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Helium–vacancy interactions in vanadium and tantalum

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ABSTRACT

In this paper we investigate the energy landscape of vacancy clusters in the presence of Helium in two materials, Vanadium and Tantalum. In order to address the relative stability of small vacancy-Helium clusters as well as the basic migration mechanisms we have used Density Functional Theory. The results of calculations are compared to experimental results, when available, and can be systematized in potentially simple laws that can be easily used subsequently in multi-scale techniques including kinetic Monte Carlo and cluster dynamics simulations.

1. Introduction

The main materials of interest for fission and fusion application are the body centered cubic (bcc) metals [1,2]. Irradiation of bcc transition metals leads to a large number of point defects in the form of self-interstitial atoms and vacancies. The interactions and migrations of defects as well as their absorption at sinks, like dislocations and grain boundaries, can influence microstructural transformations in material which can affect various properties of the metals. Experimental and theoretical studies [3] have shown that the body centered cubic lattice demonstrates improved radiation resistance compared to the close-packed face centered cubic lattice due to reduced amount of vacancy and interstitial defect clustering that occurs directly within displacement cascades as well as higher stacking fault energy. In this paper we will focus on the vacancy clusters and their interactions with Helium atoms in two materials which are good candidates for future fusion systems, V and Ta [4].

V and its alloys are promising candidates as blanket for fusion reactor thanks to their mechanical properties at high temperature and low activation [5,6]. V alloys demonstrate a good combination of strength, ductility and radiation resistance [4,5]. Ta is known for its easy manufacturing, high toughness, high-sputtering threshold energy, and low activation properties which make it a candidate for target material for spallation sources or even first wall material in fusion reactors [7,8]. As such, study of defects in those two materials, V and Ta serve as the basic foundation for future research regarding structural materials in the fusion industry.

Under irradiation, the structural materials are subject to damages such as swelling [9], embrittlement [10] and blistering [11] triggered, enhanced or suppressed [12] by He resulting of (n, α) transmutation reactions. He atoms are usually trapped at grain boundaries, dislocations or voids [13,14]. The early stages of formation of He bubbles in metals cannot be observed experimentally due to the limited spatial resolution. *Ab initio* calculations based on Density Functional Theory (DFT) are powerful tools to investigate the processes taking place at the beginning of nucleation of such objects. DFT calculations provide quantitative insight into the nature of clusters containing a small number of defects. About V relevant studies can only be found in the last years while data concerning Ta remains scarce. Hua et al. [15] went to the conclusion that alloying V with Ti enhances migration energy of He and diminishes He-vacancy binding energy. Zhang et al. [16] studied the interaction of He with monovacancy and SIA in pure V and V alloys. They showed that in V alloys, the formation and migration energies of He are larger than in pure V. The same group investigated stability of small He-vacancy clusters and migration of monovacancy. It was found that interstitial He clusters are weakly bound and need vacancy to be stable [17]. The formation of He and vacancy at grain boundary in V has been investigated in Ref. [18]. He-He and He-metal interactions have been studied in various bcc transition metals [19]. Energetics of interstitial He in several metals of *V* group and *VI* group have been detailed in Ref. [20]. Up to

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now, however, only a limited number of configurations has been studied. In this study we focus on He-vacancy type clusters in pure V and Ta, in particular we are interested in the first steps of nascent bubbles. To this end, we detail the formation and migration not only of He and monovacancy but also di-vacancies that have been proved to play a significant role in diffusion processes in Fe [21]. In the above-mentioned works, a small amount of clusters have been studied. Attempting to get the most stable clusters, we explore systematically several configurations of each He-vacancy cluster type.

This paper is organized as follows: Section 2 provides the methodology and the details of the employed techniques used for the calculations. In Section 3.1 we present the formation energies computed for vacancy and He-vacancy type clusters. In Section 3.2 the stability of He-vacancy type clusters is investigated. Finally, Section 3.3 describes the migration processes and barriers of vacancy clusters and how helium modifies the diffusion mechanisms.

2. Computational details

Ab initio calculations were performed with density functional theory (DFT) as implemented in the Vienna *Ab initio* Simulation Package (VASP) [22,23]. We employed non spin-polarised calculations with the generalised gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) [24] exchange–correlation functional, and semi-core projector-augmented wave (PAW) [25,26] as pseudo-potentials. According to Ref. [19], Van der Waals interactions (∼20 meV) can be neglected with respect to He-He and He-metal interactions. Up to 3 vacancies, the bcc supercell of 128 atoms with a $4 \times 4 \times 4$ k-points mesh grid generated by Monkhorst–Pack scheme [27] was used; for more than 3 vacancies we have used a 250 atoms supercell with a $3 \times 3 \times 3$ k-points mesh grid. The Methfessel-Paxton smearing [28] with a 0.25 eV width was used and a 350 eV cutoff energy for both V and Ta case. Atomic positions were relaxed at constant volume until forces on each atom were less than 0.01 eV/Å. The migration barriers and paths were determined using the climbing image nudged elastic band method (CI–NEB) [29,30] with 5 eV/Å^2 spring constant and a 0.01 eV/Å force convergence threshold. In addition, the converged energy it was corrected by subtracting the elastic dipole interaction energy between self-images due to periodic boundary conditions. We applied the procedure from [31]. In that paper, the elastic dipole-dipole correction is computed from the value of elastic dipole of the defects, which, in first approximation, is proportional to the stress of the simulation box. In order to have reliable value of the elastic dipole, from the stress of the simulation box containing the defect we have extracted the residual stress of the bulk reference. The magnitude of corrections are always smaller than 0.15 eV.

The equilibrium bcc lattice constant obtained for V and Ta was 3.00 Å and 3.32 Å, respectively. Those values are close to experimental data 3.03 Å for V and 3.30 Å for Ta [32].

3. Results

3.1. Formation energy of He_nV_m clusters

The energetics of isolated He in interstitial configurations as well as the vacancy and vacancy-helium clusters inserted in the bcc matrix of V and Ta are investigated.

The formation energy of the simulation box containing n He atoms inserted into the bcc matrix is given by:

$$E^f_{He_n} = E_{He_n} - E_0 - n \times E_{He}, \quad (1)$$

E_{He_n} is the DFT energy of the supercell containing n interstitials He, E_0 is the energy of the perfect bulk supercell and, finally, E_{He} is the energy of an isolated He atom. E_{He} (0.014 eV) has been computed with single He atom in a 10 Å × 10 Å × 10 Å box, a 400 eV cutoff energy and a pseudo-potential with $1s^2$ electronic structure. Firstly, we carefully checked the case $n = 1$ of only one He atom in the bcc matrix. Lately, we will discuss the case $n > 1$. In V the formation energies for interstitial configurations are 3.12 eV and 3.34 eV for tetrahedral (T) and octahedral sites (O), respectively. In Ta the same relative stability is found, the interstitial tetrahedral configuration having a formation energy of 3.47 eV, with 0.32 eV lower than interstitial octahedral configuration. For both metals, V and Ta, we found the similar hierarchy in the energy of interstitial configurations, the T interstitial site is more stable than the O site, as in other bcc transition metals, such as Fe [33], W and Nb [20].

In both metals, V and Ta, we have studied also the relative stability of vacancy clusters (V_m) up to quadri-vacancy ($m = 4$). Again we have used as indicator the zero K formation energy of clusters. The formation energy of the m vacancy cluster, V_m, is defined by:

$$E^f_{V_m} = E_{V_m} - \frac{(N-m)}{N} \times E_0, \quad (2)$$

with N the number of atoms of the perfect bcc lattice and E_{V_m} the DFT energy of the supercell containing m vacancies agglomerated in a cluster. Among many investigated configurations the lowest energy cluster, for the cases $m = 2, 3, 4$, is found to be the more compact clusters, which are reported in Fig. 1. The formation energies of mono-vacancy (Table 1) are in good agreement with experiments for both V (2.47 eV) [34,35] and Ta (2.88 eV) [34,36,37]. We point here the exception of the di-vacancy cluster. In Ta and V we find that the energy of 2nd nearest neighbour configuration (hereafter noted V_2^{2nn}) is lower than the energy of 1st nearest neighbour configuration (hereafter denoted V_2^{1nn}). The formation energy of V_2^{2nn} is lower than the formation energy of the configuration V_2^{1nn} by 0.19 eV and 0.24 eV in V and Ta, respectively (Table 1). The same tendency is observed for all *VIB* group and *VB* group metals and iron for which the most stable configuration of di-vacancy is the V_2^{2nn}. In V and Ta, the binding energy of di-vacancy, in both configurations, V_2^{1nn} and V_2^{2nn}, is positive, indicating the attraction between mono-vacancies in order to form the di-vacancy. The same tendency for the di-vacancy energy landscape is observed in iron and

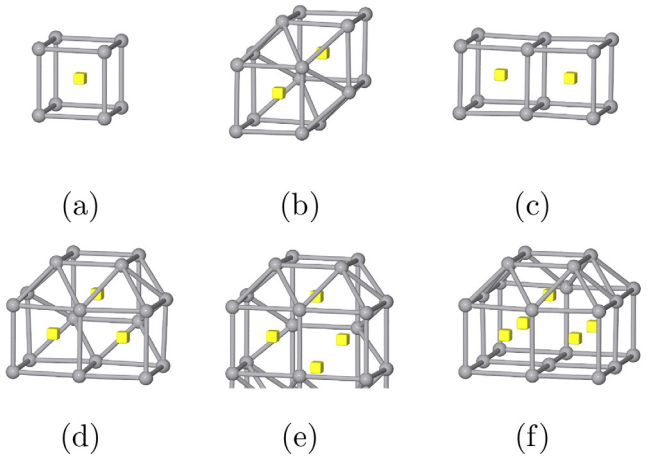

Fig. 1. The configurations of vacancy clusters ($V_m, m = 1, 2, 3, 4, 5$) with the lowest formation energy. Vacancies are represented by cubes while the atoms of the bcc lattice are represented with spheres. For the case of di-vacancy we show the first nearest neighbour $\left(V_2^{1nn}\right)$ and the second nearest neighbour configuration V_2^{2nn}: (a) V_1, (b) V_2^{1nn}, (c) V_2^{2nn}, (d) V_3, (e) V_4, (f) V_5.