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Interstitial-mediated diffusion and aggregation mechanism for Re and Os precipitation in W

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Outline

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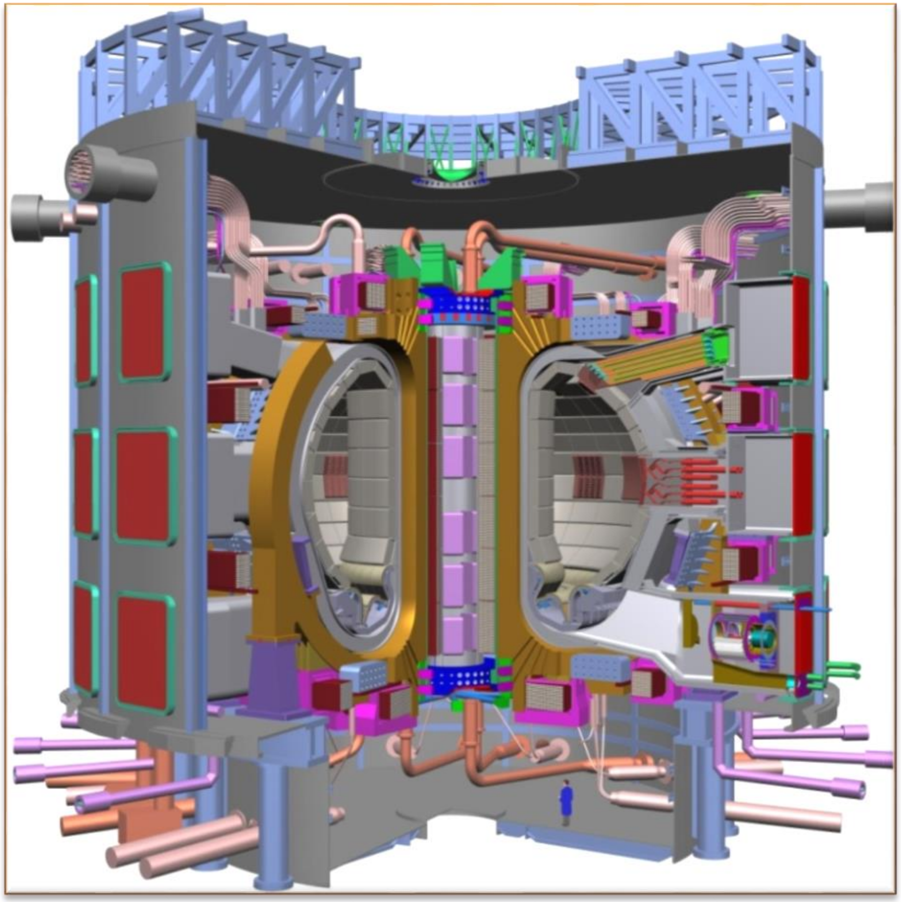
Tungsten: a promising PFM in fusion devices

Advantages

- High melting temperature
- High thermal conductivity
- Low sputtering erosion

Extreme environment

- Neutron: 14 MeV
- H/He plasma (0-100 eV)
- High heat flux (10 MW/m^{2})



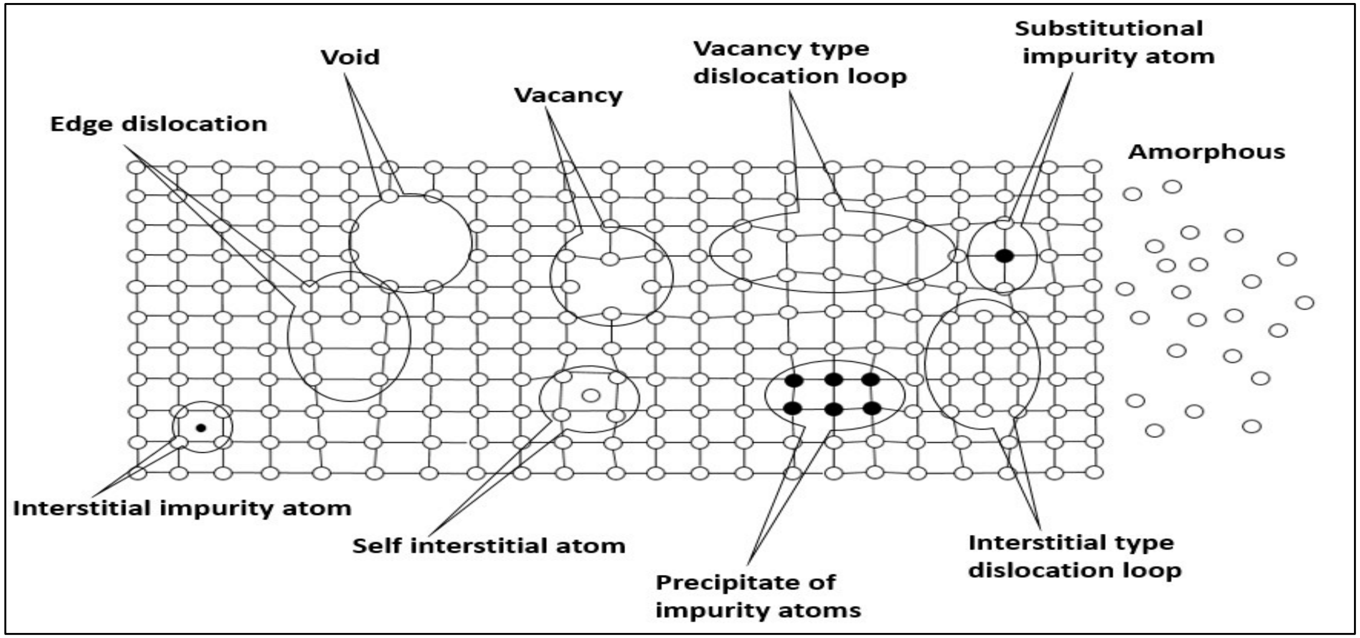
Role

- Withstand Neutron/H/He/Heat flux

Neutron irradiation

1

Displacement damage
（cascade collision）



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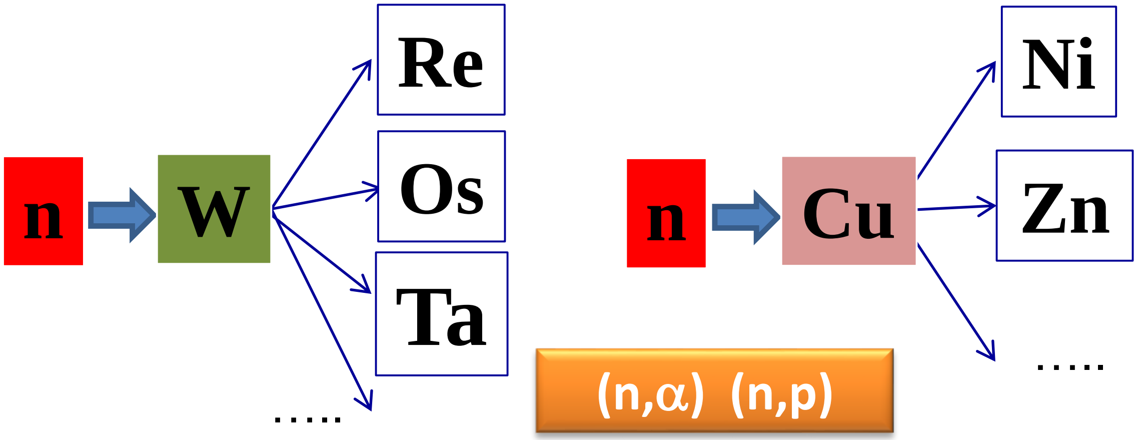
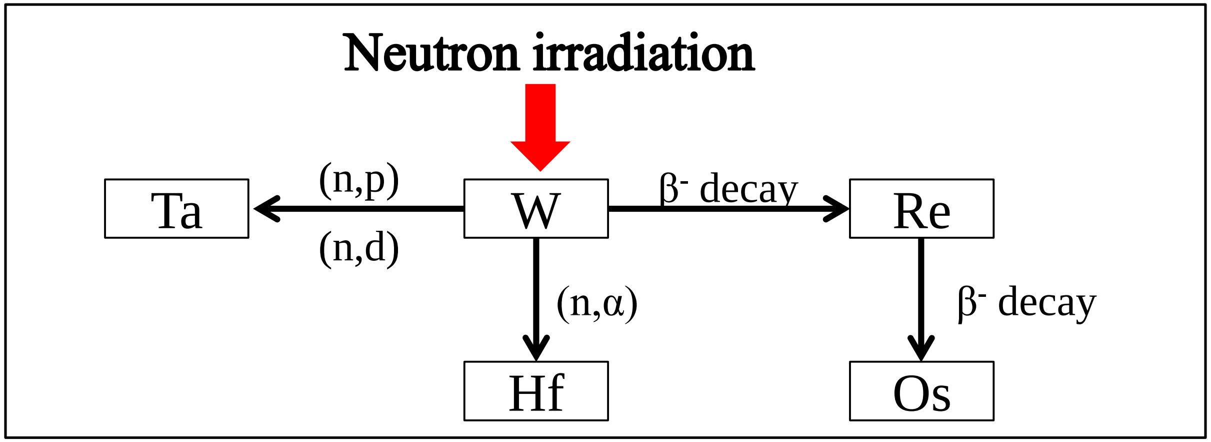
Transmutation
（chemical composition）



Nuclear transmutation of W under neutrons irradiation

Nuclear transmutation



Starting composition (at%)	Transmutation products	Concentration of product (at%) after irradiation for		
		1 year	3 year	5 year
W	W	98.9	96.3	94.0
	Re	0.91	2.59	3.80
	Os	0.06	0.53	1.38
	Ta	0.14	0.53	0.81
	Hf	/	/	0.01

Gilbert, *et al.*, Nucl Fusion 51, 043005 (2011).

- **Tungsten will undergo transmutation to its near-neighbors in the periodic table, such as Re, Os, Ta, and Hf.**

Effects of transmutation elements on the properties of W

Intrinsic properties (without irradiation)

Mechanical properties → Positive

- ✓ Reducing DBTT
- ✓ Improving both toughness and ductility
- ✓ Increasing recrystallization temperature

Thermal properties → Degradation

- ✓ Reducing melting point
- ✓ Reducing thermal conductivity
  (5 wt.% Re → ~ 50% reduction @ 300 K)

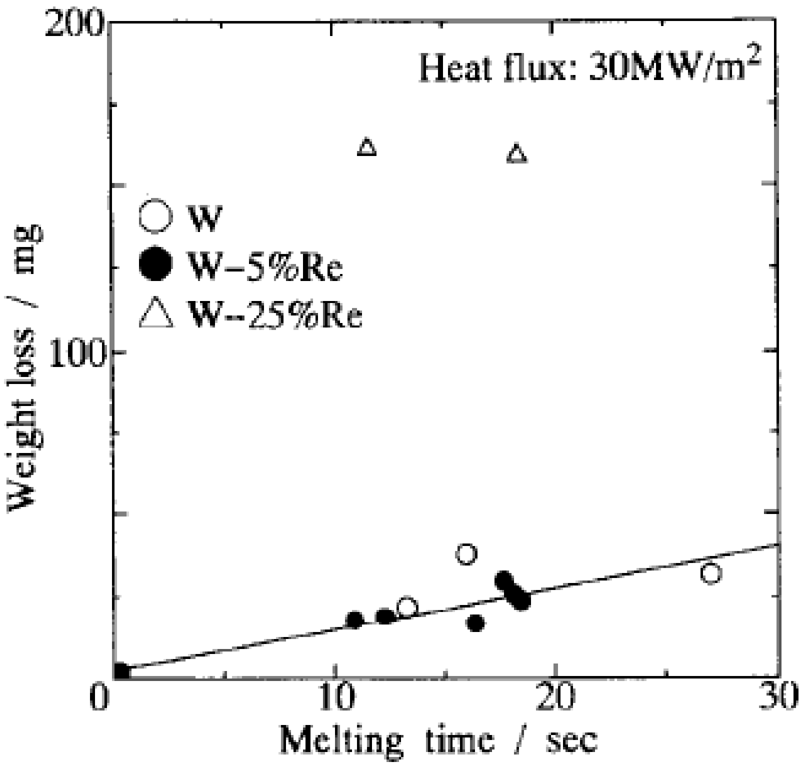
Irradiation properties (with irradiation)

High heat | Plasma | Neutron

Single + Synergistic

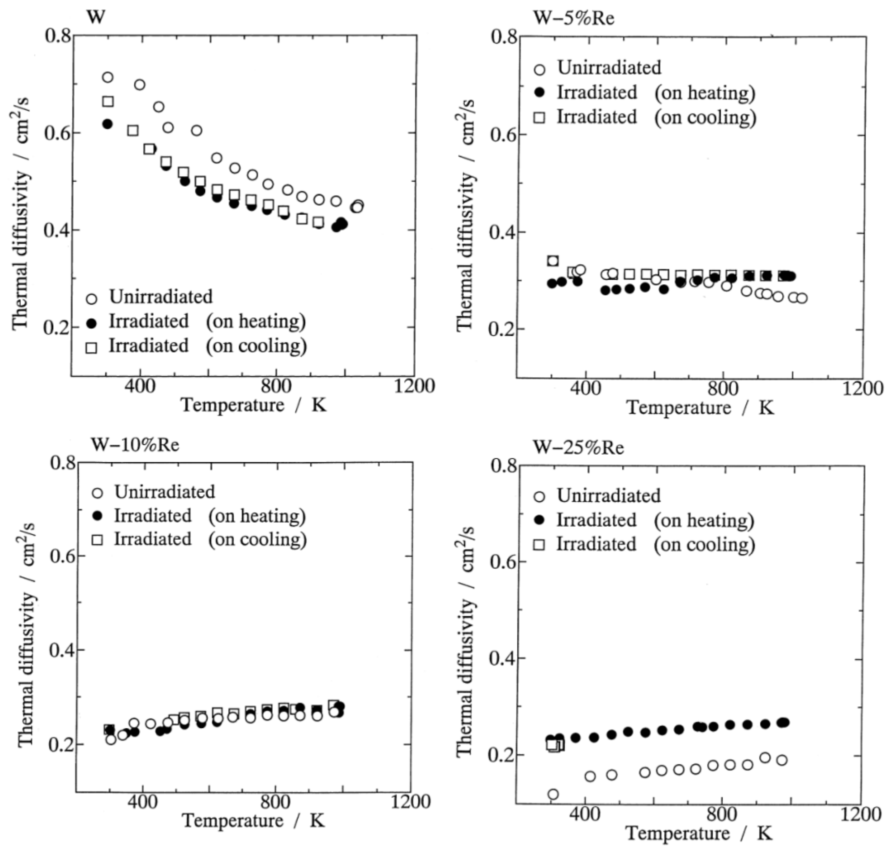
The effects of transmutation elements under **irradiation** condition are significant different from that **under irradiation-free** environment.

Effects of transmutation elements: High heat flux



Increasing weight loss under high heat load

M. Fujitsuku et al., *J. Nucl. Mater*. 233 (1996) 638

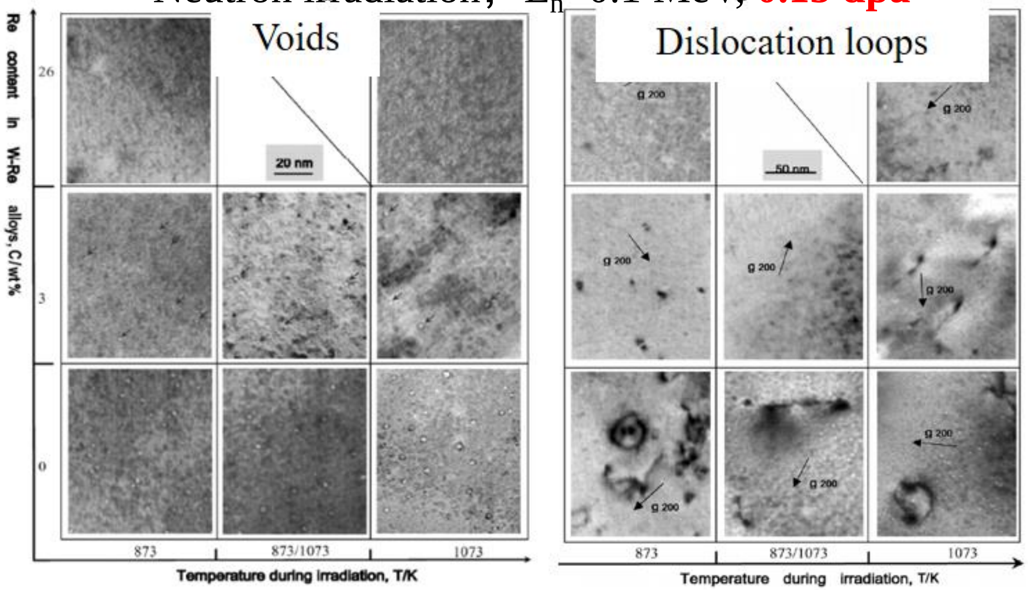


M. Fujitsuku et al., *J. Nucl. Mater*. 283 (2000) 1148

- **The presence of Re could cause severe damage of W-PFM under high heat load, due to the reduction of thermal conductivity induced by Re.**

Effects of transmutation elements: Neutron irradiation

Neutron irradiation， E_n>0.1 MeV, **0.15 dpa**



J.C. He, et al., *Nucl. Fusion* 46 (2006) 877

	Voids		Loops		Vickers hardness difference
	Radius, nm	Density, $10^{22}/m^3$	Radius, nm	Density, $10^{21}/m^3$	$\Delta HV_{irrad} - \Delta HV_{unirrad}$
Proton-irradiated to 0.15 dpa					
W (500 °C)	1.8	13.9	3.8	1.9	185
W–3Re (600 °C)	2.2	5.6	3.4	1.3	105
W–3Os (500 °C)	1.1	13.5	–	–	89
W–5Re–3Os (500 °C)	1.4	9.8	–	–	–
Neutron-irradiated to 0.15 dpa					
W (600 °C)	1.3	6.4	7.9	4.6	207
W–3Re (600 °C)	1.1	3.4	3.6	1.4	71
W–5Re (600 °C)	1.2	2.1	3.2	1.5	80
W–26Re (600 °C)	–	–	–	–	87

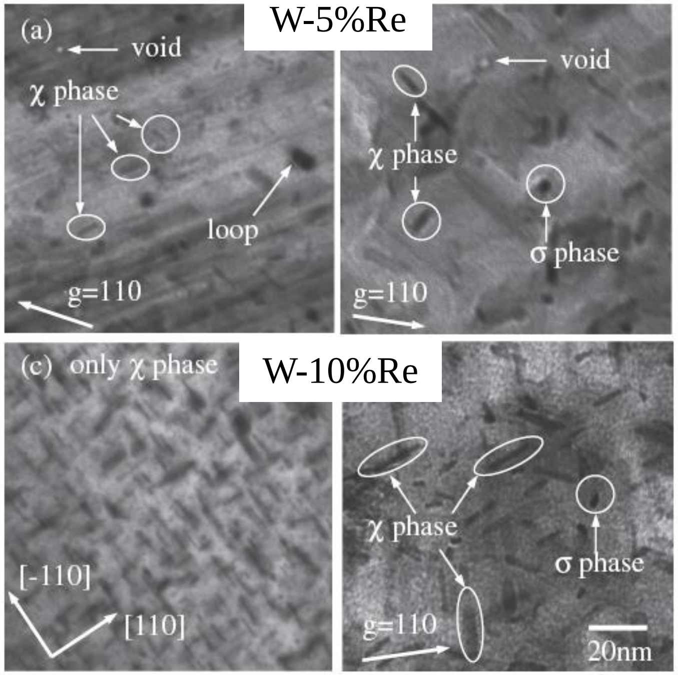
T. Tanno, et al., *Materials Transactions* 52 (2011) 1447.

Materials (Temperature during Irradiation)	Voids		Swelling	Loops		Dislocations
	Density 10^{22} m^{-3}	Radius nm	%	Density 10^{21} m^{-3}	Radius nm	Density 10^{14} m m^{-3}
W (873 K)	6.4	1.3	0.09	4.6	7.9	4.0
W (873–1073 K)	3.4	1.4	0.06	0.7	7.4	4.5
W (1073 K)	4.2	1.9	0.18	1.1	8.5	2.6
W–3Re (873 K)	3.4	1.1	0.03	1.4	3.6	—
W–3Re (873–1073 K)	2.0	1.1	0.02	—	—	—
W–3Re (1073 K)	0.9	1.3	0.01	1.1	2.8	—

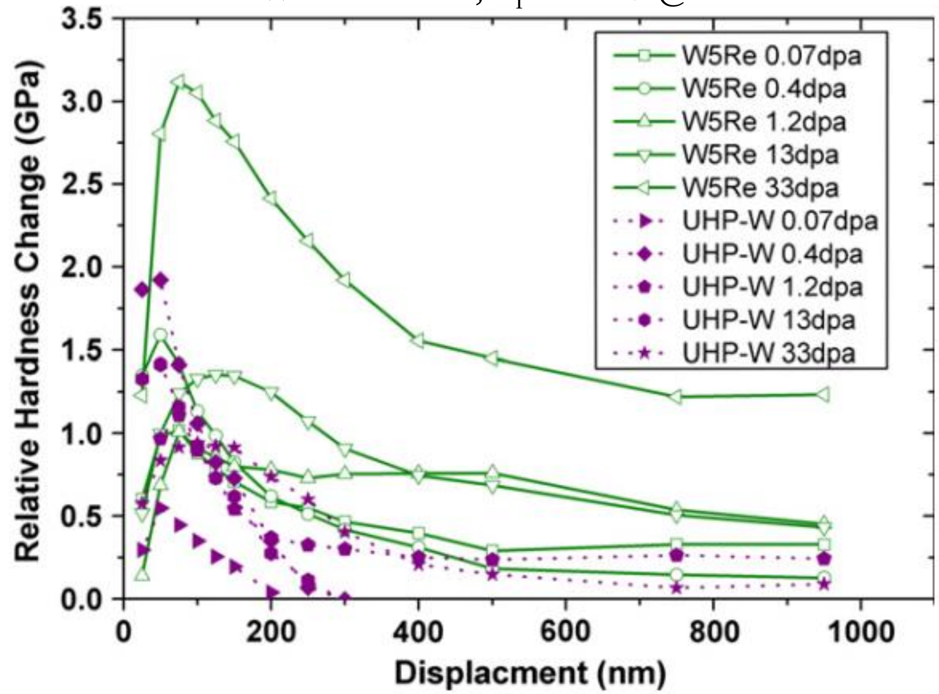
- **Under low irradiation level, Re/Os can reduce the average size of voids and dislocation loops, which contributes to the application of W-PFM.**

Effects of transmutation elements: Neutron irradiation

Neutron irradiation, E_n>0.1 MeV, **0.96~1.54 dpa**



W$^+$ irradiation, E_i>2 MeV @ 300 ℃



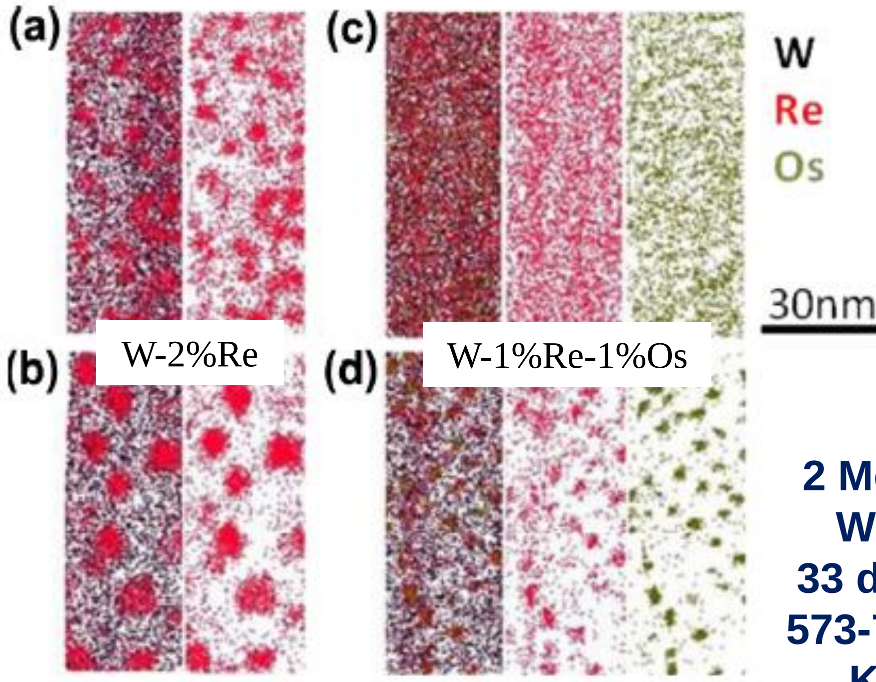
D.E.J. Armstrong et al., *J. Nucl. Mater. 432* (2013) 428.

			N [10^{22}/m^3]	d [nm]	$(Nd)^{1/2}$ [10^6/m]	ΔH_v (Calc.)	ΔH_v (Meas.)
1.54 dpa	W	Void	12.0	4.7	23.8	355	341
750°C	W-10Re	Void	3.1	1.6	7.0	104	419
		Prec.	41.7	9.5	62.9	422	
0.96 dpa	W	Void	48.7	2.1	32.1	478	363
		Loop	4.7	4.7	14.9	74	
538°C	W-10Re	Loop	<0.2	~5	<2	<10	528
		Prec.	83.7	6.8	75.6	507	

T. Tanno, et al. *Materials Transactions* 52 (2011) 1447.

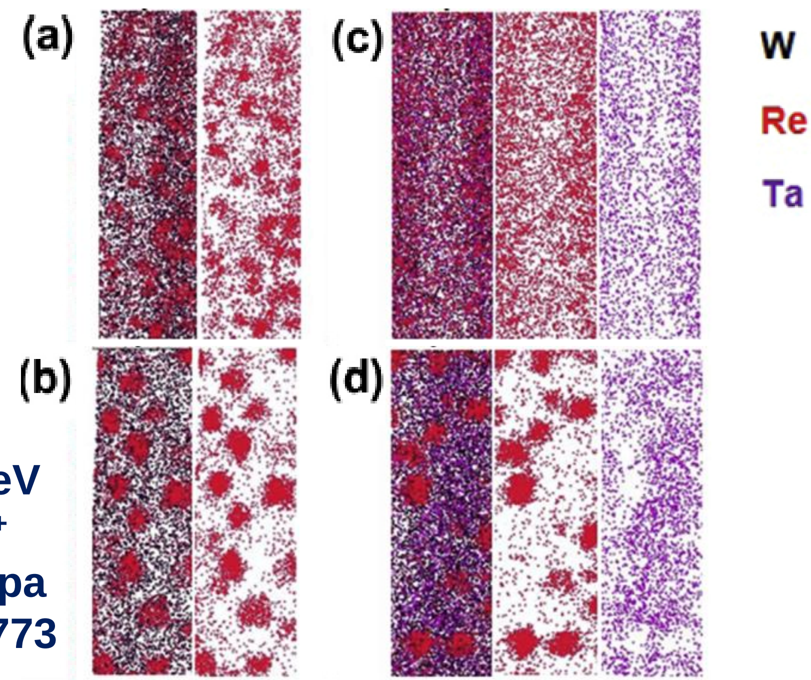
Under high irradiation level, high density of Re/Os-rich precipitate has been observed in normal W-Re/Os alloys (< 28at.% Re; < 6at.%Os), substantially enhancing the irradiation hardening and embrittlement of W

Formation of radiation-induced Re/Os precipitation



A. Xu, et al. *Acta Materialia* 87 (2015) 121.

2 MeV W$^+$ 33 dpa 573-773 K

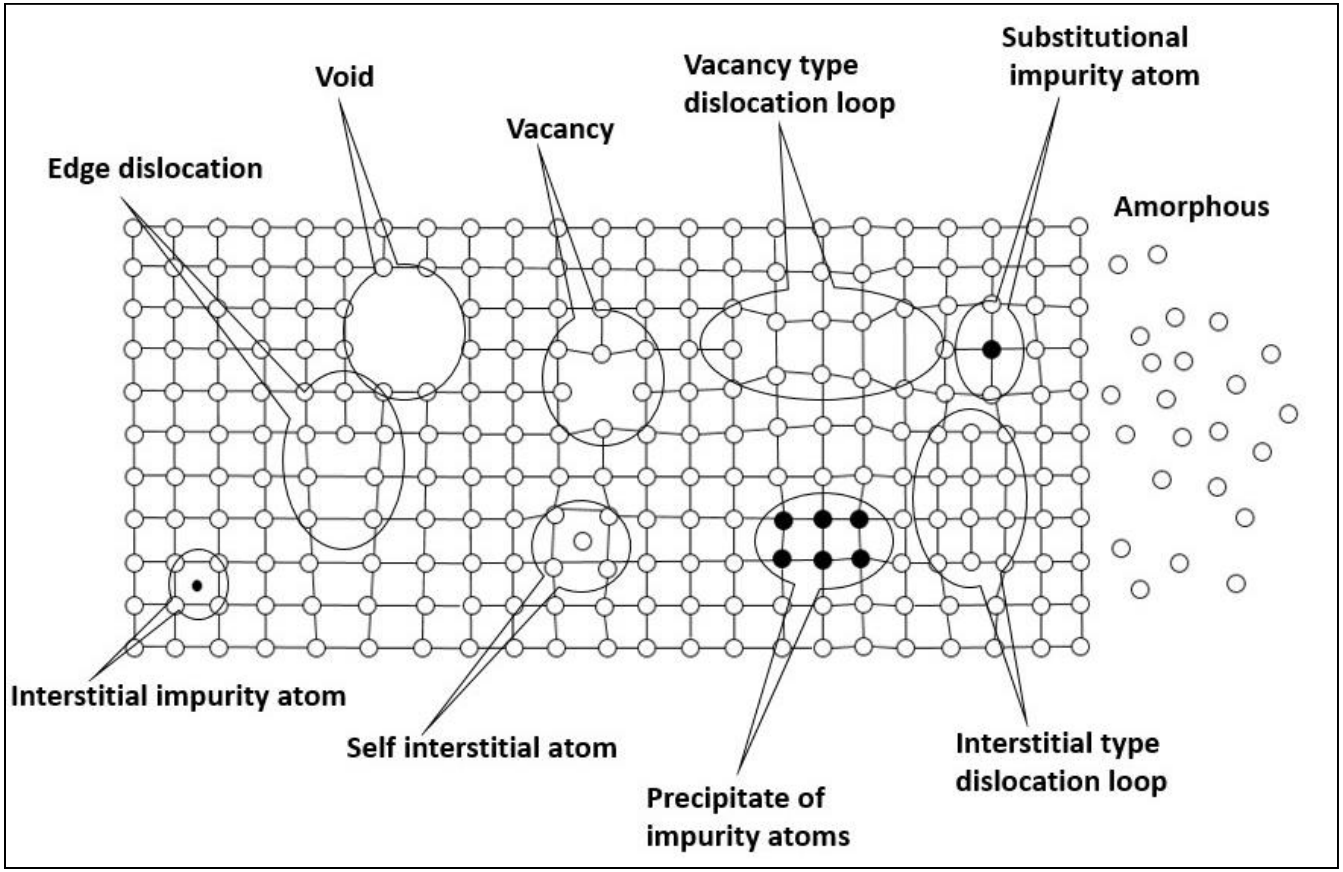


A. Xu, et al. *Acta Materialia* 124 (2017) 71.

Cluster feature	573 K 33 dpa W–2Re	573 K 33 dpa W–1Re–1Os	773 K 33 dpa W–2Re	773 K 33 dpa W–1Re–1Os
Re (at.%)	7.99 ± 1.42	1.33 ± 0.40	12.77 ± 2.86	1.88 ± 0.87
Os (at.%)	n/a	4.08 ± 0.70	n/a	6.88 ± 1.57
Radius (nm)	2.39 ± 1.03	2.77 ± 1.36	3.32 ± 1.88	1.93 ± 0.82
Number density ($\times 1000\ \mu m^{-3}$)	1717 ± 72	1095 ± 56	812 ± 54	2467 ± 112
Volume fraction (%)	9.01 ± 0.38	7.33 ± 0.38	11.21 ± 0.74	9.59 ± 0.44

- **Using Atom Probe Tomography method, it is found that even with extremely low Re/Os concentration (1~2 at.%), there is also obvious Re/Os aggregation in W.**
- **These Re/Os-rich clusters are considered as the precursors of the precipitation.**

Effects of radiation defects on Re/Os precipitation in W



- It should be noted that Re/Os precipitation only occurred under irradiation.
- The significant difference between irradiated and irradiation-free W is the radiation-induced defects (vacancy and self-interstitial atom).

Computational methods

First-principles method

- Density functional theory
- VASP code, PAW-GGA
- Ecut: 400 eV
- Force on all the atoms : less than 10^{-3}eV/Å
- Supercell size: 4×4×4 (128-atoms), 5×5×5 (250-atoms)

Thermodynamic models

- Arrhenius diffusion equation
- Classical nucleation theory

Main results

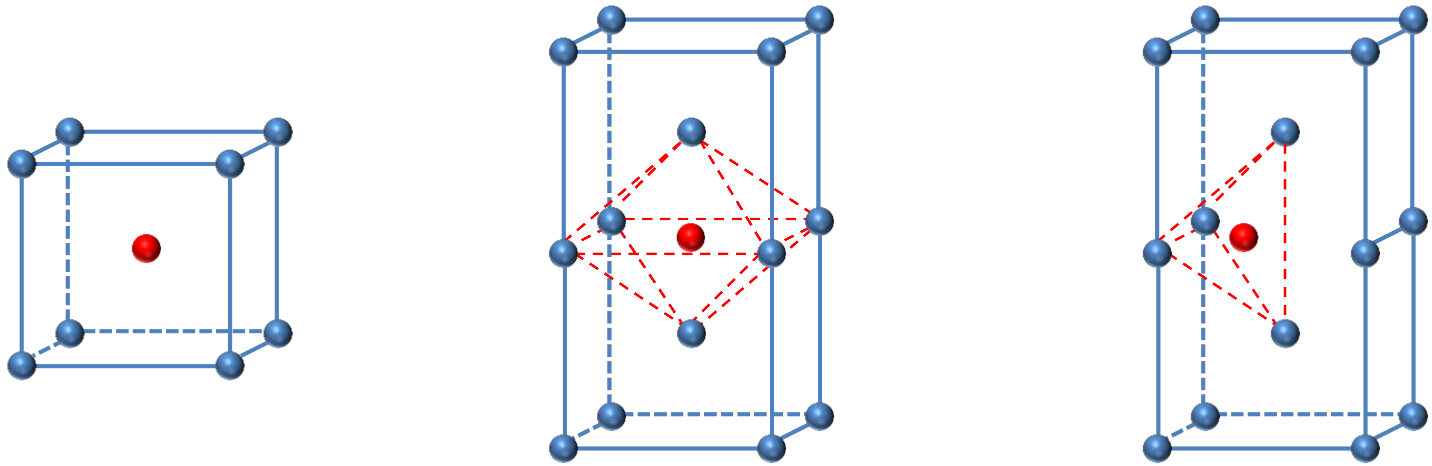
BUAA

I. **Behaviors of Re/Os in intrinsic W**

II. Behaviors of Re/Os in irradiated-W

III. Interstitial-mediated mechanism

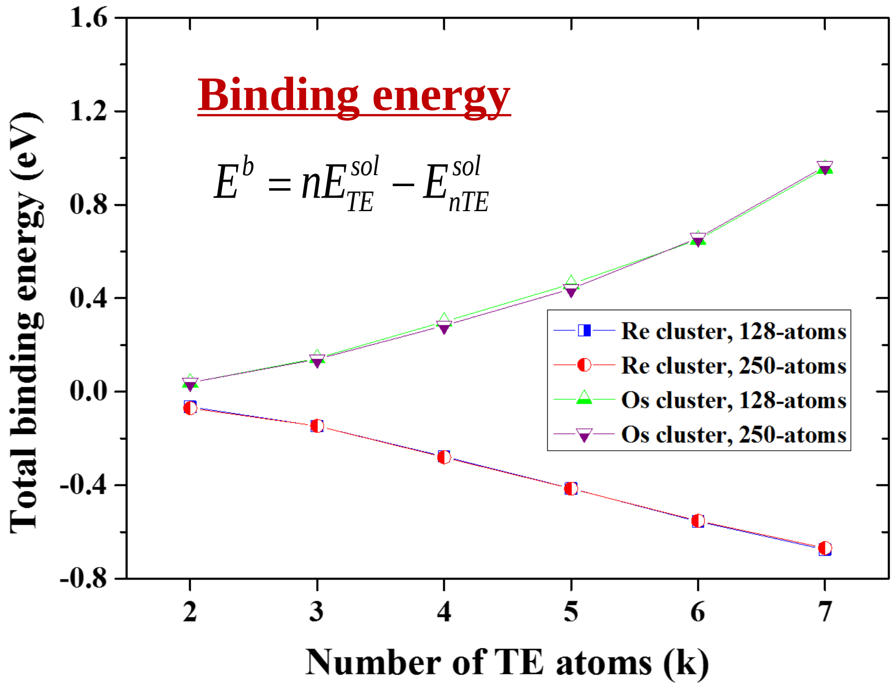
Stability of a single Re/Os in W



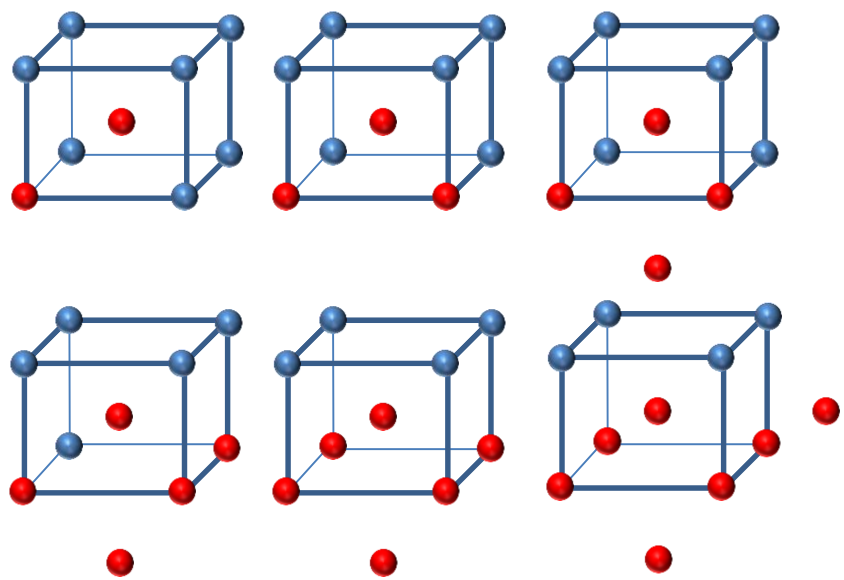
	Substitutional site	Octahedral interstitial site (OIS)	Tetrahedral interstitial site (TIS)
Re	**0.19eV**	**11.07eV**	**10.31eV**
Os	**0.76eV**	**10.83eV**	**9.77eV**

- **A single Re/Os atom is energetically favorable sitting at the substitutional site in W.**

Stability of Re/Os clusters in W

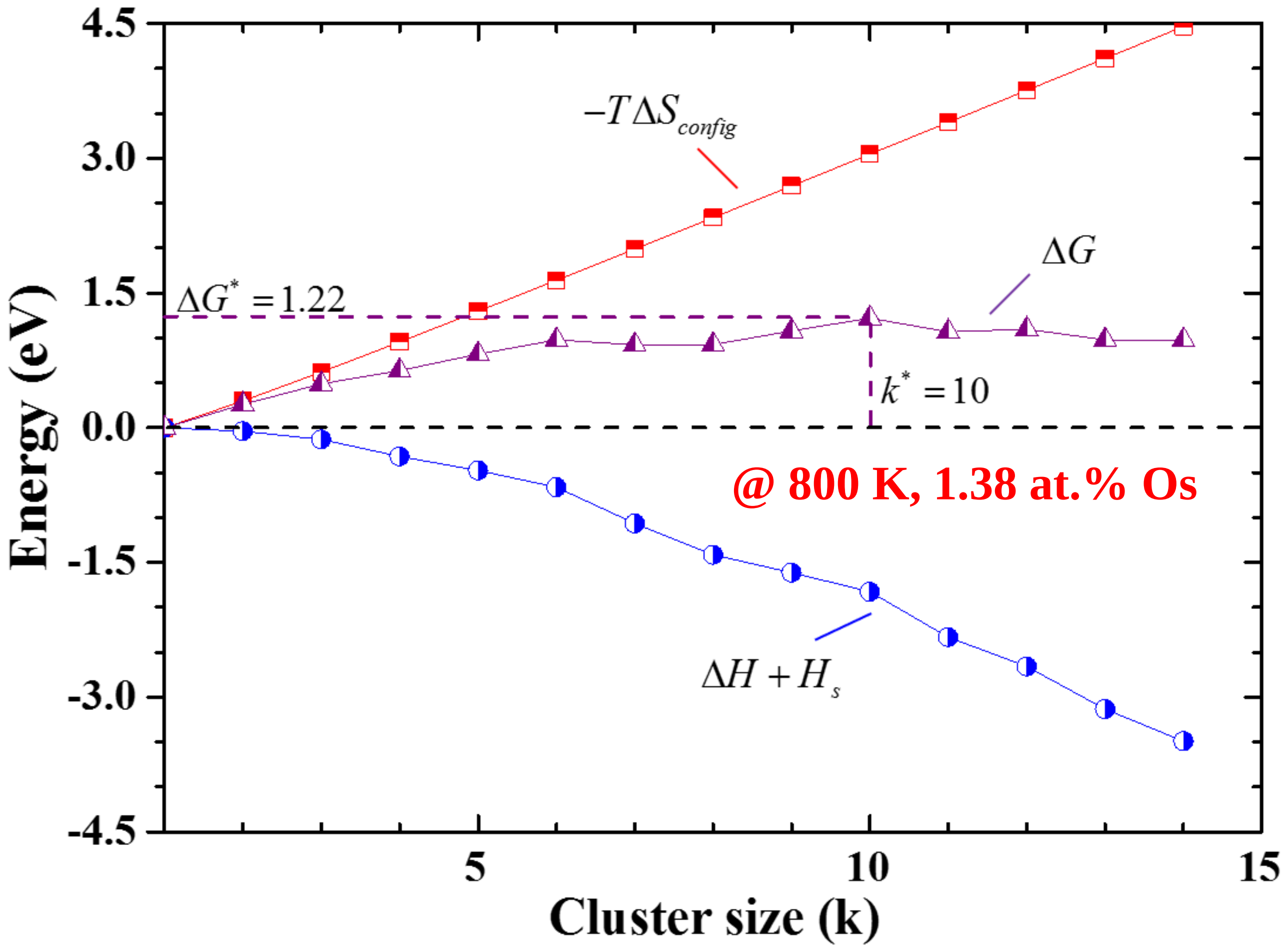


Corresponding configurations



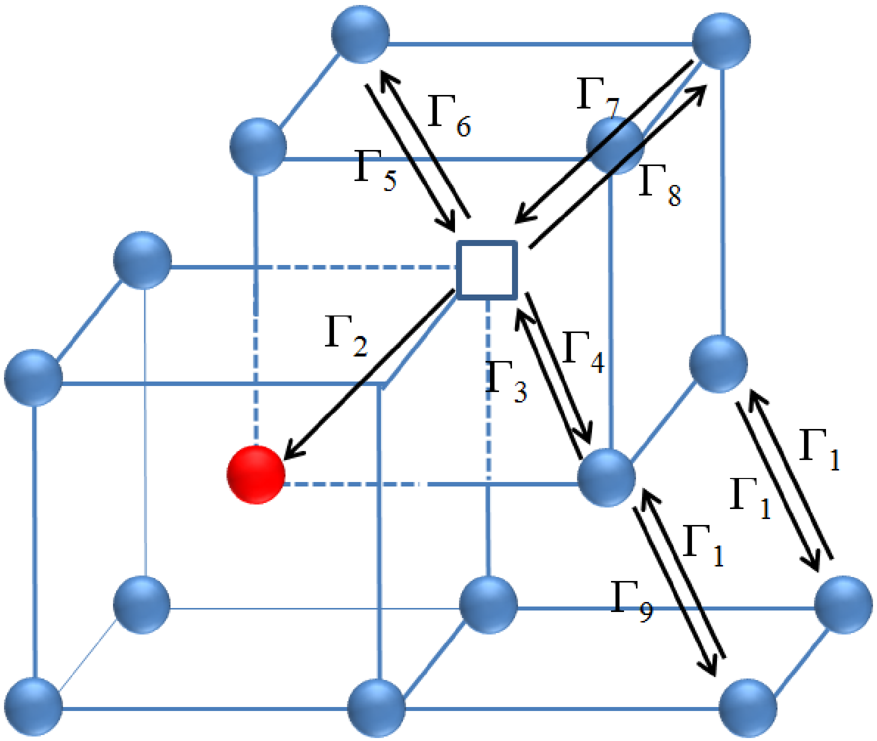
- Re atoms are energetically favorable to disperse separately in bulk W due to the Re-Re repulsive interaction (negative binding energy).
- The binding energy of Os clusters are positive, suggesting Os prefers to get together in W.

Nucleation of Os clusters in W



- **Despite the attractive interaction between Os atoms, there is still a large activation energy barrier (~ 1.10 eV) for the formation of Os clusters.**
- **Thermodynamically, the nucleation of Re/Os clusters are difficult in bulk W.**

Diffusion energy of Re/Os/W in W



path	pure W	W-Re	W-Os
1	1.65	1.56	1.40
2	1.65	1.63	1.36
3	1.65	1.56	1.38
4	1.65	1.58	1.56
5	1.65	1.56	1.40
6	1.65	1.75	1.84
7	1.65	1.49	1.27
8	1.65	1.68	1.69
9	1.65	1.73	1.70

- **The diffusion energy of Os is the lowest via the mono-vacancy mechanism, followed by Re and W.**

Diffusivity of Re/Os/W in W

Arrhenius diffusion equation

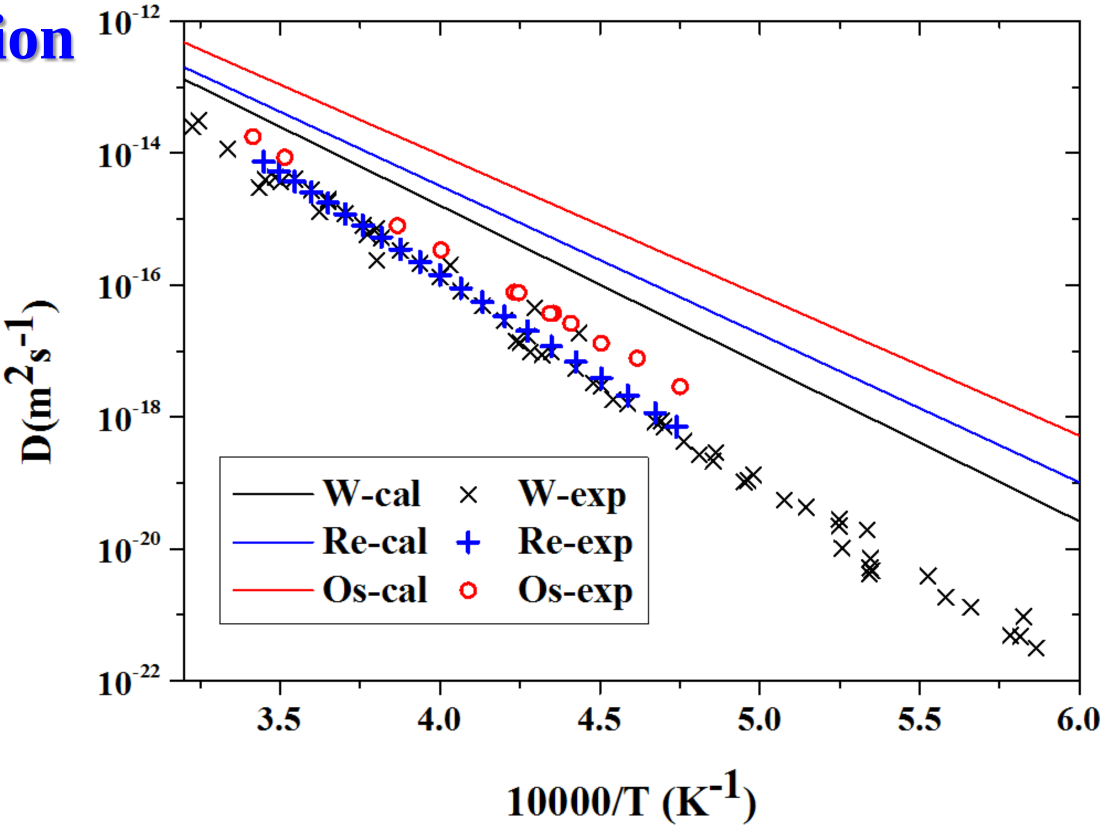
$$D = D_0 \exp(-Q_0 / k_B T)$$

D_0 : Pre-factor

Q_0 : Active energy

E_d : Diffusion energy barrier

	D_0 (10^{-6} m^2s^{-1})	Q_0 (eV)	E_d (eV)
W	5.97	4.74	1.65
Re	3.30-3.53	4.48	1.63
Os	1.04-1.05	4.23	1.36



- **The diffusion coefficient of Os is the largest via the mono-vacancy mechanism, followed by Re and W, and such sequence is in good agreement with the experiment results.**

Main results

BUAA

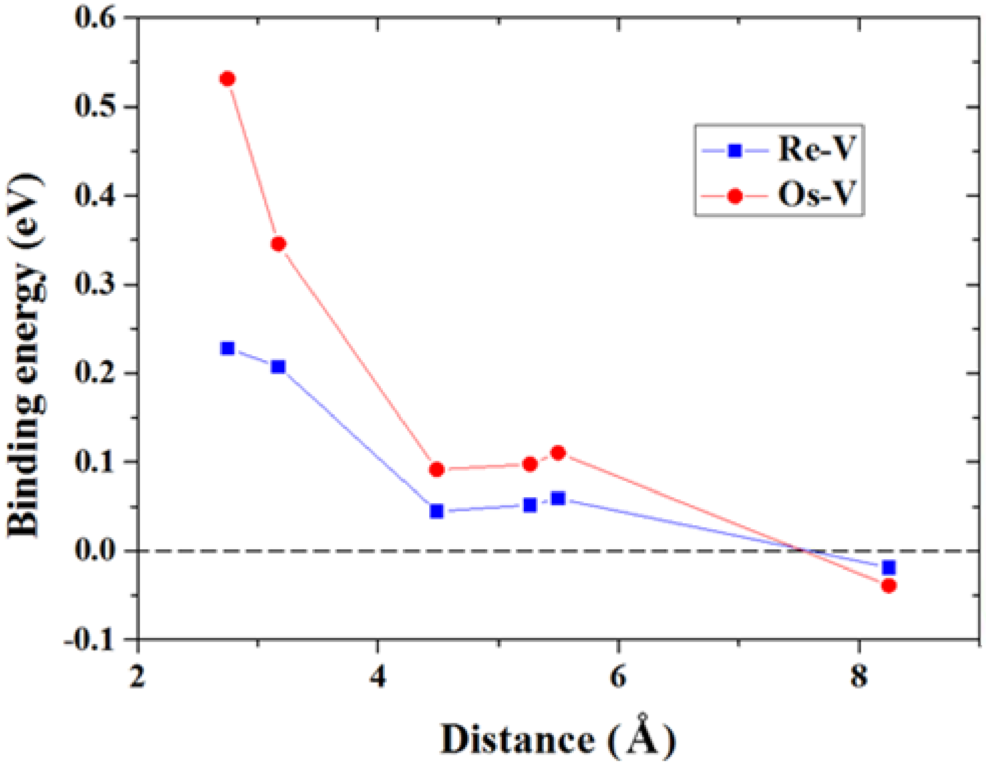
I. Behaviors of Re/Os in intrinsic W

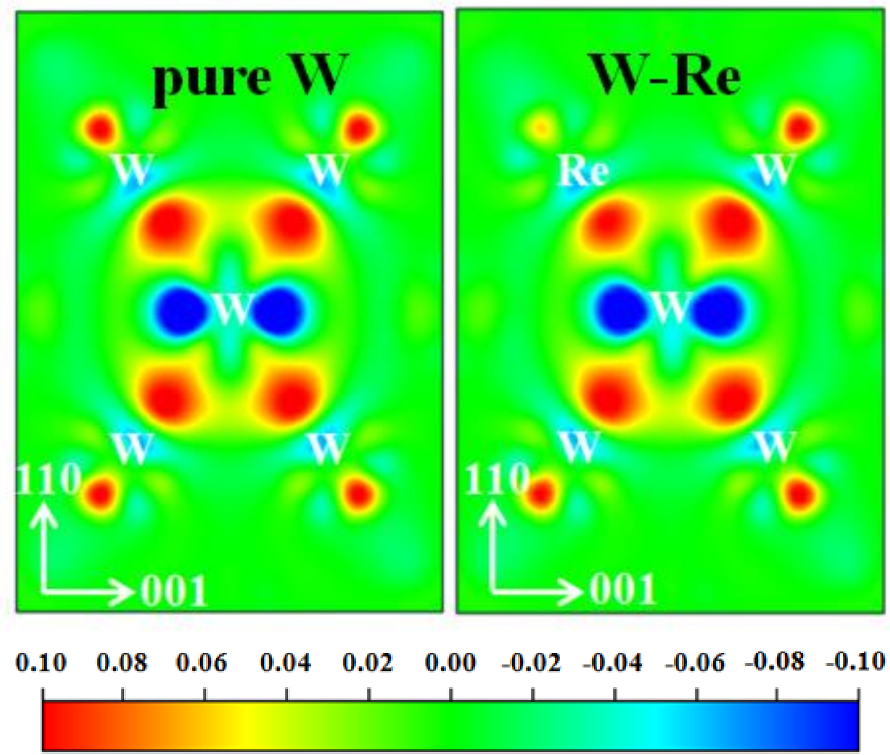
II. **Behaviors of Re/Os in irradiated-W**

- **Coupling of a point defect with a single Re/Os atom in W**

III. Interstitial-mediated mechanism

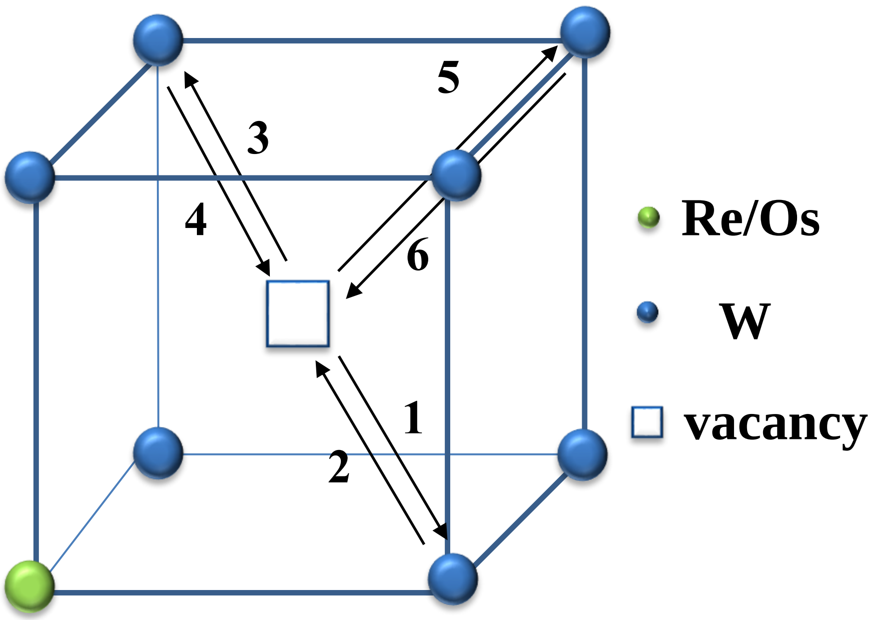
Interaction between Re/Os and vacancy





- There is strong attractive interaction of Re/Os-vacancy pair.
- The charge density between Re/Os and W is much lower than that of W-W, which means the existence of Re and Os weakens the interatomic bond of W atoms surrounding them and benefits to the vacancy formation.

Interaction between Re/Os and vacancy

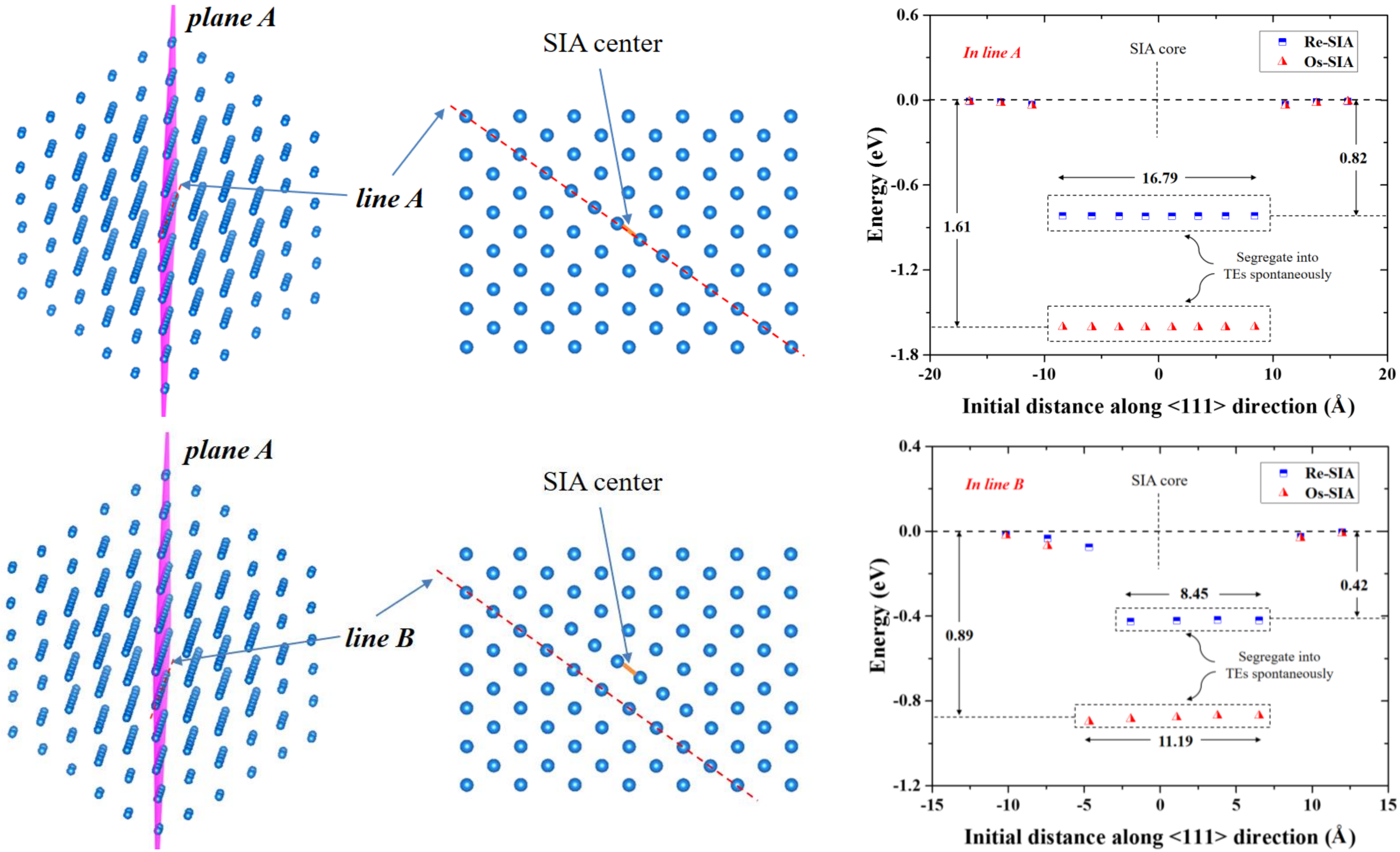


Energy barrier: eV

path	pure W	W-Re	W-Os
1	1.65	1.58	1.56
2	1.65	1.56	1.38
3	1.65	1.75	1.84
4	1.65	1.56	1.40
5	1.65	1.68	1.69
6	1.65	1.49	1.27

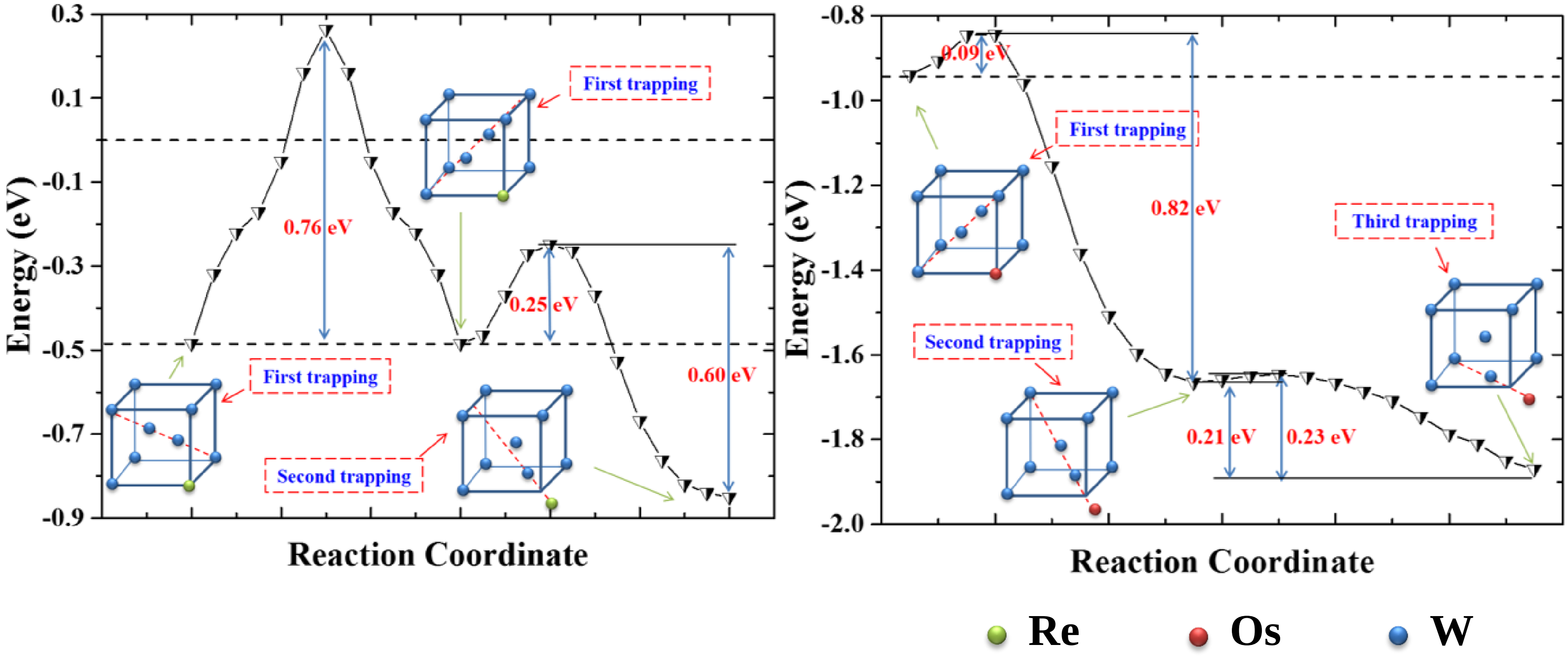
- **Due to the high diffusion energy barrier of vacancy (1.38~1.84 eV), the formation of Re/Os-vacancy must overcome a high energy barrier.**

Interaction between Re/Os and SIA



- There is strong attraction between <111> dumbbell of SIA and Re/Os.
- There exists a "spontaneously segregation region", where SIA will segregate to Re/Os via barrier-free process.

Formation of most stable Re/Os-SIA pair



- **Overcoming a low energy barrier (Re/Os: 0.25/0.09eV), the metastable Re/Os-SIA pair will transform to the most stable Re/Os-W dumbbell.**

SIA vs Vacancy

		SIA	Vacancy
Diffusion energy barrier in bulk W（eV）		< 0.05	1.65
Re	Binding energy（eV）	0.85	0.24
	Energy barrier for coupling（eV）	0.25	1.65
	Interactive region	~ 17	~ 7
Os	Binding energy	1.87	0.54
	Energy barrier for coupling	0.09	1.65
	Interactive region	~ 17	~ 7

- Compared with Re/Os-vacancy pair, Re/Os-SIA pair has a larger binding energy, a much wider interaction range and an extremely lower energy barrier.
- SIA will be preferentially trapped by Re/Os, forming IS-Re/Os.

Main results

BUAA

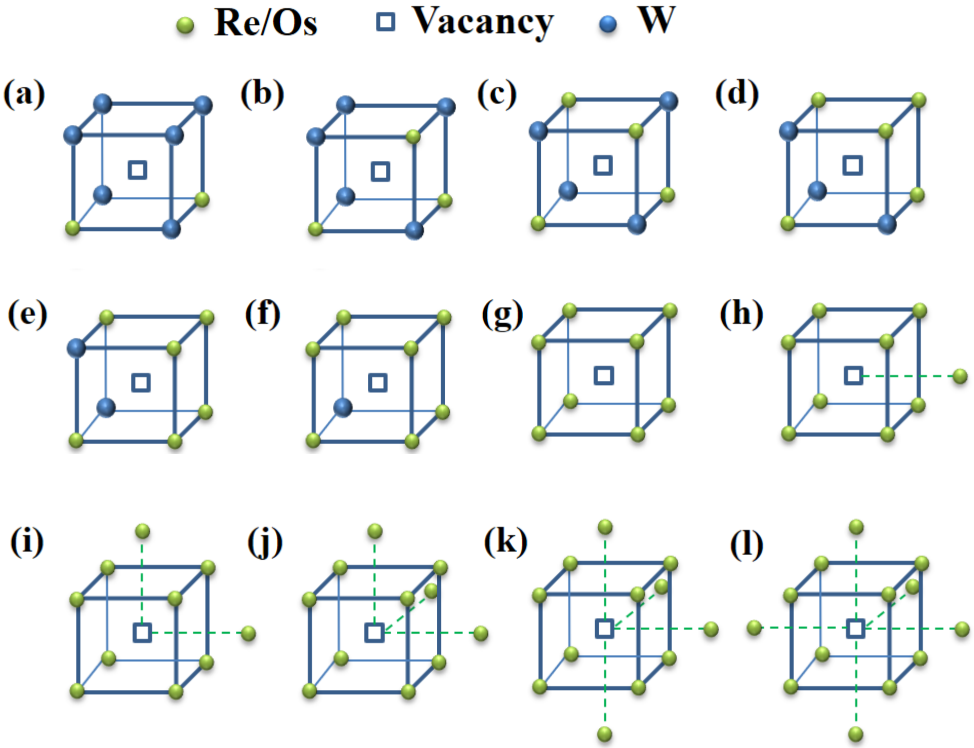
I. Behaviors of Re/Os in intrinsic W

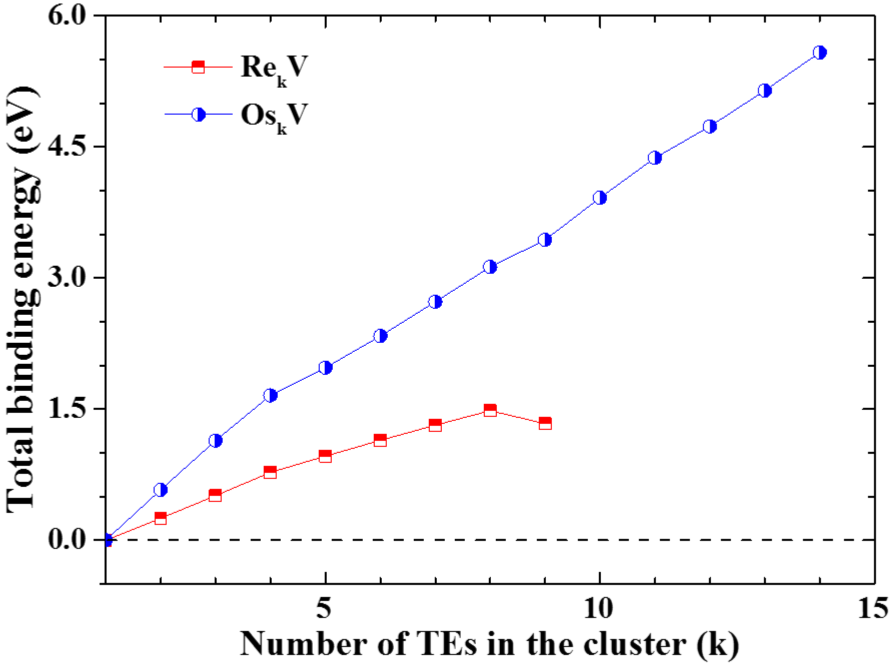
II. **Behaviors of Re/Os in irradiated-W**

- Coupling of a point defect with a single Re/Os atom in W
- **Effects of point defects on the clustering of Re/Os: Thermodynamically**
- Effects of point defects on the clustering of Re/Os: Kinetically

III. Interstitial-mediated mechanism

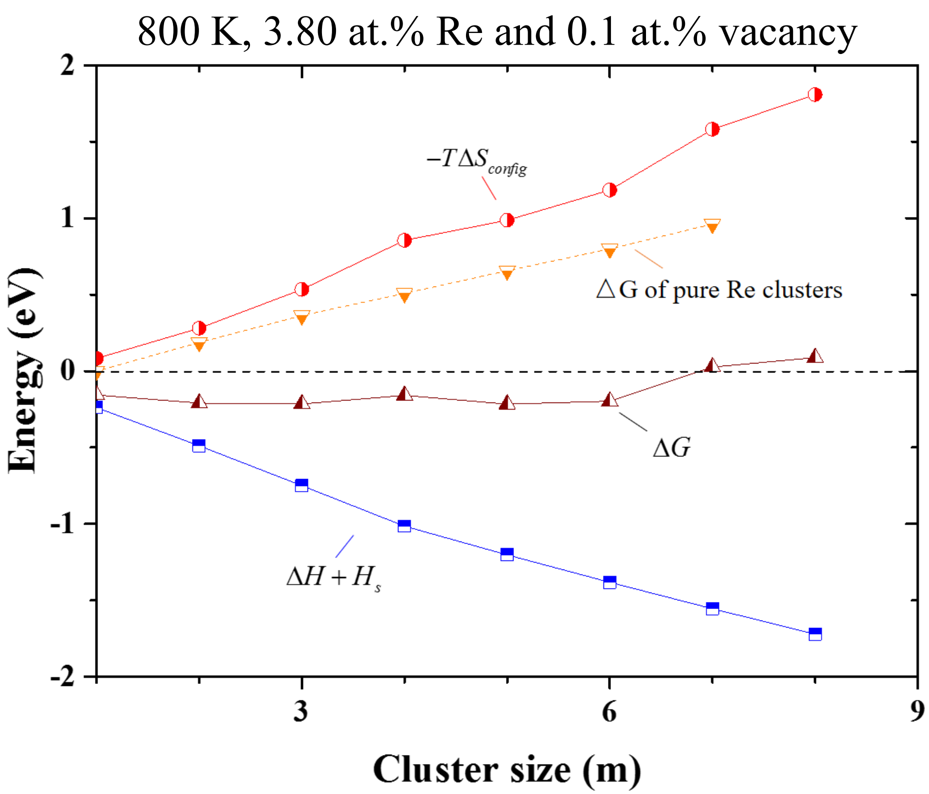
Interaction between vacancy and multi-Re/Os atoms

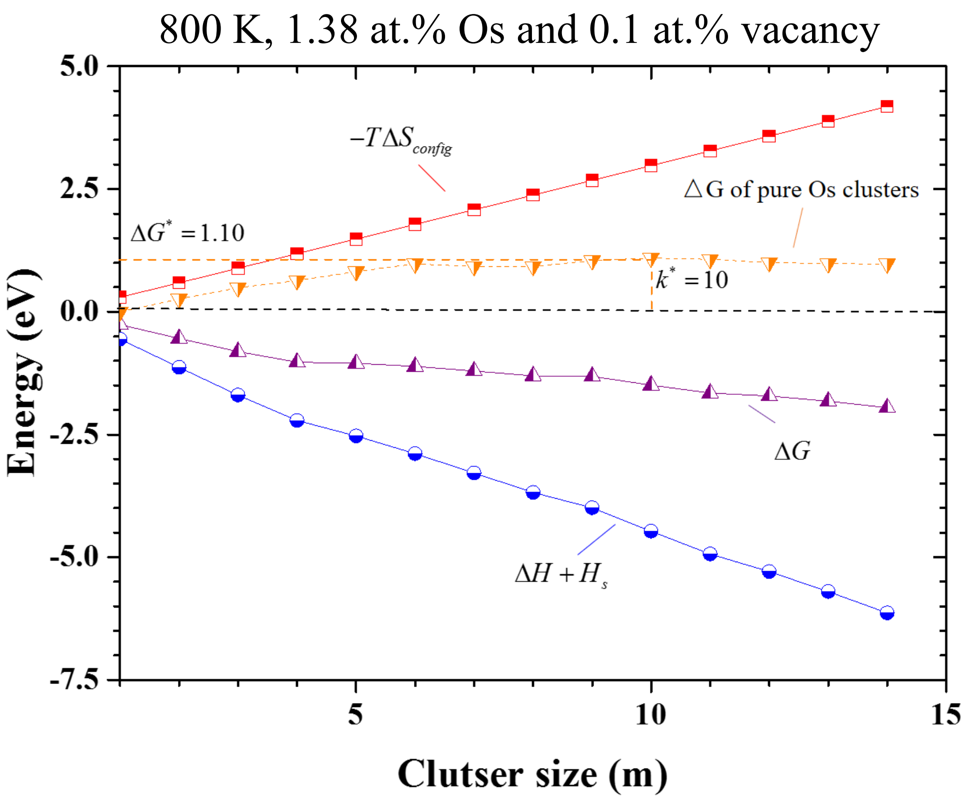




- Re/Os prefers to segregate to vacancy, forming a three-dimensional sphere-like configuration.
- The presence of vacancy will increase the binding energy of Re/Os clusters.

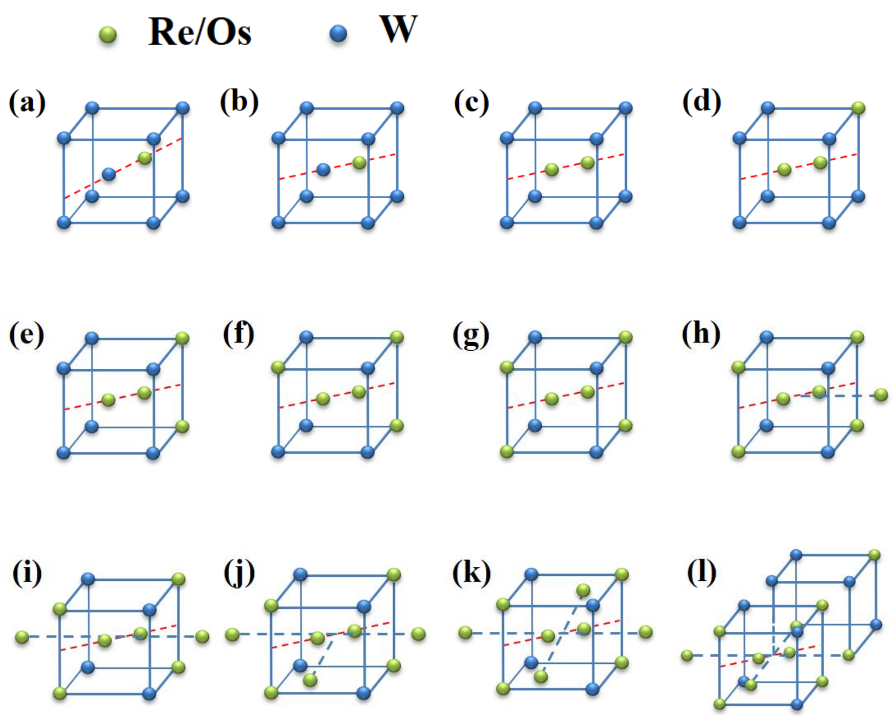
Effect of vacancy on Re/Os clustering in W

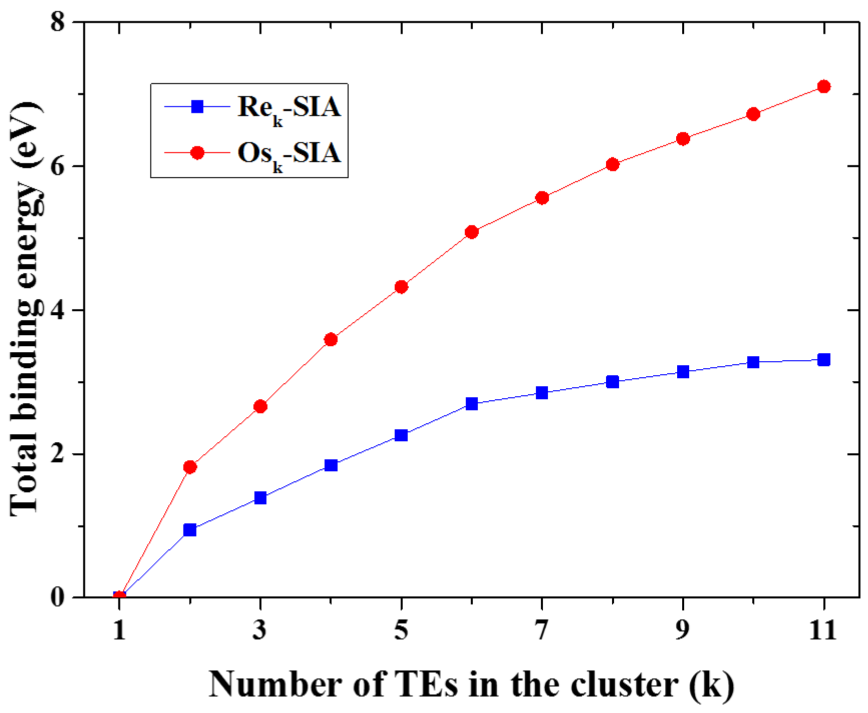




- **Vacancy can significantly reduce the total nucleation free energy change of Re/Os clusters in W.**
- **Thermodynamically, the presence of vacancy will facilitate the nucleation of Re/Os in W.**

Interaction between SIA and multi-Re/Os atoms

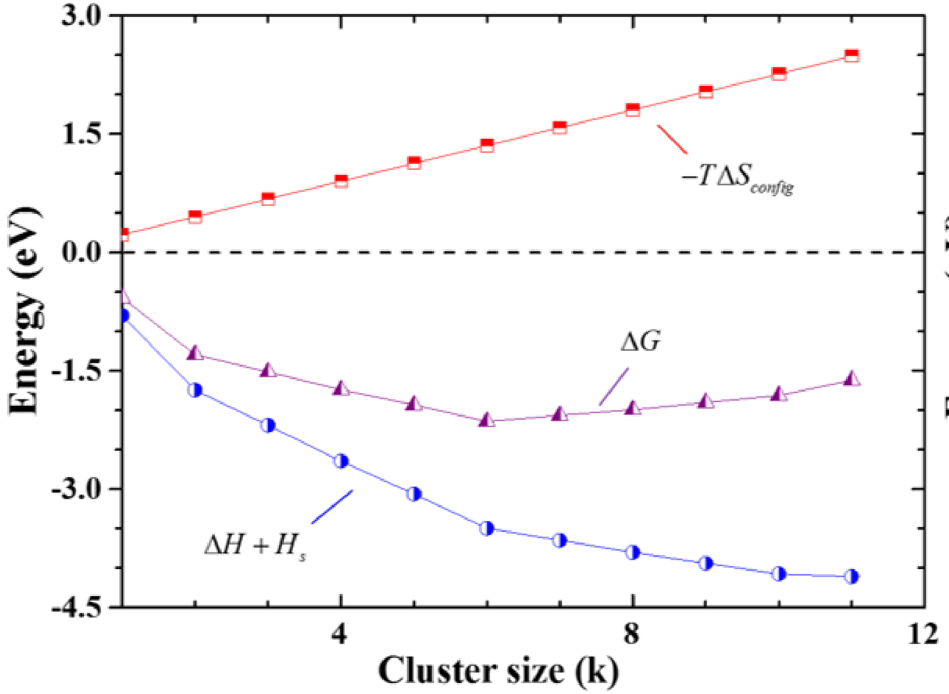




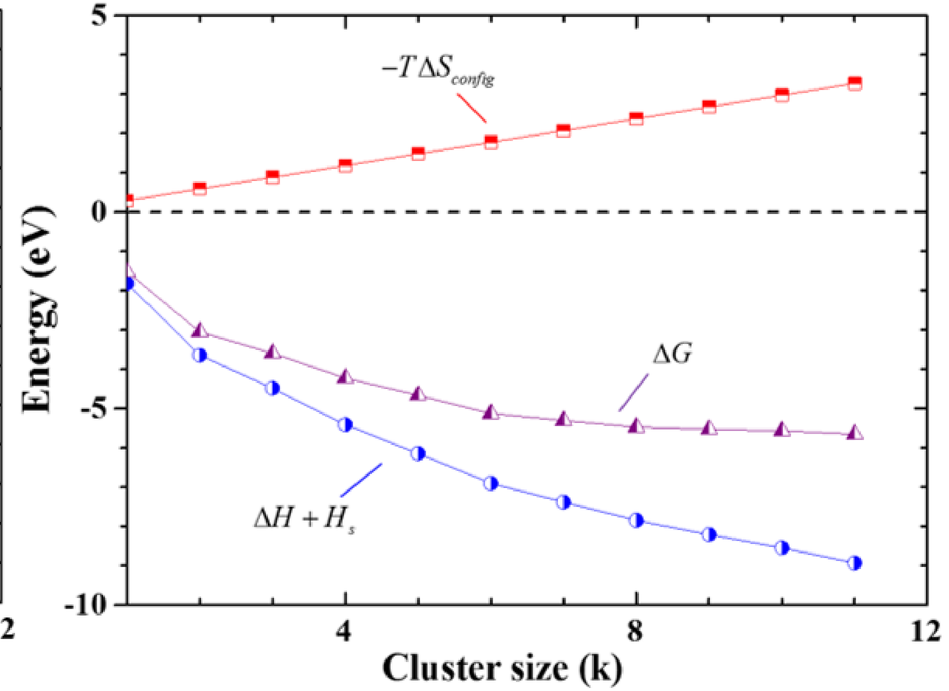
- Interstitial-mediated Re/Os clusters prefer to aggregate on the {110} planes and form two-dimensional platelet-like configurations.
- SIA can increase the binding energy of Re/Os clusters in W.

Effect of SIA on Re/Os clustering in W

800 K, 3.80 at.% Re and 0.1 at.% SIA



800 K, 1.38 at.% Os and 0.1 at.% SIA



- **Similar with vacancy, the presence of SIA also reduce the total nucleation free energy change of Re/Os clusters, and facilitate the nucleation of Re/Os in W.**
- **Because the binding energy of Re/Os-SIA is larger than that of Re/Os-vacancy, SIA has a more significant effects on the clustering of Re/Os in W.**

Main results

BUAA

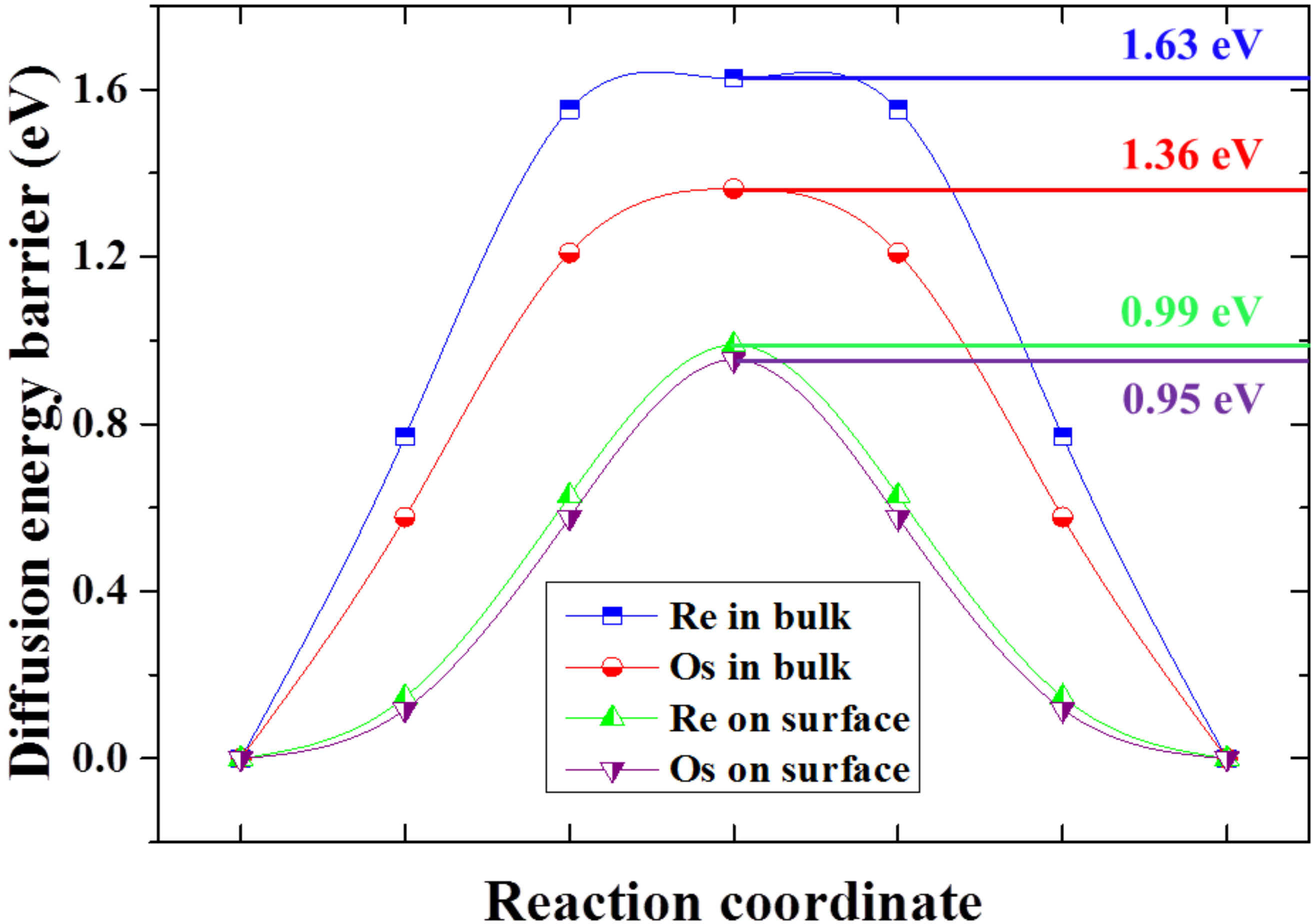
I. Behaviors of Re/Os in intrinsic W

II. **Behaviors of Re/Os in irradiated-W**

- Coupling of a point defect with a single Re/Os atom in W
- Effects of point defects on the clustering of Re/Os: Thermodynamically
- **Effects of point defects on the clustering of Re/Os: Kinetically**

III. Interstitial-mediated mechanism

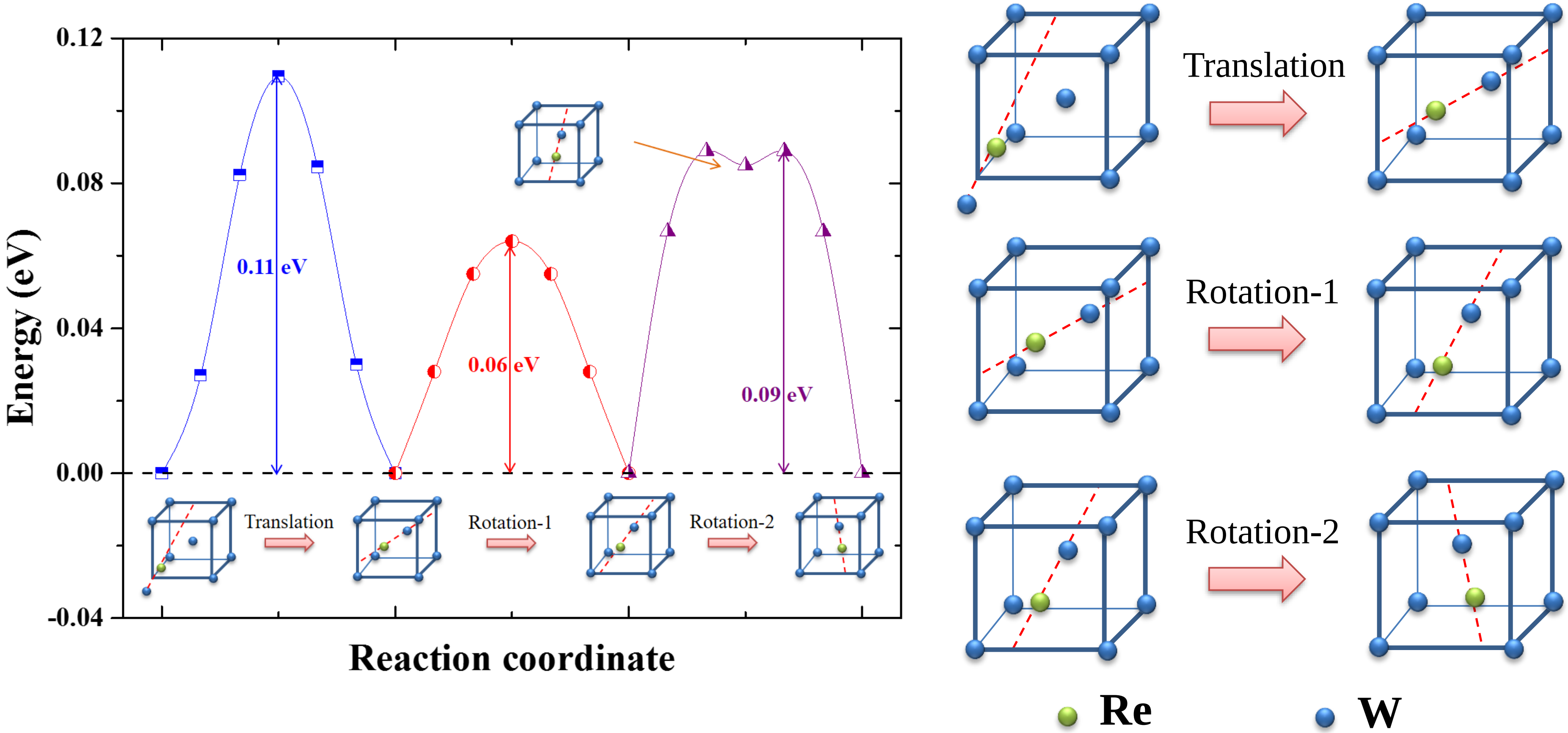
Diffusion of substitutional Re/Os



- ✓ **Bulk W：High diffusion energy barrier (Re/Os: 1.63/1.36 eV)**
- ✓ **W surface：High diffusion energy barrier (Re/Os:0.99/0.95 eV)**

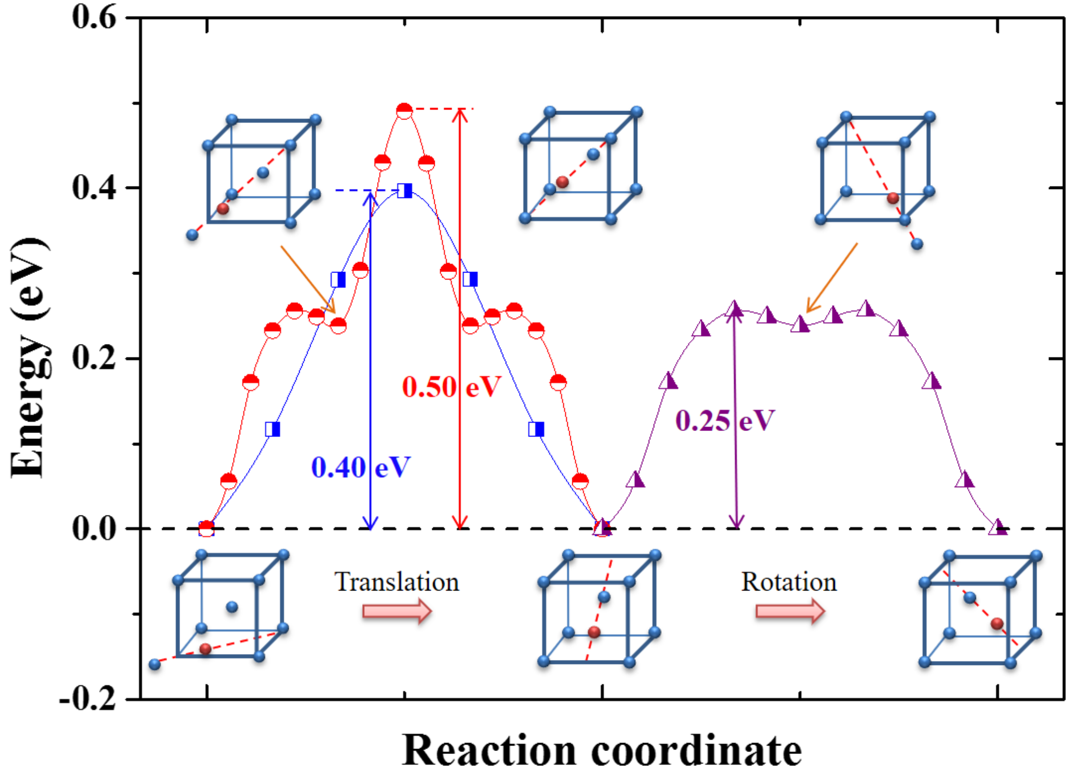
（vacancy- and vacancy cluster-mediated diffusion）

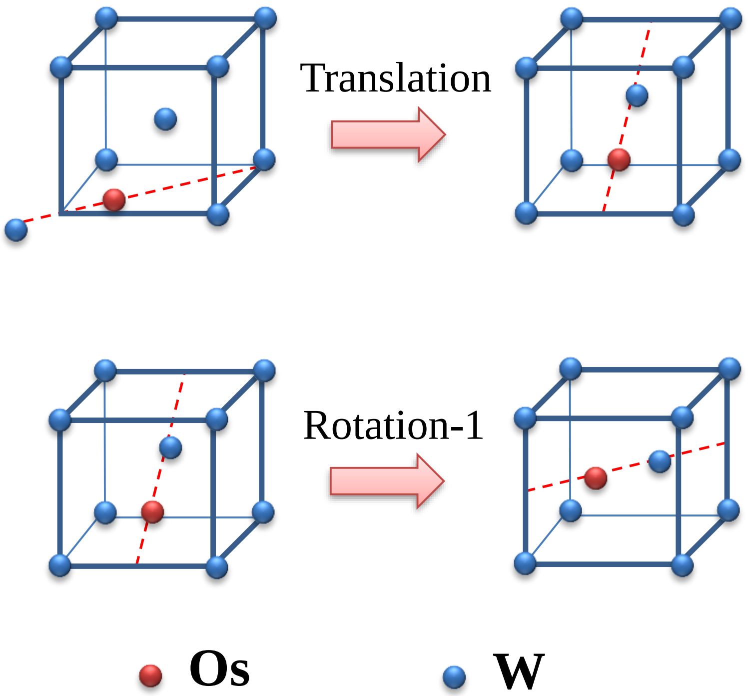
Diffusion of interstitial Re in W



- The diffusion energy barrier of IS-Re in W is only 0.11 eV, which is much lower than that of substitutional Re/Os.
- Therefore, IS-Re can easily diffuse in W via three-dimension.

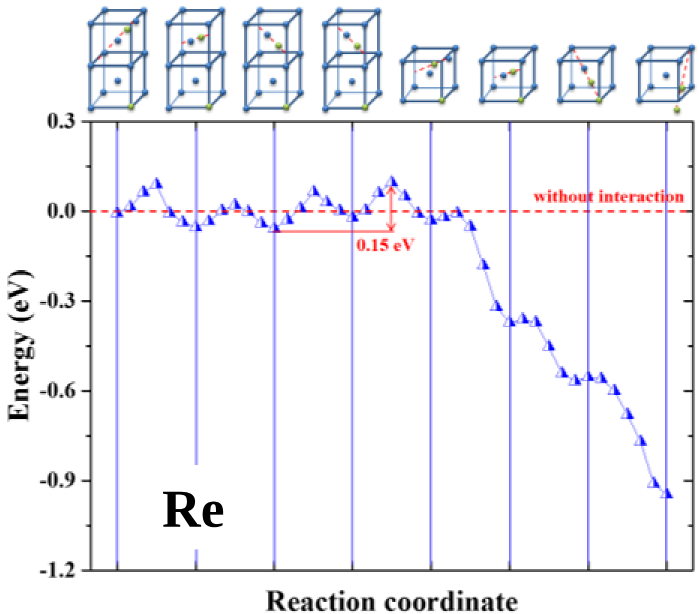
Diffusion of interstitial Os in W

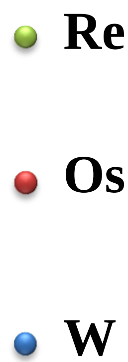


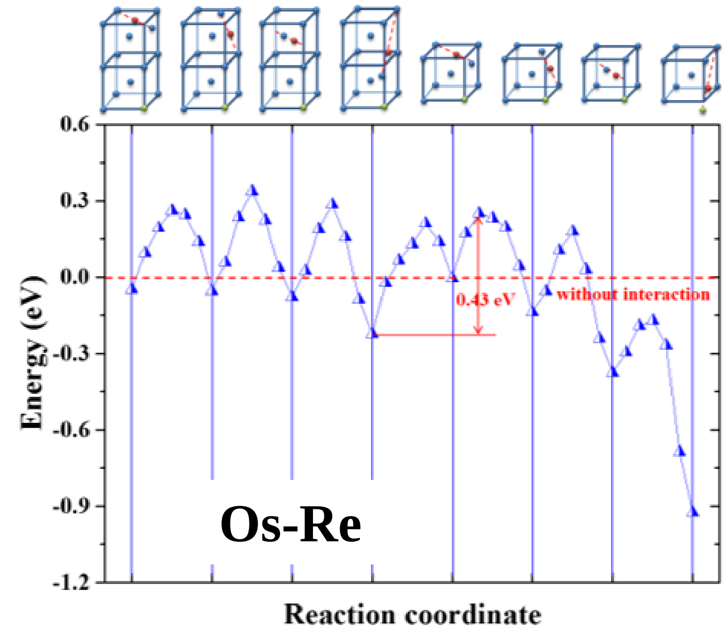


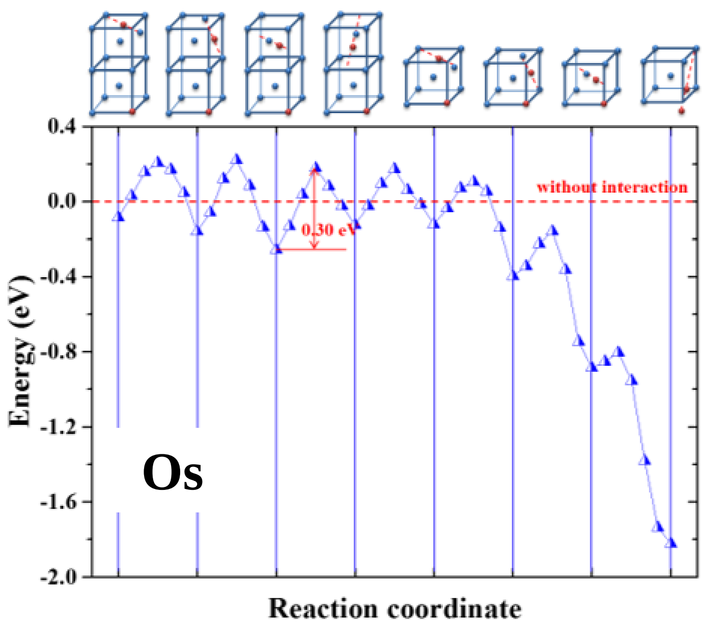
- Similar with IS-Re, IS-Os also has a much lower diffusion energy barrier (~ 0.40 eV) than substitutional Os, which means that IS-Os can also easily diffuse in W.
- Interstitial-mediated diffusion could dominate the migration of Re and Os in W under high irradiation level.

Nucleation of Re/Os (2-atom cluster)



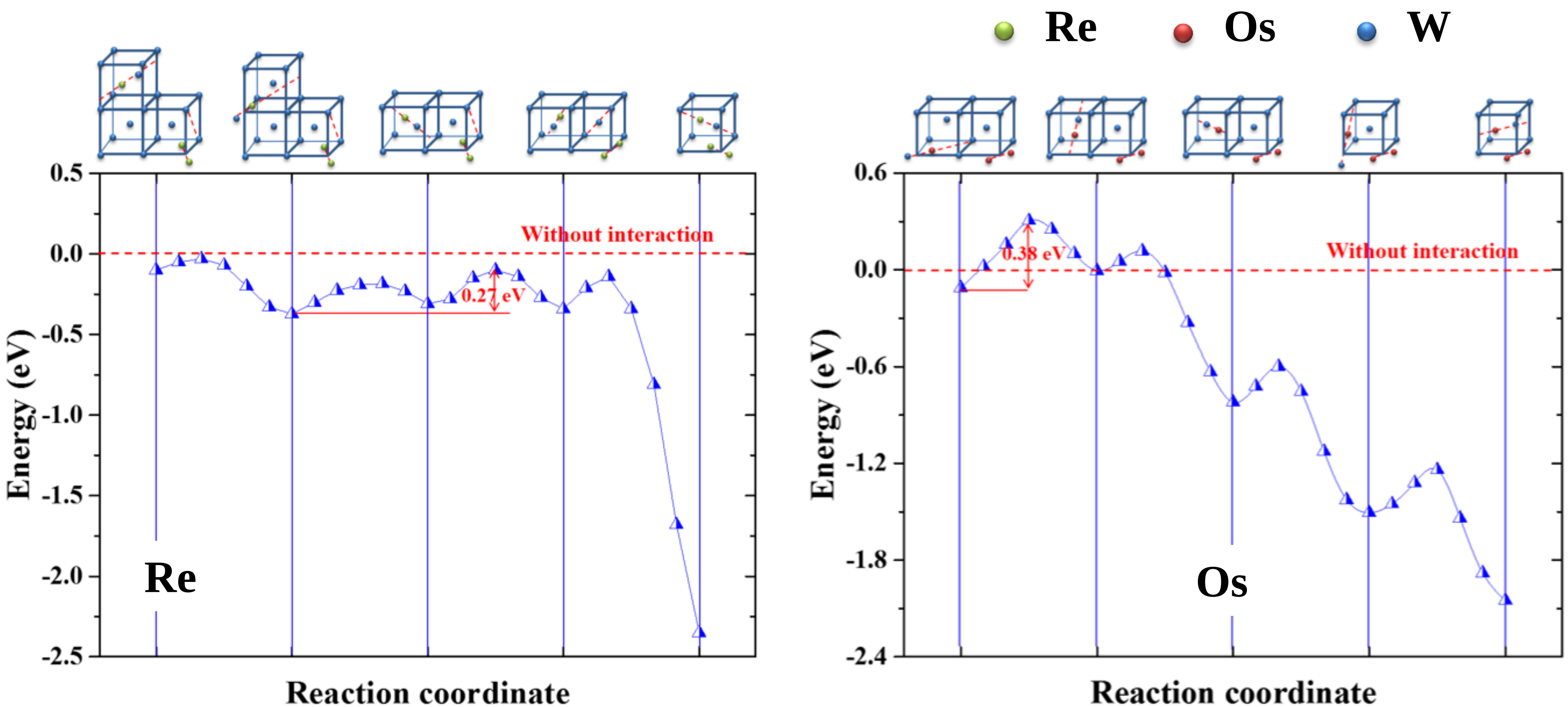






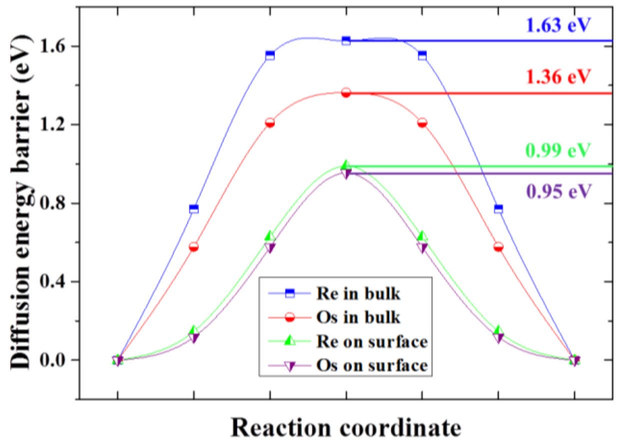
- **IS-Re/Os can be easily trapped by substitutional Re/Os, and form <110> Re/Os-Re/Os dumbbell structure.**
- **Due to high binding energy (> 0.90 eV), the <110> Re/Os-Re/Os dumbbells are very difficult to diffuse or dissociate.**

Growth of Re/Os clusters in W

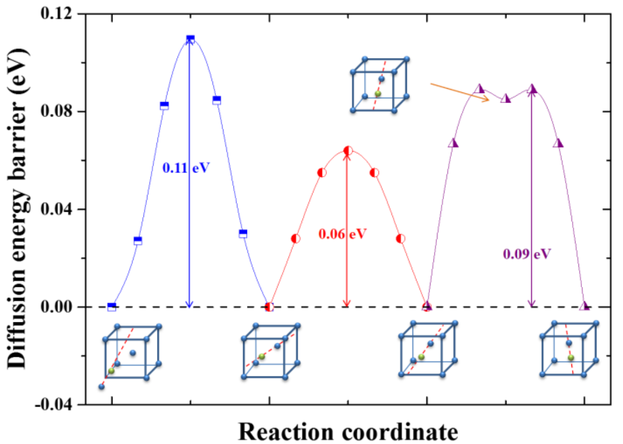


- **Stable Re-Re/Os-Os pair will serve as trapping center for subsequent IS-Re/Os, leading to the growth of Re/Os clusters in W.**

Interstitial-mediated diffusion and aggregation mechanism for Re/Os precipitation in W

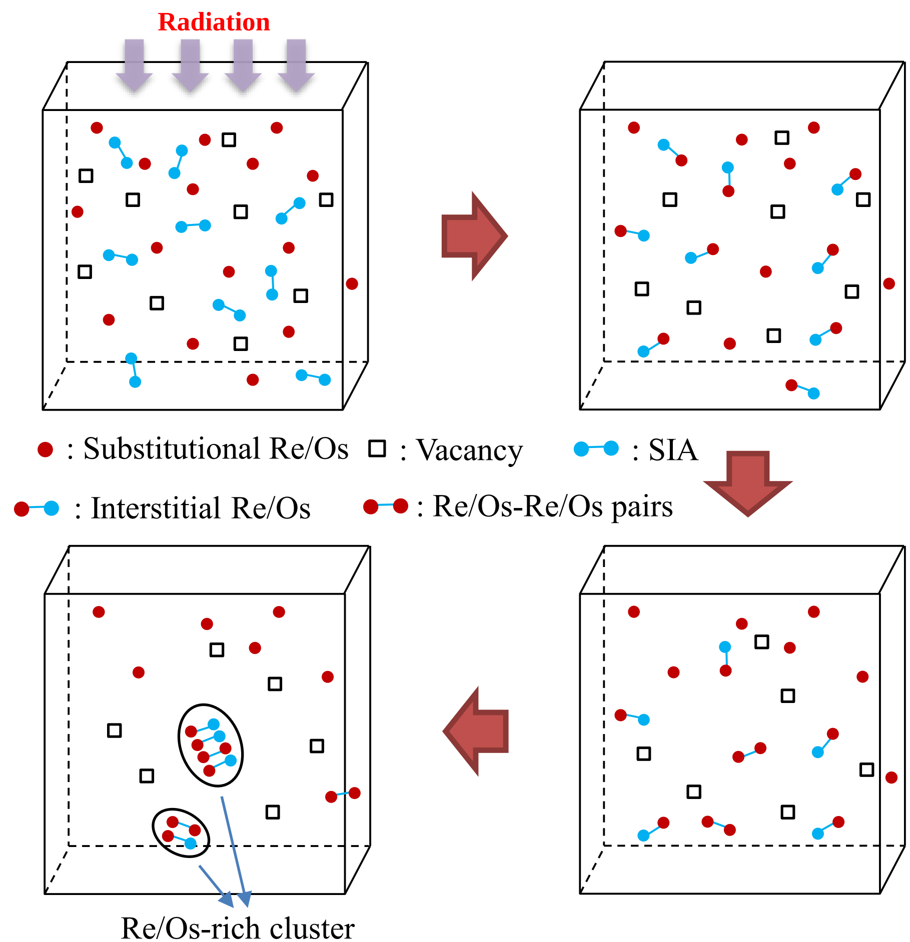


Diffusion of substitutional Re/Os



Diffusion of interstitial Re/Os

Interstitial-mediated mechanism



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Summary

Thermodynamic stability of Re/Os clusters in W

- Due to the repulsive interaction between Re atoms and the high energy barrier for the Os nucleation, the formation of Re/Os clusters in bulk W is difficult.
- Presence of radiation-induced defects (vacancy and SIA) will reduce the total nucleation free energy change of Re/Os clusters, and facilitate the nucleation.

Kinetic processes for the formation of Re/Os clusters in W

- Re/Os serves as a trapping center for vacancy and SIA with a preference for SIA.
- Interstitial-mediated diffusion could dominate the migration of Re and Os in W under irradiation condition.
- The IS-Re/Os can be easily trapped by the SS-Re/Os, and form high stable Re/Os-Re/Os <110> dumbbell.
- The Re/Os-Re/Os dumbbell can serve as trapping centre for subsequent interstitial-Re/Os, leading to the growth of Re/Os-rich clusters in W.

Thanks for your attention!