DFT calculations of vacancy formation energies and interaction energies with hydrogen atoms in tungsten

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contents

• Introduction
• DFT calculations of vacancy and di-vacancy formation energies
• H-V complex formation in W and its effects on void nucleation and hydrogen retention
• Summary
Fusion power output $\sim 3$GW

DT fusion reaction $\sim$ a few %

$\cdot$ T inventory increase (Wall pumping)

- thermal diffusion deep and trapped inside (square root of incident fluence)
- codeposition with sputtered particles (low T, linearly increase with fluence)
- microstructure develop (T dependence ?, fluence dependence ?)

$\cdot$ Reemission character $\Rightarrow$ Optimal operation temperature window

FBR $\sim 0.1$

dpa

100

microstructure

codeposit

diffusion limit

wall saturation

No experimental knowledge

$\approx 10^{24} \text{T/m}^2/\text{s}$

$\approx 10^{21} \text{n/s}$

$\approx 10^{21} \text{T/s}$

$TBR > 1$

$\approx 10^{25} \text{/m}^2$

$\approx 10^{31} \text{/m}^2$
Introduction

- Radiation damage effects on tritium retention in the tungsten divertor is a key issue for full-W option.

- **BULK/** Primary roles of n-induced radiation damage (e.g., vacancy and dislocation loop):
  D plasma exposure ($2 \times 10^{18} \text{D/m}^2/\text{s}$, $6 \times 10^{22} \text{D/m}^2$, 473K) to a damaged tungsten specimen by fission neutron (HFIR, 0.025 and 0.3dpa@373K) leads to a large enhancement (about 1%) of D concentration over a few micron depth.
  W surrogate ion (MeV) damage leads to a large increase of D retention.

- **SURFACE/** High-flux divertor plasma effects (e.g., blistering):
  Higher flux irradiation leads to a significant enhancement of D retention [e.g. Alimov, 2008].
  D+C ion-driven permeation experiments suggested super-saturated D in tungsten [Peng, Ueda, 2013].
Figure 2. Depth profiles of D in non-irradiated and n-irradiated W specimens (0.025 and 0.3 dpa) after exposure to D plasma at 473 K (a) and 773 K (b).


Hatano Y. et al 2013 Nucl. Fusion 53 073006
Radiation effects depend on character of defects. Scaling with dpa has large uncertainty.

PKA energy dependence

DEM0 \(\Rightarrow\) 10 dpa \(\Rightarrow\) Power plant \(\Rightarrow\) 100 dpa

Traps / W = \(6 \times 10^{-4} + 1.4 \times 10^{-2} \exp(-0.15/dpa)\)

Whyte, ITPA (2008)  Ueda (Osaka Univ.)

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Super-saturated D and blistering (D/C mixed irradiation)

Temperature dependence of D/W fraction at the ion range

\[ C_R - C_b \sim \phi_p d / D \]


D/C mixed irradiation increase D concentration

Blistering on W surfaces by D/C mixed irradiation (f_c = 0.7-2.1%). (No blistering observed with D only)

upper) optical microscope image
lower) SEM image

Zakharov's Diffusivity
- high-flux
- low-flux
- medium-flux
- Ref. [2]

Frauenfelder's Diffusivity
- high-flux
- low-flux
- medium-flux
- Ref. [2]
Super-saturation of H concentration by high-flux plasma irradiation

Fractional concentration of H at the surface is estimated in steady state of incident flux $\phi_{in} = 10^{24} / \text{m}^2/\text{s}$.

$$C_s = \sqrt{f \phi_{in} / k_r}$$

- Anderl’s data (Fus. Tech. v.21, 745, 1992) for recombination coefficients $k_r$, 1 keV D$^+$ ion, Frauenfelder’s diffusivity is used.
- Reflection coefficient (TRIM.SP) $0.76 \sim 0.98 @ 10 \text{ eV}$ ($f = 1e-1 \sim 1e-2$); t’Hoen et al. PRL 111, 2013, $f = 1e-5 \sim 1e-7 @ 5 \text{ eV}$. 
Divertor plasma exposure experiment at Large Helical Device (LHD)

Tokitani et al., JNM (2005)
Nano-cavity in W observed after high-flux hydrogen plasma exposure

- Discharge time: 26s (19 shots)
- \( n_e \) (core) = 2.3 – 4.0\( \times 10^{19} \) /m³
- \( T_i \) (core) = 2.1 – 3.4 keV
- \( T_e = T_i \) (divertor) = 10 – 20 eV
- Ion energy on W target: 100 – 200 eV
- Ion particle flux: \( 10^{22} \) H/m²s (Langmuir probe)
Total energy calculation in DFT

\[
E = \sum_n \int_{\Omega_{BZ}} d^3k \varepsilon_{n\tilde{k}} f \left( \frac{\varepsilon_F - \varepsilon_{n\tilde{k}}}{\sigma} \right) + E^H [\rho] + E^{xc} [\rho] + \int d^3r V^{ion}_{loc} (\vec{r}) \rho(\vec{r}) + E_{Ewald} (\{\vec{R}\})
\]

\[
\int_{\Omega_{BZ}} d^3k \varepsilon_{n\tilde{k}} f \left( \frac{\varepsilon_F - \varepsilon_{n\tilde{k}}}{\sigma} \right) \approx \sum_{\Omega_{BZ}} \omega_{\tilde{k}} \varepsilon_{n\tilde{k}} f \left( \frac{\varepsilon_F - \varepsilon_{n\tilde{k}}}{\sigma} \right)
\]

\[
f(x) = \frac{1}{2} (1 - \text{erf}(x)) + A_1 H_1(x)e^{-x^2}
\]

(Methfessel and Paxton)

Convergence of mono-vacancy formation energy in $W_{128}$

<table>
<thead>
<tr>
<th>k-point</th>
<th>$E(W_{128})$ in eV</th>
<th>$E(W_{127}V)$ in eV</th>
<th>$E_f(V)$ in eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>4x4x4</td>
<td>-1664.9194</td>
<td>-1648.6293</td>
<td>3.282</td>
</tr>
<tr>
<td>6x6x6</td>
<td>-1664.8066</td>
<td>-1648.6540</td>
<td>3.146</td>
</tr>
<tr>
<td>8x8x8</td>
<td>-1664.7713</td>
<td>-1648.6298</td>
<td>3.135</td>
</tr>
<tr>
<td>10x10x10</td>
<td>-1664.7561</td>
<td>-1648.6240</td>
<td>3.126</td>
</tr>
<tr>
<td>12x12x12</td>
<td>-1664.7531</td>
<td>-1648.6261</td>
<td>3.121</td>
</tr>
</tbody>
</table>

Calculated using VASP v4.6.34 (GGA-PBE)

\[
\alpha = 3.165\text{Å},
\]

\[
\frac{\hbar}{2m_e} \left| \mathbf{G} + \mathbf{k} \right|^2 < 223.1\text{eV}, \sigma = 0.2\text{eV}
\]

\[
E_f(V) = E(W_{127}V) - \frac{127}{128} E(W_{128})
\]
Surface-energy correction of vacancy formation energy in W

DFT results of vacancy formation energies in W

<table>
<thead>
<tr>
<th></th>
<th>$E_F$ (eV)</th>
<th>$\Omega_F$ (Å$^3$)</th>
<th>B (GPa)</th>
<th>$E_B$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perfect</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>15.9 304</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>16.0$^b$ 305$^b$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>15.8$^f$ 323$^f$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$V_1$</td>
<td>3.68(3.17)</td>
<td>10.5 309</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.5–4.1$^a$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.56$^b$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.6$^c$</td>
<td>12.4$^c$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.95$^e$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.568$^h$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$V_2(1\text{NN})$</td>
<td>7.31(6.50)</td>
<td>21.4 298</td>
<td>+0.05(-0.16)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.71$^b$</td>
<td></td>
<td>+0.41$^b$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.06$^c$</td>
<td>25.4$^c$</td>
<td>+0.14$^c$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.32$^e$</td>
<td></td>
<td>+0.7$^d$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.129$^h$</td>
<td></td>
<td>+0.007$^h$</td>
<td></td>
</tr>
<tr>
<td>$V_2(2\text{NN})$</td>
<td>7.63(6.81)</td>
<td>20.1 294</td>
<td>-0.27(-0.47)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.93$^b$</td>
<td></td>
<td>+0.19$^b$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.42$^c$</td>
<td>23.6$^c$</td>
<td>+0.78$^c$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.36$^e$</td>
<td></td>
<td>+0.54$^e$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.325$^h$</td>
<td></td>
<td>+0.29$^g$</td>
<td></td>
</tr>
<tr>
<td>$V_2(3\text{NN})$</td>
<td>7.48(6.47)</td>
<td>20.8 301</td>
<td>-0.12(-0.13)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.32$^c$</td>
<td>24.8$^c$</td>
<td>-0.12$^c$</td>
<td></td>
</tr>
</tbody>
</table>

TABLE:
Formation energy ($E_F$), equilibrium atomic volume, defect formation volume ($\Omega_F$), bulk modulus (B), and binding energy ($E_B$).
Perfect: perfect crystal, $V_1$: mono-vacancy, $V_2(1\text{NN})$: first nearest-neighbor di-vacancy, $V_2(2\text{NN})$: second, and $V_2(3\text{NN})$: third. Bold numbers are present DFT results.

a. Recommended values in Landolt-Börnstein
b. DFT-GGA with package of linear combination of atomic type orbitals (PLATO)
c. Johnson’s model potential
d. Experimental data of field ion microscopy
e. Modified embedded atom model calculation
f. Recommended values in Kittle’s text
g. Tight-binding basis calculation
h. VASP PBE-AM05
Hydrogen trapping effect on di-vacancy formation in W

$V_2H$ complex binds with H stronger than VH
A nucleus of larger vacancy clusters

$\begin{align*}
\text{1NN} \\
\text{2NN}
\end{align*}$

$DFT$ potential energy surface of $H$

Binding energy of single hydrogen atom to $V_2$
- 1.8 eV for 1NN at an octahedral site.
- 2.1 eV for 2NN at the center of a line connecting two vacancies.

(Binding energy to V is 1.4 eV)

Hydrogen effect in formation energies of $V_2$ and $V_2H$ in tungsten for 1NN and 2NN configurations. Other $DFT$ results (triangles, L.Ventelon 2012) using AM05 functional optimized to vacancy calculations are also plotted for comparison. Dotted line indicates an experimental value obtained by field ion microscopy (FIM, J.Y.Park 1983).
TABLE III. Formation energies ($E_f$) and binding energies ($E_b$), in eV, of vacancy clusters in tungsten. Positive values of the binding energy indicate attraction between the vacancies, leading to clustering of vacancies, whereas negative values indicate repulsion.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>PBE $E_f$</th>
<th>PBE-AM05 $E_f$</th>
<th>PBE $E_b$</th>
<th>PBE-AM05 $E_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.327</td>
<td>3.568</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 ((111))</td>
<td>6.624</td>
<td>7.129</td>
<td>0.029</td>
<td>0.007</td>
</tr>
<tr>
<td>2 ((100))</td>
<td>6.989</td>
<td>7.325</td>
<td>−0.365</td>
<td>−0.190</td>
</tr>
<tr>
<td>3</td>
<td>9.711</td>
<td>10.454</td>
<td>0.269</td>
<td>0.250</td>
</tr>
<tr>
<td>4</td>
<td>12.242</td>
<td>13.398</td>
<td>1.065</td>
<td>0.874</td>
</tr>
<tr>
<td>5</td>
<td>14.669</td>
<td>16.103</td>
<td>1.965</td>
<td>1.736</td>
</tr>
<tr>
<td>5 (Ref. 71)</td>
<td>15.744</td>
<td>17.230</td>
<td>0.890</td>
<td>0.610</td>
</tr>
<tr>
<td>6</td>
<td>17.847</td>
<td>19.457</td>
<td>2.113</td>
<td>1.950</td>
</tr>
</tbody>
</table>

FIG. 12. Tungsten vacancy cluster configurations ($N_v = 2–6$) investigated in the present study.

Figure 4. Atomic configuration and electron charge density of 1 1 1-crowdion. Blue balls are tungsten atoms. The crowdion is indicated by an array of bonded atoms along the [1 1 1] direction. Colors on the surface indicate electron densities; red indicates higher electron densities while blue indicates depletion of the electron density.

\[ u_n \equiv z_n - na \approx \frac{2a}{\pi} \arctan \left( \exp \left( -\frac{n - n_0}{N} \right) \right), \quad u_n \ll Na. \]
The formation energy is 12.1 eV which is 0.6 eV smaller than sum of the individual formation energies for the VH6 complex and the 111-crowdion. This indicates that the VH6 complexes can trap the 111-crowdion. Stability of the metastable state at elevated temperatures should be investigated in future studies.

HxVy complex — Nucleus of void formation under hydrogen-rich condition

The HxVy complex blocks V-I recombination. HₓVᵧ complex may be responsible for ion-driven trap and hydrogen retention.

ref. Condon and Schober, JNM 207 (1993)
Typical thermal desorption spectra of D+ irradiate W

SC, Johnson Matthey, 99.9 wt% pure with impurities of H-0.1, C-0.5, O-0.5 at%, 8.5 degrees to [001] plane

Ogorodnikova et al., JNM 313-316 (2003)
Equilibrium sites of H
- in vacancy: O site (octahedral)
- in matrix: T site (tetrahedral)
※ desorption path: O → T1 → T2

Transition states (TS1 and TS2) on the MEP. Solid circle is each image of NEB calculations. An intermediate transition state (TS1) is associated with a meta-stable T site (T1). H weakly trapped in a shallow potential well of the T1 site can be easily recombined with vacancy.
Harmonic Transition State Theory (hTST)

\[ \begin{align*}
A \Leftrightarrow A^* & \xrightarrow{\tau_{A^*}^{-1}} B \\
\Gamma_{AB} & = \tau_{A^*}^{-1} \frac{Z_{A^*} Z_A}{Z_{A^*}} \\
& = \frac{k_B T}{h} \prod_{l}^{N} \left( 1 - \exp \left( -\frac{h \nu_l}{k_B T} \right) \right) \\
& \quad \times \exp \left( -\frac{E_a}{k_B T} \right)
\end{align*} \]

Thermal desorption rate

\[ \frac{dx_A}{dT} = \left( \frac{dT}{dt} \right)^{-1} \frac{dx_A}{dt} = -\alpha^{-1} \Gamma x_A \]

\[ \frac{E_a}{k_B T_p^2} = \alpha^{-1} \frac{\prod_{l}^{N} \nu_l}{\prod_{l}^{N-1} \nu_l} \exp \left( -\frac{E_a}{k_B T_p} \right) \]

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Single H desorption was calculated using transition state theories to investigate **two-step effect**.

Branching ratio at T1 site indicates recombination dominant.

During temperature programmed desorption, population of the intermediate state ($x_m$) is vanishingly small and limited in a narrow temperature range.
Binding energy of vacancy-hydrogen complex VH\(_j\) in W

\[ e_t(V_m H_j) = E(W_{n-m} V_m H_j) - \frac{n-m}{n} E(W_n) - \frac{j}{2} E(H_2) \]

\[ e_b(H) = e_t(V_m H_{j-1}) + e_t(H) - e_t(V_m H_j) \]

DFT calculations (solid-squares, black [Kato], blue [Heinola], pink [Ohsawa]). Experimental values by gamma-ray perturbed angular correlation of \(^{111}\)In (stars, green). Insets show occupation sites (crosses) of hydrogen atoms in a tungsten cubic cell centered at a mono-vacancy.
It is noted that there is still an issue regarding the maximum number of hydrogen atoms accommodated in the single vacancy. Liu and Ohsawa have suggested 10 or 12 hydrogen atoms can be accommodated in the single mono-vacancy. It has been found that with increasing occupation numbers, the trapping sites are shifted toward the tetrahedral sites.

<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.64</td>
<td>1.22</td>
<td>1.39</td>
<td>1.43</td>
<td>1.318</td>
<td>1.16(2)</td>
<td>0.95(3)</td>
</tr>
<tr>
<td>2</td>
<td>0.67</td>
<td>1.23</td>
<td>1.40</td>
<td>1.41</td>
<td>1.308</td>
<td>0.99(2)</td>
<td>0.68(3)</td>
</tr>
<tr>
<td>3</td>
<td>0.46</td>
<td>1.10</td>
<td>1.12</td>
<td>1.22</td>
<td>1.082</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.35</td>
<td>0.82</td>
<td>0.92</td>
<td>1.11</td>
<td>1.015</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.45</td>
<td>1.12</td>
<td>1.12</td>
<td>1</td>
<td>0.929</td>
<td>&lt; 0.7</td>
<td>—</td>
</tr>
<tr>
<td>6</td>
<td>0.08</td>
<td>0.32</td>
<td>—</td>
<td>0.47</td>
<td>0.677</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Note:* Present results [20] were obtained using a reference super-cell with 54 atoms. ZPE means the results with zero-point energy correction. Results of Heinola [21] and Ohsawa [22] include the ZPE correction. Experimental values [25] and [26] are binding energies of H in InV$_2$ complexes of tungsten and those of D in mono-vacancies of a D*-irradiated single crystal tungsten, respectively (see text).
Temperature Programmed Desorption of VH\textsubscript{j} complexes

Statistical thermodynamics model proposed by Fukai with an extension.

\[ x_i = \frac{N_{i\text{H}}}{N_{i\text{w}}}, \quad x_{v0} = \exp[-f_v/kT] \]
\[ x_j = \frac{N_{vH_j}}{N_{vH}} = \left( \frac{x_i - x_t}{6} \right)^j \omega_j \exp[-\Delta f_j/kT], \quad \omega_{0-6} = 1,6,3,4,12,6,1 \]
\[ x_i = \sum_j j \times x_j, \quad x_v = \sum_{j=0}^\infty x_j \]
\[ \Delta f_j = f_j - j \times f_i \]

\( f \) : formation free energies
\[ f_j(T) = e_i(VH_j) + \sum_i^3 \left[ \frac{h \nu_i^{(VH_j)}}{2} + kT \ln(1 - \exp(-h \nu_i^{(VH_j)}/kT)) \right] \]
\[ f_i(T) = e_i(H) + \sum_i^3 \frac{h \nu_i^{(H)}}{2} + kT \ln(1 - \exp(-h \nu_i^{(H)}/kT)) \]

Rate equations for fractional concentrations of VH\textsubscript{j} complexes. Desorption rates are calculated by harmonic transition state theory (hTST).

\[
\begin{cases}
\frac{dx_j}{dT} = -\alpha^{-1} \Gamma_{j\rightarrow j-1} x_j, & j = 6 \\
\frac{dx_j}{dT} = -\alpha^{-1} (\Gamma_{j\rightarrow j-1} x_j - \Gamma_{j+1\rightarrow j} x_{j+1}), & 1 \leq j < 6 \\
\end{cases}
\]
\[ \Gamma = \frac{kT}{h \prod_{i=1}^{N-1} (1 - \exp(-h \nu_i^{(TS)}/kT))} \exp(-E_d/kT) \]

\[ \text{H concentration} = 10^{-10} \]
**Double-peak structure is obtained. Good agreement with experimental results with SCW for higher fluence.**

**No empirical parameter is used**
Summary

• Radiation damage has a primary role of tritium retention in fusion reactor plasma-facing component.

• Super-saturation of hydrogen in W divertor is anticipated. Its influence on microstructure development on the surface and tritium retention is an issue.

• DFT calculations of vacancy formation energies are improved by surface xc-energy corrections. DFT results of di-vacancy binding energies are almost zero or negative (repulsive).

• Hydrogen trapping is a clue of the abundance of di-vacancy in W (void nucleation).

• It is predicted that vacancy-hydrogen complexes can trap crowdion-SIA and suppress the vacancy-SIA annihilation.

• Detrapping of hydrogen from vacancy-hydrogen complexes are investigated based on the hTST using DFT energies and normal mode frequencies. Reasonable agreement with experimental measurements. Similar analysis will be performed for larger complexes.
UQ issues for modeling

• Numerical convergence of DFT calculations, e.g. k-point sampling and smearing, plane-wave energy-cutoff, super-cell size, energy-functional (especially for surface), pseudo-potential.

• Characterization of hydrogen traps in the model.

• How to scale-up the DFT results for larger systems, e.g. potential development for MD, parameter passing for KMC, statistical scaling (thermodynamics, CE)
Acknowledge

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