



Investigation of the interstitial oxygen behaviors in vanadium alloy: A first-principles study

Xingming Zhang^a, Yifan Li^a, Qiaoling He^b, Ruilian Li^{b,*}, Lei Deng^a, Liang Wang^a,
Xunlin Liu^a, Jianfeng Tang^a, Huiqiu Deng^c, Wangyu Hu^d

^a College of Science, Hunan Agricultural University, Changsha, 410128, China

^b College of Agriculture, Hunan Agricultural University, Changsha, 410128, China

^c Department of Applied Physics, School of Physics and Electronics, Hunan University, Changsha, 410082, China

^d College of Materials Science and Engineering, Hunan University, Changsha, 410082, China

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ABSTRACT

This study aims at characterizing the interstitial Oxygen (O) behaviors in the Vanadium (V) Alloy by means of the first-principles calculations. For this, the interactions between vacancy (Vac) and O interstitial atom are studied in detail to obtain the binding energies and stable structures of the complexes. It can be seen that monovacancy binding with two O atoms occupied the opposing octahedral site are particularly stable, and is liable to form VacO₂ cluster in the V alloys. According to the mass action analysis, the predicted temperature dependence of the concentration for VacO_n complexes are presented. Apart from monovacancy, we also consider the trapping behavior of vacancy cluster on the O atoms. The results also prove that one vacancy can trap two O atoms in the V alloys. Based the diffusion theory, we obtain the diffusion coefficients as a function of temperature with or without the vacancy effect in the V alloys. The predicted O diffusion coefficients in defect-free V alloys from our first-principles calculations are in excellent agreement with the experimental data, meanings that the vacancy-limited mechanism does not play the key role for O diffusion in V alloys. Regarding the interactions between vacancy, solutes and O atom, combining with the diffusion barriers of O affected by vacancy and solute, we infer the formation mechanism of the precipitates in the V alloys.

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1. Introduction

Vanadium (V) alloys are considered as a candidate for blanket structural materials for fusion reactor systems due to their remarkable elevated temperature strength and radiation resistance, coupled with low-induced activation characteristics in the fusion environment [1–3]. In the V alloys, the presence of Carbon (C), Oxygen (O) and Nitrogen (N) impurities in the matrix can drastically increase the ductile-to-brittle transition temperature (DBTT) and effect their mechanical behavior [4]. It is widely recognized that the reduction of these impurities is essential for maintaining the workability and weldability of V alloys [5]. However, O have very high solubility limits of (2.7 mass% at 1000 °C) in V, and can also be considered as a potent solid solution strengthener. Previous research has established that some fraction of O

should be in solid solution in the matrix after annealing at 1373 K, and the positive dependence of the hardness on O level is also found by Heo et al. [6]. Therefore, the behavior of impurities in the V alloys, especially the O, still is a open research subject.

In the matrix, dissolved O can integrate with Ti and Y solute to affect the microstructure. The mechanical strength of V alloys can be improved by high number density of tiny precipitates dispersed in the matrix [6], and many experiments proved that precipitates in V–4Cr–4Ti alloy are Ti-rich and most likely to be Ti–(O, N, C) [7]. Using high-resolution electron microscopy, Zhu et al. [8] reveal that a high density of existing precipitates are platelet-like, with NaCl structure, in three-dimensional space. Further, Impagnatiello et al. [9] characterise the local structure and chemistry at the interface between nm-thick TiO precipitates and the V-based matrix in a V–4Ti–4Cr alloy, and they found an intergrowth of the TiO fcc and V bcc structures at the precipitate/matrix interface. Both Ti and O diffuse in the V bcc matrix to form the TiO precipitates. The structure of the monolayer-thick TiO precipitate, considered as the

* Corresponding author.

E-mail address: lrl-4618155@163.com (R. Li).

early stage of precipitate in the radiation-induced aging process, is also characterised [10]. Recently, Miyazawa et al. [11] also reported that Y addition also enhanced the formation of precipitates in V–4Cr–4Ti alloy, which can improve the high temperature strength of V alloys. Considering the composition, it seems that the precipitate formation is mainly induced by bonding behavior of impurity O and solute Ti. In fact, the player of key factor to the forming process is the defect of vacancy (Vac) and its interaction with O atoms. Since vacancy is an effective tool to trap impurities [12] and stabilize the nanoclusters [13,14].

Recently, atomistic simulations gave significant insights into the behavior of interstitial O in V alloys. Several studies have addressed some of the relevant issues, including site preference [15,16], binding with solutes [17], diffusion barriers and effect on the mechanical properties of bulk [18] or grain boundary [19]. Recently, by using first-principles calculations, Li et al. [15] investigated energetic and diffusion of O, N and C impurities as well as O–O interactions in pure V. In our previous works [17], the solute-impurity interactions are systematically studied by performing density-functional theory (DFT) calculations. After digesting the results, we concluded that vacancy is one of the main reasons for the enhanced formation of precipitates/nanoclusters in V–4Cr–4Ti. Besides, much efforts [18] have been devoted to explore the effects of interstitial impurities on the mechanical properties of V alloy. The results show that C, O and N impurities not only strengthen the V alloys but also reduce their plasticity. However, these studies did not involve the interactions between interstitial impurities and vacancy deeply which is of vital importance to understand the formation process of precipitation, fine particles and phase transforming. The present work is motivated by the dearth of first-principles study of O diffusion and interaction with vacancy in V alloys. Then the calculated results and the formation mechanism of the precipitates in the V alloys are discussed.

2. Methodology

All the energies mentioned above are computed within the Vienna Ab Initio Simulation Package (VASP) [20,21] with the projector augmented wave (PAW) method [22,23] and generalized gradient approximation Perdew–Burke–Ernzerhof functional (GGA-PBE) [24]. The computations perform within a 128-atom periodic simulation cell to calculate the defects binding energies and using 54-atom periodic simulation cell to study the migration barriers for O impurity. The binding energies are obtained with 500 eV plane-wave cutoff and $5 \times 5 \times 5$ ($9 \times 9 \times 9$) k-point meshes for 128-atom (54-atom) system. Once the Hellmann–Feynman force acting on atoms is less than 0.02 eV/Å, the atoms are regard as being fully relaxed. The climbing-image nudged elastic band (CI-NEB) [25] method is used to estimate the migration barriers and determine the transition state. The required force convergence for all atoms on the CI-NEB technique is set to 0.03 eV/Å. The present equilibrium lattice constant a_0 for bulk V is 2.99 Å, which is consistent with theoretical results [16,26] and the experimental value of 3.03 Å [27]. The supercell approach [28,29] is used to calculate the phonon frequencies. The displacement of 0.05 Å around the equilibrium position of each atom in the supercell is applied, and the calculated forces acting on each atom are fitted to obtain the force constants.

In the crystal, the equilibrium concentration of vacancy defect in BCC V is normally evaluate through [30].

$$C(T) = \exp\left(\frac{-\Delta G}{k_B T}\right) \quad (1)$$

where ΔG is the Gibbs free energy. Without account for the

anharmonic effects, ΔG is defined as

$$\Delta G = H_f + T\Delta S_{el} + T\Delta S_{vib} \quad (2)$$

here H_f is the enthalpy of vacancy formation, ΔS_{el} and ΔS_{vib} are the electronic and phononic contributions to the entropy of vacancy formation, respectively. It is noteworthy that, Hu et al. [30] systematically studied the solubility behaviors of Boron, Carbon, and Nitrogen in the transition metals, and they found that the electronic entropy is seen to be negligible in all cases except for Pd and Pt, due to their exceptionally high density of states near the Fermi level. Even for transition metal Pd, the value of electronic entropy ΔS_{el} is 0.3eV, which contributes to the free energy is limited, and this temperature dependence term is negligible.

The binding energy E_{bind}^{A-B} between two point defects (A, B) in the supercell is calculated by Ref. [31]:

$$E_{bind}^{A-B} = E_{tot}^A + E_{tot}^B - E_{tot}^{A-B} - E_{tot}^{bulk} \quad (3)$$

where E_{tot}^A , E_{tot}^B , and E_{tot}^{A+B} stand for the total energies of the supercell contained defect A, B, and both two defects with the distinct nearest-neighbor (NN) distance, respectively. E_{tot}^{bulk} is the total energy of perfect V bulk. In Eq. (3), letter A or B can represent impurity atom or vacancy. The binding energies of multiple O atoms and vacancies cluster are consider using the following equation:

$$E_{bind}^{A_m B_n} = mE_{tot}^A + nE_{tot}^B - E_{tot}^{A_m B_n} - E_{tot}^{bulk} \quad (4)$$

where the n and m stand for the number of O atom and vacancy, and $E_{tot}^{A_m B_n}$ is the total energy of defect cluster $Vac_m O_n$.

Diffusion of interstitial atoms in solid solutions can be described as random jumps between interstitial positions. The diffusion coefficient can be written as [32]:

$$D = \frac{1}{6} n \lambda^2 \Gamma \quad (5)$$

where n is the number of the NN interstitial positions, λ is the jump length, and Γ represents the jump rate. For the present octahedral O diffusion in BCC V, $n = 4$ and $\lambda = a_0/2$ with a_0 being the lattice constant [33]. Based on Eyring theory [34], the jump rate can also be written as:

$$\Gamma = \frac{kT}{h} \frac{Z_{TS}}{Z_{IS}} \exp\left(-\frac{\Delta E}{kT}\right) \quad (6)$$

where Z_{TS} and Z_{IS} are partition functions for the transition state (TS) and the ground state of the initial state (IS), respectively, k the Boltzman constant, T the temperature, and h the Planck constant. ΔE is the energy difference between the TS and the IS, corresponding to the migration energy barrier which can be determined by CINEB. With the framework of the harmonic approximation at high temperatures, the jump rate can be expressed as [35]:

$$\Gamma = \frac{\prod_{i=1}^{3N-3} v_i^{IS}}{\prod_{i=1}^{3N-4} v_i^{TS}} \exp\left(-\frac{\Delta E}{kT}\right) \quad (7)$$

where v_i is the real normal modes of vibration. N is the number of the vibrating atoms. It is noteworthy that the diffusion coefficient usually meet the Arrhenius equation:

$$D = D_0 \exp\left(-\frac{Q}{kT}\right) \quad (8)$$

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