Carbon clustering and effect on hydrogen trapping in tungsten: A first-principles study

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Abstract

The clustering of carbon (C) in tungsten (W) with and without vacancies and the effects of C content at a vacancy on the hydrogen (H) trapping have been investigated by first-principles computer simulations using density functional theory. The calculations were performed in 128-atom or 432-atom supercells. The results indicate that the nascent formation of tungsten carbide is based on a pair of C atoms located at two neighbor octahedral interstitial sites along the \( \langle 111 \rangle \) direction with a distance of 0.284 nm. Small interstitial C atoms prefer to form a zigzag chain on a \( \langle 110 \rangle \) plane, and the C binding energy increases with increasing number of C until four C atoms and then remains constant at 0.7 eV for larger C clusters. The presence of vacancies enhances the interactions between C and its first nearest neighbor (1NN) W atoms because of strong hybridization between the C-p state and the d state of its 1NN W atoms. Meanwhile, the presence of C increases the stability of the \( d\)-vacancy in W. The H binding energies to carbon-vacancy-hydrogen (CmVH\( _{n-1} \)) complexes decrease with increasing C contents. For a given C content, the H binding energies to CmV complexes basically decrease with increasing number of H. The ultimate H contents that can be trapped by CmV complexes essentially decreases monotonically with increasing C content, and the C effect on H trapping is dependent on temperature.

1. Introduction

Carbon (C) based material, such as graphite, and tungsten (W) are used as plasma facing materials in a large number of operating fusion tokamaks, and recent facilities, including JET and WEST (formerly Tore Supra) have switched to all metal devices by depositing tungsten. Hydrogen plasma sputtering and found that the release behavior of the incorporated hydrogen changes depending on the atomic ratio of C and W in the layer. Moreover, Katayama et al. \cite{14} studied the incorporation of hydrogen in C-W co-deposition layers using hydrogen plasma sputtering and found that the release behavior of the incorporated hydrogen changes depending on the atomic ratio of C and W in the layer. It is known that atomistic simulations are well suited to discover fundamental mechanisms and evolution processes of materials. According to first-principles calculations based on the density functional theory (DFT), a single C atom prefers to occupy the octahedral interstitial site (OIS) in bcc W with a solution energy of 0.78 eV, and two C atoms tend to pair up at adjacent OISs along the \( \langle 210 \rangle \) direction with a distance of about 0.357 nm \cite{18}. C atoms are strongly trapped at a vacancy \cite{21,24} and the presence of C decreases the H trapping ability of a vacancy \cite{15,21}. The C in W implanted with low energies might form interstitial C clusters without the presence of vacancies. The interactions between two interstitial C as a function of distance in W are correlated with incident D+ fluence and implantation temperature. In addition, the studies of the surface morphology of W by hydrogen and C mixed ion beam irradiation show that a very small amount of C impurity (~0.3% or more) in the beam of hydrogen significantly enhanced blister formation in W \cite{5,12,13}. Therefore, investigation of C-W mixed material formation and interaction of hydrodynamic plasma with C-W mixed materials have been performed by a number of experimental and theoretical or simulation approaches \cite{4–26}. The experimental research has confirmed that C-W mixed materials, probably consisting of tungsten carbide (WC) layers, are formed near the W surface with sequential C impurity deposition \cite{4–7}. Deuterium (D) retention in C-W mixed materials and/or pure W was investigated by different experimental methods \cite{6–11} and the results show that the effect of C pre-implantation on D retention in W is dependent on the energy of the incident D+ beam. Therefore, investigation of C-W mixed material formation and interaction of hydrodynamic plasma with C-W mixed materials have been performed by a number of experimental and theoretical or simulation approaches \cite{4–26}. The experimental research has confirmed that C-W mixed materials, probably consisting of tungsten carbide (WC) layers, are formed near the W surface with sequential C impurity deposition \cite{4–7}. Deuterium (D) retention in C-W mixed materials and/or pure W was investigated by different experimental methods \cite{6–11} and the results show that the effect of C pre-implantation on D retention in W is dependent on the energy of the incident D+ beam.
were investigated by Liu et al. [18], but the clustering mechanism of more than two C atoms in W has not been found in available experimental and simulation studies. Moreover, the previous calculations [21,24] demonstrate that a mono-vacancy is able to trap four C atoms to form carbon-vacancy (CmV) complexes in W; however, only H binding to a CV complex has been investigated. In addition to single vacancies, vacancy clusters (or voids) may be produced in W under neutron irradiation in a fusion environment. Due to expensive computational cost of DFT calculations, di-vacancies were only considered for the effect of vacancy concentrations. In this work, we have used DFT calculations to investigate C clustering in bcc W without and with vacancies, including a single vacancy and di-vacancy, and evaluated the expected initial formation mechanism of WC. Furthermore, the effect of C concentration at a vacancy on H trapping has been systematically studied. The present results predict C clustering in W and explain the temperature dependence of C effect on H trapping observed in experiments. This study is helpful not only for understanding the interaction mechanism between C atoms and the effect of C clustering on H trapping in W with different vacancy concentrations, but also for guiding the experimental studies about interstitial C clusters in W and the vacancy effect on C clustering.

2. Methodology

The Vienna Ab initio Simulation Package (VASP) [27] was used in this work, along with the standard pseudopotentials of C, W and H. The interaction between ions and electrons was described by the projector-augmented wave method [28,29], while exchange and correlation interactions were obtained by the generalized gradient approximation in the Perdew-Burke-Ernzerhof form [30]. A cubic bcc supercell of 4a × 4a × 4a (128 atoms) or 6a × 6a × 6a (432 atoms) with periodic boundary conditions, where a is the lattice constant of 0.3171 nm, were used to simulate the bulk W system with and without C and H defects. The first-order Methfessel-Paxton method was applied for the Fermi surface smearing with a width of 0.1 eV. Brillouin zone sampling was performed using the Monkhorst – Pack scheme [31] with 5 × 5 × 5 and 3 × 3 × 3 k-point meshes for 128 and 432 atom supercells (named S1 and S2), respectively. The calculations in the present work were performed by a full relaxation, i.e. the atomic positions and the shape and size of the supercell were relaxed, with an energy cutoff of 360 eV for the plane-wave basis set. A summary of the test of relaxation approaches (atomic or full relaxation) and energy cutoff can be found in the Supplementary material. The energy minimization of systems was obtained until the electronic self-consistent iteration and the force on the atoms are less than 10^{-5} eV and 0.1 eV/Å, respectively. Furthermore, due to the change of supercell size and volume after relaxation, especially for high concentration of interstitial C in the 128-atom supercell, multiple calculations based on the prior converged configuration of each system were necessary until the change of the total energy was less than 10 meV.

The binding energy $E_b(C)$ of the mth C to CmVnHx complexes in bulk W with and without vacancies is defined as [18,32]

$$E_b(C) = [E(C_{mV}) + E(C_{mV-1})] - E(C_{mV}) - E_{ref}$$

(1)

where $E(C_{mV})$ and $E_{ref}$ are total energies of the supercell with and without one octahedral interstitial C atom, while $E(C_{mV-1})$ and $E(C_{mV})$ are total energies of the supercell with m-1 and m C atoms, respectively. The binding energy $E_b(H)$ of the H atom to a CmVnHx complex is given by

$$E_b(H) = [E(C_{mVH}) + E(C_{mVnH_{x-1}})] - E(C_{mVnH_x}) - E_{ref}$$

(2)

where $E(C_{mVH})$ and $E_{ref}$ are the energies of the supercell containing a tetrahedral interstitial H or without containing H, respectively, while $E(C_{mVnH_{x-1}})$ and $E(C_{mVnH_x})$ are the energies of the supercell containing a CmVnH_{x-1} and a CmVnH_x complex, respectively. m, n and x are the number of C atoms, vacancies and H atoms, respectively.

The C or H binding energy obtained in this work is based on the minimum energy configurations of C clusters and CmVnHx complexes in W. The present calculations show that a single C prefers to sit at the OIS with a formation energy of 0.78 eV (or 0.73 eV) for a 128-atom supercell (or a 432-atom supercell), which is about 1.5 eV lower than the tetrahedral interstitial site (TIS). When modeling C clustering in W, the OISs were therefore chosen for additional C atoms. Considering all possible configurations, the energy of two C atoms in W as a function of distance was first calculated. According to the stability of two C atoms, larger C clusters were further evaluated. Many configurations that might be minimum energy configurations have been considered. The rationale about how to search the minimum energy configuration of C clusters will be described in detail in Section 3.1. Similarly, the preferred sites of a C atom at a monovacancy or a di-vacancy were investigated in consideration of all possible substitutional and interstitial sites near the vacancies. Minimum energy configurations of CmVnHx complexes in W were determined among many configurations considered according to the site occupation preference of C and H near vacancies in W.

3. Results and discussion

3.1. C clustering in W

To evaluate the formation mechanism of WC with increasing C content, C clustering in W with and without vacancies was explored in the present work. First, the binding energy between two interstitial C in W without vacancies was calculated using both the 128-atom and 432-atom supercells. The results are shown in Fig. 1(a), along with the configurations of C in Fig. 1(b), where $C^0$ represents the first interstitial C atom, C$^0$ (n = 1–6) corresponds to the nth nearest neighbor (nNN) OIS of C$^0$. As demonstrated in Fig. 1(a), the negative binding energy between two C atoms with the 2NN distance of 0.244 nm (see $C^0C^2$ in Fig. 1(b)) indicates a repulsive interaction between the two C atoms. It should be noted that the distances between two C atoms shown in Fig. 1 are the final distance obtained after relaxation. The repulsive force between two C atoms increases significantly for distances shorter than 0.244 nm. For example, the (negative, or repulsive) binding energy of $C^0C^2$ is less than −1.5 eV, which is not shown in Fig. 1(a). However, the positive binding energy between adjacent C becomes attractive for a separation distance between 0.28 nm and 0.37 nm. For distances larger than 0.38 nm, the interaction between two C is negligible. It is of interest to note that the minimum energy configuration of double C atoms, which is crucial to assess the nucleation behavior of C clusters, is sensitive to the supercell size and the relaxation approach, as shown in Fig. 1s of the Supplementary material. To assess the effect of supercell size on the stability and configuration of two interstitial C, a 128 and 432-atom supercell with full relaxation was used to evaluate the same conditions. As shown in Fig. 1, although the C binding energies calculated with supercells S1 and S2 are somewhat different, the most stable configuration is the same, i.e. $C^0C^2$, a pair of C aligned along the [111] direction with a distance of 0.284 nm.

The C–C interaction in W is largely determined by the balance between elastic and electronic interactions. In general, the electronic interaction is negative (repulsive) while the elastic interaction is positive (attractive). This indicates that C atoms prefer not to locate too close to each other, as shown in the interaction between two C atoms as a function of distance (Fig. 1). But, if the distance between C atoms is too large (see $C^0C^2$ in Fig. 1), even though the repulsion from the electronic interaction approaches zero, the attraction from the elastic interaction also reduces, and thus the binding energy approaches zero.

The positive binding energy of the configuration $C^0$ and $C^2$ is mainly attributed to the elastic interactions. The stability of $C^0C^2$ in bcc W is in good agreement with that in bcc Fe from elasticity theory [32] and from the calculation of Jonson et al. [33]. The elastic model and the calculation of Jonson and co-workers reflect only the interactions of the local...
strain near the two C atoms, but do not take into account the electronic (repulsive) C–C interaction. This indicates that the C–C interaction for distances greater than 0.28 nm in W is negligible in comparison with the W–C interactions.

The present results show that the distance between C₀ and C₃, the energetically favorable pairing configuration, is 0.284 nm, which is in excellent agreement with the nearest distance (0.284 nm) between C atoms in hexagonal WC obtained in experiments [34] and is also close to DFT calculations [16,35]. This implies that a pair of C located at the two neighbor OISs along the ⟨111⟩ direction with a distance of 0.284 nm is the nascent formation step of WC in bcc W after C implantation.

Based on the interaction between C atoms as a function of distance in W, larger C interstitial clusters were further evaluated. As shown in Fig. 1, C₀C₃ has the highest binding energy, followed by C₀C₄ and C₀C₅, which indicates that the additional C is likely to occupy the 3NN, 4NN, or 5NN OIS sites of C atoms in the pre-existing C cluster. Based on this, five possible configurations of a C trimer were considered, and it is proved that a triangle configuration located between two (110) planes, which includes two 3NN and one 4NN OIS sites for each two C atoms, has a minimum energy. Similarly, for larger C clusters (C₄, C₅, C₆, and C₇), many configurations that might be minimum energy configurations have been considered based on the site occupation preference of additional C atom. The considered configurations and the total energy of the system are presented in the Supplementary material. Briefly, the additional C is likely to occupy the 3NN, 4NN or 5NN sites of C atoms in the pre-existing C cluster, and all C atoms tend to locate between two (110) atomic planes. The clustering behavior of C atoms in bcc W is similar to H clustering in bcc W [36,37]. The minimum energy configuration of a C interstitial cluster is shown in Fig. 2 and the corresponding binding energies of C to Cₙ₋₁ clusters are listed below “No V” in Table 1. It is clear that the C atoms prefer to form a zigzag chain on a (110) plane in bcc W for cluster sizes in which the number of C is less than 7. With further growth of C clusters, the zigzag chain is not the preferred configuration. Fig. 2 demonstrates that the zigzag chain C cluster consists of many isosceles triangles with length of 0.28 nm and 0.31 nm. Those C triangles on the ⟨110⟩ plane in bcc W are close to equilateral triangles of C on the ⟨0001⟩ plane in hcp WC. This indicates that with increasing C concentration in W, WC prefers to form on the ⟨110⟩ plane of bcc W with an interface of ⟨0001⟩ plane of hcp structure. This result is consistent with the first-principles calculation of the W/WC interface structure [26,38]. As seen from Table 1, for small C clusters (two or three C atoms), the supercell size effect on the C binding energy is small, while when the C cluster size increases, the
and large spheres represent vacancies and C atoms, respectively. The second C binding energy declines steeply. The C trapping ability of a single vacancy in W and the configuration of the CmV complexes obtained in the present work are similar to previous work [21,24]. Compared with interstitial C atoms, the vacancy significantly enhances the C binding energy. The second C binding energy to the vacancy and the first trapping site Cff prefer site of H near the V2-1NN [39]. Our previous calculations show that the first H prefers to trap at interstitial sites near the junction of the di-vacancy, where the H can minimize the isosurface of optimal charge density as much as possible [39]. The difference of the first trapping site between C and H near the V2-1NN in W is presumably due to different interactions of C-W and H-W. Fig. 4 shows the charge density isosurface of the first preferred site “C1” and the metastable site “C2” for C trapping by a V2-1NN (a) and the corresponding electronic density of states (DOS) of C and its 1NN W atom (b). Fig. 4(a) shows that the charge density isosurface of site “C1p” (yellow surface) is 0.117 eV/Å³, larger than that at site “C2p” (purple surface), which has a value of 0.098 eV/Å³. However, the binding energy of C at site “C1” to the V2-1NN is 0.32 eV greater than at site “C2”. This might be attributed to the observation that the first C prefers a site where it can form strong bonds with its nearest neighbor W atoms. Fig. 4(b) clearly shows the DOS distribution of the p state of C at site “C1p” is similar to the d state of its 1NN W atom (W1-p), indicating strong hybridization between C and 1NN W atoms; however, the DOS of the p state of C at site “C2p” (C2-p) is different from the W1-p state. It should be noted that after relaxation, the distance from C1 or C2 to its NN W atoms is similar and the DOS distributions of the NN W atoms are also similar.

Two C atoms form a dimer with a distance of 0.145 nm at the junction of the di-vacancy with a high binding energy. As shown in Table 1, the first C binding energy to the V2-1NN is slightly higher than the C binding to a single vacancy, while the second C binding energy to the V2-1NN increases 22%, much higher than the difference between the first and second C binding energy to a single vacancy (2%). This indicates that the second vacancy in the V2-1NN enhances the C binding

**Table 1**

<table>
<thead>
<tr>
<th>Number of C (m)</th>
<th>V1</th>
<th>V2-1NN</th>
<th>V2-2NN</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S1</td>
<td>S2</td>
<td>S1</td>
</tr>
<tr>
<td>1</td>
<td>-</td>
<td>-</td>
<td>2.01</td>
</tr>
<tr>
<td>2</td>
<td>0.45</td>
<td>0.44</td>
<td>2.09</td>
</tr>
<tr>
<td>3</td>
<td>0.61</td>
<td>0.60</td>
<td>1.76</td>
</tr>
<tr>
<td>4</td>
<td>0.78</td>
<td>0.70</td>
<td>0.65</td>
</tr>
<tr>
<td>5</td>
<td>0.79</td>
<td>0.66</td>
<td>1.90</td>
</tr>
<tr>
<td>6</td>
<td>1.01</td>
<td>0.71</td>
<td>1.14</td>
</tr>
<tr>
<td>7</td>
<td>0.73</td>
<td></td>
<td>0.32</td>
</tr>
</tbody>
</table>

**Table 2**

<table>
<thead>
<tr>
<th>Number of C</th>
<th>V2-1NN</th>
<th>V2-2NN</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.10</td>
<td>-0.44</td>
</tr>
<tr>
<td>1</td>
<td>-0.02</td>
<td>1.16</td>
</tr>
<tr>
<td>2</td>
<td>0.46</td>
<td>1.05</td>
</tr>
<tr>
<td>3</td>
<td>0.73</td>
<td>1.18</td>
</tr>
<tr>
<td>4</td>
<td>2.15</td>
<td>2.30</td>
</tr>
</tbody>
</table>

Two C atoms form a dimer with a distance of 0.145 nm at the junction of the di-vacancy with a high binding energy. As shown in Table 1, the first C binding energy to the V2-1NN is slightly higher than the C binding to a single vacancy, while the second C binding energy to the V2-1NN increases 22%, much higher than the difference between the first and second C binding energy to a single vacancy (2%). This indicates that the second vacancy in the V2-1NN enhances the C binding.

**Fig. 3.** Configuration of (a) C1V2-1NN, (b) C2V2-1NN, (c) C3V2-1NN, (d) C4V2-1NN, (e) C5V2-1NN, (f) C6V2-1NN in W, where small blue spheres represent W atoms, medium and large spheres represent vacancies and C atoms, respectively.
energy considerably. The third and fourth C prefer to trap at the other vacancy, forming a second dimer, as shown in Fig. 3(d). The fifth C is trapped at the di-vacancy with a binding energy of 1.9 eV, and the sixth C binding energy to the V2-1NN decreases dramatically. The present calculations show that the 1NN di-vacancy cannot trap more than six C atoms.

In addition to the 1NN di-vacancy, the C trapping ability of the 2NN di-vacancy (V2-2NN) was investigated and the minimum energy configurations of CmV2-2NN complexes are plotted in Fig. 5. Similar to H, the OIS that belongs to both vacancies is the most favorable position for C, which is at the junction of the isosurface of the charge density [39]. The second and third favorable sites for C around the V2-2nn are the OISs on the right and left sides of the two vacancies; therefore, the C1V2-2NN, C2V2-2NN and C3V2-2NN align in the [100] direction, as shown in Fig. 5(a)–(c), respectively. The minimum energy configuration of the C4V2-2NN is based on the configuration of the C3V2-2NN. Four C atoms in the C4V2-2NN prefer to trap by the di-vacancy on the (010) plane, see Fig. 5(d), while the C2V2-2NN has a different structure than the C4V2-2NN. In the C2V2-2NN, three C atoms from a triangle at one vacancy on the (100) plane and the two additional C atoms are trapped by the other vacancy on the (001) plane, as demonstrated in Fig. 5(e). When the number of C atoms is increased to six or seven, the configuration involves the two vacancies on two parallel (100) planes, like C trapping by two single vacancies, as shown in Fig. 5(f) and (g). The binding energy decreases to 1.5 eV and drops to 0.29 eV for the seventh C. The 2NN di-vacancy barely traps the eighth C with a sequential binding energy less than 0.1 eV.

To assess the interaction energies and mechanisms between C and W in bcc W with and without vacancies, we have calculated the DOS of C and its 1NN W atoms when C is trapped at (a) OIS site, (b) vacancy, (c) 1NN di-vacancy and (d) 2NN di-vacancy, and the results are shown in Fig. 6. One can see from Fig. 6(a), the DOS of C at the OIS is attributed to the C-\(p\) state, and the main DOS peak of C is located at about −7.0 eV. When one vacancy appears near the C, the DOS distribution of C clearly changes in comparison to the case without a vacancy. The left DOS peak of the C-\(p\) state lowers and shifts toward a high energy level.
(~−6.2 eV), as shown in Fig. 6(b). The highest DOS peak of the C-p state is close to the DOS peak of the 1NN W-d state. For the 1NN di-vacancy, the DOS distribution of the C-p state is significantly different from that of a single vacancy without a vacancy. It is of interest to note that the DOS shape of the p state of C at the V_{2-1NN} is very close to the d states of W in the whole energy range, as shown in Fig. 6(c). The distribution of the 1NN W atoms of C at the V_{2-1NN} is the same as that of C at a single vacancy (see Fig. 3(a)), but the interactions between C and its 1NN W atoms are obviously impacted by the second vacancy in the V_{2-1NN}. For the 2NN di-vacancy, the DOS shape of the C-p state is almost the same as the d state of its 1NN W. Fig. 6 demonstrates that the DOS distribution of the C-p state is dramatically influenced by the presence of vacancies. The strong similarity of DOS between the C-p state and the d state of its 1NN W atoms for the CV_{2-2NN} complex indicates the electronic states of C atoms strongly hybridize with the W atoms, which results in a very high C binding energy. Besides the C-p state, the DOS of the C-s state increases with increasing vacancy contents. The increase in the DOS of the C-s state represents charge transfer from W atoms. In general, the p state of W atoms is not attributed to the interactions between C and W. The s state of 1NN W atoms does not appear to influence the interactions between C and W in comparison with the W-d states.

As described above, the presence of vacancies enhances the interactions between C and W, strengthening the C trapping in W, meanwhile, the presence of C enhances the stability of the di-vacancy in W. The binding energy of V to C_{mV} complexes were calculated and are listed in Table 2. It is known that di-vacancies at either the first or second NN positions in bulk W are unstable, with a strong repulsion observed, especially for the 2NN configuration, despite a strong binding near W surfaces [40–42]. The instability of V_{2-1NN} and V_{2-2NN} is confirmed by the negative binding energies in this work. The binding energies of −0.10 eV and −0.44 eV for the V_{2-1NN} and V_{2-2NN} are similar to the previous values reported in Ref. [40]. It is surprising to see that with increasing C contents, the binding energy of V to C_{mV} complexes increases significantly, especially for the V_{2-2NN}. For example, the 2NN di-vacancy is the most unstable di-vacancy configuration; however, when a C atom appears, the V is strongly bound to the other V with a binding energy of 1.16 eV.

### 3.2. H binding to a C_{mV} complex

Previous experiments show that the presence of C impurities could affect the H behavior in W, and thus change the morphology of W in a fusion environment [5,12,13]. The effect of C concentration at a vacancy on the H trapping was investigated by calculating the binding energy of H to C_{mVH} complexes in bulk W and the results are shown in Table 3 and Fig. 7. The binding energy of H to a vacancy as a function of the number of H atoms has been obtained by different groups based on...
The vacancy will be a \[19\]. This suggests that C atoms are more strongly trapped by vacancies which is much higher than the H migration of 0.2 eV calculated by DFT Table 1) or 1.24 eV, respectively. Moreover, the migration energy by vacancies. The C or H binding energy to a vacancy is 1.98 eV (see Table 3). However, it is surprising to see the 11th H binding energy is one of the H atoms near the vacancy prefers to form a C–H bond with a distance of 0.109 nm. In fact, the first H near the vacancy can bind to the C atom with a binding energy of 0.84 eV, but this value is less than the binding energy of 1.21 eV for the energetically preferred configuration demonstrated in Fig. 8(a). The H binding energy becomes negative with the addition of the ninth H, which means the CV can trap eight H. This agrees well with the result in Ref. [20]. Comparing the H binding energy to a vacancy with and without C, we observe that the first H binding energy to the CV decreases slightly, while for more than one H, the C obviously is responsible for decreasing the H binding energy to the vacancy, as demonstrated in Fig. 7 and Table 3.

As the second C appears near the CV complex, representing a C dimer at the vacancy, i.e., a \( \text{C}_2 \text{V} \) complex is formed with a binding energy of 2.02 eV between the two C atoms (see Table 1). The preferred trapping sites of H to the \( \text{C}_2 \text{V} \) are shown by red spheres in Fig. 9(a) and (b), where the number 1 to 5 indicates the trapped sequential order of H. The first H prefers to trap at site “1” in Fig. 9(a), forming a triangle with two C atoms on the (001) plane. The binding energy of the first H to the \( \text{C}_2 \text{V} \) decreases to 0.96 eV due to the presence of the two C atoms. Because of the spatial locations of the second and third H trapping sites, the binding energy of the third H is similar to the second H to the \( \text{C}_2 \text{V} \); however, the fourth H binding energy drops significantly. The site of the fifth H trapped by the \( \text{C}_2 \text{V} \) is close to the first H site, as seen in Fig. 9(b) and the binding energy of the fifth H to the \( \text{C}_2 \text{V} \) is similar to the fourth H. The calculations show that no more than six H can be trapped by the \( \text{C}_2 \text{V} \) due to a negative binding energy of the sixth H. Three C atom at the vacancy form a trimer or a \( \text{C}_2 \text{V} \) complex on the (001) plane, which can trap only three H atoms. The trapping sites of the three H by the \( \text{C}_2 \text{V} \) are represented by the red spheres in Fig. 9(c). The binding energy of the first H to the \( \text{C}_2 \text{V} \) has a lower value of 0.6 eV. The second H binding energy is close to the first H binding energy because of the symmetry of the two trapping sites. The sequential binding energy of the third H to the \( \text{C}_2 \text{V} \) is only 0.24 eV and there is no more room near the \( \text{C}_2 \text{V} \) energetically left for the fourth H. As discussed above, a vacancy can trap four C atoms, forming a \( \text{C}_4 \text{V} \) complex; however, this \( \text{C}_4 \text{V} \) complex cannot trap any H atoms.

According to the sequential H binding energy (greater than 0.0 eV), the maximum number of H \( (N_H) \) trapped by complexes \( \text{C}_2 \text{V} \), \( \text{C}_4 \text{V} \) and \( \text{C}_6 \text{V} \) are 10, 8, 4 and 0, respectively. However, as shown in Fig. 7 and Table 3, the H binding energies exhibit significant decreases at the 7th, 5th, 4th and 3rd H atoms in the cases of no C, one, two or three C atoms, respectively, and approach 0.1–0.3 eV for higher H contents. This suggests that the H trapping by \( \text{C}_m \text{V} \) complexes becomes weak at high H contents. The stability of \( \text{C}_m \text{VH}_x \) complexes at temperature \( T \) is correlated with the dissociation energy \( (E_d) \) of H from \( \text{C}_m \text{V} \) complexes. Based on the work of Janotti and Van de Walle [50], the relation of \( T \) to \( E_d \) can be estimated by the following equation:

![Fig. 7](image-url)
where the dissociation energy of H from defects $E_d$, i.e. trapping energy, is equal to the sum of the migration energy of H ($E_m$) and the binding energy of H to defects ($E_b$). The details about the derivation of Eq. (3) from Ref. [50] are shown in the Supplementary material. Using Eq. (3) and the calculated $E_m$ of H (0.20 eV) and $E_b$ of H to a single vacancy in W (1.24 eV), the H desorption peak temperature $T$, corresponding to vacancy trapping, is estimated to be 558 K. If considering the increase in the binding energy of H to vacancy clusters [39] and the effect of surface barriers or recombination of H at surfaces, the estimated H desorption peak temperature should be closer to the value of 600 K observed in experiments [51]. Based on Eq. (3), at 300 K and 500 K, the dissociation energies of H from defects are about 0.77 eV and 1.29 eV, and thus a single vacancy can trap six and two H atoms at these two temperatures, respectively. Similarly, assuming that the migration energy of H is still 0.2 eV without considering the effect of C at low C concentrations, the maximum number of H ($N_{H1}$) trapped by $C_mV$ complexes at 300 K and 500 K can be evaluated. Fig. 10 shows the maximum number of H trapped by $C_mV$ complexes with and without considering temperature effects as a function of the number of C ($N_C$). It is of interest to see that the maximum number of H that can be trapped by $C_mV$ complexes almost linearly decreases with increasing number of C at a single vacancy, and this decrease becomes slow when the temperature increases. These results imply that the difference in H retention in W with and without C might decrease with increasing temperature at low C concentrations, in other words, the effect of C on H retention is dependent on temperature. Based on the present simple

![Fig. 8](image_url)

*Fig. 8. Configuration of (a) CVH$_1$, (b) CVH$_2$, (c) CVH$_3$, (d) CVH$_4$, (e) CVH$_5$, (f) CVH$_6$, (g) CVH$_7$, (h) CVH$_8$ in W, where small blue spheres are W atoms, medium red and large green spheres represent H and C atoms, respectively. The dotted lines represent C-H bonds.*

![Fig. 9](image_url)

*Fig. 9. Configuration of (a) C$_2$VH$_4$, (b) C$_2$VH$_5$, (c) C$_3$VH$_3$ in W, where the representations of spheres are the same as those in Fig. 8. The number (1–5) indicates the sequential order of H binding to $C_mV$ complexes.*

![Fig. 10](image_url)

*Fig. 10. Maximum number of H ($N_{H1}$) trapped by $C_mV$ complexes as a function of number of C ($N_C$), where squares represent $N_{H1}$ without considering temperature effect, circles and triangles denote $N_{H1}$ at 300 K and 500 K, respectively.*
estimation, when the temperature is greater than 558 K, the effect of C on H trapping by Cn,V complexes can be negligible. The temperature dependence of H trapping in pure W, C-containing W, and WC has been investigated by different groups [8,9,52,53]. The inference based on the present DFT calculations is somewhat consistent with the experimental observations in Refs. [8] and [9], which showed the difference in the trapped deuterium in C-containing W and C-free W sharply decreased at the temperatures between 300 K and 500 K and then disappeared at higher temperatures.

4. Conclusion

We investigated the C clustering in W with and without vacancies and the effect of C concentration at a vacancy on the H trapping by DFT calculations performed using VASP. The results show that the nascent formation of WC is based on a pair of C located at the two neighboring OISs along the (111) direction with a distance of 0.284 nm. With increasing interstitial C atoms, the C atoms prefer to form a zigzag chain on a (110) plane for cluster sizes in which the number of C is less than 7, and the binding energy increases with increasing number of C until four C atoms and remains constant at 0.7 eV for larger interstitial C clusters.

The presence of vacancies enhances the interactions between C and W, strengthening the C trapping in W. One single vacancy can trap four C atoms, while a first and a second nearest neighbor di-vacancy can trap six and seven C atoms, respectively. The binding energy of C to vacancies increases with increasing number of vacancies and decreases with increasing number of C. The hybridization between the C-p state and the d state of its 1NN W atoms becomes stronger with increasing vacancy contents, resulting in larger C binding energy. In addition, the presence of C enhances the stability of di-vacancy in W.

C atoms located near a vacancy will decrease H trapping at the vacancy, because the H binding energies to Cn,VHn+1 complexes decrease with increasing C contents. For a given C content, the H binding energies to Cn,VHn+1 complexes basically decrease with increasing number of H. The maximum number of H that can be trapped by Cn,V complexes almost linearly decreases with the rising number of C at a single vacancy. The effect of C on H binding to Cn,V complexes is dependent on temperature.

CRediT authorship contribution statement

L. Yang: Conceptualization, Methodology, Software, Data curation, Visualization, Writing - original draft. B.D. Wirth: Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.commatsci.2020.109932.

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