DFT study of H-vacancy/O/C complexes and MD+MS study of interactions of vacancy and interstitial with the grain boundary

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Outline

- DFT study of H-vacancy/O/C complexes.
- MD+MS study of interactions of vacancy and interstitial with the grain boundary.
- Future Study.

DFT study of H-vacancy/O/C complexes

In order to evaluate energetically the vacancy, oxygen and carbon role in modifying the hydrogen retention behavior.

Background: low-energy H/He ions produce bubbles?

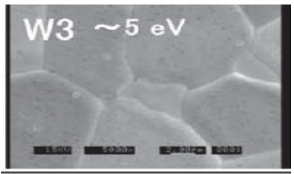
D ion → 940 eV

He ion → 500 eV

displacement threshold energy in W: 40 eV
E_V=3.20 eV, E_{SIA}=9.68 eV

H bubble formation: under irradiation with high flux of 10^{22} /m^2 s and low-energy D ions (~38 eV)

Shu et al., Nucl. Fusion 47, 201 (2007); Appl. Phys. Lett. 92, 211904 (2008)



He bubble formation: under irradiation with high flux of 1.1*10^{23} /m^{2}s and low-energy He ions (~5 eV, which is the surface barrier potential energy for He penetrating into the W).

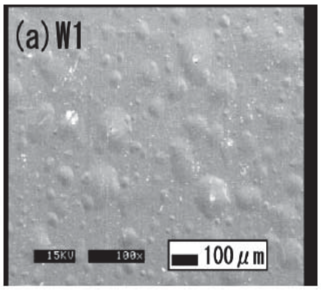
Nishijima et al., J. Nucl. Mater. 329–333 ,1029 (2004)

Background: low-energy H/He ions produce bubbles?

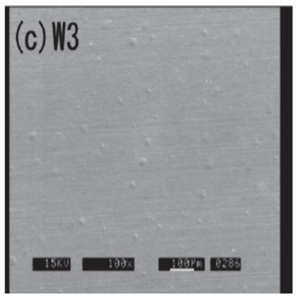
In sharp contrast with the case of W, the experimental result reported no bubbles formation in Pd implanted by 10keV D to a very high supersaturation of about 1.7 D/Pd mole ratio.

S. M. Myers, et al., Phys. Rev. B 43, 9503(1991).

Background: He pre-exposure suppressing H bubbles



D implanted W surface without He pre-exposure

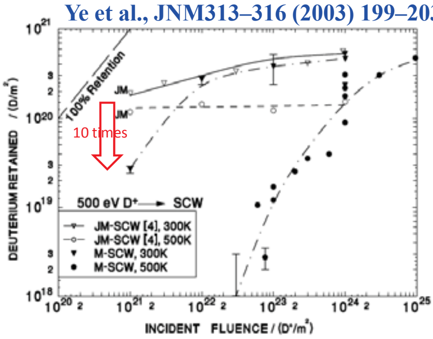


D implanted W surface with He ion pre-exposure (80 eV He ions at a flux of 4.2*10^{21} /m^{2}s, 700K, 7200s)

(500K, 80 eV , a flux of 2.5×10^{21} /m^{2}s D ions, 3h)
Nishijima et al., Nucl. Fusion 45, 669 (2005)

Background: Impurity effect on D retention

Ye et al., JNM313–316 (2003) 199–203

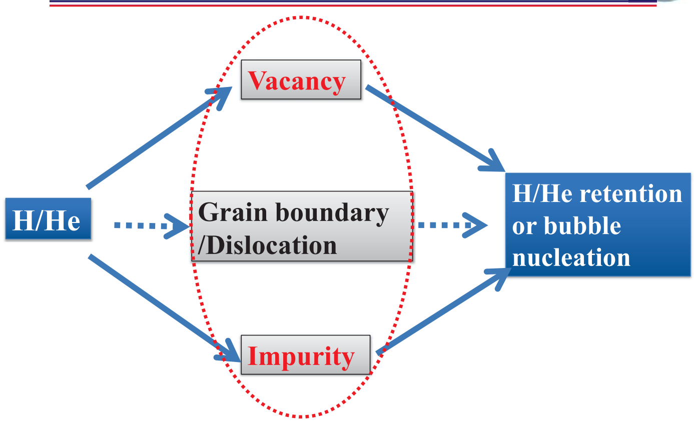


J-M SCW(99.9%)
5000appm C/O

Moscow
SCW(99.99%)
500appm C/O

This suggests that the primary trap sites for deuterium clusters in annealed SCW should be related to impurities. The impurity can increase the hydrogen retention in W.

Background: Three possible sites for retention/bubble



Methods:

Defect (A_1) formation energy:

$$E_f^{A_1} = E_{tot}^{A_1} - E_{tot}^{bulk} - \Sigma_i \Delta n_i \mu_i$$

Binding energy of defects A_1 and A_2:

+: attraction
-: repulsion

$$E_b^{A_1-A_2} = E_{tot}^{A_1} + E_{tot}^{A_2} - E_{tot}^{A_1-A_2} - E_{tot}^{bulk}$$

Trapping energy of H/He in a vacancy:

$$E_{tr}^{V-A_n} = E_{tot}^{V-A_n} - E_{tot}^{V-A_{n-1}} - (E_{tot}^{A_{tet}} - E_{tot}^{bulk})$$

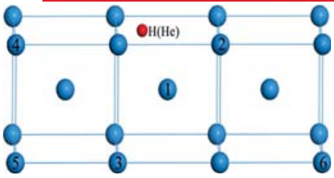
Concentration of defect (A_1):

$$c = N_{sites} N_{config} exp(E_f^{A_1}/kT)$$

New vacancy formation energy nearby the existed defect (A_1):

$$E_f^{V_{A_1}} = E_{tot}^{A_1-V} - E_{tot}^{A_1} + \mu_W$$

Results: Interstitial H/He reducing E_v



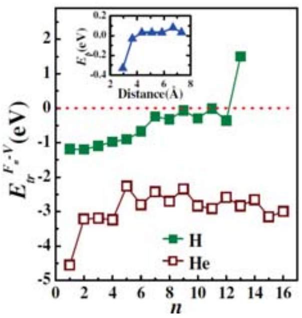
Vacancy formation energy in the perfect system:
3.20eV in W(2.65 eV in Mo)

Vacancy formation energy nearby interstitial H/He

n	W H (eV)	W He (eV)	Mo H (eV)	Mo He (eV)
1	2.01	-1.36	1.45	-1.12
2	2.91	-0.43	2.25	-1.12
3	3.08	2.92	2.43	2.35
4	3.11	3.04	2.45	2.42
5	3.16	3.12	2.48	2.49
6	3.19	3.17	2.51	2.54

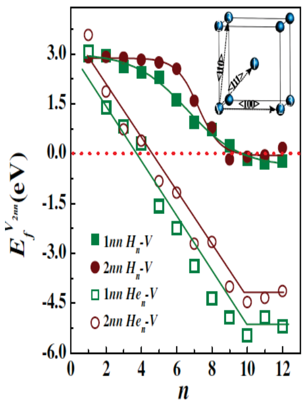
- Interstitial H reduce its first neighboring vacancy formation energies remarkably;
- The effect of He leads to negative vacancy formation energy at the first and second nearest neighboring sites around the interstitial He, indicating W atom at these sites is unstable, and forms a vacancy spontaneously.

Results: Vacancy traps multiple H/He atoms



- One vacancy could trap up to 12 H atoms or 14 He atoms (additional He atoms move out of the cell containing the vacancy);
- Additional H atoms are repulsive with H_{12}-V complex, while additional He atoms are still attractive to He_{14}-V complex.

Results: E_v(new) closest to the already existed V + H/He



- The new vacancy formation energy decreases in a "step-like" way with the number of trapped H atoms, while the new vacancy formation energy decreases linearly with the trapped He atoms;
- The accumulation of 9 H or 4 He in a vacancy surprisingly reduce the formation energy of first and second nearest vacancy to ~0 eV.

Results: E_v(new) closest to the already existed V + H

In Pd

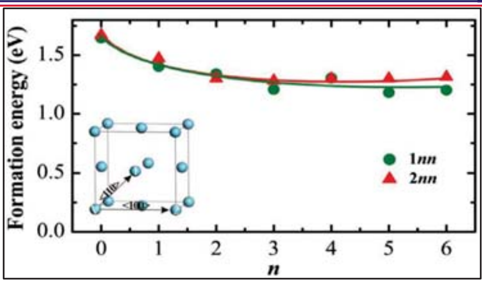
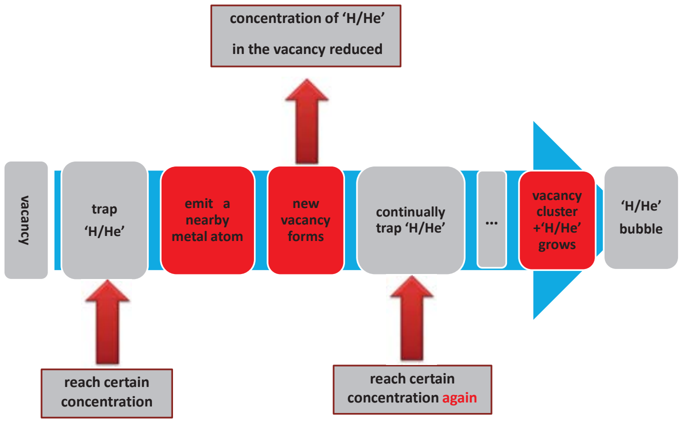


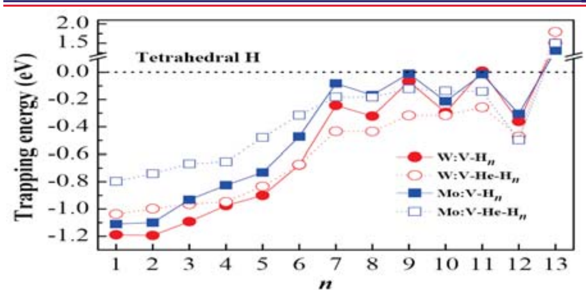
Fig. S4: The 1*nn* and 2*nn* vacancy formation energies around V-H_n complex as a function of H

- The new nearest neighboring vacancy formation energy decreases only slightly, the formation energy is still larger than 1.2 eV when the vacancy has trapped 6 hydrogen atoms.

Results: H retention or H/He bubbles Nucleation from V

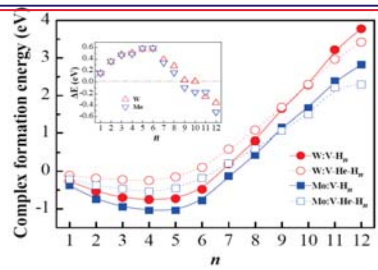


Results: Influence of preexisted He on vacancy trapping H



- Compared to the pure vacancy, the He-vacancy complex traps H atoms less strongly when trapped H atoms are not larger than 6 in both W and Mo.

Results: Influence of preexisted He on vacancy trapping H



- The formation energy of **V-He-H*n*** complex is higher than that of **V-H*n*** complex before *n* exceed 8 in W and 9 in Mo.
- The maximum discrepancy is ~0.60 eV when the number of H atoms add up to 5 in a vacancy and V-He complex in both W and Mo.

---He located in a vacancy could hinder, to sorme extent, the accumulation of H atoms in the vacancy (low incident fluence??)

Results: Interstitial O/C reducing E_v

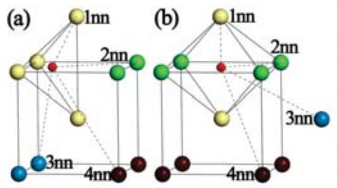


TABLE II. The vacancy formation energies of lattice sites nearby the stable interstitial hydrogen, oxygen and carbon (unit in eV).

	Hydrogen	Oxygen	Carbon
$1nn$	2.01	0.15	1.23
$2nn$	2.91	0.15	2.74
$3nn$	3.08	3.03	2.91
$4nn$	3.11	2.25	2.76

TABLE I. Formation energies (eV), $E_f^{i_t}$ and $E_f^{i_o}$, and formation-energy difference, $\Delta E = E_f^{i_o} - E_f^{i_t}$, between tetrahedral and octahedral sites for hydrogen and LE atom in tungsten. The previous DFT results ($\Delta E^{Previous}$) of formation-energy difference are listed in the fifth column for comparison.

	$E_f^{i_t}$	$E_f^{i_o}$	ΔE	$\Delta E^{Previous}$
Hydrogen	0.93	1.31	0.38	*0.38*[a]
Oxygen	0.57	0.84	0.27	*0.315*[b]
Carbon	2.23	0.76	-1.47	*-1.46*[c]

- **O is energetically preferable to occupy tetrahedral interstitial site, while C prefers to take octahedral interstitial site.**
- **Both the formation energies of the *1nn* and *2nn* vacancy close to C/O are reduced.**

Results: O/C-H complex reducing E_v

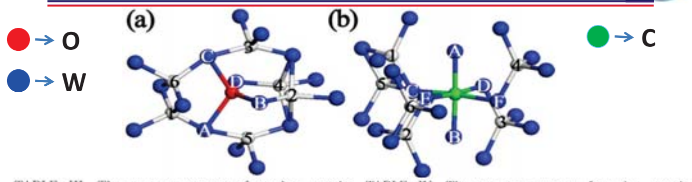


TABLE III. The tungsten vacancy formation energies ($E_f^{V_{O-H_n}}$) of lattice sites nearby the $O-H_n$ complex (unit in eV). Configuration of $O-H_n$ complex is shown in Fig. 4 (a) and positions of tungsten vacancies are indicated by *A*-*D*.

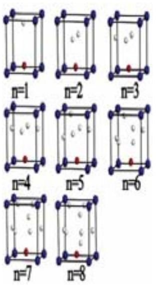
n	A	B	C	D
1	-0.64	0.37	0.56	0.37
2	-0.41	-0.41	0.78	0.77
3	-0.10	-0.28	-0.07	0.88
4	0.06	-0.09	0.09	-0.09
5	-0.85	-0.08	0.31	-0.08

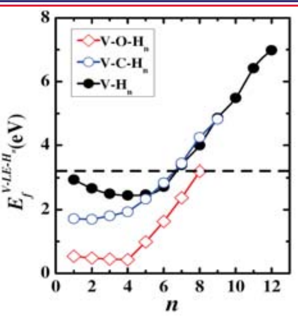
TABLE IV. The tungsten vacancy formation energies ($E_f^{V_{C-H_n}}$) of lattice sites nearby the $C-H_n$ complex (unit in eV). Configuration of $C-H_n$ complex is shown in Fig. 4 (b) and positions of tungsten vacancies are indicated by *A*-*F*.

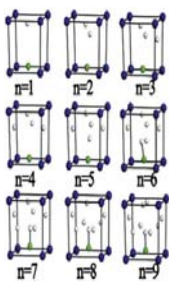
n	A	B	C	D	E	F
1	1.04	1.11	1.63	2.69	2.65	2.72
2	0.93	0.93	1.56	2.68	1.56	2.68
3	0.84	0.74	1.53	1.60	1.58	2.62
4	0.66	0.66	1.55	1.55	1.55	1.55
5	0.60	0.57	0.55	1.50	1.53	1.56

- **O/C-H complex could further reduce its neighboring vacancy formation energy compared with interstitial O/C atom, especially O-H complex.**

Results: Comparison of formation energies of 3 complexes

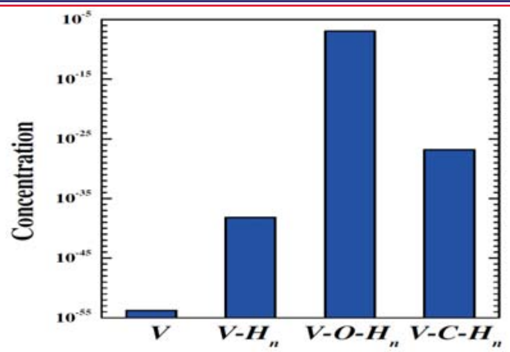






- **The formation energies of the V-O/C-H*n* complex are significantly lower than V-H*n* complex;**
- **The formation energy of V-O-H*n* is the lowest, that is V-O-H*n* is most energetically favorable to form.**

Results: Comparison of the concentrations 3 complexes

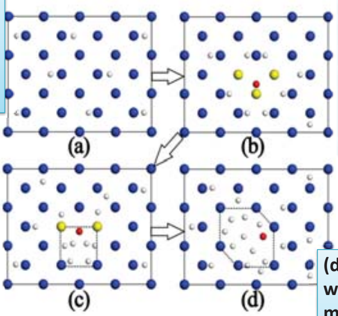


- **Both C and O could considerably increase the concentration of vacancy, especially O;**
- **The concentration of V-O-H*n* is highest.**

Results: Mechanism of H retention/bubble from O interstitial

(a) Assuming H equally distributed in bulk due to the repulsive interaction between interstitial H

(b) H atoms accumulate around O, forming O-H*n* complex, reducing the formation energy of neighboring vacancy



(c) New vacancy is created close to O-H$_n$, forming V-O-H$_n$ complex

(d) The increase in H will lead to the mutation from V-O-H*n* into V2-O-Hn, the vacancy-H complex grows in both V and H

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5. Y.W. You, X.S. Kong, X.B. Wu, Q.F. Fang, J.L. Chen, G.N. Luo, and C.S. Liu, **Effect of vacancy on the dissolution and diffusion properties of hydrogen and helium in molybdenum**. ***J. Nucl. Mater.*** 2013, 433, 167-173.
6. Y.W. You, X.S. Kong, Q.F. Fang, C.S. Liu, J.L. Chen, G.N. Luo, and Y. Dai, **A first-principles study on hydrogen behavior in helium-implanted tungsten and molybdenum**, ***J. Nucl. Mater.*** 2013, http://dx.doi.org/10.1016/j.jnucmat.2013.04.026
7. X.B. Wu, X.S. Kong, Y.W. You, C.S. Liu, Q.F. Fang, J.L. Chen, G.N. Luo, and Z.G. Wang, **Effects of alloying and transmutation impurities on stability and mobility of helium in tungsten under a fusion environment.** ***Nucl. Fusion*** 2013, 53, 073049

Summary of first part:

(New) Vacancy formation energy

3.20 eV (in pure W)

2.01 eV (closest to Interstitial H)

1.23 eV (closest to Interstitial C)

0.15 eV (closest to Interstitial O)

-1.36 eV (closest to Interstitial He)

~ **0** eV (closest to V+H9 complex)

~ **0** eV (closest to V+He4 complex)

Defect complex formation energy

$$V+O+H_n < V+C+H_n < V+H_n$$

MD+MS study of interactions of vacancy and interstitial with the grain boundary

In order to investigate the role of the grain boundary in radiation-induced defects evolution (vacancy and interstitial segregation and their annihilation) near the GB in W.

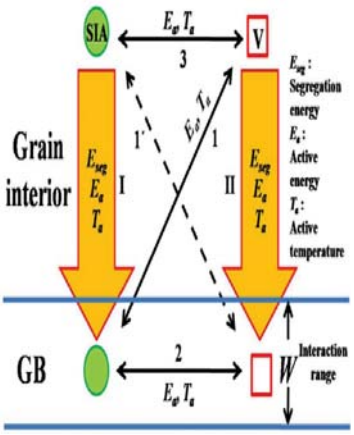
Backgrounds

- Some nanocrystalline materials have been shown to have improved radiation resistance compared with their polycrystalline counterparts. It is naturally speculated that GBs serve as effective sinks for radiation-created defects and thus benefit the recovery of vacancies and interstitials.
- Dislocations and GBs are at microscopic and mesoscopic scales and critical players on the stage of the change in mechanical properties of polycrystals.
- Thus, it arises reasonably: the radiation-induced-point-defects (vacancies and interstitials) related processes in which GBs and radiation-induced defects are involved should be critical. It becomes especially important to study the interactions between radiation-induced defects (vacancies and interstitials) and GBs.

Backgrounds

- The interactions are captured through energetic and kinetic behaviors of these point defects near the GB. The energetics is often characterized by the defect formation energy or binding energy, while the kinetics is described by the defect diffusion barrier and interstitial-vacancy annihilation barrier, and the corresponding activation temperature.
- Once these interactive parameters are obtained, they not only are able to provide insight into the above-mentioned processes but also are necessary parameters to some high-level simulation techniques such as kinetic Monte Carlo (KMC) and rate theory (RT) that can evaluate the defect evolution and the resulting material performance at long time-scales.

Results: Critical atomic processes of defect evolution



The involved processes include segregation of interstitials and vacancies (**processes I** and **II**).

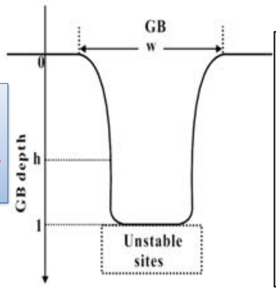
Also include interstitials and vacancies annihilation and respective diffusion in the bulk, near the GB and within the GB (**processes 1, 2 and 3**).

Segregation Processes *I*, *II* and processes *1*, and *3* contribute to healing grain interiors. Process *2* is critical to healing the GB.

Results: V/SIA-GB interaction

In W

GB as a sink for V and SIA to understand the segregation processes I and II



Formation energy:

In bulk,
V: 3.75 eV;
SIA: 10.19 eV.

In GB,
V: ↓~0.86eV (segregation energy);
SIA: ↓~7.5eV

The GB depth (*h*) is defined as the segregation energy divided by the defect formation energy in the bulk, and that is the reduction in defect formation energy scaled by the bulk value.

The influence range (*w*) is defined as the distance perpendicular to the GB within which the deviation of defect formation energies from the bulk value is larger than 0.05eV.

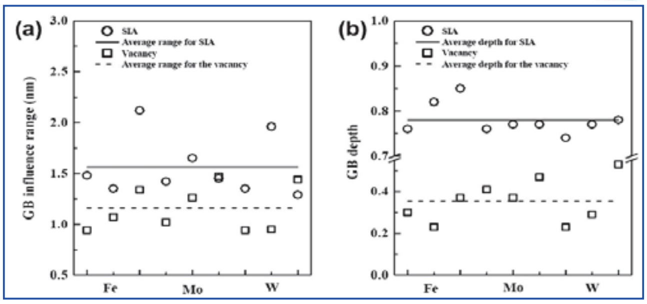
Results: V/SIA-GB interaction

Table 1. The energetic and interactive range parameters of interactions between vacancies, interstitials and GBs. Here the symbols are defined as follows. Θ: inclination angle; E_{GB}: GB energy; w_V: GB influence range for the vacancy; E_b^V: the binding energy for the vacancy; h_V: GB depth for the vacancy; w_{SIA}: GB influence range for the interstitial; E_b^{SIA}: the binding energy for the interstitial; h_{SIA}: GB depth for the interstitial.

Results: V/SIA-GB interaction

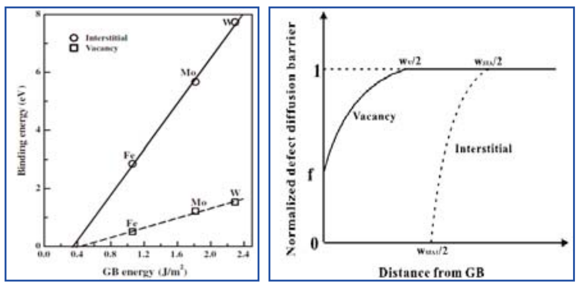
	GB	Θ (°)	E_{GB} (J/m²)	w_V (nm)	E_b^V (eV)	h_V	w_{SIA} (nm)	E_b^{SIA} (eV)	h_{SIA}
Fe	Σ5(310)/[001]	36.87	0.9886	0.94	0.52	0.30	1.48	2.7	0.76
	Σ13(320)/[001]	67.38	1.1764	1.07	0.4	0.23	1.35	2.9	0.82
	Σ25(430)/[001]	73.74	1.0085	1.34	0.63	0.37	2.12	3.0	0.85
Mo	Σ5(310)/[001]	36.87	1.7766	1.02	1.2	0.41	1.62	5.6	0.76
	Σ13(320)/[001]	67.38	1.8716	1.26	1.1	0.37	1.65	5.7	0.77
	Σ25(430)/[001]	73.74	1.8052	1.47	1.4	0.47	1.45	5.7	0.77
W	Σ5(310)/[001]	36.87	2.3322	0.94	0.86	0.23	2.65	7.5	0.74
	Σ13(320)/[001]	67.38	2.3455	0.95	1.75	0.29	1.96	7.8	0.77
	Σ25(430)/[001]	73.74	2.2043	1.44	2.00	0.53	1.29	7.9	0.78
	Average value			1.16		0.36	1.73		0.78

Results: V/SIA-GB interaction



- The GB influence range is small and nearly independent of the system; averagely, the GB range for interstitials is larger than for vacancies;
- There exists to a certain extent a general level of the GB depth for vacancies and interstitials, respectively, particularly for the interstitial.

Results: V/SIA-GB interaction



- **Binding energies strongly correlate with GB energies averagely;**
- **Within the range of w_{SIA} the absorption of interstitials into the GB is spontaneous. In the GB core, the normalized barrier of vacancy diffusion is reduced to *f* from 1 in the bulk.**

Results: V/SIA-GB interaction

- The following table summarized the kinetic parameters describing the GB as the sink for the vacancy and interstitial, and the catalyst for vacancy-interstitial annihilation.
- These include the barrier of vacancy (interstitial) diffusion in the bulk, near the pure GB, and the barrier of vacancy-interstitial annihilation within the spontaneous region and near this region.
- The corresponding activation temperature is defined as the temperature that gives the transition time one second, which the attempt frequency is about 10^{12}/s.
- The fraction of GB region is calculated according to the GB influence range, here the grain size is assigned to be 100 nm.

Results: V/SIA-GB interaction

	SIA_m^{bulk}	$SIA_m^{near-GB}$	V_m^{bulk}	$V_m^{near-GB}$	$V-SIA_{ann}^{near-GB}$	$V-SIA_{ann}^{GB}$
Barrier (eV)						
Fe	0.33	0	0.629	0.46	0.16	0
Mo	0.03	0	1.67	1.17	0.24	0
W	0.002	0	1.80	0.98	0.31	0
T_a (K)						
Fe	128	0	244	178	62	0
Mo	12	0	649	455	93	0
W	1	0	702	382	121	0
Range (nm)						
Fe		1.65		1.12	1.12	0.30
Mo		1.57		1.25	1.25	0.45
W		1.97		1.11	1.16	0.76
Fraction (%) (when Grain size = 100 nm)						
Fe		5		3	3	1
Mo		5		4	4	1
W		6		3	3	2

Spontaneous annihilation region

Results: V-Interstitial-loaded-GB interaction

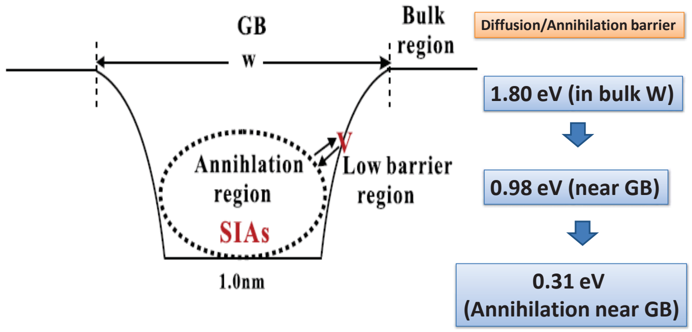


Illustration of the annihilation between the vacancy near the GB and the interstitial trapped at the GB.

Conclusions:

- Binding energies strongly correlate with GB energies averagely and have a general level when scaled by the bulk defect formation energy. Defect diffusion is enhanced near the GB. The diffusion barrier of the vacancy gradually decreases as it approaches to the GB. For interstitials, there exist several layers near the GB in which the absorption of interstitials is spontaneous and out of which orientation-dependent.
- For the interstitial-rich GB, the vacancy near the GB can be annihilated at a low barrier, independent of the system.
- The GB influence range is limited of 1.0–2.0 nm from the GB. This leads to a limited fraction of the GB region working as a sink for defects and/or the catalyst for vacancy-interstitial annihilation.
- Our obtained principal physical parameters may be applied to build the master framework for defects' generation, transport and fate and thus to evaluate the damage rate in nano/poly-crystalline materials.

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2. X.Y. Li, W. Liu, Y.C. Xu, C.S. Liu, Q.F. Fang, B.C. Pan, and Z.G. Wang, **Energetic and kinetic behaviors of small vacancy clusters near a symmetric Σ5(310)/[001] tilt grain boundary in bcc Fe.** ***J. Nucl. Mater.*** 2013, 440, 250-256.
3. X.Y. Li, W. Liu, Y.C. Xu, C.S. Liu, Q.F. Fang, B.C. Pan, J. L. Chen, G.-N. Luo and Z.G. Wang, **An energetic and kinetic perspective of the grain-boundary role in healing radiation damage in tungsten**, ***Nucl. Fusion*** 2013, 53 123014.
4. X.S. Kong, X.B. Wu, Y.W. You, C.S. Liu, Q.F. Fang, J. L. Chen, G.-N. Luo and Z.G. Wang, **First-principles calculations of transition-metal solute interactions with point defects in tungsten**, ***Acta Mater***., to be published.

Future work

Specific objectives of this research

Interactions of hydrogen with irradiation-generated defects at entire temporal evolution stages.

1) Understanding on the irradiation damage of W

2) Understanding on the nature of hydrogen traps

3) Understanding the status of hydrogen in small vacancy clusters

Research schemes

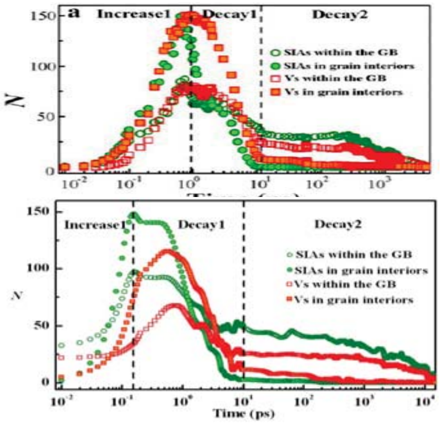
MD simulations of primary radiation damage in W

KMC investigation of the further evolution of the primary damage structure

First principles study of interactions of hydrogen with above identified defects.

Development of W-H and W-He empirical potentials.

Future work: example



Thanks for your attention!