H trapping and migration in tungsten: a DFT investigation that includes temperature dependency

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How to contribute?

DFT world

Nanometric scale – 0K

ITER world

Macroscopic scale
## Different Strategies

### Laboratory experiments

| TDS, HREELS, NRA, XPS ... | S. Markelj (O), P. Pelicon, I Cadez | JSI – Ljubljana, Slovenia  
| R. Bisson (O), T. Angot, J.M. Layet | PIIM – AMU, France  

*Talks on Friday*

### Multi-scale approaches

| MD, KMC, MRE ... | C. Becquart (O) | UMET – Université de Lille, France  
| E. Hodille (P), C. Grisolia | CEA – Cadarache, France  

### Statistic models

| DFT  
| TST | D. Kato (O) | NIFS, Toki City - Japan  

*THIS WORK*
1 – DFT model and parameters

2 – H trapping in Vacancies

3 – Toward macro-scale understanding

4 – Conclusion
DFT parameters / Error Bars

**Accuracy** - $\Delta E_f$ vacancies, solubility, $E_a$ diff.

**Wave-function expansion**
- **Used**: 36 – 40 Ry
- **Literature**: ≈ 25 (36) Ry

**K-points sampling**
- **Used**: 18 - 20 $k$ points
- **Literature**: 12 – 15 $k$ points

**Pseudo-potentials**
- **Used**: 14 valence $e$
- **Literature**: 6 (12) valence $e$

**Functional**
- **Used**: PBE
- **Literature**: PBE (PW91)

**Functional**
- **Vacancies**
  - most sensitive prop.
  - can rise to 11%

**Deviation**
- below 0.7%

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Models / Error Bars

Models

W3 - 3×3×3 unit cells, 54 W atoms
W4 - 4×4×4 unit cells, 128 W atoms

These data can be tuned in the range of 3-4% to fit with exp.

Deviation

- Size of the Unit-cell 3.0%
- DFT param. 0.7%

Total Deviation ≈ 3.1%

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1 – DFT model and parameters

2 – H trapping in Vacancies
   DFT - H trapping in Vacancies
   Statistic model

3 – Toward macro-scale understanding

4 – Conclusion
**H trapping in vacancies**

**H interstitial as solute**

*Vacancies*  Stability $V_1$ vs $V_2$

D. Kato (O)

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**Multi-trapping**

*Up to 12 H atoms in a vacancy*

Y. W. You et al., *AIP ad. 3* (2013) 012118
De-trapping from VHj

De-trapping path

\[ e_{\text{diff}} \]

\[ e_b \]

\[ e_{dtp} \]

\[ e_{dnn} \]

Reaction coordinate

Energy (eV)

(i) (ii) (iii) Td Td

\( e_{b} \)

\[ e_{dtp} = e_{b} + e_{\text{diff}} \]

\[ e_{dnn} \]

Thermodynamic

Kinetic

NEB generalized paths to \( j=1, 6 \)

Y.L. Liu et al. PRB 79 (2009) 172103

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Filling level at RT

Polanyi-Wigner equation

Previous results at 0K

\[
\frac{e_{\text{dip}}}{k_B T_{\text{max}}^2} = \frac{\nu}{\beta} \exp\left( -\frac{e_{\text{dip}}}{k_B T_{\text{max}}} \right)
\]

- Rump in temperature \( \beta \)
- Attempt frequency \( \nu = \frac{k_B T}{h} \frac{Z_{\text{vib}}^+}{Z_{\text{vib}}} \)
- mean value \( 300K < T < 1000K \)

\[ 0.85 \times 10^{13} \text{ Hz} < T < 1.45 \times 10^{13} \text{ Hz} \]

Desorption \( T \) at peak maximum

\[ \beta = 1 \text{ K.s}^{-1} \]

\[
\begin{array}{ccccccc}
\beta = 1 \text{ K.s}^{-1} & 6H & 5H & 4H & 3H & 2H & 1H \\
E_{\text{des}} (\text{eV}) & 0.86 & 1.11 & 1.17 & 1.25 & 1.42 & 1.43 \\
T_{\text{max}} (\text{K}) & 311 & 399 & 420 & 447 & 507 & 511 \\
\end{array}
\]

Filling level at RT

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1 – DFT model and parameters

2 – H trapping in Vacancies
   DFT - H trapping in Vacancies
   Statistic model

3 – Toward macro-scale modeling

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## Statistic Model

### What we have ...

- DFT parameters – error bars
- Quantum effects - ZPE
- Temperature dependency
  - Polanyi-Wigner
  - Filling level at RT – VH6

### What want ...

- Full temperature dependency
- Energies and free energies
- Equilibrium conditions

### How

\[ e(T) = e^{\text{DFT}}(0) + e_{\text{vib}}(T) \]

\[ s(T) = s_{\text{vib}}(T) \]

\[ f(T) = e - T s(T) \]

\[ e_{\text{vib}}(T) = k_B \sum_{i=1}^{3n} \left( \frac{h v_i}{2 k_B} + \frac{h v_i}{k_B} \frac{1}{e^{\frac{h v_i}{k_B T}} - 1} \right) \]

\[ s_{\text{vib}}(T) = k_B \sum_{i=1}^{3n} \left( \frac{h v_i}{k_B T} \frac{1}{e^{\frac{h v_i}{k_B T}} - 1} - \ln \left(1 - e^{\frac{h v_i}{k_B T}}\right) \right) \]

\[ F = -k_B T \ln Q \]

\[ Q = Z_{\text{vib}} Z_{\text{conf}} \]
Equilibrium

Tungsten sample

H implantation
Ion gun / plasma source
Low energy particles

Equilibrium in tungsten

Constant H concentration
H inserted as interstitial
VH_j are induced

Thermo. Equilibrium is reached

\[
F = n_{H_i} \Delta f_{H_i} + \sum_{j=0}^{6} N_j \Delta f_{VH_j} - k_B T \ln(Z_{\text{conf}})
\]

Proposed by D. Kato

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VHj vacancies fractions

VHj fractions at Thermo Equilibrium

300K < T < 550K – VH6 - PW eq.
550K < T < 1000K – pop inverted
T > 1000K – vacancies depopulated

Excellent agreement

Numerically solved – D. Kato

J.P. Roszell et al. JNM 429 (2012) 48
Total vacancy fraction

Total vacancy fraction induced
Thermodynamic Equilibrium

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Max. 300K&lt;T&lt;550K</th>
<th>ITER</th>
<th>Decreases 550K&lt;T&lt;1000K</th>
<th>AS in pure W for T&gt;1000K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000K</td>
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<td>550K</td>
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<tr>
<td>300K</td>
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</tbody>
</table>

**H concentration = 10^{-5}**

- **VH₆**
- **w/o vibration entropy**
- **ITER**
- **Thermal vacancy concentration**

**Excellent agreement**

All implanted H at RT create VH₆ vacancies
A safety issue for ITER

From J.P. Roszell et al. JNM 429 (2012) 48
1 – DFT model and parameters

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3 – Toward macro-scale understanding

   TDS
   Diffusion coefficient

4 – Conclusion
DFT vs TDS

TDS - What are the mechanisms taking place during desorption

Simple kinetic model

- diffusion is neglected (0.2eV)
- the surface of the sample is neglected
- hydrogen is assumed to desorbed as released from a vacancy type VH_j
- kinetics of order one are assumed

\[-\frac{dx_{VH_j}(T)}{dT} = x_{VH_j}(T) \frac{\nu_j}{\beta} \exp\left(-\frac{e_{dip_j}}{k_BT}\right)\]

TDS conditions

- H implantation T=300K
- VH_j fraction from stat. model
- \(\beta=5\text{Ks}^{-1}\)
- 0.85 \(10^{13}\) Hz < \(\nu\) < 1.45 \(10^{13}\) Hz
This work

Low temperature peak VH3-5
T=420K

High temperature peak
VH1,2
T=540K

Not observed
Already desorbed

Exp.

TDS peaks include desorption from multiple VH_j traps

A. D. Quastel et al, JNM 359 (2006) 8

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De-trapping mechanisms

**Experiment**

- Poon et al. weighing LT40 : HT60
- Using Polanyi-Wigner
- $e_{\text{exp1}} = 1.34 \text{eV}$, $e_{\text{exp2}} = 1.07 \text{eV}$

**These are mean values**

- LT $j=4,5$ and HT $j=1-3$

**3-4% error bars**

- Small deviations affect assignment
- Mean values of de-trapping energies
  - HT $- e_{\text{dtp} j=1-3} - e_{\text{HT}} = 1.37 \text{eV}$
  - LT $- e_{\text{dtp} j=4-5} - e_{\text{LT}} = 1.14 \text{eV}$

M. Poon et al. JNM 374 (2008) 390
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**Experimental results**

\[ D_{\text{exp}}^F = 4.1^{+5.10^{-7}} \exp(- \frac{0.39 \pm 0.08}{k_B T}) \]


**NEB from Td to Td sites**

**DFT result**
\[ e_{\text{diff}} = 0.20 \text{ eV} \]
Experimental results

\[ D_{\text{exp}}^F = 4.1^{+5-2}.10^{-7} \exp\left(-\frac{0.39 \pm 0.08}{k_B T}\right) \]


\[ D_{\text{exp}}^Z = 6^{+2-1}.10^{-4} \exp\left(-\frac{1.04 \pm 0.08}{k_B T}\right) \]


\[ D_{\text{FitH}}^F = 1.58^{+1.9-0.77}.10^{-4} \exp\left(-\frac{0.25 \pm 0.08}{k_B T}\right) \]

Heinola et al., *PRB* 82 (2010) 094102

**DFT result**

\[ e_{\text{diff}} = 0.20 \text{ eV} \]
**Experimental results**

\[ D_{\text{exp}}^F = 4.1^{+5}_{-2}.10^{-7} \exp\left(-\frac{0.39 \pm 0.08}{k_B T}\right) \]


\[ D_{\text{exp}}^Z = 6^{+2}_{-2}.10^{-4} \exp\left(-\frac{1.04 \pm 0.08}{k_B T}\right) \]


\[ D_{\text{FiiH}}^F = 1.58^{+1.9}_{-0.77}.10^{-4} \exp\left(-\frac{0.25 \pm 0.08}{k_B T}\right) \]

Heinola *et al.*, PRB 82 (2010) 094102

**This work**

- **High Temp.**
  \[ D_{\text{DFT}}^{\text{HT}} = 1.38.10^{-7} \exp\left(-\frac{0.20}{k_B T}\right) \]

- **Low Temp.**
  \[ D_{\text{DFT}}^{\text{LT}} = 6.10^{-4} \exp\left(-\frac{1.07}{k_B T}\right) \]
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Conclusion

VHj fractions at equilibrium and evolution with Temperature

The amount of trapped H/T is maximum in the range 300K – 550K

TDS and desorption mechanisms – mean values of VHj contributions

Diffusion coefficient – mean value of two regimes due to vacancies

Results to be compared with and included in

Experiment
OKMC, RE ...
Comparison to other works

DFT + Thermo

MRE – C. Grisolia, E Hodile

OKMC – C. Becquart

Exp: T. Angot, R Bisson,

After 2h
Thank you for your attention