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Numerical Study on Hydrogen Retention at a Grain Boundary in Tungsten

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Abstract

In this thesis the hydrogen retention at a Σ3(111) regular grain boundary in tungsten and its effect on the mechanical strength are investigated based on the first principles methods. The trapping energy for hydrogen at each site is calculated to show which one is most stable. Then, we studied on hydrogen segregation at the grain boundary region by calculating the hydrogen segregation energy ΔE_{seg}. we estimate the dependence of γ_{int} on the hydrogen density. We performed a tensile test of the tungsten block under the effects of hydrogen segregation using numerical simulations and estimated the maximum tensile strength after hydrogen induced embrittlement had occurred. In addition, the same test was performed with helium.

Key words : *tungsten, hydrogen, first principle simulation, grain boundary, cohesive energy*

1. Introduction

Tungsten and its alloy are one of the plausible candidates for divertor armor tiles of International Thermonuclear Experimental Reactor (ITER) due to their low solubility for hydrogen, excellent thermal properties and low sputtering property etc. However, plasma facing materials are exposed to heat and plasma particles with very high flux for a long time. As the results, a large amount of deuterium and tritium is expected to be retained in the plasma facing materials. In particular, tritium retention over 700g in the plasma facing wall in total is strictly restricted in ITER. Besides, hydrogen and its isotope in metals are supposed to induce embrittlement. Hydrogen is expected to be trapped in vacancy-type lattice defects and on the surface of metals rather than in bulk. In the present work, we perform first principle calculations on the basis of the density functional theory [1] to investigate the mechanism of the hydrogen retention and hydrogen induced embrittlement at the coincidence grain boundary by using Vienna ab initio simulation package (VASP)[2,3].

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2. Simulation Method

We calculate trapping energy of hydrogen by using a bcc tungsten Σ3 (111) symmetrical grain boundary, as shown in Fig. 1. The supercell is composed of 72 tungsten atoms and 3.17nm vacuum region (VAC). Periodic boundary conditions are imposed on a, b, and c directions, where $a=<110>$ $b=<112>$ $c=<111>$. We use cutoff energy 270 eV, the Monkhorst-Pack (3,4,1) k-point mesh, and iterate lattice relaxation until every force exerted on each atom is lower than 0.1eV/nm. The cell shape and volume do not change during the lattice relaxation. The lattice constant of tungsten used in the present work is determined as 0.31735855 nm which is estimated in a preparatory simulation of bulk tungsten.

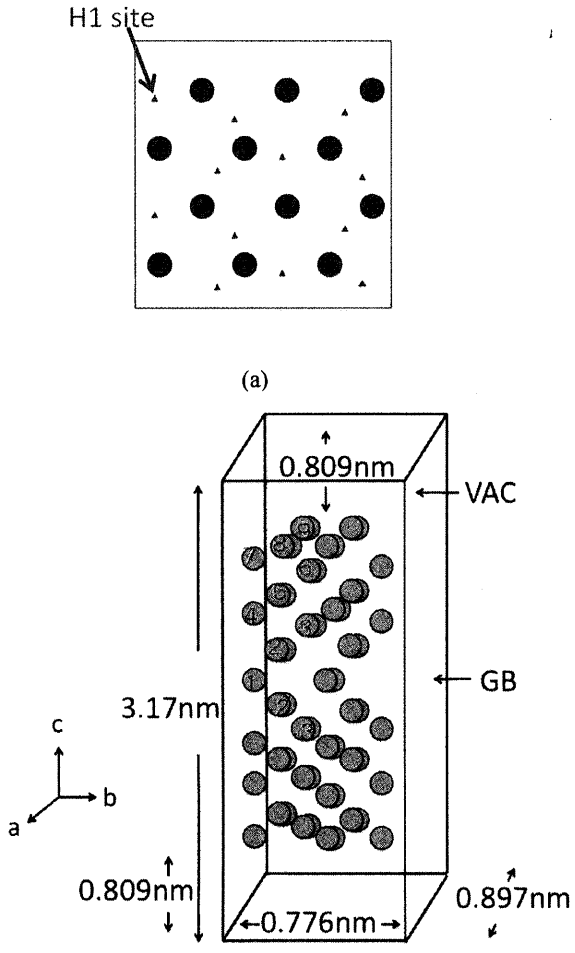

Fig. 1 (a) Top view of the fracture (111) surface of the grain boundary. The H1 site expressed by triangles indicates trapping site of hydrogen located at the grain boundary. The numbers labeled on atoms indicates the atomic layers of tungsten. (b) Schematic view of the supercell containing a regular grain boundary (GB) Σ3 (111) composed of 72 tungsten atoms. The circles indicate tungsten atoms. Atomic layers of tungsten are labeled by numbers from the grain boundary to the vacuum region (VAC) in the supercell, that is, atomic layer 1 is located at the grain boundary, while atomic layer 9 is located on the surfacing to the VAC.

3. Results

3-1 Trapping Energy

Hydrogen is expected to be trapped at some definitive sites around the grain boundary. We investigate the trapping energy of hydrogen depending on the trapping site. We calculated dependence of the trapping energy of one hydrogen atom on the trapping site. Trapping energy of hydrogen atom at grain boundary is defined as

$$\Delta E = E_{gb}(\mathrm{W}_n\mathrm{H}) - E_{gb}(\mathrm{W}_n) - (E_{bk}(\mathrm{H}) - E_{bk}), \quad (1)$$

where $E_{gb}(\mathrm{W}_n\mathrm{H})$ means calculated formation energy of a relaxed supercell containing a regular grain boundary Σ3 composed of n tungsten and one hydrogen atoms. Similarly, $E_{gb}(\mathrm{W}_n)$ indicates the formation energy of a supercell composed of n tungsten atoms containing the grain boundary. Third term $E_{bk}(\mathrm{H})$ indicates formation energy for a relaxed structure of a supercell that indicates one hydrogen atom in bulk tungsten. Similarly, the fourth term E_{bk} means formation energy for a supercell of bulk tungsten [4]. In the present simulations, we took into account 9 plausible layers H_n as trapping sites of hydrogen, where n indicates the order from the grain boundary. For example, H1 is located at the grain boundary and H9 is facing to the vacuum region (Fig. 1). We found that hydrogen is trapped on the almost same plane of the first tungsten layer at the grain boundary, that is, the first tungsten layer is nearly includes the trapping site H1.

We investigate the trapping energy of one hydrogen atom depending on the trapping site in the tungsten block of Fig. 1. The trapping energy for one hydrogen atom into the H1, H2, H8, and H9 are -0.974 eV, -0.53eV, -1.28eV and -1.47 eV respectively, where negative sign indicates endothermic reaction (Fig. 2). So, we can see that grain boundary and free surface region are favorable for hydrogen. On the other hand, the trapping energies into other trapping sites, H3, H4, H5, and H6, are almost zero because circumstance of these sites is similar to that of the bulk tungsten.

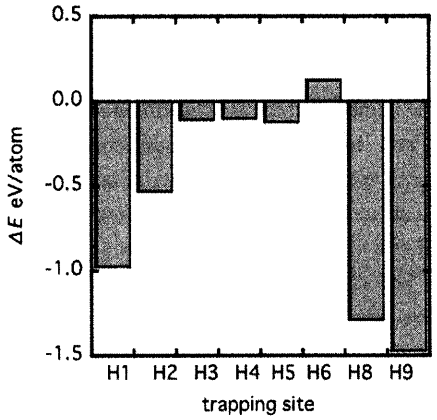

Fig. 2 Calculated trapping energy of one hydrogen atom depending on the trapping site H*n*. Sites H1, H2 are located at the grain boundary region, and H8 and H9 are located on the surface facing to the vacuum region. Hydrogen trapping into H7 site does not occur in the present simulation.

3-2 Segregation Energy

We investigated dependence of grain boundary segregation energy ΔE_{seg} for hydrogen on the hydrogen density in the grain boundary region. The ΔE_{seg} indicates the total energy gain by segregated hydrogen at the grain boundary region, which is defined as follows

$$\Delta E_{seg} = E_{gb}(W_n H_m) - E_{gb}(W_n) - m \times (E_{bk}(H) - E_{bk}), \quad (2)$$

where ΔE_{seg} means calculated formation energy of the relaxed supercell composed of n tungsten and m hydrogen atoms containing the grain boundary. The other terms in Eq. (2) has been already explained in Eq. (1). We calculate the ΔE_{seg} by progressively adding hydrogen atoms to the grain boundary region. The hydrogen is supposed to be trapped at a variety of trapping sites and it is possible to have many configurations in the tungsten block. However, according to Fig. 2, we found that sites, H1 and H2, at grain boundary are favorable for hydrogen and H1 site have larger trapping energy than H2 site. We determined optimized hydrogen configurations with the limited segregation sites H1, H2, H(-2), H(3) and H(-3), where H(-2) and H(-3) are located on the symmetrical positions with respect to the grain boundary in Fig. 1. Hydrogen segregate to H1 sites shown in Fig. 1, if the total number of hydrogen atoms less or equal to 12. However, being over 12, the hydrogen atoms segregate to not only H1 sites but also other trapping sites. A part of hydrogen atoms are distributed between H1 and H2 sites, and between H2 and H3 sites. Besides, we found metastable configurations of hydrogen in addition to the stable ones.

We show dependence of ΔE_{seg} on the hydrogen density at the grain boundary region in Fig. 3. We know that the maximum segregated hydrogen density is about 35 atom / nm^2 because the absolute value of ΔE_{seg} dose not increases any more.

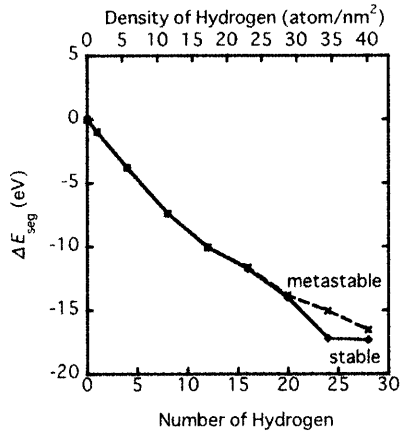

Fig. 3 Grain boundary segregation energy (ΔE_{seg}) for hydrogen depending on the hydrogen density in the grain boundary region. Solid line and dashed lines indicate ΔE_{seg} for stable and metastable configurations of hydrogen at the grain boundary region, respectivery.

3-3 Grain Boundary Cohesive Energy

Grain boundary cohesive energy $2\gamma_{int}$ implies the work necessary for crystals to be fractured at grain boundary. Furthermore, it is directly related to the surface energy $2\gamma_s$ and grain boundary energy γ_{gb}

$$2\gamma_{int} = 2\gamma_s - \gamma_{gb} \quad (3)$$

according to Rice-Wang thermodynamic theory of intergranular fracture by solute segregation[5,6]. We estimate it directly as energy necessary for making fracture surface at the grain boundary in the present simulations to complete simulations earlier. Occasionally, the grain boundary cohesive energy is calculated by the original definition in Eq. (3) in order to compare the result derived form the direct method. However, we cannot see a big difference between the grain boundary cohesive energies estimated by the both methods.

We investigate the dependence of the grain boundary cohesive energy on the segregated hydrogen density in the grain boundary region, as shown Fig. 4. The hydrogen segregation causes the reduction of the grain boundary cohesive energy. The magnitude decreases up to about one fourth of the original value at the maximum segregated hydrogen density at the grain boundary region.

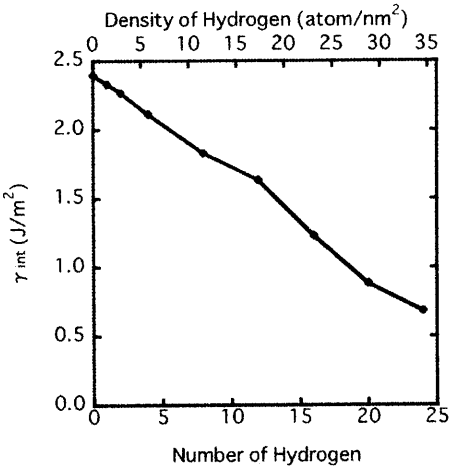

Fig. 4 Calculated grain boundary cohesive energy depending on the segregated hydrogen density at the grain boundary.

3-4 Tensile Test

We performed uniaxial tensile test to obtain stress-strain curve and maximum tensile stress (tensile strength) of the tungsten block with hydrogen segregated at the grain boundary. In the present simulations, tungsten block as shown in Fig. 1 is elongated to the c axis direction by applying an additional displacement to the tungsten atoms located on the layers facing to the vacuum region. Then, the upper and lower tungsten layers gradually separated to the opposite c directions. At first, we applied a small strain to the tungsten block and gradually increase the strain. The stress is approximately proportional to the applied strain. But eventually the tungsten block is fractured at the maximum tensile stress. We investigate the stress-strain curves of the tungsten blocks for a variety of number of segregated hydrogen, as shown in Fig. 5. The maximum tensile stress is 40 GPa for the original tungsten block without hydrogen segregation. However, the maximum tensile stress decreases with increasing the number of hydrogen (density of hydrogen) at the grain boundary region. Eventually, it decreases up to about 15 GPa in the case of the maximum hydrogen segregation at the grain boundary region.

In order to compare the above results, we performed tensile test of tungsten block with helium segregation at the grain boundary, as well. We show the stress-strain curves in Fig. 6. In the case of helium, we obtained similar results for hydrogen, that is, the maximum tensile stress decreases with increasing the number of helium. In addition to it, we can see that helium has larger effect on tensile strength reduction than hydrogen, according to Fig.5 and Fig.6. Segregation sites of helium are quite different from those of hydrogen. Helium segregate to the middle point between tungsten atoms labeled by 3 and -3, which is the largest vacancy type space in the grain boundary region.

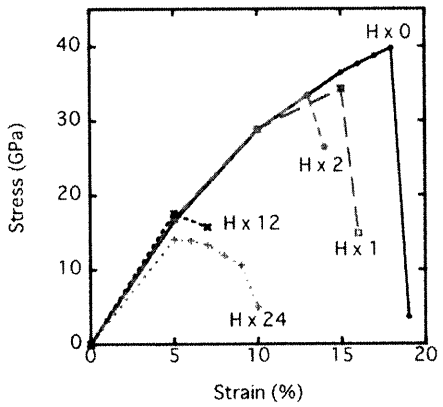

Fig. 5 Calculated stress-strain curves of tungsten blocks with hydrogen segregation at the grain boundary region. The symbols of H x n in the present figure means the number of hydrogen segregated at the grain boundary region, where n =1, 2, 12, 24. For the comparison, tungsten block without hydrogen segregation is investigated (H x 0).

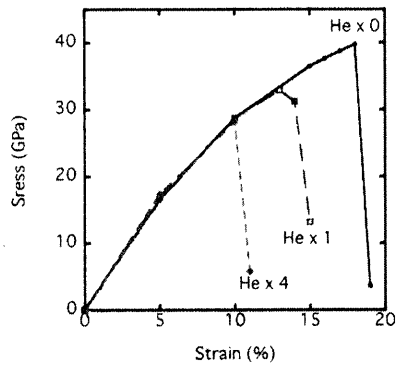

Fig. 6 Calculated stress-strain curves of tungsten blocks with helium segregation at the grain boundary. The symbols of He x n in the present figure mean the number of helium segregated at the grain boundary, where n =1 and 4.

4. Summary and Discussion

In this thesis the hydrogen retention at a $\Sigma 3(111)$ regular grain boundary in tungsten and its effect on the mechanical strength are investigated based on the first principles methods using VASP. The trapping energy for hydrogen at each site is calculated to show which one is most stable. Then, we studied on hydrogen segregation at the grain boundary region by calculating the hydrogen segregation energy ΔE_{seg}. We estimate the dependence of γ_{int} on the hydrogen density. We performed a tensile test of the tungsten block under the effects of hydrogen segregation using numerical simulations and estimated the maximum tensile strength after hydrogen induced embrittlement had occurred. In addition, the same test was performed with heliumfor.

1. The hydrogen trapping site in the bulk tungsten is investigated. It is found that t-site is energetically most favorable for hydrogen in the perfect crystals.
2. The dissolution energies of hydrogen in the bulk tungsten are found to be positive, which, indicates an endothermic reaction. The trapping energy is estimated to be 0.889 eV per one hydrogen atom. Hence, it is concluded that tungsten has quite a low solubility in hydrogen, which corresponds well with experimental results.
3. The dependence of the trapping energy for hydrogen on the trapping site is investigated in the tungsten block containing a $\Sigma 3(111)$ regular grain boundary. It is found that the trapping energy for the H1, H2, H8, and H9 sites are -0.97 eV, -0.53 eV, -1.28 eV, and -1.47 eV respectively. Therefore, it is concluded that the grain boundary and surface region are favorable for hydrogen deposition.
4. The segregation energy of hydrogen ΔE_{seg} is estimated by progressively adding hydrogen atoms at the grain boundary. It is found that the atoms segregate to the grain boundary up to about 35 atom/nm^2.
5. The dependence grain boundary cohesive energy γ_{int} on hydrogen density is calculated, which is expected to be a key cause of intergranular fracture and therefore, a good measure of the mechanical strength. With increasing the hydrogen density, the value of γ_{int} decreases up to about one fourth of the original value.
6. The uniaxial tensile test is performed using numerical simulations. The tungsten block is elongated to the <111> direction. (1) It is found that the stress is proportional to small applied strains, but eventually the tungsten block fractures at the maximum tensile stress. (2) The maximum tensile stress decreases with increasing the segregated hydrogen density at the grain boundary region up to about one forth of the original tensile strength.
7. A tensile test for tungsten block with helium segregation is performed, as well. The similar results are obtained compared with that of the hydrogen segregation. However, the effect of helium on the strength reduction is larger than that of hydrogen.

The hydrogen trapping energy at the grain boundary is smaller than at the surface in Fig. 2. So, hydrogen is embrittling element in terms of the theory of fracture mechanism. Furthermore, the more hydrogen segregates to the grain boundary, the less the grain boundary cohesive energy becomes as shown in Fig. 4, which corresponds to the previous works well[6].

Hydrogen segregates to the H1 site in the grain boundary up to the number of the hydrogen atom 12. According to Fig. 3, the slope to of the line is almost constant up to 12. So, we suppose the hydrogen atoms segregated at the H1 site do not strongly interact with each other, that is, the hydrogen atoms are trapped independently of one another at the H1 site. However, the hydrogen density in the grain boundary region eventually becomes saturated at about 35 atom/nm^2.

Hydrogen atoms tend to be trapped on the inner surface of vacancy-lattice defects, e.g. single vacancy, grain boundary, etc. On the other hand, helium atoms tend to be located at the center of the vacancy-type lattice defects. We suppose the reason is that helium is a rare gas with little chemical activity. In the present simulations, we can see the helium atom located in between tungsten atoms 3 and -3, as shown in Fig.6. It is the largest space in the $\Sigma 3(111)$ type grain boundary.

Helium has not been regarded as embrittling element. However, we find that helium also has quite large embrittlement effect on the tungsten block containing the grain boundary. The effect of helium is probably larger than that of hydrogen, which is an important conclusion of the present simulations. The helium induced embrittlement of metals will be an important subject in the field of metallurgical science.

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