRACT

Employing the first-principles simulation, we investigate the energetics of oxygen (O) and the influence of O on the mechanical behaviors of vanadium. O atom prefers to occupy the octahedral interstitial site with the solution energy of −4.942 eV. Along the [100] direction, the ideal tensile strength of vanadium doped with an O occupying the octahedral interstitial site is 17.4 GPa, which can be reduced by ~8.9% compared to 19.1 GPa of pure vanadium. This demonstrates that impurity O has a large effect on the tensile strength of vanadium. We further calculate the generalized fault energies including the unstable stacking energy (γ_{us}) and the cleavage energy (γ_{cl}) in pure vanadium and O-vanadium system in the most preferable {110}<111> slip system. The cleavage energy can be decreased from 1.705 J/m^2 of pure vanadium to 1.681 J/m^2 of O-vanadium system and simultaneously the unstable stacking energy can be increased from 0.308 J/m^2 of pure vanadium to 0.325 J/m^2 of O-vanadium system. The ratio of γ_{cl}/γ_{us} alters from 5.536 to 5.172 and can be thus decreased by 6.57%. This means that the ductility of vanadium will significantly decrease owing to the appearance of impurity O.

1. Introduction

Developing a key structural material is one of the most crucial subjects in the course of realizing commercial fusion power reactors. Many efforts have been made to search this kind of material, which must exhibit attractive characteristics such as low induced activation, good tolerance to high operating temperature and stress, long-term reliability under operating conditions, good fabricability and weldability, and reasonable production cost. Vanadium and vanadium-alloys are regarded as the most promising candidates of the structural materials in a fusion reactor at a long term study. The good performance in high temperature [1–3] and intrinsic low activation property [4–7] of vanadium can meet the demand for safety operation in the cruel conditions. Also, the high corrosion resistance in the reactor coolant lithium (Li) makes it possible to equip with liquid Li blankets in reactors [8–10]. Although the theoretical and experimental data base of V and its alloys are limited, a lot of scientific and industrial attentions have been paid on these materials. Many progress have been achieved on the critical issues for the vanadium and its-alloys such as fabrication technology and materials performance [11].

Previous studies have shown that vanadium possesses reasonable tensile properties and creep properties [12]. But in the harsh environment of fusion reactors, vanadium, as structural material, has to suffer the high flux of heat and particles such as high energy neutrons (14.1 MeV), which leads to host atom cascade. Correspondingly, large amount of defects such as vacancies and self-interstitial atoms are present, which will severely deteriorate the performance and finally result in the failure of materials.

Oxygen (O) is generally the most frequent foreign impurity atom in material. Over O solubility limit, O and host atoms can easily form the oxides, which might be favorable to enhance the strength and the hardness of metals. Under the solubility limit, even a very little amount of impurity O atoms in the interstitial position can significantly change the thermal and mechanical behaviors, owing to the strong interaction between impurity O and host atoms. On the other hand, the interstitial O atoms can effectively capture the migrating vacancies so as to decrease the defect vacancy diffusivity, as well as easily interact with the defect vacancies and produce a strong impact on various properties of vanadium [13]. Reducing the level of O is an important step to maintain the material's mechanical strength. Alloy element Ti can precipitate with O in the matrix of vanadium-based alloys and lower down the O content in

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the crystal [14]. The experimental evidences have demonstrated that the harmful consequences of vanadium under high energy neutrons irradiation are alleviated [11]. The swelling behaviors of perfect vanadium and vanadium-alloys after neutron irradiation have been investigated. The results reveal that the addition of Ti in vanadium can substantially suppress the swelling of crystal [15,16].

Although the experimental results have hinted that O exhibits the significant effects on vanadium, the theoretical investigations on the thermodynamic behavior of impurity O in vanadium and its effects on the mechanical properties of vanadium such as the ideal tensile/shear behaviors have been not received a lot of attentions. For example, how can impurity O in the interstitial position alter the basic mechanical properties of vanadium crystal such as the ideal tensile and shear strengths. The ideal tensile/shear strength of a perfect crystal can be determined by the maximum tensile/shear stress at elastic instability when an increasing strain is applied to a perfect crystal [17], and the ideal tensile/shear strength is the upper limit of the real crystal. Similarly, the impurity-material system also exhibits a ideal tensile/shear strength when the impurity is present in material. Moreover, the existing impurity can either raise or reduce the ideal tensile/shear strength of material. In the past, a lot of researches in this respect have been performed, in order to obtain the basic mechanical properties such as tensile/shear strengths of single crystal such as W, Cu, Ir, Al, Ni, Mo, Nb, Fe, and NiAl [18–27], and the defective systems containing only one defect such as a point defect [28], an interface or a grain boundary [29–32].

Motivated by the above descriptions, in this study we employ the first-principles calculations to investigate the basic properties of impurity O in vanadium from thermodynamic stability to tensile/shear deformation. We first study the site preference of O in the interstitial positions. Then, the effects of impurity O on the theoretical tensile/shear strength of vanadium single crystal are further explored. Using the first-principles computational tensile test (FPCTT), we present the ideal tensile strengths of vanadium crystal with and without impurity O atom. On the other hand, the generalized stacking fault energy and cleavage energy of vanadium crystal with and without impurity O atom have been also calculated. Using the criteria of the ratio of “cleavage energy” and “unstable stacking fault energy”, we can determine the alteration of ductility of a vanadium crystal when it is doped with an impurity O atom. These results will be regarded as the first step to further study the interaction between impurity O and vanadium-alloy. Simultaneously, we believe that these results can also provide a very useful reference for vanadium as a candidate structural material in a fusion reactor.

2. Computational methods

We have performed the first-principles calculations using the Vienna Ab-initio Simulation Package (VASP) code [33,34] based on the density functional theory. The exchange-correlation function is described by the generalized gradient approximation of Perdew and Wang [35] and the ion-electron interaction is defined by the projector augmented wave potentials [36]. The plane wave energy cutoff is 350 eV, which is sufficient for the total energy and geometry of vanadium supercell. The calculated equilibrium lattice constant of bcc vanadium is 2.98 Å, in good agreement with the corresponding experimental value of 3.03 Å [37].

2.1. Energetic stability calculations

For the calculations of O solution energy, we use the 128-atom supercell containing ($4 \times 4 \times 4$) unit cells with the lengths of 11.92 Å in [100], [010], and [001] directions, respectively. The supercell Brillouin zone was sampled by the Monkhorst-Pack scheme [38] and the Methfessel-Paxton smearing with a width of 0.10 eV. We tested k-point sampling and kinetic energy cutoff convergence for the supercell without and with impurity O. First, we choose the different energy cutoff to perform the convergence test using a large k-points mesh of $8 \times 8 \times 8$ for the supercell. Table 1 lists the tested results on the solution energies of O in vanadium. Next, using the tested energy cutoff of 350 eV, we choose the different k-points mesh to further carry out the convergence test. As seen from Table 1, the k-points mesh of $3 \times 3 \times 3$ can make all the relevant energies mentioned above converge to within less than 0.01 eV/atom. By the convergence test, we find that the size of 128-atom supercell can fully produce the reliable total energies required for single impurity O atom in vanadium. Further, the supercell size, shape, and atomic positions are allowed to relax to the equilibrium, and the energy relaxation iterates until the forces on all the atoms are less than 10^{-3} eV Å^{-1}.

The solution energy of interstitial O atom in perfect vanadium is defined as

$$E_O^s = E_{vanadium,O} - E_{vanadium} - \mu_O, \tag{1}$$

where $E_{vanadium,O}$ is the energy of the vanadium supercell with one impurity O atom, $E_{vanadium}$ is the energy of ideal perfect vanadium supercell, and μ_O is the chemical potential of O. The chemical potential of O is calculated to be −4.416 eV, which is half of the energy of an O_2 molecule putted into one vacuum box.

2.2. Tensile/shear calculations

Concerning the FPCTT, we choose the [001] as the tensile direction, due to that the [001] direction is often regarded as the weakest crystal direction under tension in bcc lattice according to prior work [39]. In the FPCTT, we employ the 128-atom supercell with an impurity O atom (i.e., O-vanadium system) to determine the ideal tensile strengths. A uniaxial tensile strain will be applied for the [001] crystalline direction. The corresponding tensile stress σ can be calculated according to the following equation

$$\sigma(\varepsilon) = \frac{1}{\Omega(\varepsilon)} \frac{\partial E}{\partial \varepsilon}, \tag{2}$$

where E is the total energy and $\Omega(\varepsilon)$ is the volume at given tensile strain ε. The lattice vectors are incrementally increased in the strain direction. At each strain step, the structure is fully relaxed until all other five stress components disappear except that in the tensile direction. The tensile stress of each strain step can be obtained, and thus the stress-strain relationship and the ideal tensile strength can be obtained.

As to the calculations of cleavage energies and generalized unstable stacking fault energies, we employ the 288-atom supercell containing ($4 \times 6 \times 2$) unit cells with the lengths of 10.32 Å, 25.28 Å, and 14.60 Å in [111], $[\bar{1}10]$, and $11\bar{2}$ directions, respectively. The size of the supercell was also indicated to yield reliable total energies needed for single impurity O atom after convergence test. The Brillouin zone was sampled with ($4 \times 2 \times 2$) k-points by the Monkhorst-Pack scheme [38]. During the shear slip, the 288-atom supercell including the {110}<111> slip system is divided into the upper and lower halves by the fault {110} plane. Thus, to calculate the cleavage energy, the slabs have to be formed by six atomic layers (i.e., 144 atoms) for (110) surface. While the thickness of the vacuum layer was correspondingly set to 12.64 Å, which is half of the length of the $[\bar{1}10]$ direction in the supercell. The atoms are relaxed until the remaining forces were less than 10^{-3} eV Å^{-1}. Moreover, we required numerical precision to compute the change

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