Uncertainties in modeling of diffusion of hydrogen interacting with traps in bcc metals

Takuji Oda

Department of Nuclear Engineering Seoul National University

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- The calculations in this study were carried out using HELIOS supercomputer system at the Computational Simulation Center of the International Fusion Research Center (IFERC-CSC) in Japan.

Appendix-2) potential model construction

	# structures	Conditions	
bcc-W bulk	8,000	300-5700 K	
bcc-W surface	4,800	(100), (110), (111), (211) surfaces, 300-1500 K	
bcc-W with vac.	28,400	1-9 vac. clusters, 300-4500 K	
bcc-W with SIA	2,600	1 SIA, 300-4500 K	
bcc-W with H atoms	5,600	1-12 H atoms, 300-4500 K	
bcc-W with vac. and H atoms	28,400	1-9 vac. clusters, 1-12 H atoms, 300-4500 K	
bcc-W with SIA and H atoms	4,000	1 SIA, 2-12 H atoms, 300-2100 K	
Molecules	150	H_2 , WH, W_2 , WH ₆	

Hydrogen diffusivity in bcc-W: experimental data

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

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



Hydrogen diffusivity in bcc-W: DFT v.s. experiment



Figure 1. Calculated H diffusivity in W in comparison with the experimental values.

*G.H. Lu et al., Nucl. Fusion 54 (2014) 086001.

Hydrogen diffusivity in bcc-W: diffusion mechanisms

Location of T-sites and migration paths between neighboring T-sites.

In (a), 4 first neighboring T-sites (#2-#5) and 2 second neighboring T-sites (#6-#7) for a T-site (#1) are described together with migration paths between them with small pink and yellow spheres.

In (b), Tri-site on the way between #1 and #2 sites is emphasized with an enlarged pink sphere.

In (c), O-site on the way between #1 and #7 sites is shown with an enlarged yellow sphere.



→ a

A(0.25 0.50 1.00), B(0.25 0.50 0.00) C(0.75 0.00 0.50), D(0.75 1.00 0.50) #1(0.50 0.50 0.50) #2(0.25 0.25 0.50), #3(0.25 0.75 0.50) #4(0.75 0.50 0.75), #5(0.75 0.50 0.25) #6(0.00 0.50 0.50), #7(1.00 0.50 0.50)

Hydrogen diffusivity in bcc-W: transition state analysis



0.4	0.6 0.8	1.0				
Reaction coordinate						
	T-site	Tri-site	O-site			
	1160 cm ⁻¹	ⁱ 846 cm⁻¹	ⁱ 872 cm ⁻¹			
	1557 cm⁻¹	1552 cm⁻¹	ⁱ 872 cm ⁻¹			

1557 cm⁻¹

2106 cm⁻¹

2517 cm⁻¹

Mode-1

Mode-2

Mode-3

Expression of diffusion coefficient: with TST

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

(1) Classical transition state theory (TST) with harmonic approximation by Vineyard

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

 $\langle N \rangle \langle N-1 \rangle$

$$\Gamma_{Vine}^* = \nu_{Vine}^* \exp\left(-\frac{\Delta E}{RT}\right) \qquad \qquad \nu_{Vine}^* = \left(\prod_{i=1}^N \nu_i\right) / \left(\prod_{i=1}^N \nu_i'\right).$$

(2) Classical TST with quantum mechanical partition functions within harmonic

approx.
$$\Gamma_{qHTST}^{*} = \nu_{q-hTST}^{*} \exp\left(-\frac{\Delta E}{RT}\right),$$
$$\nu_{qHTST}^{*} = \frac{kT}{h} \times \left\{ \prod_{i}^{N-1} \left(\frac{\exp\left(-\frac{h\nu_{i}^{*}}{2kT}\right)}{1-\exp\left(-\frac{h\nu_{i}^{*}}{kT}\right)}\right) \right/ \prod_{i}^{N} \left(\frac{\exp\left(-\frac{h\nu_{i}}{2kT}\right)}{1-\exp\left(-\frac{h\nu_{i}}{kT}\right)}\right) \right\}$$

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

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

Model validation: H in bcc-Fe

- ✓ Both classical MD and PIMD include an-harmonic effects.
- ✓ PIMD additionally includes quantum effects (including tunneling effect).

*H. Kimimzuka et al, Phys. Rev. B 83 (2011) 094110.





Comparison of various DFT functionals



Heinola's suggestion on H diffusivity in bcc-W



*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) $D = 1.58 \times 10^{-7} \exp(-0.25 \ e V/k T)$

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



Approach with 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.

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



Isn't it too simple? - focus on high temperature (>1100 K) of pure W + H₂ absorption-

✓ Impurities

- ✓ Non-metallic (~ 0.3 eV)
- ✓ Metallic (~0.7 eV for substitutional Fe)
- ✓ Vacancy clustering (pre-treatment at 2400 K)
- ✓ Dislocation (~0.7 eV)
- ✓ Grain boundary (~1.1 eV)

V-H interaction model



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

V-H interaction model



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.

KMC results: Influence of traps (vacancy)



- ✓ Diffusivity from Einstein's equation.
- ✓ 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)

KMC results:

Correlation between solute fraction and apparent diffusivity



✓ If we know the fraction of solute H atoms, we can determine the effective H diffusivity: $D_{eff} = D \times f$

KMC results: Influence of H/V ratio on apparent 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 apparent diffusion coefficients are comparable with the true diffusion coefficient, which is given by Eq. (2).



Obviously, the upper limit of the apparent diffusion coefficient appears in the region (iii) and is equal to the true hydrogen diffusivity. The lower limit can be obtained assuming that <u>a vacancy can trap only 1 H atom at most</u>.

$$f_{trap} \times \Gamma_{detrap} = 24 \times (f_{solute}/N_{T-site}) \times \Gamma_{trap} , \qquad (9)$$

$$f_{trap} + f_{solute} = 1, \qquad (10) |$$

$$\Gamma_{trap} = \nu_{trap} \times \exp(-E_{migration}/kT), \qquad (11)$$

$$\Gamma_{detrap} = \nu_{detrap} \times \exp(-E_{detrap}/kT), \qquad (12)$$

$$c_{vacancy} = N_{vacancy}/N_{lattice-site} = 1/N_{lattice-site}, \qquad (13)$$

$$N_{T-site} = 6N_{lattice-site} \cdot (14)$$

$$lute = \Gamma_{detrap}/(\Gamma_{detrap} + 4c_{vacancy}\Gamma_{trap}) = 1/(1 + 4c_{vacancy} \times \exp(E_{binding}/kT))$$

 f_{so}



Appendix-1) Influence of XC-functionals Overall comparison in the deviation of results

- ✓ Migration energies are not largely affected by functional, due to error cancelation.
- ✓ The deviation in vacancy formation energy is large, because the electron density is largely changed at the surface (inner surface of vacancy).
- $\checkmark~$ AM05 and TPSS give values around the average.
- \checkmark In most key properties, the error level in DFT is around 10-15 %.



- ✓ Uncertainties/Errors in DFT
 - ✓ Cut-off energy (plane-wave)/basis-set quality
 - ✓ K-point sampling/smearing
 - ✓ XC functionals
 - ✓ Code (more or less due to pseudo-potentials)

✓ But, we really need "very accurate"?

✓ How inaccurate is acceptable enough?

- ✓ Rate-equational model / KMC
 - ✓ DFT → TST → rate equation* ("theoretical")
 - ✓ MD → TST → rate equation → [Refinement with DFT/GAP]