Assessment and modeling of trap effects on hydrogen diffusivity in tungsten

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Contents

1. Hydrogen diffusivity in W

- Migration paths for H
- ✓ Modeling of migration with transition state theory (TST)
 - ✓ Model validation with "H in Fe"
- ✓ Kinetic Monte Carlo simulation for trap effects
- ✓ Overall comparison with available experimental results

(Frauenfelder) $D = 4.1 \times 10^{-7} \exp(-0.39 \ e \ V/k \ T)$

(Heinola; high-T data fitting) $D = 1.58 \times 10^{-7} \exp(-0.25 \ e V/kT)$

- 2. Rate theoretical model for vacancy trap effects on hydrogen diffusivity
- 3. Experimental studies in SNU

1. H diffusivity in bcc-W: review of experimental data



1. H diffusivity in bcc-W : diffusion mechanisms

✓ Stable site for hydrogen atom is tetrahedral sites. (T-site)

- : W
- : T-site (of interest) 💫 : 1st neig. T-site 💫 : 2nd neig. T-site

- \checkmark Migration to the 1st neighboring T-site passes Trigonal site (\bigcirc).
- Migration to the 2nd neighboring T-site passes Octahedral site (O-site;).



1. H diffusivity in bcc-W : transition state analysis



- ✓ The migration via Trigonal-site (E_m =0.20-0.21 eV [1.2]) is the minimumbarrier path, and thus is the most probable migration path for H [1,2].
- ✓ Although the migration via Octahedral-site (E_m=0.40 eV [3]) gives a closer barrier to the experiment, it should be inappropriate.

[1] Y.L. Liu et al., J. Nucl. Mater. (2009) 1032; [2] K. Heinola et al., J. Appl. Phys. 107 (2010) 113531; [3] D.F. Johnson et al., J. Mater. Res. 25 (2010) 315.

1. H diffusivity in bcc-W: expression of diffusion coefficient



$$D = \frac{1}{6}fd^2\Gamma$$

- D [m²/s]: diffusion coefficient
- \succ *f* []: correlation factor
 - F=1 as no correlation in sequential jumps.
- d [m]: jump distance

$$ightarrow d = a_0/2\sqrt{2} = 1.12$$
 Å

$$\Gamma = n\nu e^{-\frac{\Delta E}{kT}}$$

n [-]: the number of equivalent paths

▶ n = 2 or 4

A L

- ➤ v [1/s]: jump attempt frequency
- $\succ \Delta E$ [eV}: migration barrier

1. H diffusivity in bcc-W: determination of v and ΔE by TST

*J. Phys. Chem. Solids 3 (1957) 121.

(1) Classical transition state theory (TST) with harmonic approx. by Vineyard*.

$$\Delta E = E_{Tri-site} - E_{T-site}$$

$$v_{Vine} = \left(\prod_{i=1}^{N} v_i \right) / \left(\prod_{i=1}^{N-1} v'_i \right).$$

(2) Classical TST with quantum mech. partition functions within harmonic approx.

$$\Delta E = E_{Tri-site} - E_{T-site}$$

$$\nu_{qHTST} = \frac{kT}{h} \times \left\{ \prod_{i=1}^{N-1} \left(\frac{\exp\left(-\frac{h\nu_i^*}{2kT}\right)}{1 - \exp\left(-\frac{h\nu_i^*}{kT}\right)} \right) \right/ \prod_{i=1}^{N} \left(\frac{\exp\left(-\frac{h\nu_i}{2kT}\right)}{1 - \exp\left(-\frac{h\nu_i}{kT}\right)} \right) \right\}.$$

(3) Explicit correction of zero-point energies to the Vineyard model

$$\Gamma_{ZPE} = \nu_{Vin}^* \exp\left(-\frac{\Delta E + E_{ZPE}}{RT}\right) \qquad E_{ZPE} = \frac{1}{2} \sum_{i=1}^{N-1} h\nu_i' - \frac{1}{2} \sum_{i=1}^{N} h\nu_i$$

1. H diffusivity in bcc-W: application to "H in W" with DFT results

✓ DFT calculation was done with VASP code using PBE functional.



*R. Frauenfelder, J. Vac. Sci. Technol. 6 (1969) 388.

1. H diffusivity in bcc-W: Heinola's suggestion



*K. Heinola and T. Ahlgren, J. Appl. Phys. 107 (2010) 113531.

(Frauenfelder) $D = 4.1 \times 10^{-7} \exp(-0.39 \ e \ V/k \ T)$

(Heinola; high-T data fitting) $D = 1.58 \times 10^{-7} \exp(-0.25 \ e V/k T)$

1. H diffusivity in bcc-W: summary of available experimental data

(Original: Eq. 1) $D = 4.1 \times 10^{-7} \exp(-0.39 \ e \ V/k \ T)$ (High-T only: Eq. 2) $D = 1.58 \times 10^{-7} \exp(-0.25 \ e \ V/k \ T)$



1. H diffusivity in bcc-W: Kinetic Monte Carlo (KMC) method

KMC simulation pursues a system evolution by repeating some atomic-scale kinetic events which are relevant with a phenomenon of interest. Judgment whether an event attempt will succeed or fail is made using Monte Carlo simulation technique.

$$v_{event} = v_{attempt} \times p = v_{attempt} \times \exp(-E/kT)$$



1. H diffusivity in bcc-W: Isn't it too simple? - focus on high temperature (>1100 K) of pure W + H₂ absorption-

- ✓ Vacancy trapping energy: (~1.4 eV)
- ✓ Impurities
 - ✓ Non-metallic (~ 0.3 eV)
 - Metallic (~0.7 eV for substitutional Fe)
 *X.S. Kong et al., J. Nucl. Mater. 433 (2013) 357;
 G.H. Lu, Nucl. Fusion 54 (2014) 086001
- Vacancy clustering (pre-treatment at 2400 K); V clusters are decomposed at around 1700 K
 *H. Eleveld and, A. van Veen, J. Nucl. Mater. 212-215 (1994) 1421;

F. Ferroni et at., Acta Mater. 90 (2015) 380.

✓ Dislocation (~0.7 eV)

* D. Terentyev et al., Nucl. Fusion 54 (2014) 042004.

✓ Grain boundary (~1.1 eV)

* Σ5(310)/[001] tilt GB H.B. Zhou et al., Nucl. Fusion 50 (2010) 025016.

1. H diffusivity in bcc-W: V-H interaction model



*K. Ohsawa et al., Phys. Rev. B 82 (2010) 184117; D.F. Johnson, E.A. Carter, J. Mater. Res. 25 (2011) 315; K. Heinola et al., Phys. Rev. B 82 (2010) 094102; Y.W. You et al., AIP Adv. 3 (2013) 012118; N. Fernandez, et al., Acta Mater. 94 (2015) 307.

1. H diffusivity in bcc-W: simplification of potential energy profile



1. H diffusivity in bcc-W: i.e. DFT results



* N. Fernandez, Acta Mater. 94 (2015) 307.

1. H diffusivity in bcc-W: trap/detrap process



✓ [● : 1st neig. O-site to vacancy] The sites for trapped H atoms
 ✓ [○ : 2nd neig. T-site to vacancy] Some sites for solute H atoms
 ✓ Detrap event: From Red to Blue (via Green)
 ✓ Trap event: From Blue to Red (via Green)

1. H diffusivity in bcc-W: KMC results on trap effects (vacancy)

cpretreatment>
2400 K for 10 h in H₂ (8x10⁴
Pa) and in vacuum (10⁻⁴ Pa)

<H-loading>
1120-2080 K In H₂ (8x10⁴ Pa); 400
min at 1120 K, 60 min at 2080 K





- $\checkmark\,$ H concentration is set according to H solubility of Frauenfelder's experiment.
- ✓ Equilibrium vacancy concentration at 2400 K (pre-treatment temperature of Frauenfelder's experiment) is 0.01 ppm with 3.8 eV vacancy formation energy.



1. H diffusivity in bcc-W: KMC results -effects of uncertainty in DFT-



1. H diffusivity in bcc-W: KMC results -Influence of H/V ratio on effective diffusivity-

- 3 characteristic regions:
- I. low H/V ratio region (H/V < 1), where apparent diffusion coefficients are almost constant;
- II. intermediate H/V ratio region (1 < H/V < 100), where the apparent diffusion coefficient increases as the H/V ratio increases;
- III. high H/V ratio region (H/V > 100), where effective diffusion coefficients are comparable with the true diffusion coefficient (Heinola's equation).



1. H diffusivity in bcc-W: sumary

 $D_{lower-limit} = D/(1 + 4c_{vacancy} \times \exp(E_{binding}/kT))$

 $E_{binding} = 1.32 \text{ eV}$ of V1H1 complex

*A. McNabb, P.K. Foster, Trans. Metall. Soc. AIME 227 (1963) 618.



Appendix-1) Influence of XC-functionals of DFT calculation Results in hydrogen related properties in W

	LDA	PBE	PBEsol	AM05	TPSS	RTPSS	M06L	Exp.
V formation	3.330	3.221	3.397	3.555	3.710	3.772	5.037	3.67 ^a
(eV)	(3.344)	(3.267)	(3.453)	(3.616)		(3.832)		±0.2
V migration	1.748	1.717	1.762	1.787	1.797	1.789	1.545	1.78 ^a
barrier (eV)	(1.756)	(1.722)	(1.760)	(1.783)		(1.786)		±0.1

		LDA	PBE	PBEsol	AM05	TPSS	RTPSS	M06L
Solution (eV)		0.633	0.904	0.773	0.862	0.982	1.063	-
		(0.627)	(0.897)	(0.761)	(0.850)		(1.052)	
Migration barrier		0.206	0.203	0.207	0.208	0.214	0.216	0.233
(e)	V)	(0.205)	(0.203)	(0.207)	(0.208)		(0.216)	
V-H	V1-H1	1.243	1.176	1.249	1.292	1.289	1.344	1.567
interacti		(1.255)	(1.204)	(1.270)	(1.316)		(1.370)	
on	V1-H6	5.786	5.462	5.810	6.038	6.040	6.281	7.339
energy		(5.762)	(5.473)	(5.802)	(6.034)		(6.286)	
(eV)	V1-H12	7.185	7.011	7.223	7.380	7.627	7.875	8.073
		(7.027)	(6.881)	(7.029)	(7.183)		(7.712)	

Contents

- 1. Hydrogen diffusivity in W
- 2. Rate theoretical model for vacancy trap effects on hydrogen diffusivity
 - ✓ <u>Deqiong Zhu</u>, Takuji Oda

3. Experimental studies in SNU

2. Derivation of rate equations for V-H interaction in "H in W"

[Motivation] In KMC simulation, we simplified the potential energy profile. In this study, we construct rate equations considering changes in potential energy profile as a function of the number of trapped H.

For this purpose, we study with "H in Fe", because a good potential model is available.

*Fe-H potential; A. Ramasubramaniam et al., Phys. Rev. B 79 (2009) 174101.



2. Derivation of rate equations for V-H interaction in "H in W" -comparison between Fe (with potential model) and W (with DFT)-



* N. Fernandez, Acta Mater.

94 (2015) 307.

2. Derivation of rate equations for V-H interaction in "H in W" -Rate equations for trap and detrap-



2. Derivation of rate equations for V-H interaction in "H in W" -validation of the model: VH_k complex fraction at a steady state-



2. Derivation of rate equations for V-H interaction in "H in W" -validation of the model: time evolution of solute H fraction-



Time evolution of solute-H fraction

2. Derivation of rate equations for V-H interaction in "H in W" -validation of the model: time evolution of VH_k complex fractions-



Time evolution of V-H complexes

- 1. Hydrogen diffusivity in W
- 2. Rate theoretical model for vacancy trap effects on hydrogen diffusivity
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 - ✓ Younggil Jin, Nam-Kyun Kim, Jae-Min Song, Ki-baek Roh, Gon-Ho Kim

Experimental Setup : ECR-TDS



The ion irradiation condition is relevant to ITER PFC condition: 1st wall ~ 1 x 10²¹ D⁺/m² (8-300eV), divertor dome ~ 2 x 10²⁰ D⁺/m² (33-80eV)

SIMS depth profile of Deuterium (Qualitative measurement)





Determination of Defect Generation Rate

1. Olga's method ^[2]

 The original model of Olga was design to describe the effect of ion energy, fluence, and the maximum defect fraction. It's not the physical model but empirical form which has high accordance with experiment nevertheless its simplicity.



But the dW/dt is hard to measure directly, thus, Olga arbitrarily take the η (10⁻³ for ion-induced trap [1]) which shows good agreement with experimentally obtained retention data.
 [2] Ogorodnikova, Roth, and Mayer, J. Appl. Phys. 103, 034902, 2008

Estimation of Defect Fraction for Ion Irradiated W 33/14

- Defect fraction estimation: Olga's model + determined η (using dh/dt)
- Conditions:
 - Using defect generation rate (η): 0.000786.
 - Incident ion backscattering yield (f_{bs}) determined by TRIM with incident ion energy and angle.
 - Assumption: Maximum defect fraction in tungsten= 0.05 atomic fraction.
 - Fluence = effective ion flux (D^+/m^2 -s) x time.

Defect fraction

$$W(x,t) = W_m \left(1 - \exp\left(-\left(1 - f_{bs}\right)I_0\Psi(x)\eta t / W_m\right)\right)$$

W(x,t)	defect fraction at time t and position x				
I ₀	Effective incident ion flux x area [D/s]				
η	defect generation rate = 0.78x10 ⁻³ (expected minimum value)				
Ψ	Defect depth distribution factor, 1 in oversaturation depth but 0 for beyond oversaturation depth				
W _m	maximum defect fraction in tungsten = 0.05 atomic fraction				
f _{bs}	backscattering yield of incident D ion): 50eV → 0.4836, TRIM				



Determination of Effective Diffusion Coefficient 34/14

Effective diffusion coefficient in Olga's model taken into oversaturation depth

$$D_{eff}(x,t) = D_{\text{intrinsic}}\left(1 - 0.75 * \exp\left(-\left(1 - f_{bs}\right)I_0\Psi(x)\eta t\right)\right)$$



Plasma permeation simulation using TMAP4						
with Ion-induced defect + Neutron-induced defect Model						
Plasma exposu	re condition	Defect parameter				
Parameter	Parameter Value		Value			
D Ion flux, Γ _i	5.6 x 10 ²¹ D+/m ² - s	Intrinsic defect faction, W _{intrinsic}	0.0004 (dislocation, uniform in volume.)			
f _{backscattering}	0.486 (TRIM result)	Ion-induced defect factio W _{ion-induced}	where, $W x, t = W_m 1 - \exp(-1 - f_{bs} I_0 \Psi x \eta t / W_m)$			
Fluence	~ 4.0 x 10 ²⁵ D/m ²	Defect growth rate <i>n</i>				
Effective ion flux	2.72 x 10 ²¹ D ⁺ /m ² -s		0.78810°			
Impact energy, E _i	50 eV/D+	Effective diffusion				
lon implanting depth	1.5 nm	coefficient , D D_{eff} <i>x</i> , <i>t</i>	$= D T 1 - 0.75 * \exp - 1 - f_{bs} I_0 \Psi x \eta t / u_m$			
W _{m,intrinsic}	0.0004 (const.)	Trapping rate	$K_t = 2.92 \times 10^{12} \exp -0.39 eV / kT$			
W _{m,ion-induced}	0.05 (function of time)	De-trapping rate	$K_{r,\text{intrinsic}} = 8.4 \times 10^{12} \text{ exp } -0.85 eV / kT$ $F_{r,\text{ion-induced}} = 8.4 \times 10^{12} \text{ exp } -1.43 eV / kT$			

Retention Scaling Law for Ion-induced W



Scaling laws

(based on ion induced defect considered TMAP4 results)



- Parameters in scaling law (a ~10³⁻10⁶, b=0.6-0.8) are a function of ion flux (Γ_i), ion energy (E_i) and PFC temperature (T) and ion-induced defect generation rate (η)
- The new scaling law narrow down the Tanabe's scaling law (b=0.3-1.0): reduce uncertainty in expectation.

Scale Law for ion+neutron induced defect W



 The higher slope 'a' and The lower exponent 'b' (0.4-0.5 < 0.6-0.8) resulted from ion-induced defect trapping energy (Eb for ion = 1.45 eV, Eb for n = 1.85 eV) and spatial distribution (ion ~ 16 nm, n ~ entire bulk)

Summary

1. Hydrogen diffusivity in W

(Frauenfelder) $D = 4.1 \times 10^{-7} \exp(-0.39 \ e \ V/k \ T)$

(Heinola; high-T data fitting) $D = 1.58 \times 10^{-7} \exp(-0.25 \ e \ V/k \ T)$

2. Rate theoretical model for vacancy trap effects on hydrogen diffusivity

- ✓ The rate constants are established using transition state theory.
- ✓ [Plan] We will apply this method to determine trap/detrap rate constants for V-H interactions in W using DFT.
- 3. Experimental studies in SNU
 - \checkmark How should we consider effective diffusivity in TMAP.