Effects of transmutation elements in tungsten as plasma-facing material

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Abstract

Under fusion neutron irradiation, transmutation elements, Re, Os and Ta, are generated in tungsten due to transmutation reaction. We performed first-principles calculation, based on density functional theory, to investigate the effects of transmutation elements on the performances of tungsten as the plasma-facing material in fusion reactor. There is no strict correlation between the content of the transmutation element and its effects on the mechanical properties of tungsten. Generation of transmutation elements does not lead to the neutron irradiation hardening of W, on the contrary, transmutation elements enhance the ductility of it. The transmutation elements change the formation energies of H/He atom near the transmutation elements atom in W, but they do not change the most favorable sites of H/He atoms. An attractive interaction exists between the transmutation elements and H/He atoms except a repulsive interaction exists between Ta atom and He atom in W. Our works might shed some light on the development of tungsten-based plasma-facing material.

Keywords: Plasma-facing material, Tungsten, Transmutation elements, Density functional theory

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1. Introduction

Nuclear fusion is considered as the most promising sustainable energy source, and the best solution to solve the energy crisis the world will face in the future[1]. Tungsten (W) is generally considered as the most potential plasma-facing material (PFM) used in fusion reactor[2]. Naturally occurring tungsten is made up of five stable isotopes: $^{180}$W(0.1%), $^{182}$W(26.3%), $^{183}$W(14.3%), $^{184}$W(30.7%), and $^{186}$W(28.6%). Under fusion neutron irradiation, tungsten undergoes ($n$, $\gamma$) and ($n$, 2n) transmutation reaction that mainly produce rhenium (Re), and Osmium (Os) isotopes, and neutron absorption in $^{180}$W produce traces of tantalum (Ta) through $\beta^+$ decay of $^{181}$W[3, 4]. Therefore, Re, Os and a lesser extent Ta, are the main concerns in regard to the effects of transmutation elements (TEs) on tungsten properties degradation. These solutes will eventually lead to the formation of brittle intermetallic phase that is detrimental to the mechanical properties of tungsten[5, 6].

Using the first-principles calculation method, Chouhan et al. investigated the influence of Re content on the thermodynamics properties of W-Re alloys[7]. Giusepponi and Celino researched the effect of Re and Ta on the ideal tensile strength of tungsten[8]. Wei et al. studied the structure stability and mechanical properties of W-Re and W-Ta alloy[9]. Hossain et al. tested the effects of stress on the diffusion of Re in W-Re alloy[10]. Zhao et al. explored the crystal structure and the mechanical properties of W-Re-Os system[11]. Setyawan et al. studied the interstitial cluster interaction with Re, Os, and Ta in tungsten[12]. Nguyen-Manh et al. researched the abnormal gathered behavior of Re in W-Re alloy contain vacancies[13]. Bonny et al. studied the elastic properties of sigma phase W-Re alloy[14]. Liu Changsong’s group investigated the interaction between 16 kinds of elements (including the transmutation elements) and hydrogen (H) or helium (He) in tungsten[15–17].

Although research work of transmutation elements in W-based PFM received more and more attention from researchers in the world, the most works are concern on the effects of Re, Os and Ta on the crystal structure, mechanical properties and thermodynamics properties of tungsten. The study on the interaction between transmutation elements and H/He in tungsten is very rare. In this paper, we systematic studied the effects of Re, Os and Ta on the mechanical properties of tungsten and the interaction between transmutation elements and H/He in tungsten. Our works might shed some light on
the development of W-based PFM.

2. Methodologies

Tungsten belongs to the body centered cubic (BCC) crystal system, its space group is Im-3m. Simulation supercell composed 54 lattice points (3 × 3 × 3) was used in this paper. Some W atoms in the supercell were replaced by Re, Os and Ta atoms in a form of a symmetric as far as possible, and we formulated them as W$_{1-x}$Re$_x$, W$_{1-x}$Os$_x$ and W$_{1-x}$Ta$_x$, respectively. $x$ stands for atom percent of Re, Os and Ta in the supercell, the value of $x$ vary between 0 and 0.5, inclusively. To study the interaction between TEs atom and H/He atom in W, the center W atom that in the supercell is replaced by a TEs atom (W(Re), W(Os) and W(Ta)), and H/He atom in substitutional site (SS), tetrahedral interstitial site (TIS) and octahedral interstitial site (OIS) near the TEs atom. Previous works have suggested that the supercell will keep the BCC structure until the value of $x$ larger than 0.7\cite{18}, we choose a BCC supercell structure in this paper.

Computations in present work were performed by using density functional theory (DFT) and plane-wave pseudo-potential method\cite{19, 20}, as implemented in the Cambridge sequential total energy package (CASTEP)\cite{21}. Generalized gradient approximation (GGA)\cite{22, 23} developed by Perdew and Wang (PW91) functional\cite{24} was used for describing the exchange-correlation interaction among the electrons, and the ultrasoft pseudo-potential were employed for the ion-electron interaction. H atom only has one valence electron and He atom is a closed-shell atom, the van der Waals force has an important role on the interaction between transmutation elements and H or He in W. We used the Ortmann-Bechstedt-Schmidt(OBS)\cite{25} dispersion correction DFT(DFT-D) to describe the van der Waals interactions between transmutation elements and H or He in this paper. Basic parameters of the calculation were chosen as follows: The energy cutoff is 390 eV for all calculations, space representation equals reciprocal, SCF tolerance equals 1.0 × 10$^{-6}$ eV/atom, and $k$ sampling with 5 × 5 × 5 $k$-point mesh in Brillouin zone was used. The atomic positions were determined until satisfying the conditions: (1) the maximum force on them was smaller than 0.05 eV/nm; (2) the maximum change of energy per atom was smaller than 1.0 × 10$^{-5}$ eV; (3) the maximum displacement was smaller than 0.001 Å; and (4) the maximum stress of the crystal was smaller than 0.02 GPa.
The Re, Os and Ta atoms in $W_{1-x}Re_x$, $W_{1-x}Os_x$ and $W_{1-x}Ta_x$ have 2 possible positions, substitutional site and interstitial site, and formation energy of them are obtained by the equation:

$$E_f(W_mX_n) = E_t(W_mX_n) - nE(X) - mE(W) \quad (1)$$

Where, X stands for Re, Os and Ta, m and n stand for the number of W and X atoms, $E_t(W_mX_n)$ represents the total energy of $W_mX_n$ supercell, $E(X)$ stands for the energy of an X atom in pure X, and $E(W)$ represents the energy of a W atom in perfect W crystal, respectively.

Formation energy of an H or He atom in $W_mX_n$ supercell and binding energy between X and H/He in W supercell are calculated by follows equations:

$$E_f(W_mX_nA) = E_t(W_mX_nA) - E(A) - E(W_mX_n) \quad (2)$$

$$E_b(X, A) = E(W_mX_n) + E(W_yA) - E(W_mX_nA) - yE(W) \quad (3)$$

Where, A stands for H or He atom, y is the number of W atoms, $E_t(W_mX_nA)$ stands for total energy of an H or He atom in $W_mX_n$ supercell, $E(A)$ stands for the energy of an A atom, $E(W_mX_n)$ represents the total energy of $W_mX_n$, $E(W_yA)$ is total energy of W supercell contains an a atom, respectively.

As a BCC crystal structure, the elastic properties of W can be described by three independent elastic constants, $C_{11}$, $C_{12}$ and $C_{44}$. When $C_{11} + 2C_{12} > 0$, $C_{44} > 0$ and $C_{11} - C_{12} > 0$, the BCC structure of W can exist stably. The mechanical properties, like bulk modulus ($B$), shear modulus ($G$), Young’s modulus ($E$) and Possion’s ratio ($\nu$), can be calculated according to the following formulas:

$$B = (C_{11} + 2C_{12})/3 \quad (4)$$

$$G = (C_{11} - C_{12} + 3C_{44})/5 \quad (5)$$

$$E = 9BG/(3B + G) \quad (6)$$

$$\nu = (3B - 2G)/(2(3B + G)) \quad (7)$$
Table 1. Formation energy (in eV) of Re, Os and Ta doped in tungsten.

| Elements | Re  | Os  | Ta  |
|----------|-----|-----|-----|
| SS       | -0.526 | -0.016 | -1.04 |
| IS       | 10.412 | 10.103 | 11.978 |

3. Results and discussion

In order to investigate the effects of TEs on the performance of W, first we calculated the formation energy of Re, Os and Ta in W, according to the results we can get the most possible site the TEs occupied. Tab. 1 shows the results, the values of these TEs atoms that in interstitial site (IS) are much bigger than that of the TEs atoms are in substitutional site (SS), and we infer that these TEs atoms are insoluble in W when them are in IS. All of the study models in this paper are based on that all of the TEs atoms are located in the substitutional site.

As the most potential PFM, the mechanical properties of W is very important for the stable operation of fusion devices. Tab. 2 shows the mechanical properties of perfect W, the results of our calculation are in good agreement with the theoretical\cite{26} and experimental\cite{27} results of others. Fig. 1 shows the effects of TEs on shear modulus, bulk modulus, Young’s modulus and poisson’s ratio of W. The generation of all of the three TEs atoms make the shear modulus of W become smaller than that of perfect W. Re and Os atoms make the bulk modulus of W become bigger than that of perfect W. The effect of Re and Os on bulk modulus of W is not very obvious when they are compared with that of Ta atoms, and bulk modulus of W decreases as the increase of the content of Ta. Young’s modulus of W becomes smaller than that of perfect W when TEs atoms are generated in W. Generation of TEs atoms make the Poisson’s ratio of W become bigger than that of perfect W. There is no strict correlation between the content of the transmutation element and its effects on the mechanical properties of tungsten. Nevertheless, all of the three TEs atoms really have some effects on the mechanical properties of W. Pugh presents an empirical correlating and predicting the brittleness and ductility of metal\cite{28}, that is the ratio of shear modulus and bulk modulus, the metal is malleable when the ratio is less than 0.57, and the metal is brittle when the ratio is greater than 0.57. Fig. 2 shows the effect of TEs on the ratio of shear modulus and bulk modulus of W, result shows all of the TEs, Re, Os and Ta, make the ratio less than that of the perfect W,
Table 2. Shear modulus, bulk modulus, Young’s modulus and Poisson’s ratio of perfect tungsten.

| parameters | G(GPa) | B(GPa) | E(GPa) | ν     |
|------------|--------|--------|--------|-------|
| W         | 171.16 | 307.23 | 418.63 | 0.27  |
| Cal.[26]  | 149.42 | 313.61 | 386.83 | 0.29  |
| Exp.[27]  | 163.40 | 314.33 | 417.80 | 0.28  |

the ductility of W enhanced when TEs atoms are generated in W. According to the change of Poisson’s ratio of W, we can get the same conclusion. Previous others research work shows the generation of TEs atoms is the reason which for the neutron irradiation hardening of W[29–31]. Our results suggest that the neutron irradiation hardening of W is not due to the generation of TEs atoms, some other reasons, such as the irradiation-introduced voids and dislocation loops[32], should be responsible for the neutron irradiation hardening. After the TEs atom were generated in W, some changes have taken place on the mechanical properties of W. The reason which for these changes is the change of the interaction between atoms. Tab. 3 shows the bond population of W, W(Re), W(Os) and W(Ta), the generation of TEs atoms make the value of W-W bond population become greater than that of the perfect W, most of the distance between two adjacent W atoms become shorter than that in the perfect W and a small percentage of the distance become longer than that in perfect W. For these reasons, the effects of the TEs atoms on W are produced.

During operation of fusion reactor, H and He inevitably enter in W. The research of the interaction between TEs atoms and H/He atom in W is very important for the development of the W-based PFM. Formation energies of H and He in perfect W are shown in Tab. 4 and Fig. 3. Our calculation results are in agreement with the theoretical research works of others[26, 33, 34], the difference may arise from the difference in the computation method and the size of the supercell, their works performed using the VASP code with a 128-atom supercell. Although the absolute value of the formation energy have a discrepancy between our work and theirs, the energy difference among the SS, TIS and OIS agree with each other. A single He atom favors a substitutional site while a H atom spontaneously incorporates at a tetrahedral interstitial site with a negative formation energy. There is an electron in H atom s orbit, and two electrons in He atom s orbit. In the supercell, closer to 2 the number
Table 3. The typical bond population of W, W(Re), W(Os) and W(Ta), and bond length (in Å) did approximate processing.

| System | Bond   | Length | population |
|--------|--------|--------|------------|
| W      | W-W    | 2.755  | 0.38       |
| W(Re)  | W-W_1  | 2.751  | 0.39       |
|        | W-W_2  | 2.746  | 0.40       |
|        | W-W_3  | 2.762  | 0.39       |
|        | W-Re   | 2.751  | 0.40       |
| W(Os)  | W-W_1  | 2.746  | 0.39       |
|        | W-W_2  | 2.746  | 0.40       |
|        | W-W_3  | 2.747  | 0.39       |
|        | W-W_4  | 2.752  | 0.39       |
|        | W-W_5  | 2.754  | 0.39       |
|        | W-W_6  | 2.754  | 0.40       |
|        | W-W_7  | 2.757  | 0.39       |
|        | W-W_8  | 2.759  | 0.40       |
|        | W-W_9  | 2.764  | 0.39       |
|        | W-Os   | 2.762  | 0.36       |
| W(Ta)  | W-W_1  | 2.729  | 0.38       |
|        | W-W_2  | 2.751  | 0.39       |
|        | W-W_3  | 2.753  | 0.39       |
|        | W-W_4  | 2.753  | 0.40       |
|        | W-W_5  | 2.759  | 0.41       |
|        | W-W_6  | 2.760  | 0.42       |
|        | W-W_7  | 2.761  | 0.40       |
|        | W-W_8  | 2.773  | 0.37       |
|        | W-Ta   | 2.789  | 0.60       |
Fig. 1. The mechanical properties of $W_{1-x}Re_x$, $W_{1-x}Os_x$ and $W_{1-x}Ta_x$, and a, b, c and d show shear modulus, bulk modulus, Young’s modulus and Poisson’s ratio, respectively. Dot lines stand for the corresponding value of perfect W.

Fig. 2. $G/B$ of $W_{1-x}Re_x$, $W_{1-x}Os_x$ and $W_{1-x}Ta_x$. Dot line stands for the ratio of perfect W.
Table 4. Formation energy of H atom and He atom in perfect W.

| Reference       | H_{SS} | H_{TIS} | H_{OIS} | H_{SS} | H_{TIS} | H_{OIS} |
|-----------------|--------|---------|---------|--------|---------|---------|
| This paper      | 1.468  | -2.202  | -1.836  | 4.660  | 5.695   | 5.837   |
| Cal.[33]        | 0.92   | -2.47   | -2.07   | 5.00   | 6.23    | 6.48    |
| Cal.[26, 34]    | 0.78   | 2.44    | 2.06    | 4.70   | 6.16    | 6.38    |

of electron in s orbit is, more stable both H atom and He atom are. Fig. 4 shows the number of electron in s orbit of H atom and He atom, the number in s orbit of H atom that is in TIS is closer to 2, and the number in s orbit of He atom that is in SS is closer to 2 over the He atom is in TIS and OIS. Fig. 3 shows formation energy of a H and He atom in the supercell which contains a TEs atom, respectively. The TEs, Re, Os and Ta, make formation energy of H atom, that is located in SS, TIS and OIS near the FEs atom, becomes smaller than that of the perfect W. Os and Ta make formation energies of the H atom is in the three possible site are negative value. These results suggest the point defects that formed by H atom, near the TEs atom, become more easy to formation than that in the perfect W, but the H atom still favors the tetrahedral interstitial site. Re and Os make the point defects formed by a He atom, near Re and Os atom, become easier to formation than that in perfect W, and Ta make the point defect formed by a He atom is more difficult to formation than in perfect W. Although the formation energy of the point defects formed by H/He atom are changed due to the generation of TEs atoms, the favor site of H atom and He atom are not changed. Because the number of electron in s orbit of H atom and He atom is still more close to 2 when they are in TIS and SS, respectively.

Fig. 5 shows the binding energies between TEs atom and a H atom in W and the binding energies between TEs atom and a He atom in W. The results indicate there is an attractive interaction between TEs atom and H atom in W. The attractive interaction between TEs atom and H atom in the substitutional site is stronger than in the tetrahedral interstitial site and octahedral interstitial site, the attractive interaction between TEs atom and H atom in the tetrahedral site is the weakest of the three possible site for H atom in W. There is an attractive interaction between Re/Os atom and He atom in W, and the interaction between Os atom and He atom is stronger than the interaction between Re atom and He atom in W. While there is a repulsive interaction between Ta atom and He atom in W, and the strength of the repulsive interaction between Ta atom and He atom follow the order: SS
Fig. 3. Formation energy of H atom (a) and He atom (b) in supercell with and without TEs atom.

Fig. 4. Number of electron in H atom (a) and He (b) atom s orbit.

> OIS > TIS. The changes of binding energy value are in agreement with that of formation energy. The attractive interaction between the TEs atom and H atom is due to the change of the electronic structure and the generation of local stress in the supercell, only one electron in s orbit of H atom and
it tends to obtain charge from its surrounding atoms to keep stability. The interaction between TEs atom and He atom is due to the local stress that produced by the TEs atoms, He atom is a closed-shell atom and the influence of charge can be neglected when it compared with that of the local stress. The atomic radius of Ta atom is bigger that of W atom and the atomic radius of Re and Os atom is smaller than that of W atom, as a results there is a force field from Ta atom to its adjacent W atom and a force field from the surrounding W atom to Re atom and Os atom.

Fig. 5. Binding energy between H/He atom and TEs atom in W. H atom (a) and He atom (b).

4. Conclusion

Transmutation elements, Re, Os and Ta, are produced in W during the operation of fusion rector, investigating the effects of transmutation elements on the performance of W clearly is very important for the development of fusion energy. In this paper, using the first-principles calculation method, we investigated the effects of transmutation elements on the mechanical properties of W, and the interaction between H/He atom and TEs atoms in W. Results show that, the generation of Re, Os and Ta increases the ductility of W, previous others researches indicated the generation of TEs will results in neutron irradiation hardening of W, but our results suggest that the generation of transmutation elements in W should not be responsible for the
hardening. Although the formation energies of the point defects formed by H/He atom are changed, the most favorable sites of H and He in W are not changed. There is an attractive interaction exists between TEs atoms and H/He atom in W, except a repulsive interaction between Ta atom and He atom in W. The works, in this paper, might shed some light for the development of W-based PFM.

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