Migration Energy of He in W Revisited by *Ab Initio* Calculations

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We use state of the art *ab initio* calculations to obtain the diffusion properties of He in tungsten. The calculated migration energy of He is very low, around 0.06 eV. This value is much lower than the experimental field-ion microscopy results which lead to a migration energy of the order of 0.24—0.32 eV. The reason for this discrepancy is the high propensity for He to form He-He clusters characterized by a very large binding energy of the order of 1 eV. Such a large binding energy indicates that He atoms can be trapped by other He atoms and can explain the formation of He blisters close to the surface of He implanted tungsten.

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During its lifetime the divertor plate will be subject to high flux, steady state hydrogen isotopes as well as helium plasma bombardment. Meanwhile, transmutation reactions can also induce the buildup of an appreciable concentration of H and He. Much attention has been paid and is still devoted to the study of the behavior of helium in metals. In particular, its migration properties are of fundamental as well as of practical interest as they eventually will influence physical and mechanical properties, the most significant example being the high-temperature helium embrittlement. Theoretical and experimental results indicate that helium is mobile already below room temperature. The basic experimental problem in the study of He in metals is its essential negligible solid solubility. He is virtually insoluble in metals; however, if introduced by implantation at high energies and doses is trapped, forming platelets and bubbles. He implantation is thus a mean to investigate the properties of He in metals. The properties of He are subsequently studied by, for example, thermal helium desorption spectroscopy (THDS) [1] or channeling [2]. Another mean of studying the properties of He in tungsten is the use of atomistic simulations. There exist a few interatomic potentials able to model the interactions between tungsten and helium atoms. Wilson and Johnson [3] obtained a W-He potential by an approximate quantum mechanical method to study the properties of interstitial and substitutional He. This potential is limited to the study of a single He atom in a W matrix as no He-He interactions exist. Caspers and co-workers [4] have determined activation energies for the interaction of He with vacancies and vacancy clusters using the W-He and W-W potentials derived by Wilson and Johnson [3,5]. The potential given by Abrahamson [6] was used for He-He. Wilson and Bisson [7] have calculated specific helium tungsten defect configurations suggested by Kornelsen [8] to result from ion implantation following irradiation. They also used the W-He and W-W potentials derived by Johnson and Wilson [5] but the He-He was developed by Beck [9]. Much more recently, Henriksson and co-workers [10] derived a new potential to simulate the initial stages of blistering in He implanted tungsten. To describe the W-W interaction, they used the potential derived by Ackland and Thetford [11]; the W-He interaction was obtained from an *ab initio* potential for the W-He diatom and the He-He potential was calculated using the *ab initio* DMOL package [12].

Because of the highly important role of He in metals, we have investigated, using state of the art *ab initio* calculations, some properties related to diffusion of the He atom in tungsten. More precisely, we have determined: the most favored configuration in interstitial position, the migration energy of an He atom, and the binding energies between He atoms for different configurations.

Our calculations have been performed using the Vienna *ab initio* Simulation Package VASP [13]. They were performed in the framework of Blöchl's projector augmented-wave (PAW) method [14,15] within the generalized gradient approximation (GGA) of Perdew and Wang [16]. The pseudopotentials were taken from the VASP library. The supercell approach with periodic boundary conditions was used to simulate point defects as well as pure phases. Brillouin zone sampling was performed using the Monkhorst and Pack scheme [17]. The plane wave cutoff energy was 350 eV. The error induced by this lower cutoff energy was checked to be negligible. The equilibrium lattice parameter obtained was 3.1741 Å. All the calculations were done at constant volume fully relaxing the atomic positions in the supercells.

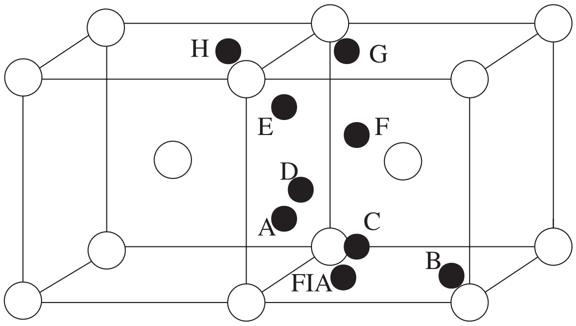

FIG. 1. Labeling of the He-He positions. The first He atom is situated in the site labeled FIA.

The formation energies were calculated as follows:

$$\Delta H_f = E(NW + \mathrm{He}) - NE(W) - E(\mathrm{He}_{\mathrm{isolated}}), \qquad (1)$$

when the He atom is in substitutional or interstitial position, where $E(W)$ is the reference energy of bulk bcc W, $E(NW + \mathrm{He})$ the energy of the supercell containing N W atoms and 1 He atom, and $E(\mathrm{He}_{\mathrm{isolated}})$ the energy of the He atom isolated (a single He in a large supercell).

The binding energy between two He atoms was determined for different configurations. For a supercell containing N atoms, the binding energy is obtained as:

$$E_b(A_1, A_2) = [E(A_1) + E(A_2)] - [E(A_1 + A_2) + E_{\mathrm{ref}}], \qquad (2)$$

where E_{ref} is the energy of the supercell without A_1 and A_2, $E(A_1)$ [respectively $E(A_2)$] is the energy of the supercell with A_1 (respectively A_2), $E(A_1 + A_2)$ is the energy of the cell containing both A_1 and A_2 interacting. All the supercells contain the same number of sites, i.e., have the same size.

With such a scheme a positive binding energy means attraction between the entities, while a negative binding energy indicates a repulsion. The migration energy was determined by positioning the He atom in the close neighborhood of the saddle point situated on the right bisector of two first neighbor tetrahedral sites, at 0.504 lattice parameter from the octahedral site.

He atoms in a metal may occupy either substitutional or interstitial lattice sites. As interstitials, they are very mobile at room temperature, but will be trapped at lattice vacancies, impurities, and vacancy-impurity complexes [1,2,8]. We have determined the formation energies for different configurations of He in interstitial position as well as in substitution using Eq. (1). The migration energy was calculated as described above. The binding energies between two He atoms were computed using Eq. (2) for the positions described in Fig. 1. All the results are collected in Table I and II and compared with the experimental data available as well as with the data obtained with some empirical potentials.

The location of He in tungsten is of interest since it influences its solubility and migration, which in turn is important for the understanding of such effects as damage trapping, bubble nucleation, embrittlement, and blistering. Our calculations predict that the most stable configuration for He in interstitial position is the tetrahedral site, as was recently calculated in Fe [20,21]. The octahedral site is a metastable configuration, more precisely, it is a rank-2 saddle point as observed for H in Fe [22]. Indeed, if one introduces a slight perturbation when the He atom lies in the octahedral site, it changes site and goes either to a tetrahedral position or to the saddle point. The empirical potentials, as was the case for Fe [20], predict the octahedral site to be the most stable. Seletskaia and co-workers [21] explain the preferred interstitial location by an unexpected influence of magnetism on the properties of He in Fe. The introduction of He in a tetrahedral site induces less magnetic moment quenching than when He is in an octahedral position. As the empirical potentials are not well suited to reproduce correctly the influence of magnetic properties (the electrons are not explicitly taken into account in such models) it is thus not so surprising that empirical potentials fail to reproduce correctly the favored position of He intersititials in Fe. Contrary to the case of hydrogen or more precisely deuterium (D) for which all

TABLE I. Formation energies (in eV) for a single He atom positioned in the octahedral or tetrahedral interstitial sites as well as in substitution. He migration energy (in eV). The calculations were done using 54 atom supercells and 125 k points as well as 128 atom supercells and 27 k points. The reference for He is the isolated He atom.

Configuration	54 atoms	128 atoms	Experiment	Empirical potentials
Octahedral	6.40	6.38	···	7.83[a] 5.47[b]
Tetrahedral	6.18	6.16	···	5.71[b]
Substitutional	4.77	4.70	···	
Migration	0.06	0.06	^{3}He: 0.28[c]	0.29[a]
Energy			^{4}He: 0.24–0.32[d]	0.24[b]

[a] Reference [10].
[b] Reference [3].
[c] Reference [18].
[d] Reference [19].

TABLE II. He-He binding energies (eV). The calculations were done using 54 atom supercells and 125 k points as well as 128 atom supercells and 27 k points. The positions refer to Fig. 1, the first He being located at the position noted by "FIA", the second one at the letter. The final configurations are given for the 128 atom supercell calculations. *: see Fig. 2. **: see text.

Position	54 atoms	128 atoms	He-He initial distance	He-He final distance	Final configuration
A	0.68	0.74	$a\sqrt{2}/4 = 0.354a$	1.44 Å	A
B	0.87	0.94	$a/2 = 0.5a$	1.49 Å	B
C	0.98	1.01	$a\sqrt{6}/4 = 0.612a$	1.51 Å	C
D	0.29	0.31	$a\sqrt{2}/2 = 0.707a$	1.64 Å	D
E	0.96	1.03	$a\sqrt{10}/4 = 0.791a$	1.50 Å	*
F	0.43	0.99	$a\sqrt{14}/4 = 0.935a$	1.48 Å	**
G	−0.06	−0.04	a	3.17 Å	G
H	0.98	1.03	$a\sqrt{5}/2 = 1.113a$	1.50 Å	*

experiments indicate that D occupies the tetrahedral site [23–25], no experimental data is available for the lattice location of He in tungsten despite careful studies such as the ones of Picraux and co-workers [2]. This, according to Picraux [2], is due to the strong tendency for multiple helium trapping at defect centers presumed to be vacancies. The results of our calculations indicate also, as will be shown in what follows, that another possible reason is the formation of He-He clusters.

The migration energy was found to be very low, around 0.06 eV. This seems to be in contradiction with the experimental data available [18,19]. However, Soltan and coworkers [26] in a careful study of H, D, and He implantation at 5 K with energies from 0.25 to 3 keV into thin films of 80–320 nm of Au and W, followed by isochronally heating of the specimens up to 400 K, demonstrated that concentrations as low as 350 ppm of He suppressed He migration because of the clustering of this element. They calculated that in the experiments of Wagner *et al.* [19] as well as that of Amano [18], the concentration of implanted He was 5%. They thus explain why in their own experiments, He becomes mobile at temperatures below 6 K, in contradiction to the previous results [18,19] where mobility of ^{3}He and ^{4}He was observed only above 90 K. Furthermore, the results of Soltan *et al.* [26] are supported by the large binding energy (close to 1 eV) found between two He atoms in interstitial position (Table II). When exploring the different configurations involving tetrahedral sites situated at different distances, it appears that in many configurations, the atoms relax quite a lot, tending to reduce the distance between the two He atoms. Configuration C is a typical example. For configuration F, the 54 atom supercell calculation relaxed in a configuration where both He atoms are situated close to saddle point for the migration. For the 128 atom supercell calculation, the He atoms relax a lot and are situated far away from tetrahedral sites. Configurations E and H relax towards the same and most bound configuration represented in Fig. 2. Such a large binding energy indicates that clustering of two single He atoms is very probable and that the clusters will be very stable.

This tendency to form He clusters is confirmed by the large total binding energies obtained for clusters of size up to five as can be seen in Table III.

This large binding energy also explains why experiments show that even at temperatures where the migration of He is larger than for H (at 500 K, for example), He will form bubbles right below the surface, i.e., as soon as it will encounter another He atom, at depths 100 Å [27,28], while H clusters are formed at micrometer depths [29]. These results indicate also that similarly to what has been observed in Ni [30] and Au [31], He can be trapped without any prior damage, i.e., defects, in agreement with the experiments of Nicholson and co-workers [27] who used an ultrahigh vacuum field-ion microscope to bombard tungsten with 200 eV He atoms. Despite the fact that the energy transferred in such bombardment was below the threshold displacement energy, they observed small voids and dislocations, even though no damage, i.e., no vacancies were created during the implantation. Our results can also explain why as observed by Yoshida and co-workers [28],

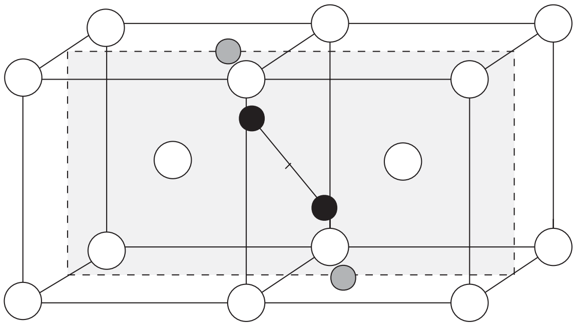

FIG. 2. Final configuration for initial positions E and H. The initial positions of configuration H are represented by gray spheres, the final ones by black spheres. During the relaxation, both He atoms remain in the same plane, represented in light gray in the figure. The white spheres are the W atoms.

TABLE III. He cluster binding energies (eV). The calculations were done using 54 atom supercells and 125 k points as well as 128 atom supercells and 27 k points.

Cluster size	54 atoms	128 atoms
He_2	0.98	1.03
He_3	2.35	2.39
He_4	4.07	3.90
He_5	5.31	5.54

the distribution of interstitial loops of He observed after the implantation of He with energy less than 5 keV coincides with the He atom distribution, whereas in the case of the implantation of H, the distribution of interstitial loops coincides with the damage distribution.

As for the empirical potentials, Wilson and Johnson [3] determine the migration energy by taking the energy difference between the octahedral position and the tetrahedral position (as is the case for instance for carbon in bcc Fe [32]). In our calculations this energy difference equals 0.22 eV which is in very good agreement with the value obtained by Wilson. However, this is not the migration energy, as the lowest energy path to go from one tetrahedral site to another does not pass through the octahedral site.

To summarize, we have determined some elementary properties of He in tungsten by *ab initio*. The most stable configuration for He in interstitial configuration is the tetrahedral site. The calculated migration energy of He is very low, around 0.06 eV. This value is much lower than the experimental results. The discrepancy between the experimental results and our *ab initio* results can be explained by the large binding energy which exists between He atoms. Because of this binding energy He atoms tend to form clusters very easily and to obtain the migration energy of one single He atom, one must implant only a very reduced amount of He atom. Such a large binding energy can also explain the formation of He blisters close to the surface of He implanted tungsten. Furthermore, it is well known that He is easily trapped at lattice vacancies, impurities, and vacancy-impurity complexes. Our results indicate that He can be also easily trapped by other He atoms, i.e., without prior damage. This tendency of He to form clusters can thus explain the lack of experimental results on the lattice location of He in tungsten, by, similarly to the case of He migration energy, the difficulty of having single He atoms in the W matrix.

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