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# First-principles investigation of grain boundary morphology effects on helium solutions in tungsten

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ABSTRACT

Helium solutions at eight symmetric tilt grain boundaries (GBs) in tungsten (W) have been investigated through first-principles calculations. The GBs are constructed by the coincidence site lattice (CSL) model and all interstitial sites at GBs are identified with convex deltahedra. For each GB, helium atom prefers to dissolve in interstitial sites with the lowest charge density. Interactions between the helium atom and the GBs atoms are rather localized for all eight GBs studied here, and the helium solution explicitly relates to the local environment of the interstitial site. It is found out that the helium solution energies decrease as the Voronoi volumes of interstitial sites increase, and they can be quantitatively determined by helium solution energy in tungsten clusters $W_n$. Based on this quantitative relationship, it is easy to estimate the helium solution energy in various interstitial sites in tungsten without massive first-principles calculations. Our result provides a sound theoretical guide to design favorite grain boundaries to suppress helium segregations at GBs.



## 1. Introduction

Macroscopic radiation damage effects of materials served in nuclear devices are consequences of two types of interactions between projectile particles and atoms included in the irradiated materials, that is, atomic displacements which will result in lattice defects vacancies and self-interstitials, and nuclear reactions which can create foreign elements [1,2]. The creation of helium atoms in metals has caused wide concerns since helium atoms tend to assemble in vacancies, dislocations and GBs, and form helium bubbles [3–6], which can significantly degrade the mechanical properties of metals [7–10]. One well-known example is the high-temperature helium embrittlement, which is the drastic embrittlement of metals at temperatures above 0.5 $T_m$ ($T_m$: melting temperature) due to helium bubbles formation at GBs, even at extremely low overall helium concentration [1,8–11]. To enhance the helium embrittlement resistance of metals, it is necessary to study solutions and segregations of helium atoms at GBs first.

It has been experimentally demonstrated that the segregation of helium atom at GBs is sensitive to morphology of GBs. N. Sakaguchi et al. recently observed that helium atoms tended to aggregate at random GBs rather than Σ3 twin boundary in austenitic stainless steel under high-temperature annealing [12]. This result suggests that it is possible to enhance the helium embrittlement resistance of materials by increasing the fraction of certain kinds of GBs which are resistant to aggregation of helium atoms through GB engineering. To provide a rational guidance for the GB engineering, it is of fundamental importance to explore the relationship between the solutions and segregations of helium atom at GBs and the characteristics of GBs.

Tungsten is one of the promising candidates for plasma facing materials (PFMs), such as the first wall materials and divertor of the magnetic confinement fusion reactor due to its high melting temperature, high thermal conductivity and low sputtering erosion. The PFMs will be exposed to a high flux of hydrogen and helium atoms [13]. Combining experimental results and density functional theory data, Gonzalez et al. studied trapping and mobility of hydrogen in nanostructured tungsten grain boundaries and their results showed that a non-coherent W(1 1 0)/W(1 1 2) interface is favorable of hydrogen retention [14]. A first-principles calculation by Zhou et al. indicated that helium may segregate in ∑5(3 1 0)[0 0 1] GB in tungsten [15]. And a large number of helium bubbles have been experimentally observed at GB in irradiated tungsten samples [16]. However, there is a lack of

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**Table 1**
Sizes, number of atoms, GB energies γ as well as k-meshes used in calculations for the eight symmetric tilt GBs.

| GB systems | Number of atoms | k-mesh | $L_a$(Å) | $L_b$(Å) | $L_c$(Å) | γ (J/m$^2$) This work (Ref.[a]) |
|---|---|---|---|---|---|---|
| ∑3(1 1 0)[1 1 1] | 144 | 1 * 3 * 3 | 31.55 | 9.01 | 8.25 | 0.65 (0.70) |
| ∑3(1 1 1)[1 1 0] | 120 | 1 * 5 * 3 | 28.54 | 7.76 | 8.97 | 2.28 (2.29) |
| ∑5(3 1 0)[0 0 1] | 160 | 1 * 3 * 5 | 41.11 | 10.05 | 6.36 | 2.22 (2.23) |
| ∑5(2 1 0)[0 0 1] | 152 | 1 * 3 * 5 | 27.86 | 14.17 | 6.35 | 2.64 |
| ∑9(1 1 4)[1 1 0] | 136 | 1 * 3 * 3 | 26.34 | 9.55 | 8.95 | 2.35 |
| ∑17(4 1 0)[0 0 1] | 128 | 1 * 3 * 5 | 25.52 | 13.07 | 6.35 | 2.42 |
| ∑11(3 3 2)[1 1 0] | 168 | 1 * 3 * 3 | 29.10 | 10.53 | 9.03 | 2.27 |
| ∑19(1 1 6)[1 1 0] | 148 | 1 * 3 * 3 | 39.19 | 6.93 | 9.00 | 2.75 |

[a] Ref [28].

comparative and systematic study of helium solutions and aggregations at different GBs.

The aim of this paper is to systematically study the solution of helium atoms at GBs in tungsten. Eight symmetric tilt GBs constructed by the coincidence site lattice (CSL) model [17] are selected to carry out this investigation. Interstitial sites at GBs are identified by convex deltahedra. The effects of charge density on the helium solutions at GBs have been discussed, and changes in charge density of tungsten atoms induced by helium atom occupying the interstitial sites have been analyzed. The helium solution energies in different interstitial sites at the eight symmetrical tilt GBs have been computed through the first-principles total energy calculations. Our results show a quantitative relationship between the helium solution energy in interstitial site and the Voronoi volume of the interstitial site. Finally, a method to estimate the helium solution energy is proposed.

## 2. Structural models and computational details

First-principles total energy calculations [18] were carried out with the Vienna Ab initio Simulation Package (VASP) [19–21] based on the density functional theory (DFT) [22,23]. The projected augmented wave (PAW) [24] pseudopotentials were employed in the calculations within the generalized gradient approximation (GGA) with Perdew and Wang [25] functional for the exchange and correlation energies. A cutoff energy of 400 eV was used for the plane-wave expansion. The internal structural relaxations stopped when the residual force on each atom was less than 0.01 eV/Å. Both atomic positions and volumes of supercells were allowed to relax in all our calculations. The Monknorst-Pack k-mesh varied for difference systems, which are listed in Table 1. As an example, the k-mesh convergence was checked for ∑17(4 1 0)[0 0 1] GB, in which the total energy converged to be within 1 meV per atom. Periodic boundary condition was employed for all our current calculations.

By least-square-fitting total energies to the 4th Murnaghan's equation of state, the calculated equilibrium lattice parameter of the body centered cubic tungsten was 3.19 Å, which is slightly overestimated as compared to the experimental value of 3.165 Å [26]. A $4 \times 4 \times 4$ supercell (128 atoms) with calculated lattice parameter was employed to calculate the helium solution energies in tetrahedron (TET) and octahedron (OCT) interstitial sites in the bulk. To investigate the solution behavior of helium at GBs, eight low sigma number symmetric tilt GBs with [0 0 1], [1 1 0], and [1 1 1] as tilt axes were constructed with the CSL model. GB energy γ was determined by the difference between the total energy $E_{GB}$ of relaxed supercell consisting of the GB and the total energy $E_{bulk}$ of an equal number of tungsten atoms in a perfect bulk, divided by the cross sectional area $S$ on the GB plane in the supercell. There are two equal GBs in a supercell due to the periodic boundary conditions, so γ is defined as,

$$\gamma = \frac{E_{GB} - E_{bulk}}{2 * S}, \tag{1}$$

Around some GBs constructed by the CLS model the nearest atoms distance is so short that the GB energies are very high. In these cases, one of the nearest atoms was removed as these GBs were constructed. The GB energies with and without removal of one of the nearest atoms for Σ9(1 1 4)[1 1 0] GB (the nearest atoms distance is 1.50 Å in the CSL model) and Σ3(1 1 1)[1 1 0] GB (the nearest atoms distance is 1.84 Å in the CSL model) were calculated. It was found out that the GB energy was lower when one of the nearest atoms was deleted than that in which the nearest atom was not removed for the Σ9(1 1 4)[1 1 0] GB and the opposite result was obtained for the Σ3(1 1 1)[1 1 0] GB. Therefore, in our following study, one of the nearest atoms would be removed if their distance was less than 1.50 Å as the structures of the eight tilt GBs were constructed. The relaxed GB structures agree well with GB structures reported in literature [27] and are shown in Fig. 1.

The GB energy convergence to supercell size was checked. Taken GB ∑5(3 1 0)[0 0 1] as an example, GB energy difference for two supercell sizes of 21.00 Å and 41.11 Å along the direction normal to GB plane while sizes for the other two directions were kept as the same, was calculated. The difference of the GB energies was about 0.03 J/m$^2$, indicating that the size of 21.00 Å along the vertical direction was large enough to study the GB energy for GB ∑5(3 1 0)[0 0 1]. That is, the GB-GB interaction induced by the periodic boundary condition can be neglected with this large supercell size. Since the sizes for all other GBs along the vertical direction to GBs are all larger than 21.00 Å, we believe that these supercell sizes are rational and the GB energy accuracies of all these GBs are within 0.03 J/m$^2$. Calculation parameters and the resultant GB energies in this study as well as reference results are listed in Table 1.

To explore helium solutions at GBs, it is essential to identify different interstitial sites around the GBs. Based on the rigid model, it was demonstrated that the structure of any GBs could be described by packing of eight basic convex deltahedra, and the host atoms located at the vertexes of these deltahedra [29]. This approach has been applied to investigate GB related properties in materials, such as solutions and segregations of impurity elements at GBs [30,31]. There are five types of deltahedra, that is, TET, OCT, pentagonal bipyramid (PBP), cap trigonal prism (CTP), and bitetrahedron (BTE) at the eight GBs studied here. Taken GB Σ5(2 1 0)[0 0 1] as an example, these convex deltahedra are illustrated in Fig. 2. The helium solution energy $E_{He}^{S,i}$ in the i$^{th}$ interstitial site at GBs (bulk) can be calculated by,

$$E_{He}^{S,i} = E_{GB(bulk)}^{He,i} - E_{GB(bulk)}^{Perf} - E_{He}^{iso}, \tag{2}$$

where $E_{GB(bulk)}^{He,i}$ is the total energy of the supercell with a helium atom inserted into the i$^{th}$ interstitial site at a GB (bulk), $E_{GB(bulk)}^{Perf}$ is the total energy of the supercell containing clean GB (bulk), and