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First principles study of helium trapping by solute elements in tungsten

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ABSTRACT

The behavior of helium in metals is particularly important in fusion research due to the He induced degradation of materials. A small amount of impurities introduced by alloying or transmutation reactions will interact with He and lead the microstructure and mechanical properties of materials to change. In this paper, we present the results of first-principles calculations on the interactions of He with impurities in tungsten (W), including the interstitials C, N, O, and substitutional 3d, 4d and 5d transition metals. We find that the trapping radii of interstitial atoms for He are almost twice larger than those of substitutional solutes. A preliminary evaluation of the effective trapping of He is also given when considering the detrapping of He at high temperature. The binding energies between the substitutional impurities and He increase linearly with the relative charge densities at the He occupation site, implying that He atoms easily aggregate at low charge density sites. The present results suggest that Ta might be chosen as a relatively suitable alloying element compared to other possible choices.

1. Introduction

Tungsten (W) and W alloys are most promising for use as the divertor material in the International Thermonuclear Experimental Reactor (ITER) and in future fusion reactors due to their high melting point, good thermal conductivity, low tritium inventory, and low sputtering rate [1,2]. In ITER and future fusion devices, the surface of W will be exposed to extremely large fluxes of hydrogen and helium, and special surface structures can form on the W surface by impact of low energy hydrogen and helium, which may influence the surface stability [3]. Experimental results show that exposure of W to He leads to blisters and bubbles confined to a depth of more than 140 nm [3–5]. Moreover, it was found that He irradiation generates a fuzzy structure on the surface, which consists of a very porous W network and is mechanically unstable [3,6]. Understanding these macroscopic effects requires detailed knowledge of the processes controlling microstructural evolution, such as the He atom configuration in the W lattice, diffusion of He atoms, their trapping and dissociation from other defects, as well as bubble nucleation and growth [7,8].

In addition, the practical use of W is hindered by its high ductile–brittle transition temperature (DBTT) and consequently high brittleness at the operation temperature. It has been proposed that the ductility of W can be improved by the addition of certain alloying elements such as Re, Ta, Tc, Os, Ru, Ti and V [9–11]. Transmutation reactions during neutron irradiation also generates some new elements such as Re, Os, Ta [10,12]. These impurities will inevitably interact with the emitted He from neutron-induced reactions, consequently leading the change of microstructure and mechanical properties of materials [13]. Therefore, it is necessary to clarify the interactions of impurities with He in W. Previous results showed that the substitutional impurities such as Ag and Cu and inert gas atoms are capable of trapping He atoms in W [14]. Recently, Becquart et al. have investigated the binding energies of a series of impurities with He and He clusters, and found that most of the substitutional impurities can trap He atoms as well as small He clusters except for Re [15,16]. These investigations have certainly advanced our understanding of helium trapping by solutes in W, but as the authors of Ref. [16] pointed out the relationship between the binding energies of impurities with He and the electron densities is not clear and requires further investigations.

The results of our earlier studies by first-principles suggest that there is a linear relation between the binding energies and the relative charge densities at the He occupation site for some common alloying and transmutation impurities in W such as Re, Ta, Os and Ti [17]. The diffusion behaviors of He around these impurities were also studied. However, it should be further confirmed if the relationship between binding energies and electron densities

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exists for more alloying elements in W. Another purpose of this study is to present a quantitative comparison of the trapping radii of interstitial atoms and substitutional solutes for He. In this paper, we carry out a systematic first-principles calculation to quantify the binding energies and the trapping radii of He around impurities in W. These impurities include interstitial C, N and O atoms and substitutional 3d, 4d and 5d transition-metal (TM) solutes, which are chosen to construct an extensive first-principles database of He-solute binding and gain insight into fundamental and general trends. We believe the general conclusion of He behavior in W are also applicable to other metals.

2. Computation method

The present calculations are performed within density functional theory as implemented in the Vienna Ab-initio Simulation Package (VASP) [18,19]. The interaction between ions and electrons is described by the projector augmented wave potential (PAW) method [20]. Exchange and correlation functions are taken in a form proposed by Perdew and Wang within the generalized gradient approximation (GGA) [21,22]. The supercell composed of 128 lattice points ($4 \times 4 \times 4$) is used. The plane wave cutoff and k-point density are both checked for convergence for each system to be within 0.001 eV per atom. Following a series of test calculations a plane wave cutoff of 500 eV is used and a k-point grid density of $3 \times 3 \times 3$ is employed. The structural optimization is truncated when the forces converge to less than 0.01 eV Å^{-1}. In order to accurately account for the dilation effects of He in the W lattice [23], the supercell shape and volume are allowed to fully relax in our calculations. It should be noted that the constant volume relaxation is also found acceptable to describe helium trapping by solutes in W by Becquart et al. [16,24], because these two different strategies to relax the system will approach the same value when the system is large enough to reach the asymptotic behavior [24,25]. To test the validity of the size of supercell, a larger supercell containing 250 atoms ($5 \times 5 \times 5$) with $2 \times 2 \times 2$ k-points is calculated for comparison. The binding energies between He and the impurities such as vacancy, N, O and V are nearly the same to those by using the $4 \times 4 \times 4$ supercell, which means that the 128 atom supercell is big enough for this investigation.

The binding energy of two defects (A_1, A_2) is calculated as follows:

$$E_b^{A_1-A_2} = E_{tot}^{A_1} + E_{tot}^{A_2} - E_{tot}^{A_1+A_2} - E_{tot}^{bulk},$$

where $E_{tot}^{A_1}$ and $E_{tot}^{A_2}$ are total energies of the supercell with A_1 and A_2, respectively, $E_{tot}^{A_1+A_2}$ is total energy of the supercell containing both A_1 and A_2, and E_{tot}^{bulk} is total energy of perfect W bulk in supercell.

3. Results

The site preference of impurities in bulk W is considered first before studying their influence on trapping He. We examine the substitutional site and two interstitial sites of the W lattice, i.e., tetrahedral (t) and octahedral (o) site. The calculations of W with impurities at different sites show that transition elements prefer substitutional sites, and small elements C and N favor to occupy the o-site, while He and O prefer the t-site. These results are in good agreement with previous theoretical results [23,26]. Further calculations show that these individual equilibrium sites do not change when impurities and He form a stable pair. In order to determine the lowest energy configurations of a solute-He pair, a number of possible configurations are investigated, which are as follows: a solute is first placed on its most stable interstitial/substitutional site and then a He atom is placed on the tetrahedral/octahedral site surrounding the solute. The obtained binding energies between the solutes and He as a function of their separation distances are shown in Fig. 1. For all the solutes considered, the binding energies are positive within a certain separation distance, implying that there exists an attractive interaction between the solutes and He. Such attraction may lead to the accumulation of He around impurities and an increase of the local He concentration. It should be noted that the binding energies between the interstitial C/N/O atom and He have different values at the same distance due to their different arrangements, as shown in Fig. 1a. The most stable solute-He pair separation distance is about 2.1 Å for the interstitial C, N or O atom. The distances (r_t) within which He spontaneously migrates to the most stable position are 3.9 Å for O and 3.3 Å for C/N. The trapping radius is the distance beyond which the attraction of He towards impurities is considered negligible. From the stable separation distance, the positive binding energies between the solutes and He decrease with increasing separation distance and ultimately decrease to almost zero at a certain distance (~9 Å). The small negative binding energies at larger distances indicate that there is no attractive interactions between the interstitial atoms and He. So the trapping radius of interstitial atoms on He is ~9 Å. For the substitutional atoms shown in Fig. 1b, the trapping radius is ~5 Å because the positive binding energies decrease to zero when the separation distance of the solute-He pair reaches ~5 Å. There is an exception for Re, where the binding energy is always low at about 0.01 eV. The binding energies of

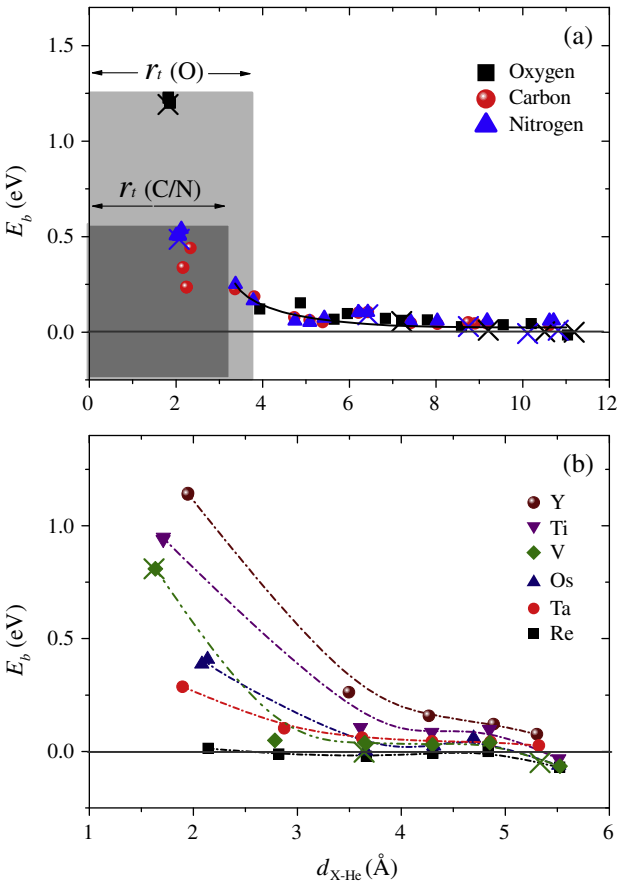

Fig. 1. Variation in the binding energy of (a) the interstitial C, N and O and (b) the substitutional Y, Ti, V, Os, Ta and Re with He as a function of the separation distance between He and the solutes. r_t is the distance within which He spontaneously migrates to its most stable position around the solutes without any energy barrier. The symbol (×) represents the calculation results using 250 atom supercell and others represent the results using 128 atom supercell.