He effects in concentrated equiatomic refractory alloys with increasing chemical complexity: From medium to high entropy alloys (HeRHEA)

EUROFUSION ENR-MAT.02.VTT-T002-D001

01/01/2024 ⟶ 31/12/2025

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Partners of the HeRHEA project

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HerHEA

Timeline of HeRHEA project

2024	2025

WP1a(exp): Synthesis and characterization of REAA with different compositions

WP2(th): Development of ML-KMC model of vacancy clustering in REAAs in the presence of He atoms

WP3(exp): He irradiation of REAA in three energy regimes (low, medium, and high) at fusion reactor relevant temperatures. In-situ and ex-situ characterization of He bubble growth in REAA of different compositions

HerHEA

WP4(th): Simulations of He bubble growth in REAA due to He irradiation with different irradiation energies by means of ML-KMC and ML-MD

WP1(exp) "Synthesis and characterization of REAA with different compositions"

Samples

Material fabrication at VTT
Available material(s) to be studied
W, W-Ta, W-Mo, W-V

Other materials from Portugal
W-Ta-V, W-Ta-Mo

Cutting of the bulk as-fabricated material

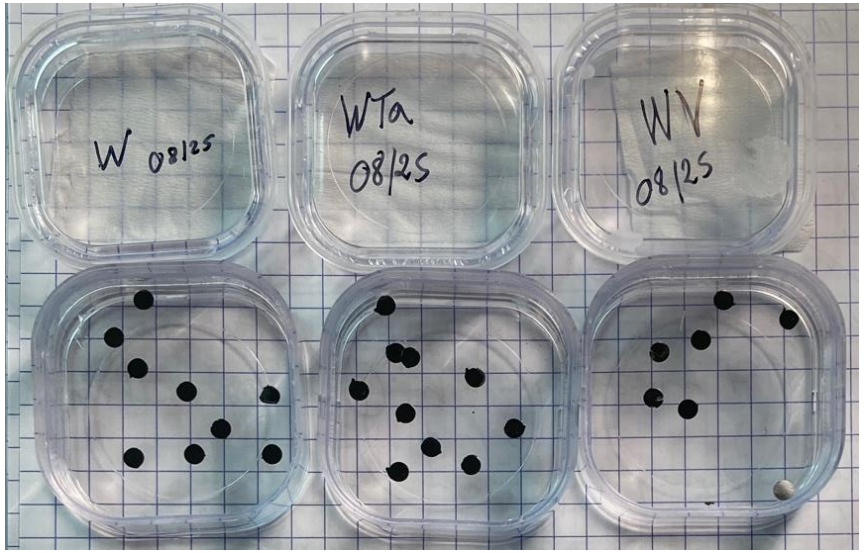
subcontractor in France for EDM cutting
Electrical Discharge Machining

squares → Materials sent to CNRS-CEMHTI and UHEL for ex situ ion implantation and characterizations

3 mm diameter discs

half discs

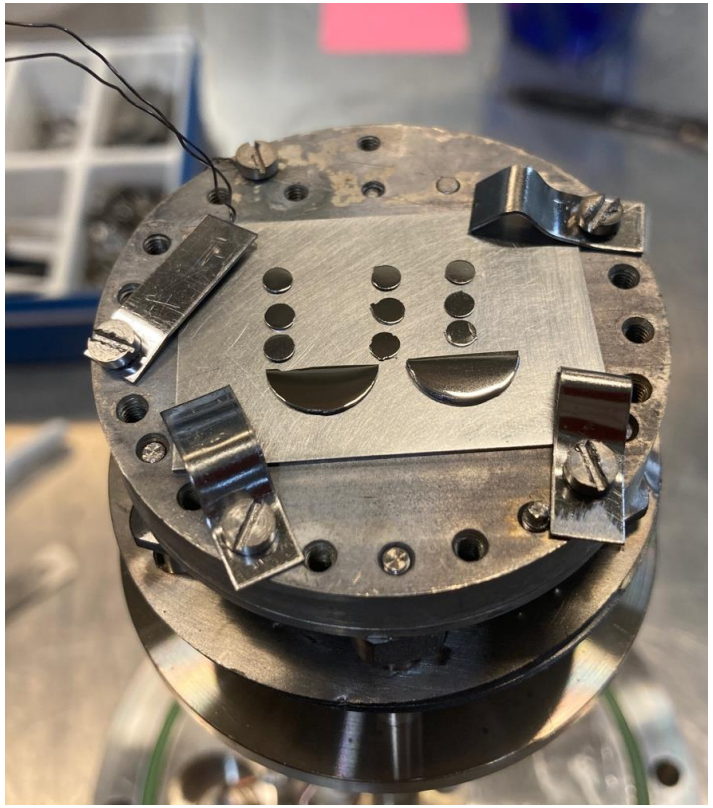
Quick SEM-EDX characterization of binary alloys
Surface mechanical polishing



Polishing performed on W, W-V, W-Ta and the ternary alloys WTaV, WTaMo

Mirror-polished samples (mid August / Sept.)

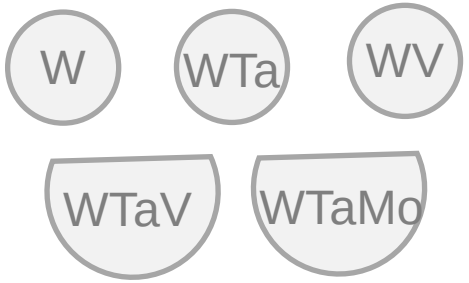
Samples

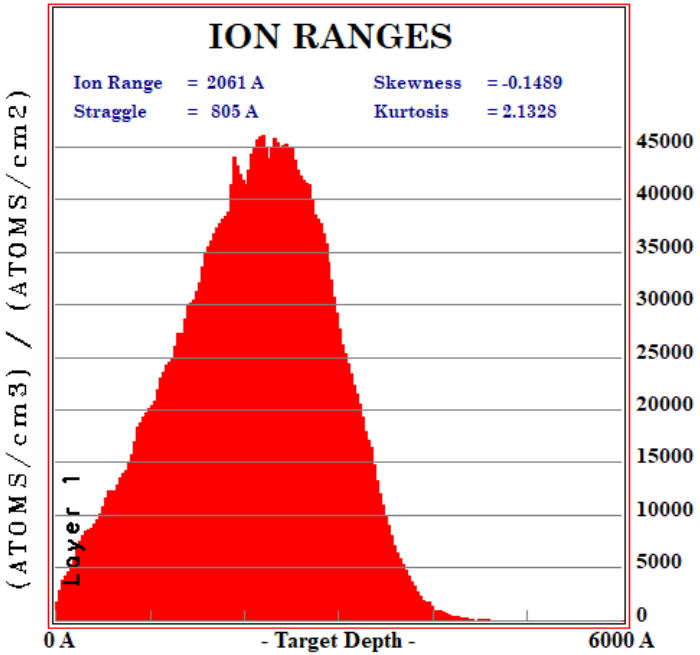


Samples attached on the implantation sample holder

Ion implantation performed in Sept. 2025 using 190 kV IRMA ion implanter

He energy: 100 keV
He fluence : $1x10^{17}$ cm^{-2}
Temperature of the samples: 500°C





From literature: should be enough He to see bubbles in W

- SRIM calculations using average Ed = 44 eV, see J. Byggmästar, F. Djurabekova, and K. Nordlund, Phys. Rev. Materials 8 (2024) 115406
- He bubbles observed in W by TEM starting $5x10^{15}$ cm^{-2} fluence (12 keV, 600°C), see F. Luo *et al*, Fusion Engineering and Design **125** (2017) 463, dx.doi.org/10.1016/j.fusengdes.2017.04.014

WP2(th) "Development of ML-KMC model of vacancy clustering in REAAs in the presence of He atoms"

Diffusion of helium in tungsten-based refractory alloys by molecular dynamics simulations

Potential He-refractory alloys

$$f(r_{ij}) = \begin{cases} \text{ZBL}, & r_{ij} \leq r_1, \\ e^{b_0 + b_1 r_{ij} + b_2 r_{ij}^2 + b_3 r_{ij}^3}, & r_1 \leq r_{ij} \leq r_2, \\ \sum_{n=1}^{12} a_n (r_n - r_{ij})^3 H(r_n - r_{ij}), & r_{ij} \geq r2, \end{cases} \quad (1)$$

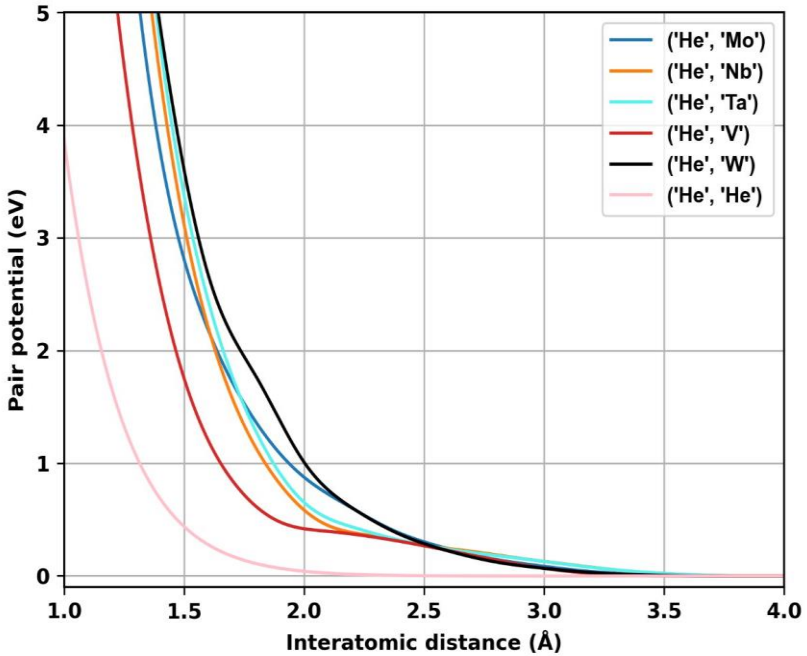


Table 2: Properties used for fitting and testing the interaction between refractory metals and He. Tetra. and Octa. means the formation energy of a He at the tetrahedral and octahedral positions. Reference values are from the corresponding DFT, ab-initio and MD calculations. All the units are eV.

W-He	Present value	Reference values	**Mo-He**	Present value	Reference values
Tetra.	6.18	6.15[9,24],6.16[4,13],6.22[25,16],6.23[26]	Tetra.	5.33	5.16[27],5.28[28],,5.31[18] 5.33[29]
Octa.	6.34	6.31[13],6.34[16],6.37[9,24],6.38[4],6.44[25],6.48[26]	Octa.	5.44	5.33[27],5.45[28],5.48[29],5.49[18]
E_{binding}	4.76	4.57[9,4],4.62[26],4.63[25],4.75[18],4.91[16]	E_{binding}	3.65	3.64[28],3.65[18],3.66[29],3.67[27]
E_{mig}	0.09	0.06[4,18],0.07[25,26],0.09[16]	E_{mig}	0.09	0.06[18]
Ta-He	Present value	Reference values	**Nb-He**	Present value	Reference values
Tetra.	3.46	3.16[27],3.34[30],3.41[31,24],3.45[16],3.46[18]	Tetra.	3.18	3.05[27],3.13[18]
Octa.	3.59	3.42[27],3.60[16],3.65[30],3.68[24],3.74[31],3.79[18]	Octa.	3.34	3.26[27],3.40[18]
E_{binding}	1.79	1.62[31],1.67[32],1.79[18],1.81[16]	E_{binding}	1.49	1.49[18],1.67[27]
E_{mig}	0.09	0.09[30,18],0.10[32],0.11[16]	E_{mig}	0.11	0.09[18]
V-He	Present value	Reference values			
Tetra.	3.20	2.94[27],3.09[24],3.17[18]			
Octa.	3.35	3.17[27],3.31[24],3.40[18]			
E_{binding}	1.16	0.91[27],1.16[18]			
E_{mig}	0.11	0.09[18]			

- We have developed the interatomic potential to describe the interaction of He atoms with all atoms in HEA composition. The interactions are purely repulsive, the HEA is described by previously developed tabGAP potential
  - [J. Byggmästar, K. Nordlund, and F. Djurabekova, Simple machine-learned interatomic potentials for complex alloys, Phys, Rev. Materials 6 (8),2022.]
- Tabel 2 illustrates the comparison of formation, migration and binding energies for He atoms in monoelemental metals.

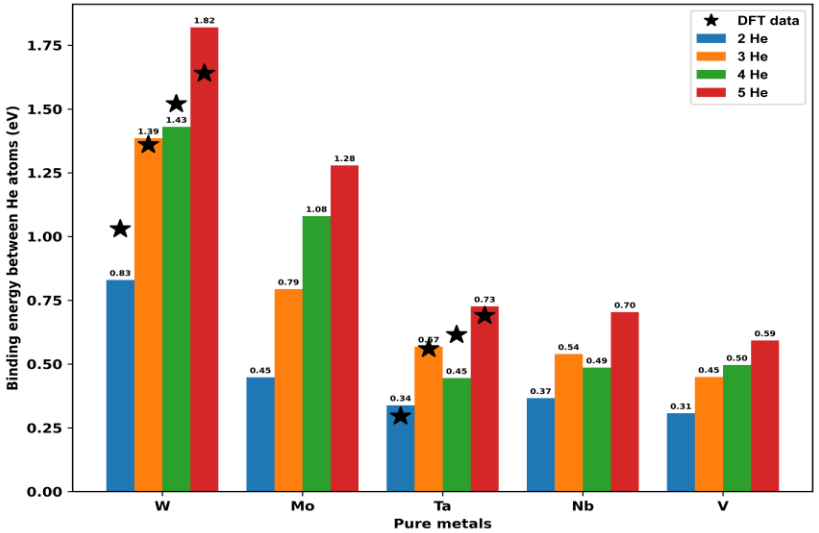
Binding energy

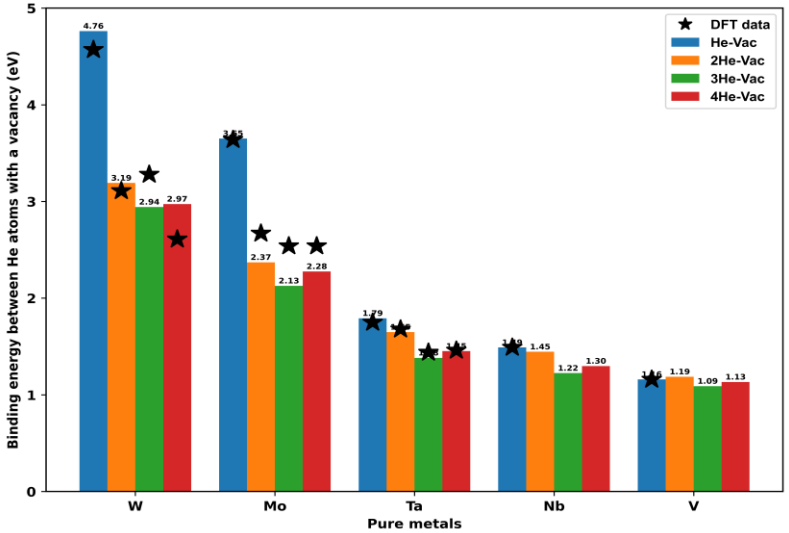
$$E_{\text{binding}}(D_1, D_2) = E(D_1) + E(D_2) - E(D_1 + D_2) - E_{ref}$$

References for the DFT values:
Ta: You et al, Jour. of Nucl. Mat., 2018(499).
W: Becquart et al, Jour. of Nucl. Mat., 2009(385).

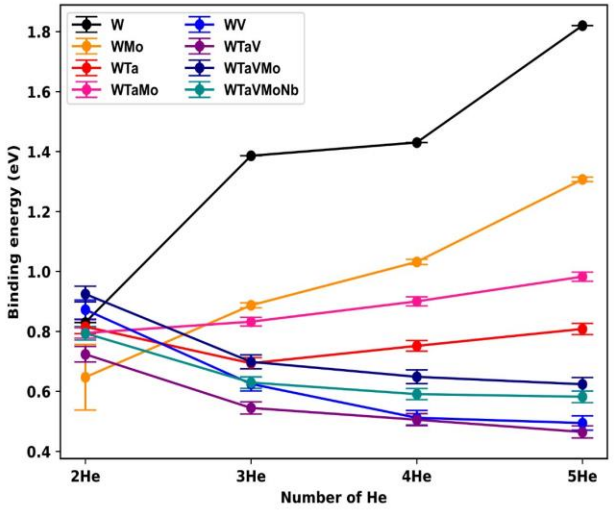
W: Becquart et al, Jour. of Nucl. Mat., 2009(385).
Mo: Runnevall et al, Jour. of Phys.: Cond. Mat., 2009(21).
Ta: Omori et al, Nucl. Mat. and Ener., 2018(16).
Nb & V: Jiang et al, Phys. Chem. Chem. Phys., 2018(25).

Pure metals

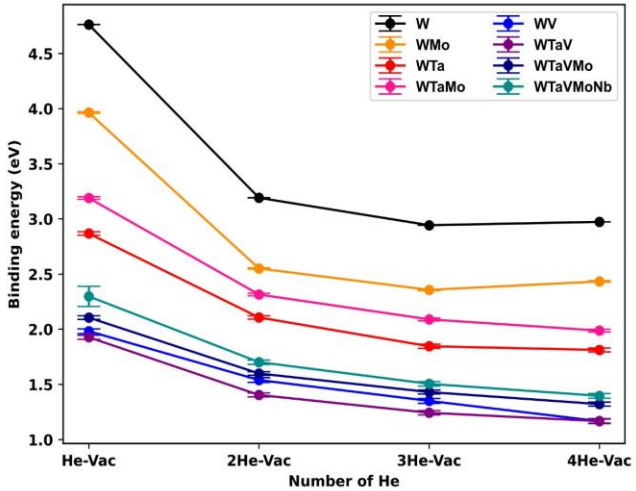




W and W-based alloys



He-He

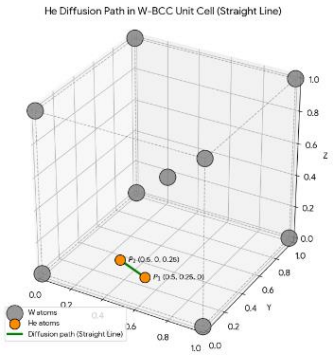


He-Vac

Average migration energy of a He atom

(calculated by NEB)

He position	WMo	WTa	WTaMo	WV	WTaV	WTaVMo	WTaVMoNb
(0.5,0.25,0)*a ⬇ (0.5,0,0.25)*a (a: lattice constant)	0.2576± 0.0034	0.3021± 0.0056	0.3234± 0.0040	0.6313± 0.0095	0.5300± 0.0068	0.5152± 0.0060	0.4584± 0.0049



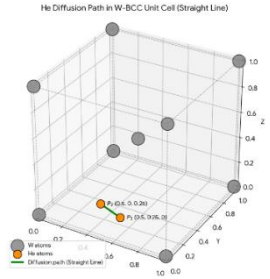
Migration path

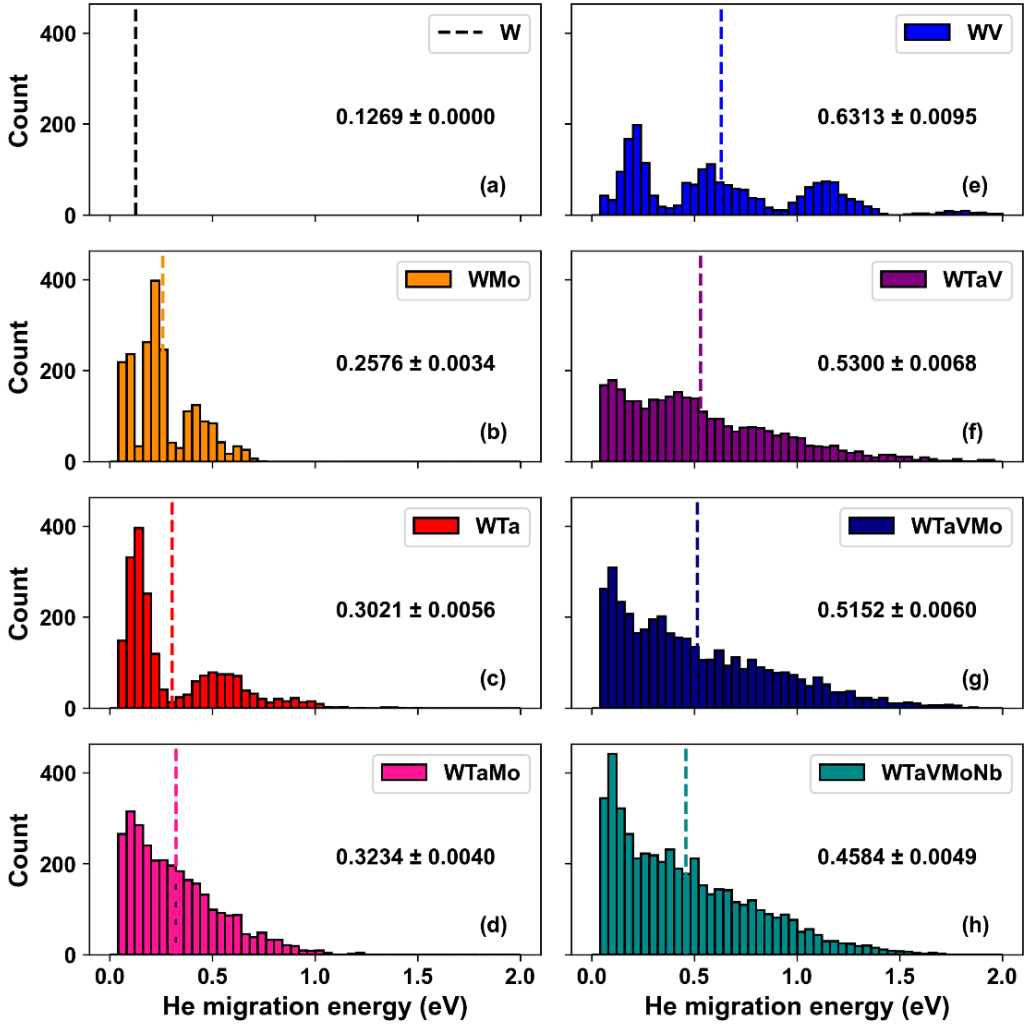
Pure metals

Migration energy	Mo	Nb	Ta	V	W
DFT data[1]	0.07	0.11	0.09	0.11	0.12
Our results	0.06	0.09	0.09	0.09	0.06

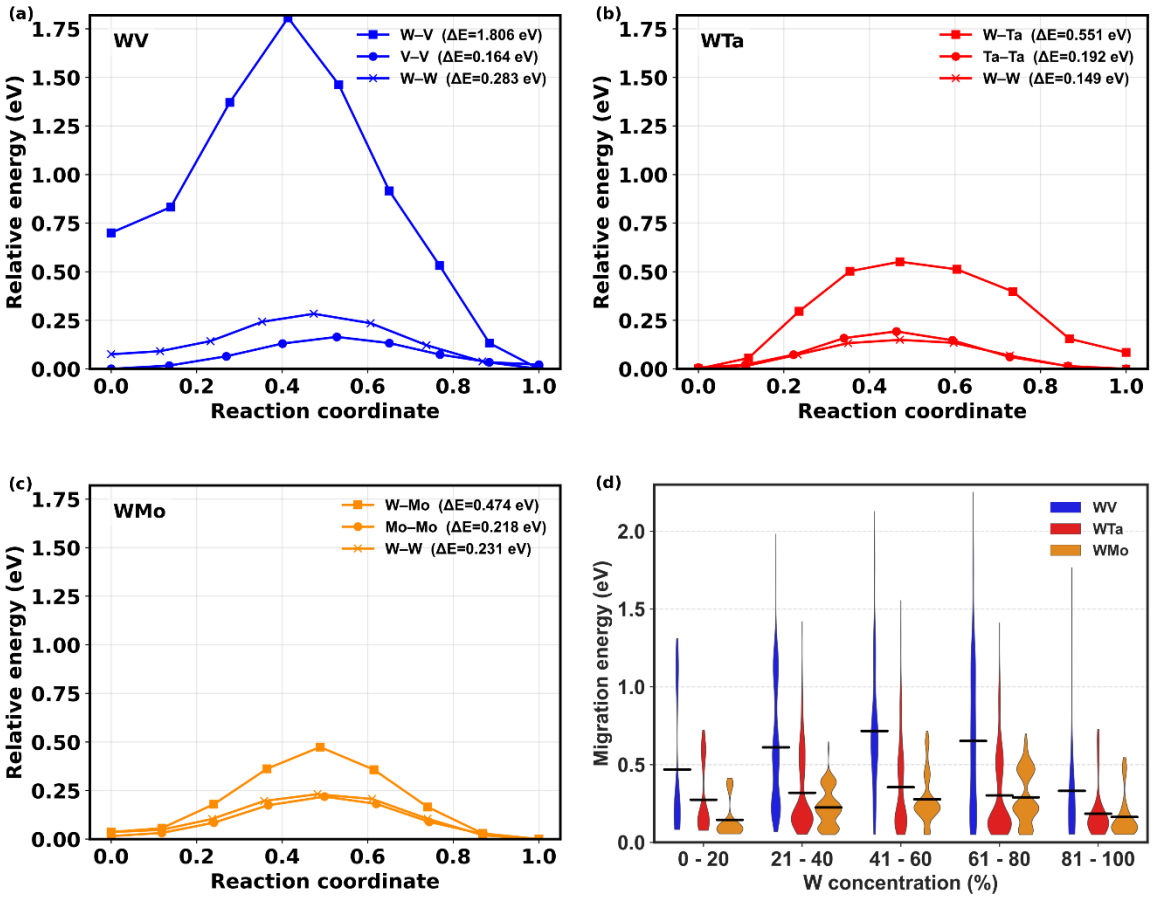
[1]: Jiang et al, Ab initio theory of noble gas atoms in bcc transition metals, Physical Chemistry Chemical Physics, 2018(25).

Migration energy of a He atom



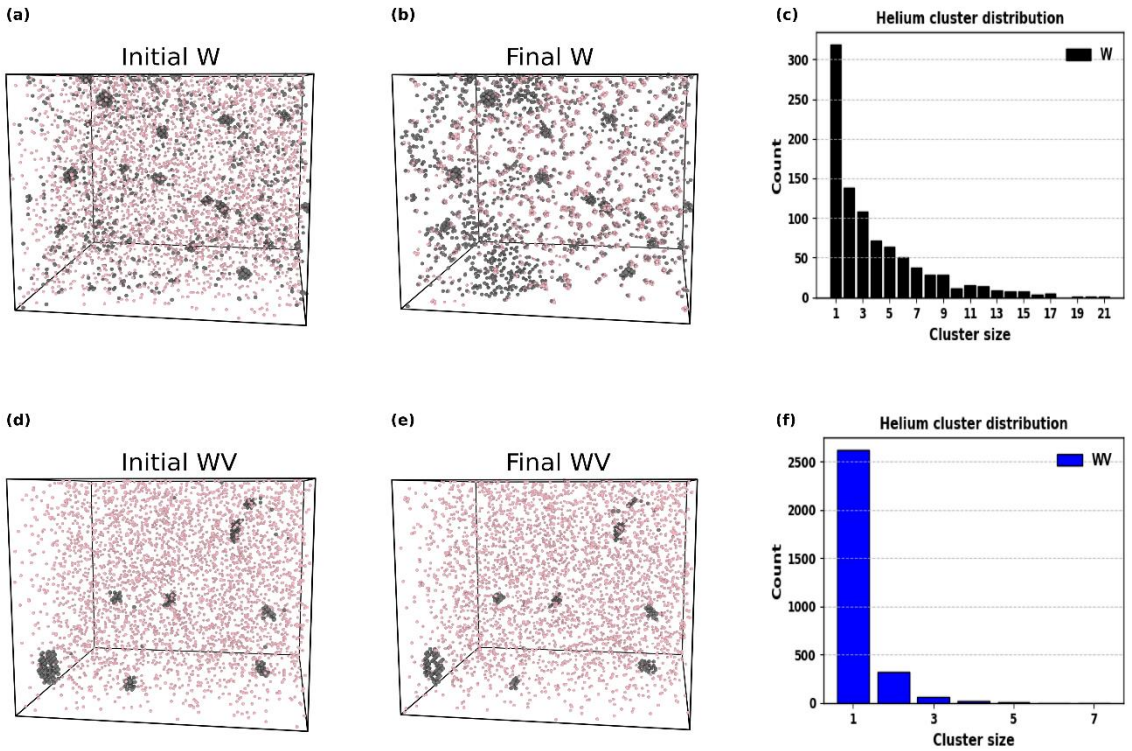


The distribution of migration energies

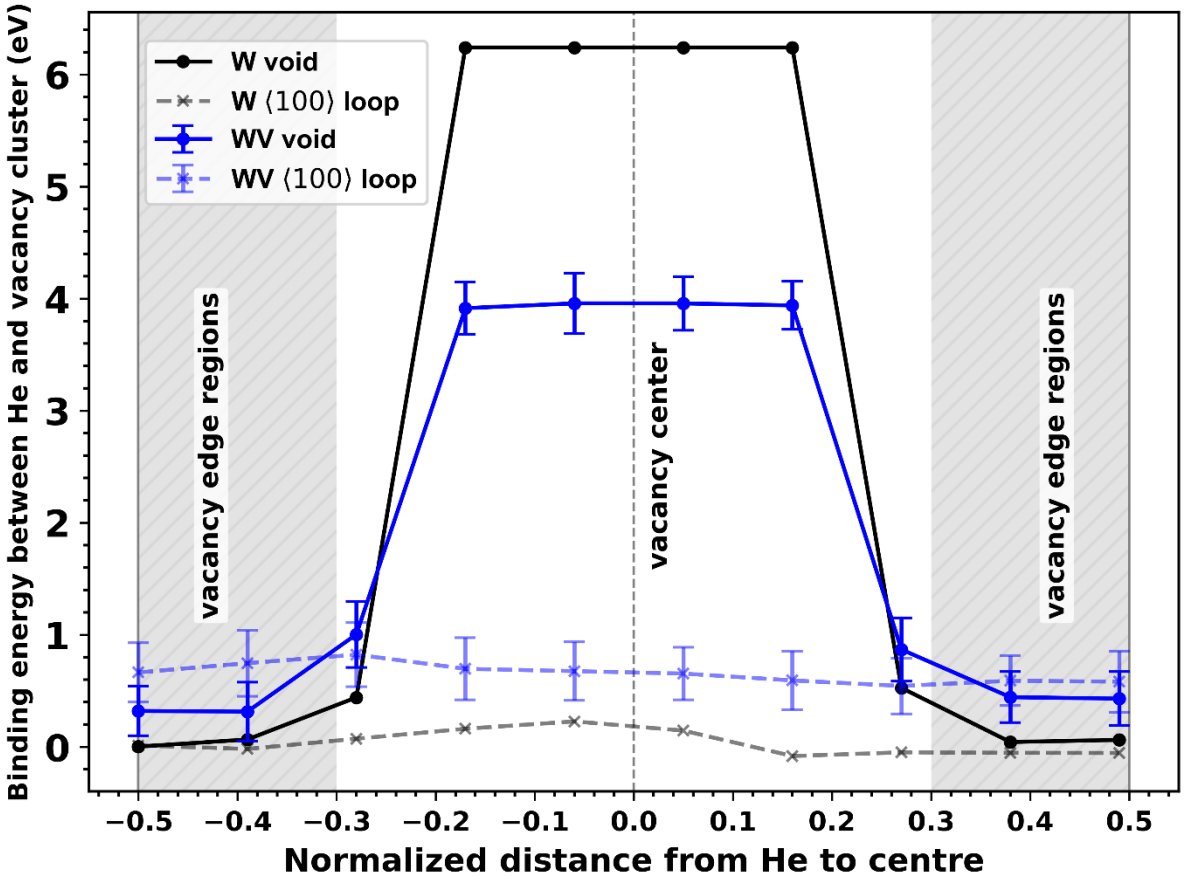


Effect of W concentration in the environment on the migration of He atoms

Cascade simulations with He implantation



Snapshots of He atoms in systems of 0.3 dpa radiation damage, showing vacancies (gray atoms) and He (pink atoms).



Binding energy of a single He atom with a void (100vacancies) and a ⟨1 0 0⟩ vacancy loop (101 vacancies) in W and WV .

WP3(exp) "He irradiation of REAA in three energy regimes (low, medium and high) at fusion reactor relevant temperatures. In-situ and ex-situ characterization of He bubble growth in REAA of different compositions"

Samples and methodology

- We have prepared two types of samples:
  1. Bulk samples (*Sample preparation : cutting, polishing)*
     - from VTT (Arc Melting binary alloys, WMo, WTa, WV, + pure W)
     - from IPFN (Institute for Plasma Research and Nuclear Fusion, Portugal)
  2. Thin layers (Magnetron sputter deposition, WV binary alloys, 50-100nm on MgO substrates)
     - University of Helsinki
- Two ways to insert ^{3}He into the samples:
  1. ^{3}He plasma exposure (low energy 300 eV, medium flux 10^{14} $cm^{-2}.s^{-1}$
  2. ^{3}He implantation (Pelletron accelerator) 0.5 MeV, low flux $7x10^{10}$ $cm^{-2}.s^{-1}$
- Characterization techniques:
  - Nuclear reaction Analysis (NRA): Detection of ***^{3}He*** with a deuteron beam (900 keV) using ^{2}H (^{3}He, ^{4}He)^{1}**H** reaction
  - Rutherford Backscattering (RBS)
  - Scanning Electron Microscopy Electron Dispersive spectroscopy (SEM-EDS)
  - Atomic Force Microscopy (AFM)

^{3}He plasma exposure in thin layers + bulk samples

^{3}He plasma exposure in thin layers in PIMAT:

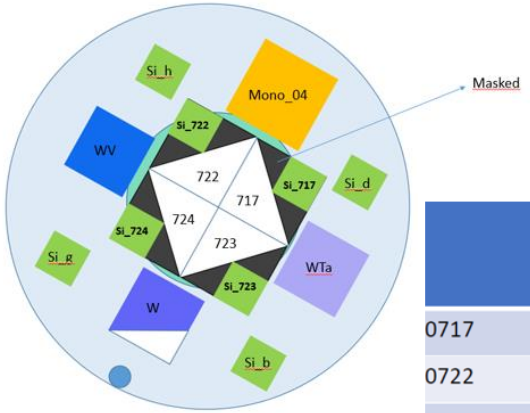
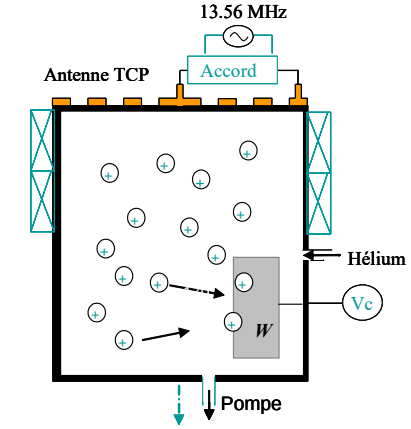


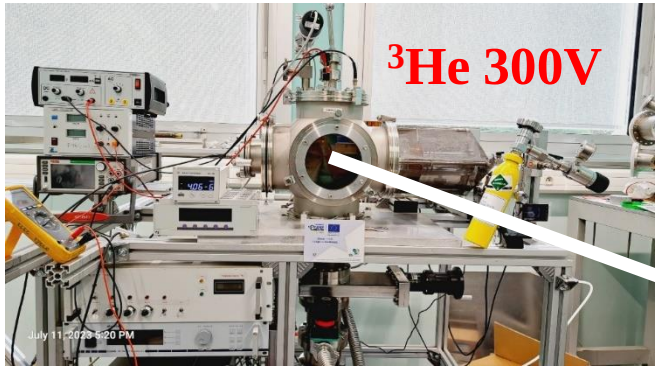
Table 1 : Exposed thin-layer samples

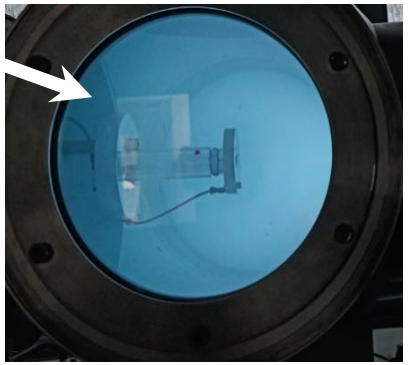
	Sample (MgO substrate)	Temperature (C)	Thickness estimate(nm)	Surface Oxygen estimate(%) Measured at 09/05/2025
0717	W	300	150-200	~ 4%
0722	W+C	300	100-150	0
0723	WV+C	300	50-100	~3%
0724	WV	300	50-100	~10%

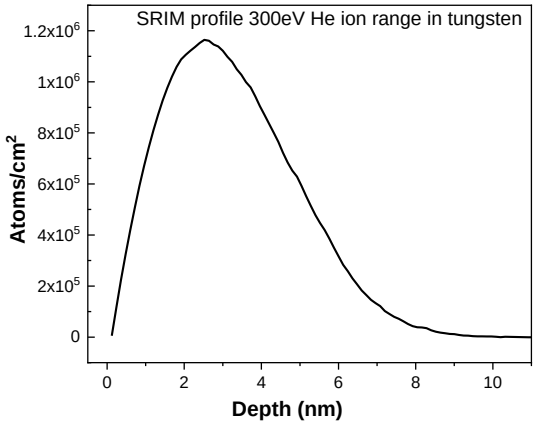


a. Schéma de principe du réacteur plasma

[1]







Flux 1,5x10^{14} cm^{-2}s^{-1}

Fluence estimated at 8x10^{16} cm^{-2}

[1] PE Lhuillier, PhD thesis (2010) Université d'Orléans

He release in DIADDHEM

- He release as a function of temperature () in W bulk alloys and thin layers exposed to ^{3}He in PIMAT:

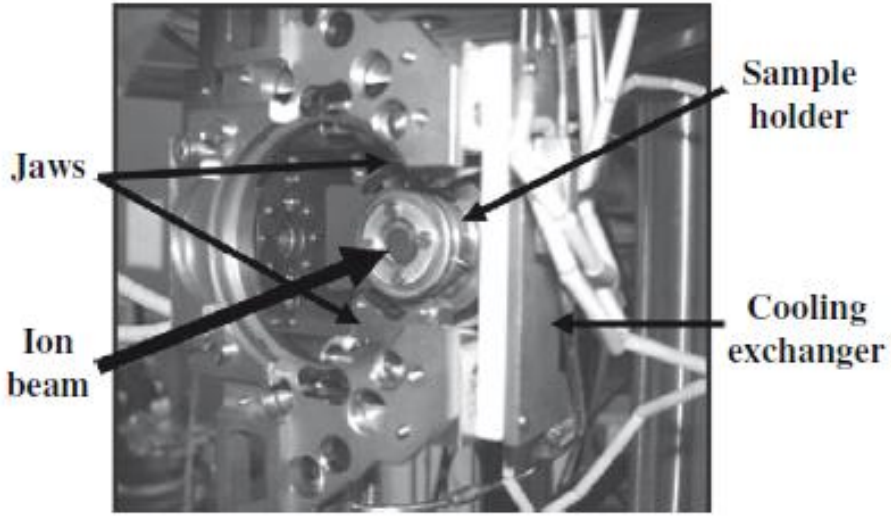
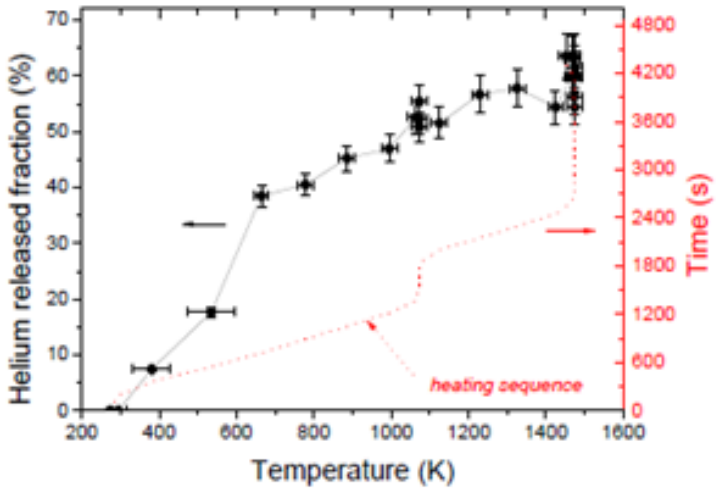


Fig. 1. Photography of the DIADDHEM core.

DIADDHEM - Device for Analyzing the Diffusion of Deuterium and Helium in Materials

Table 1 : Exposed thin-layer samples

	Sample (MgO substrate)	Temperature (C)	Thickness estimate(nm)	Surface Oxygen estimate(%) Measured at 09/05/2025	Holes	Grain sizes
0717	W	300	150-200	~ 4%	No	Same as 0718
0722	W+C	300	100-150	0	No	Same as 0718
0723	WV+C	300	50-100	~3%	No	Single crystal
0724	WV	300	50-100	~10%	No	Single crystal

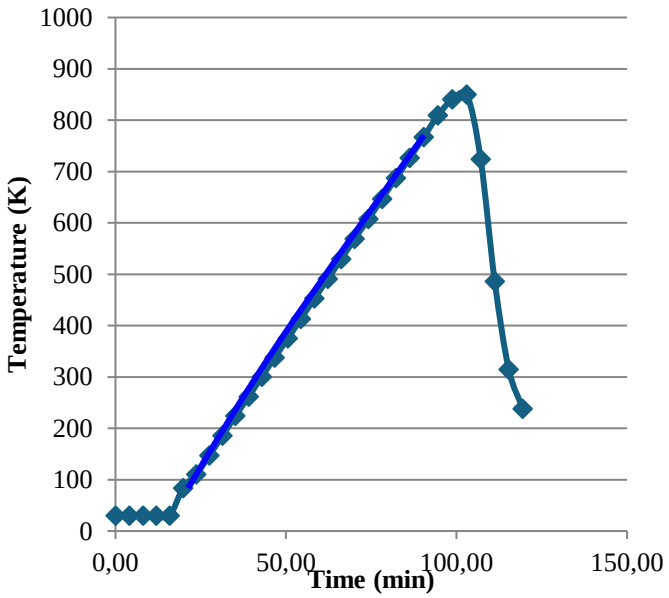


[1]

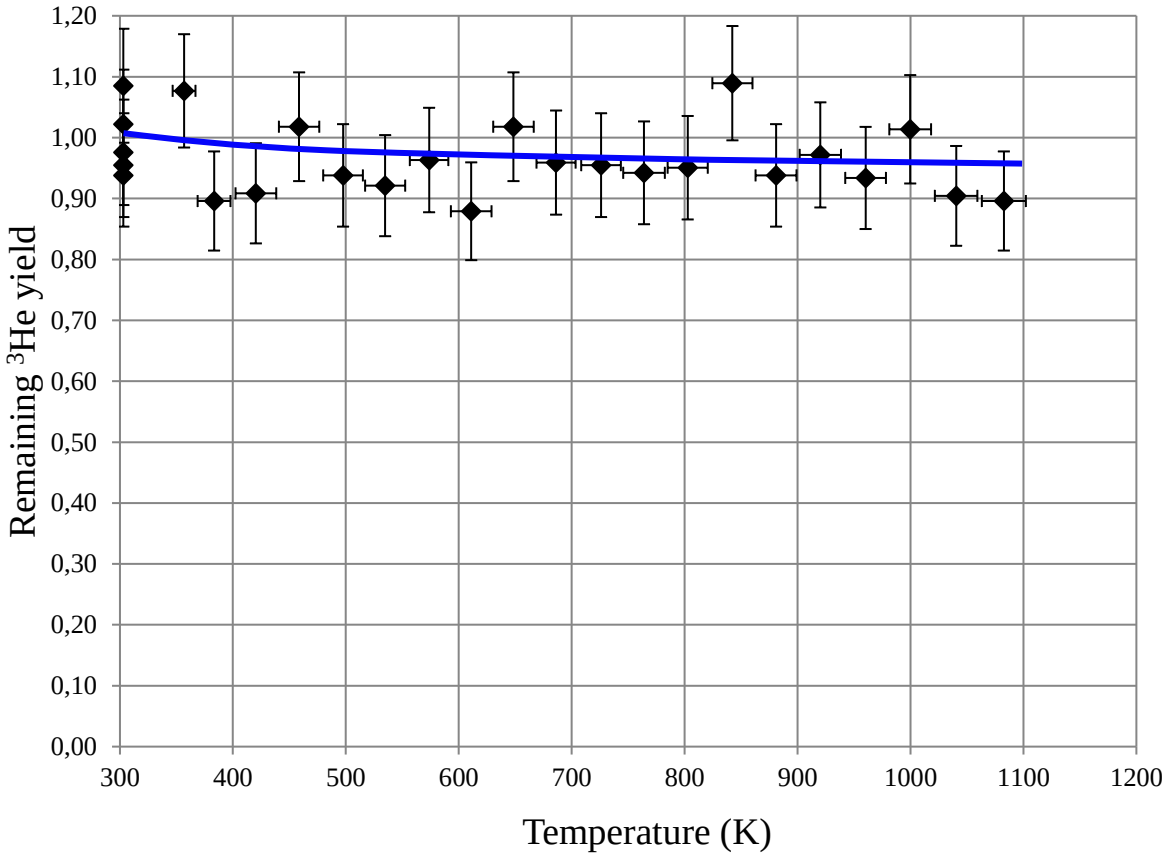
[1] PE Lhuillier, PhD thesis (2010) Université d'Orléans

In situ release in DIADDHEM

- W single crystal (W-M-M-04)



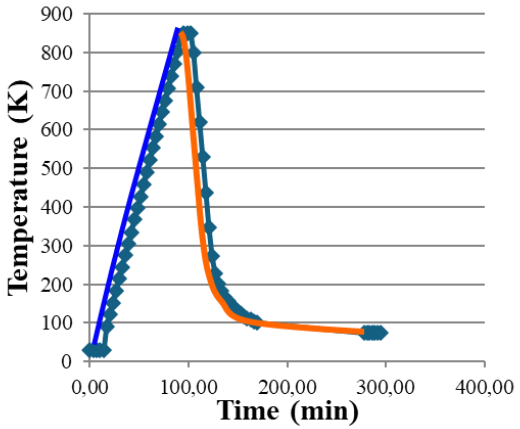
Temperature ramp : 10°/min

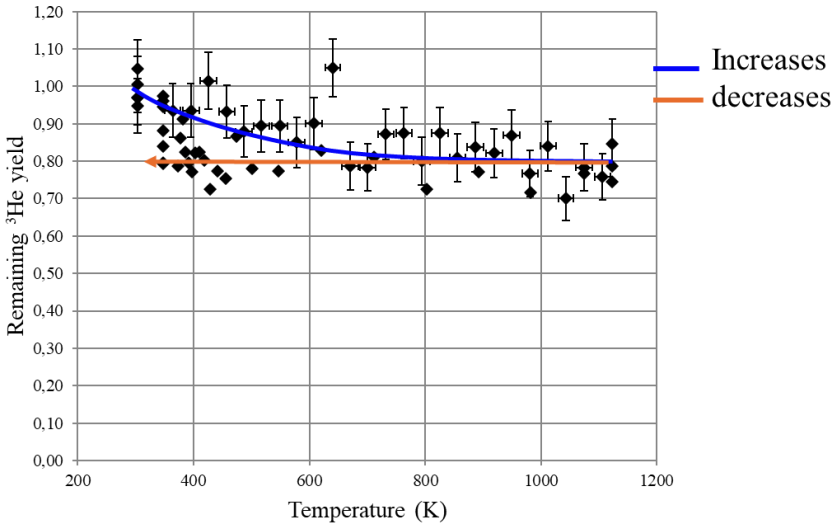


Release = ~ 0% at 1073K

In situ release in DIADDHEM

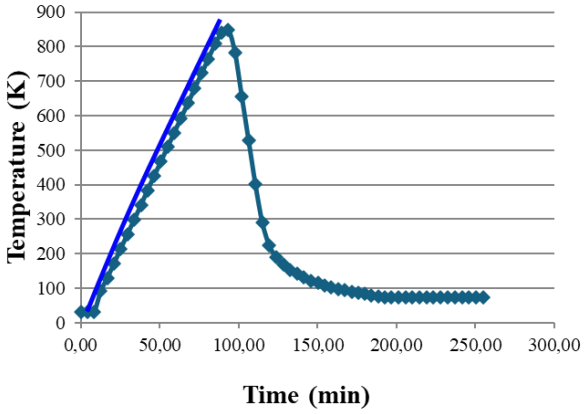
- WV/MgO (0724, $W_{50}V_{50}$)
  - Temperature ramp : 10°/min

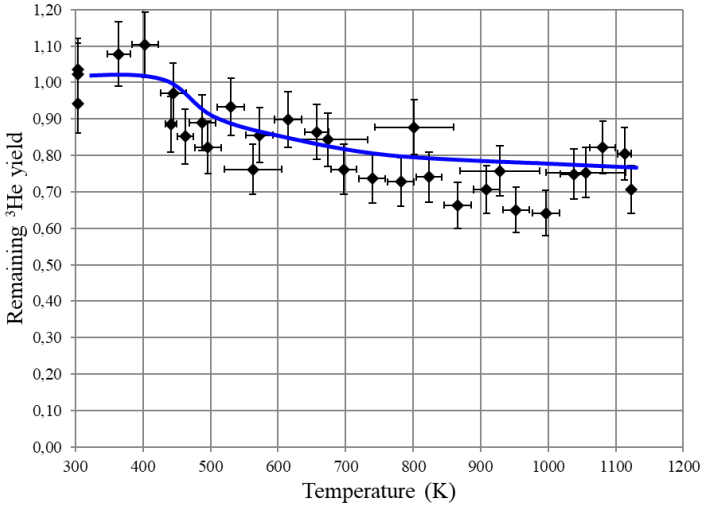




Release = 20% at 1073K

- WV/MgO (723, $W_{51}V_{49}$+C)
  - Temperature ramp : 10°/min



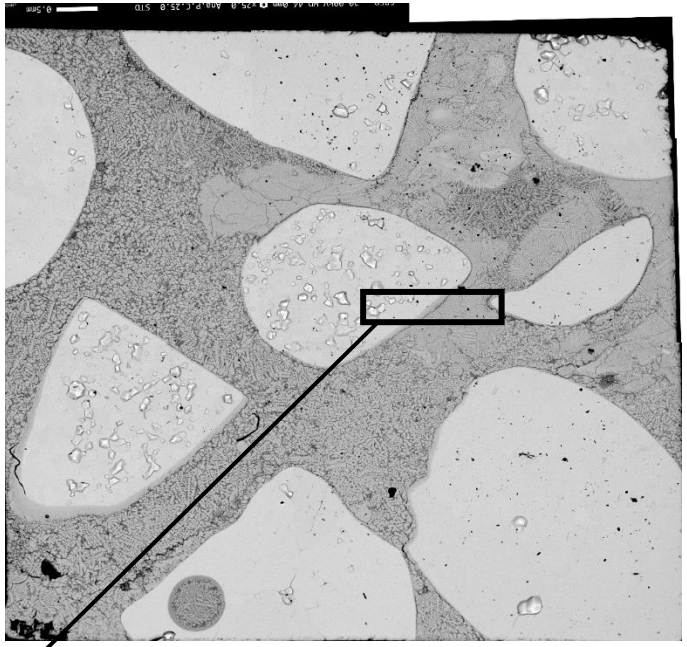


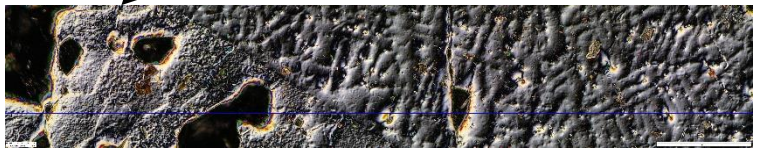
Release = 25% at 1073K

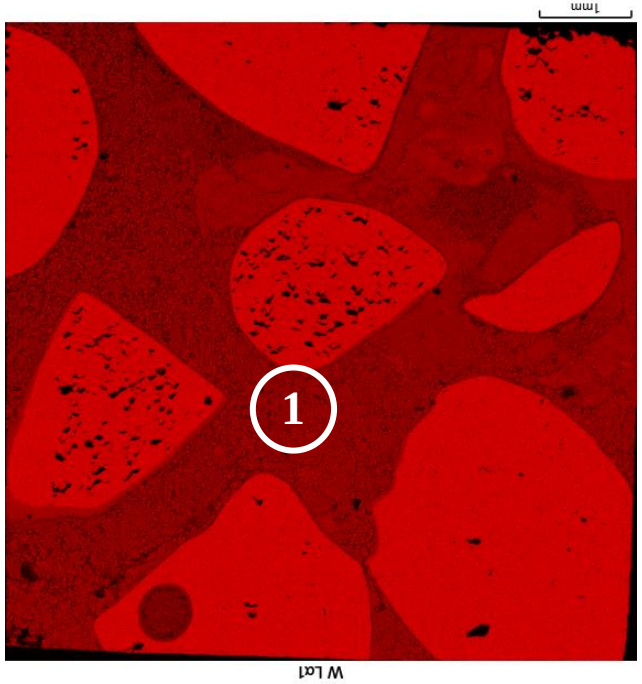
SEM-EDS

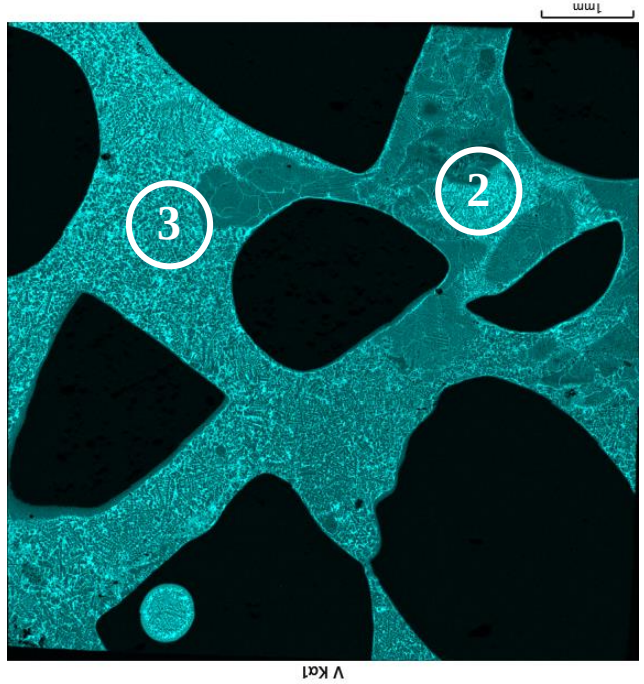
ZH-WV-VTT-C1B

VTT : Evaporation of V during arc melting





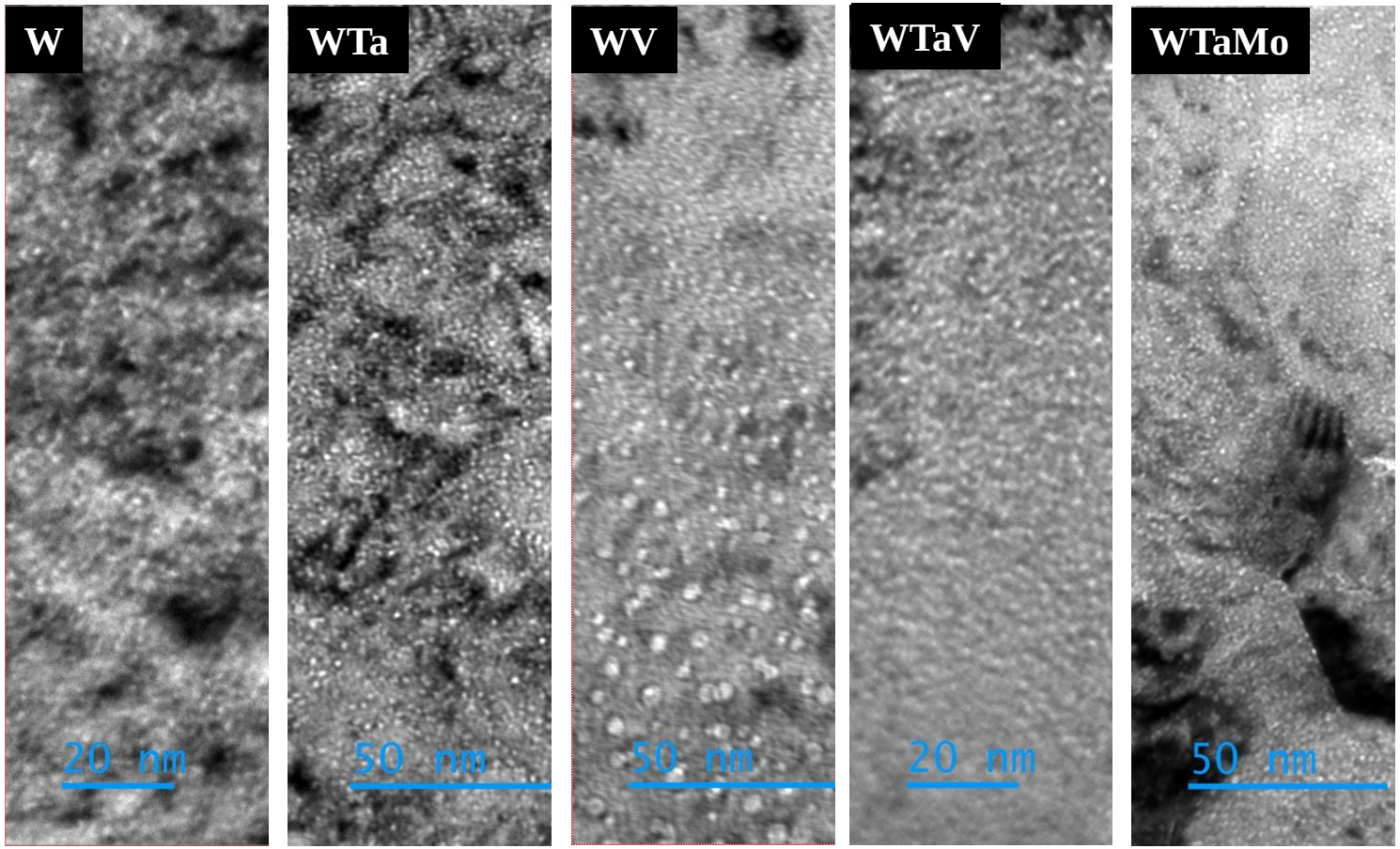


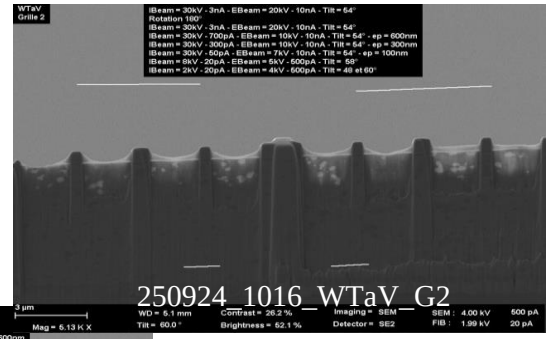


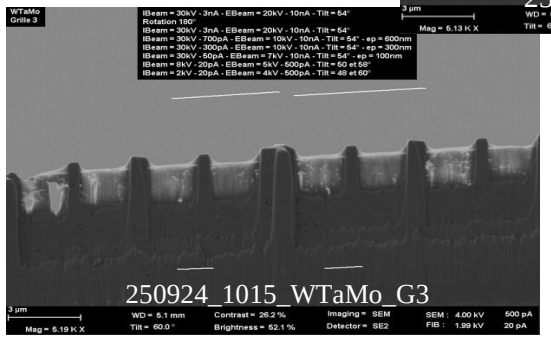
1. Zones with pure W and pores
2. Zones with heterogeneous concentration of V
3. Zones enriched in V

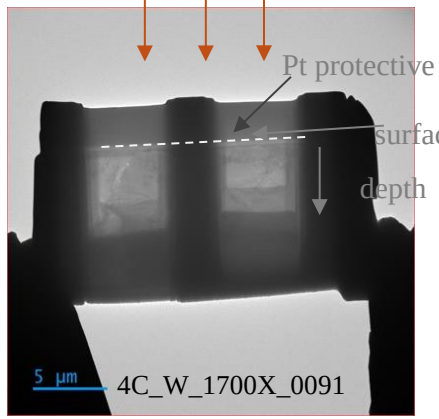
TEM results

Beware ! Not the same scale (to be updated ;-))









Through focus series of bright field images showing bubbles

See details next slides

Observation if any He bubbles are seen

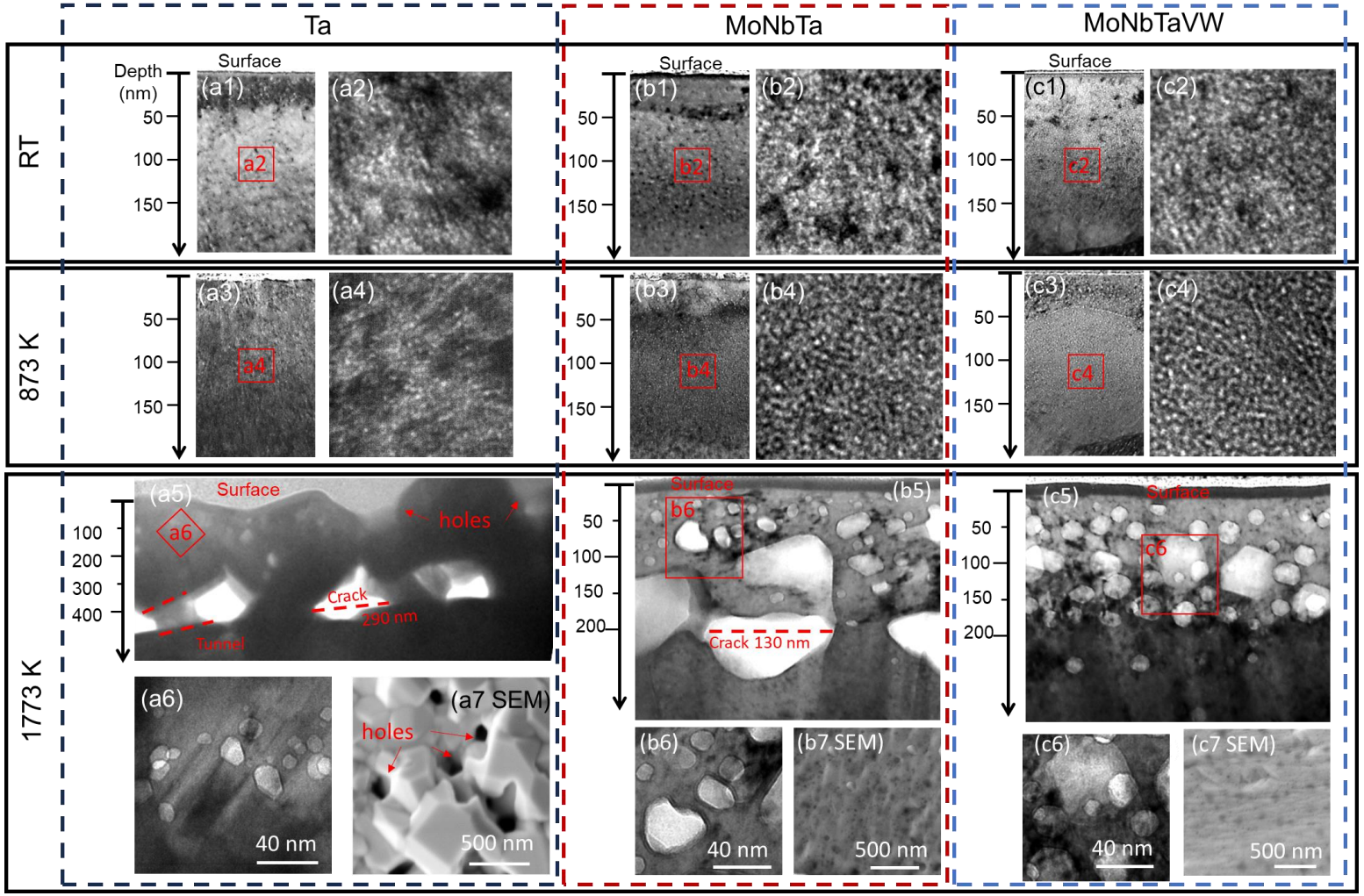
Transmission Electron Microscopy

ex situ (in October/November)

TEM thin foils preparation by FIB

(end Sept./Oct., IEMN and NCBJ)

Alternative BCC HEA with Ta-based composition: He distribution after annealing---microstructure

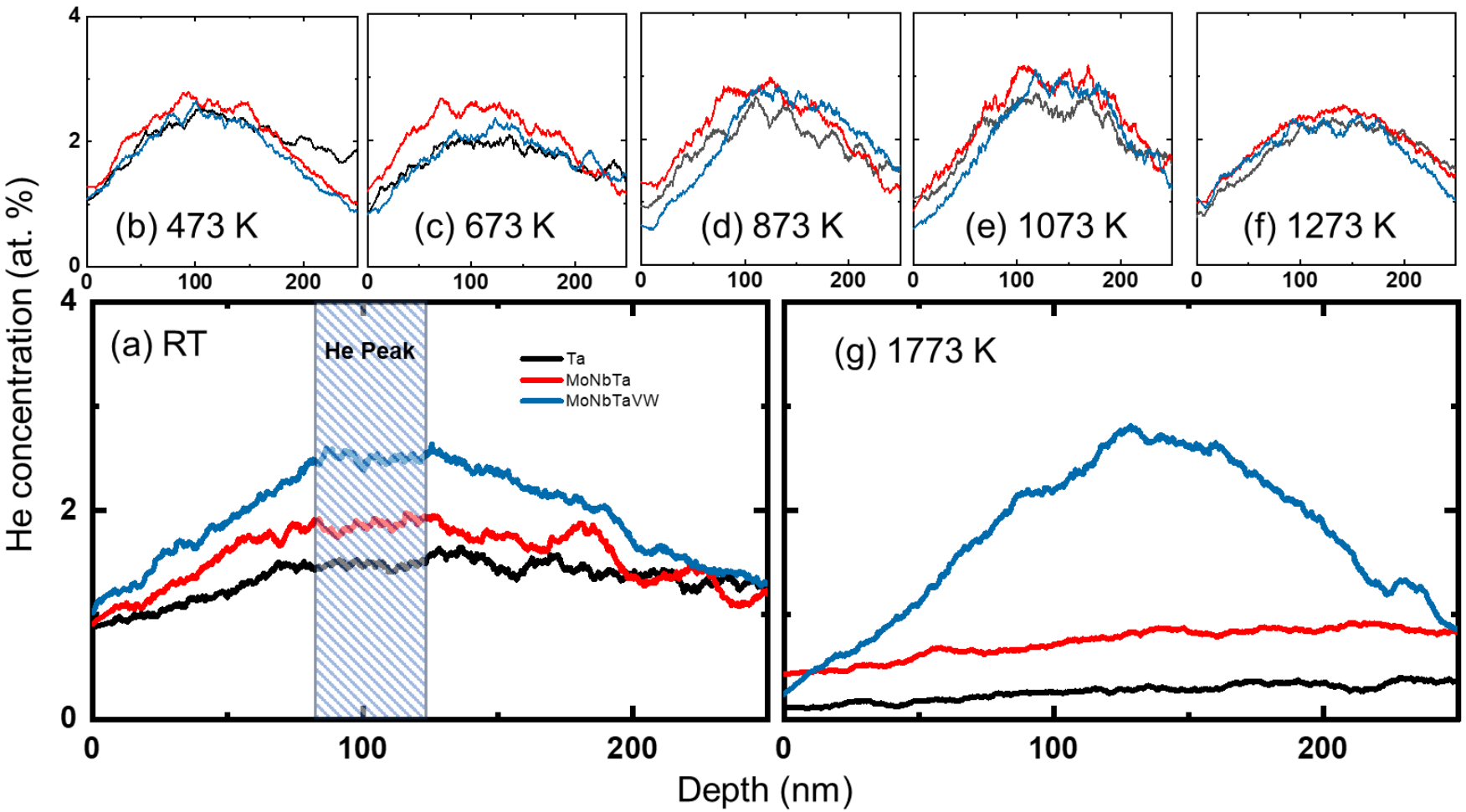


Samples: **Arc-melted Ta, MoNbTa, MoNbTaWV,** BCC, large grain size (around 100 um),

Irradiation: 5×10^{16} 25 keV He (ions/cm^2) , at room temperature

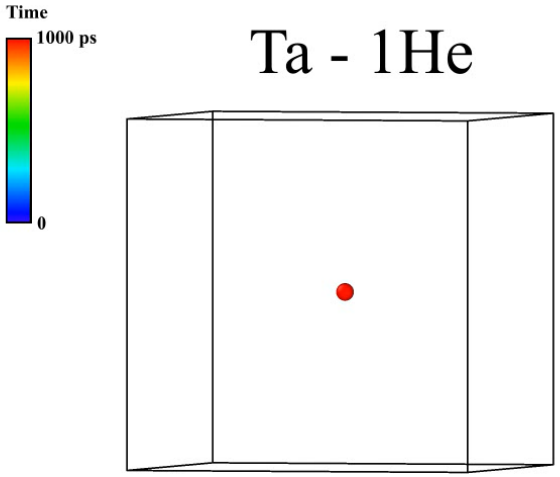
- He bubbles are more concentrated at the damage peak in BCC HEA.
- In pure metal Ta, long-range He migration leads to cracks and holes

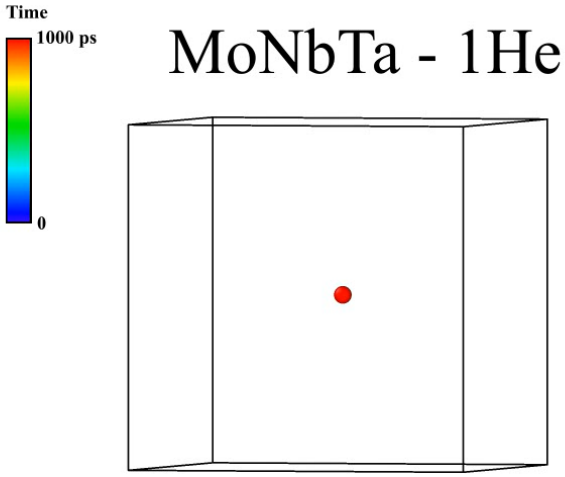
He depth profile by ERDA

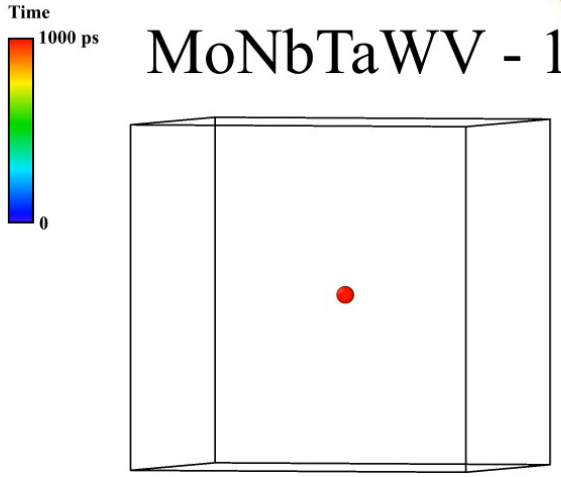


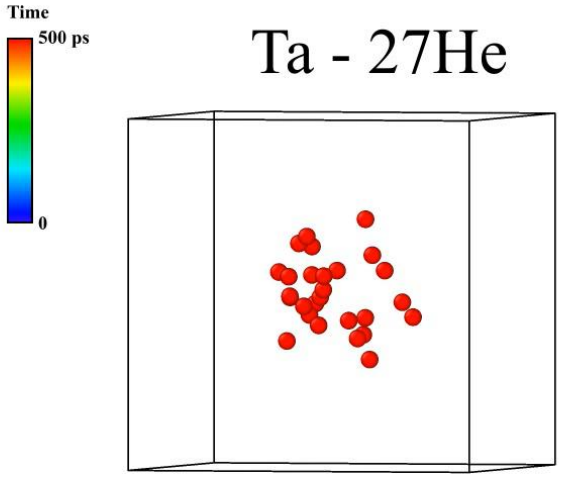
He profiles obtained by ERDA (=Elastic Recoil Detection Analysis) support TEM microstructure results, which suggest that long-range helium migration is limited in BCC HEA

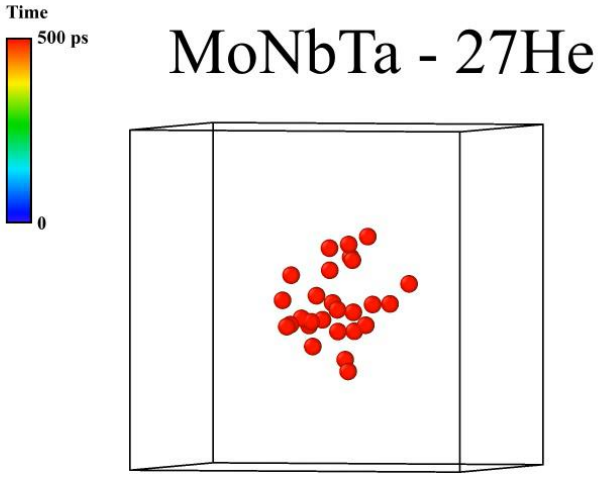
Molecular Dynamics simulation

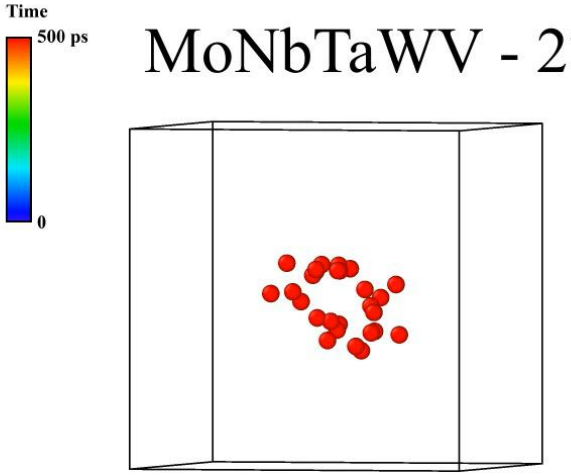




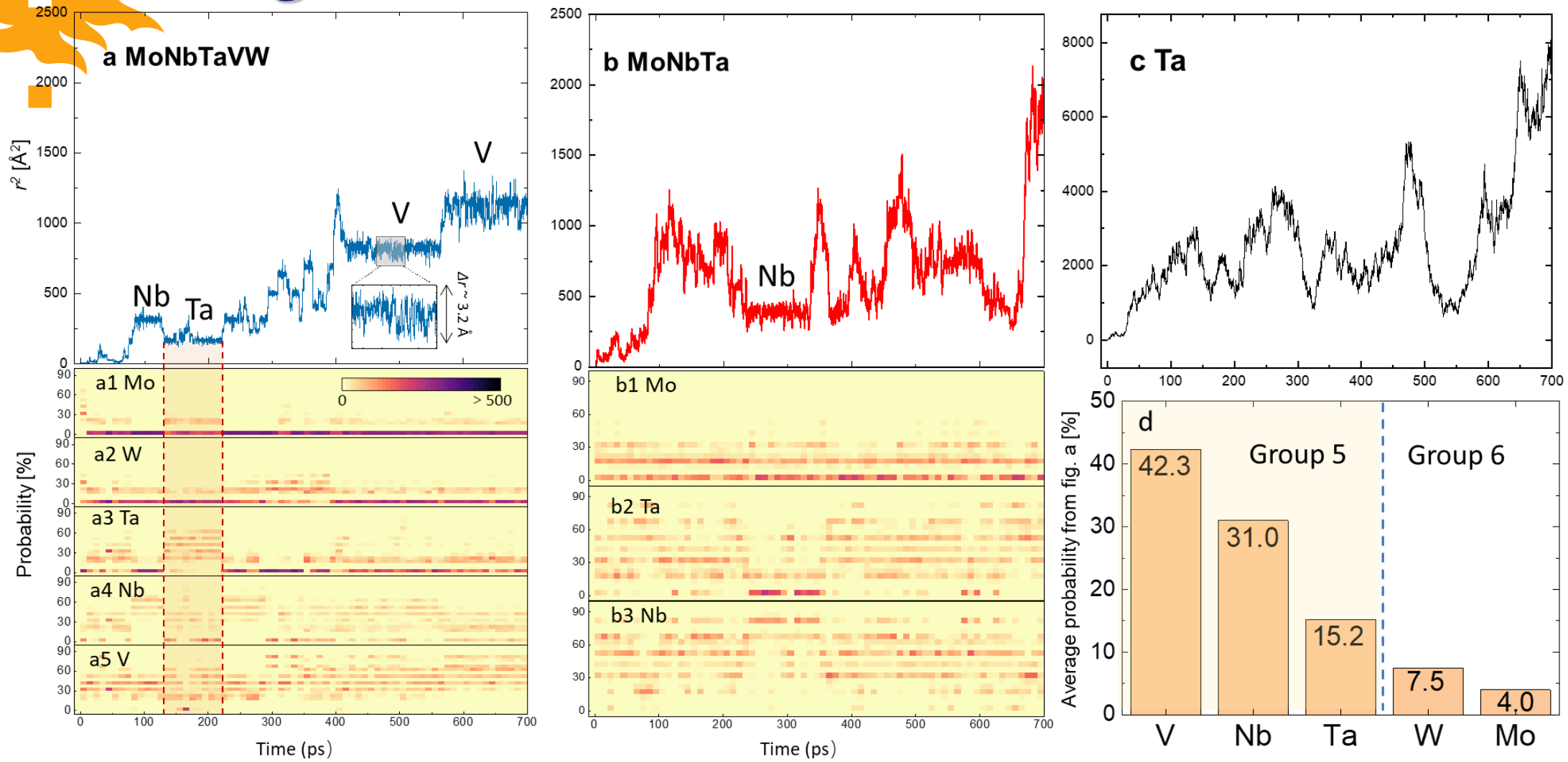








Single He atom diffusion



He tend to trap around Group 5 elements (V, Nb and Ta)

WP4(th) "Simulations of He bubble growth in REAA due to He irradiation with different irradiation energies by means of ML-KMC and ML-MD"

Suppression of He clustering in W across temperature via dilute V alloying

AKMC simulation of He-vacancy complex mobility in W and WV

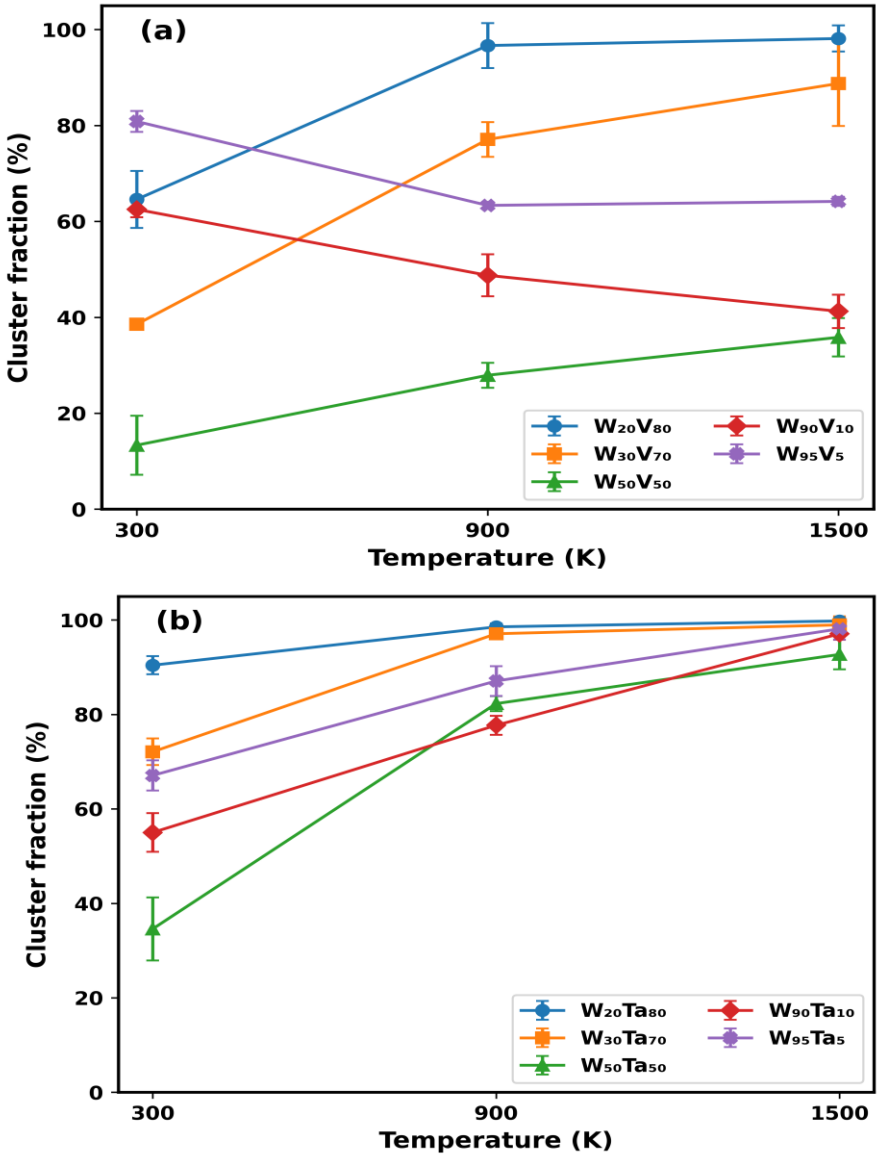
He cluster fraction in WVx and WTax

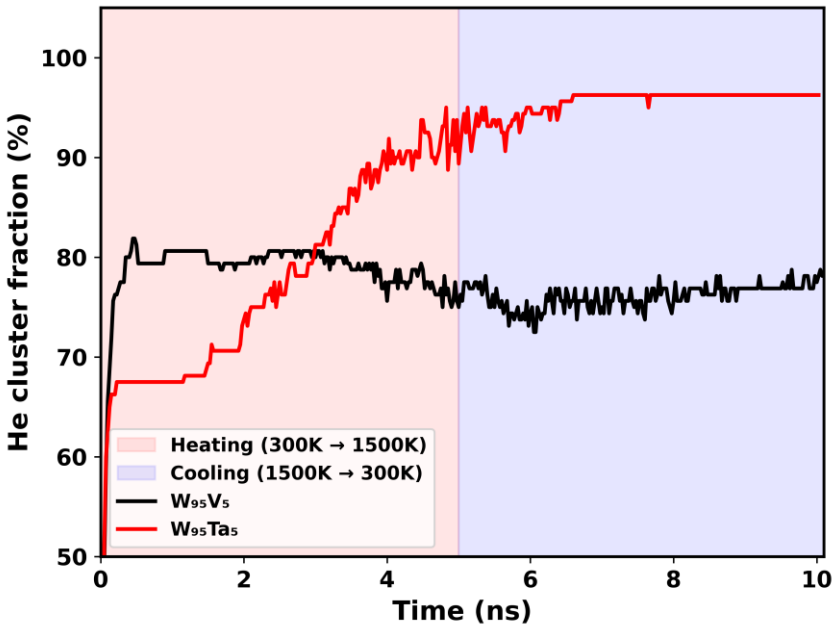
He cluster fraction = 1 – Number of single He atom / Total He number

Box size: $20 \times 20 \times 20$ unit cells = 16000 atoms + 1% He (160 atoms)

Minimize first

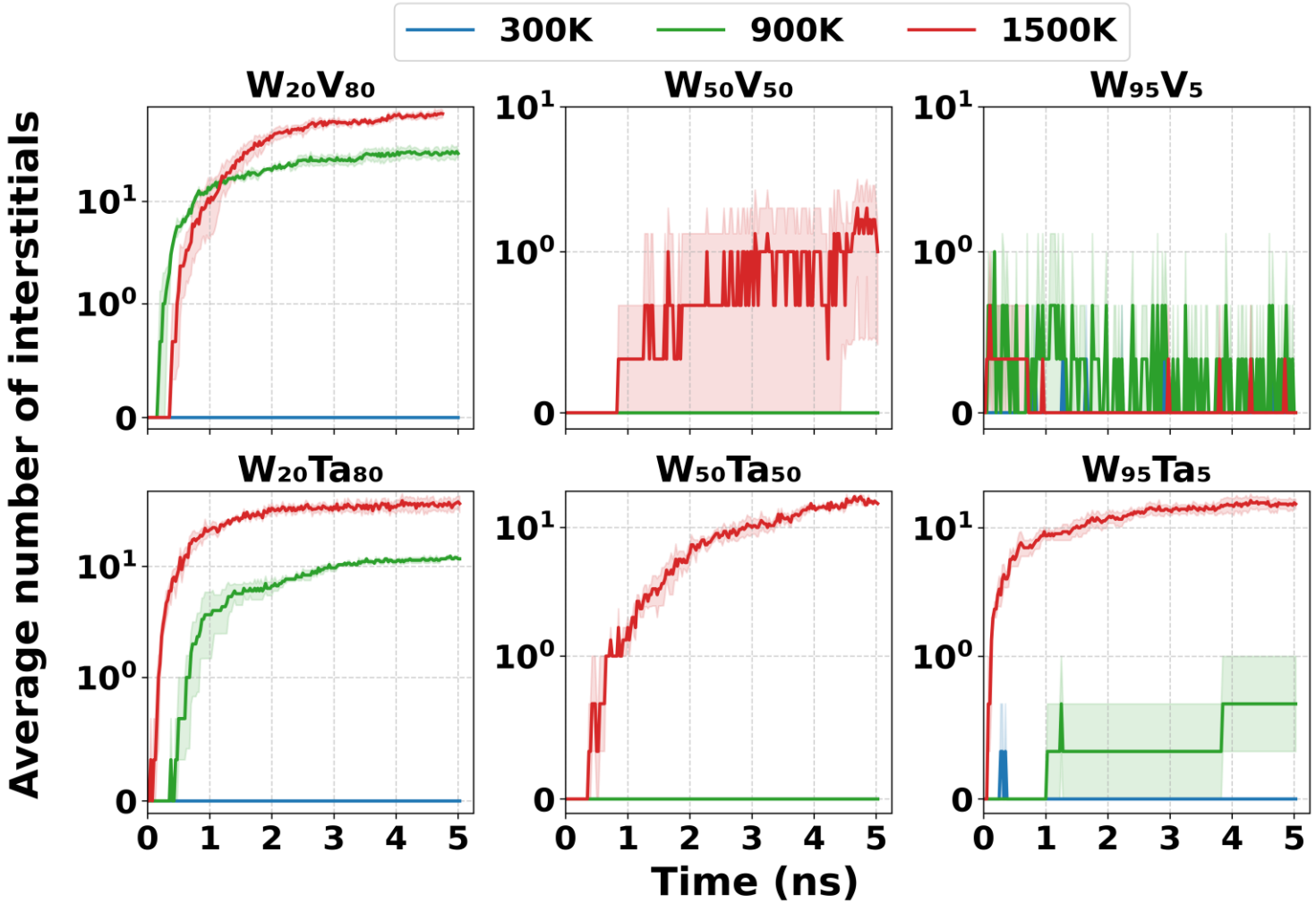
NPT relax 5 ns at 300 K, 900 K and 1500 K





Verification by a thermal cycle.

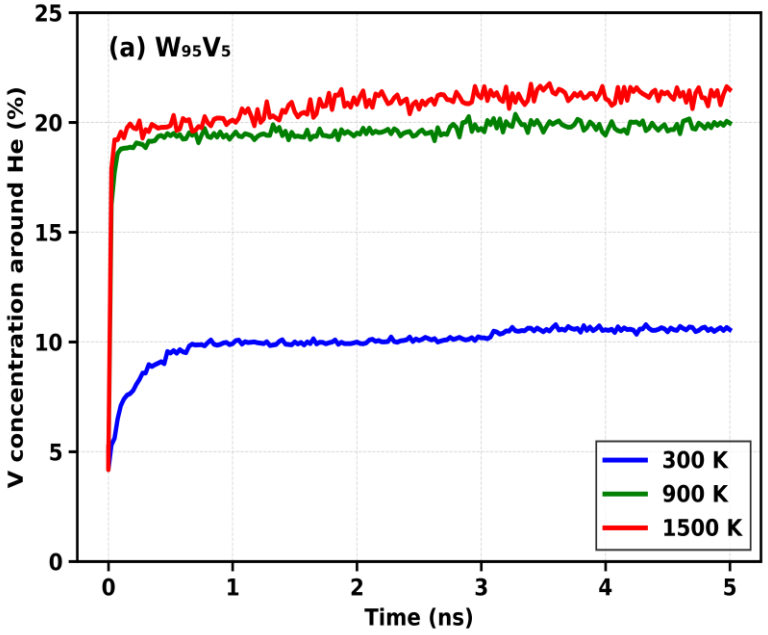
Self trapping

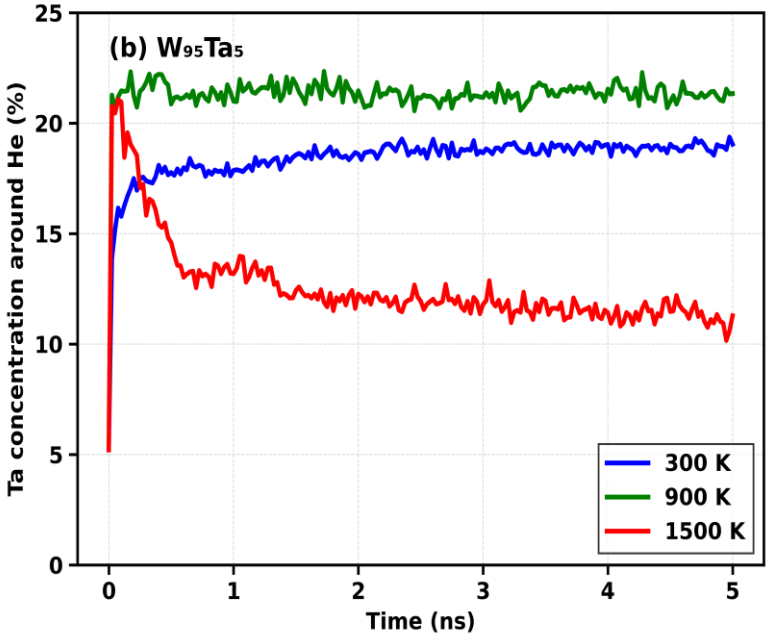


Evolution of the average number of interstitials in W–V and W–Ta alloys at 300 K, 900 K, and 1500 K without He atoms. (Statistics is given by the three independent runs)

Elements around He

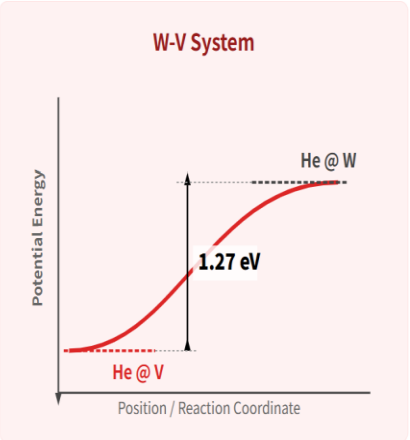
The energy differences were calculated using a 20 * 20 * 20 W supercell with a central solute atom. Values represent the potential energy change when a He atom moves from a bulk-like W environment to a tetrahedral site adjacent to the solute (V/Ta).

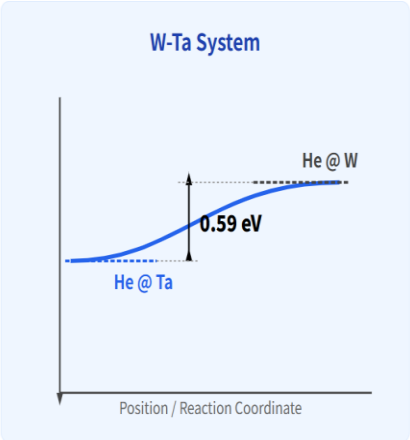




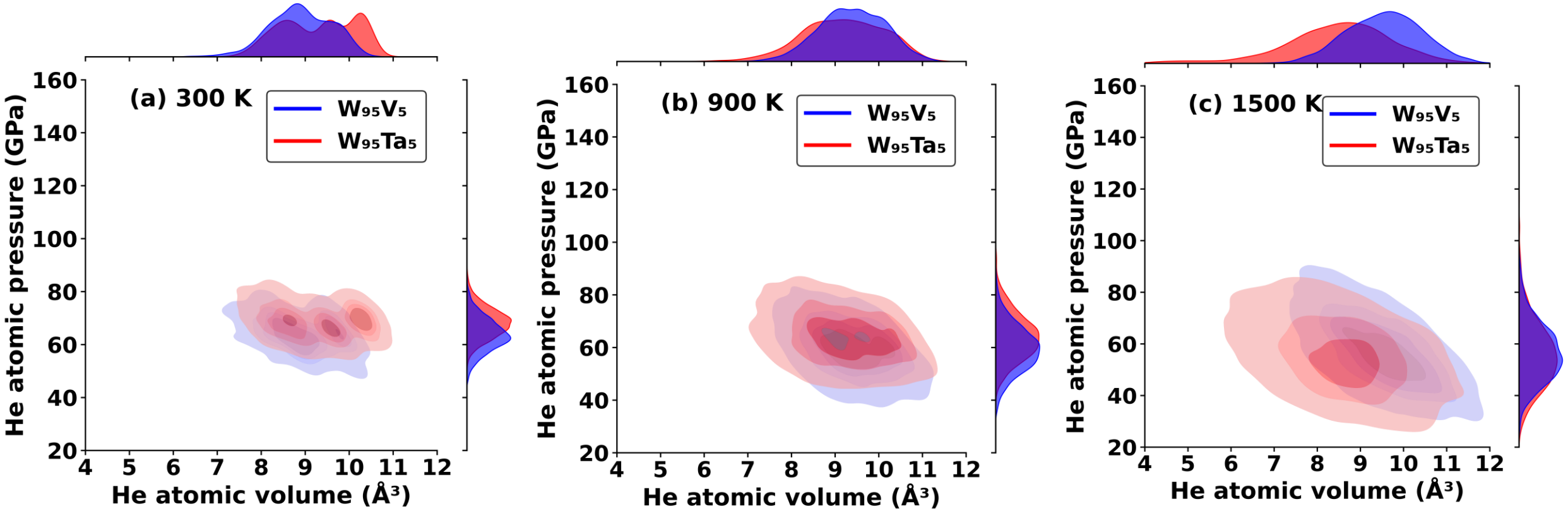
Evolution of the solute concentration around He atoms, in $W_{95}V_5$ and $W_{95}Ta_5$ alloys at 300 K, 900 K, and 1500 K (Statistics is given by 3 independent runs)

Energy Difference between He@Trap and He@W



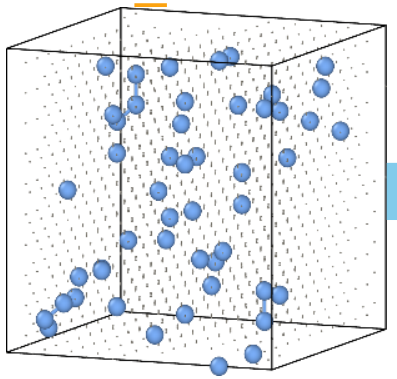


Pressure-volume



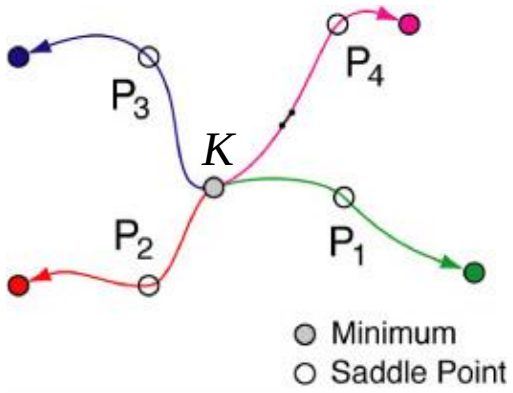
He atomic pressure-volume contour plots and corresponding distributions for $W_{95}V_5$ (blue)and $W_{95}Ta_5$ (red) at (a) 300 K, (b) 900 K, and (c) 1500 K.

MLP-AKMC Flowchart



Atomic Defect

Search for transition events



High-temperature MLP-MD simulation

$R_{k,1}$ $R_{k,2}$ $R_{k,3}$

$$r_{k,i} = Aexp(\frac{-E_{k,i}}{k_b T})$$

$$R_{k,i} = \frac{\sum_{j=1}^{i} r_{k,i}}{\sum_{j=1}^{N_k} r_{k,i}}$$

Update Rate Table

Generate a random number $\mu \in (0,1]$

Select the ith event if $R_{k,i-1} < \mu \leq R_{k,i}$

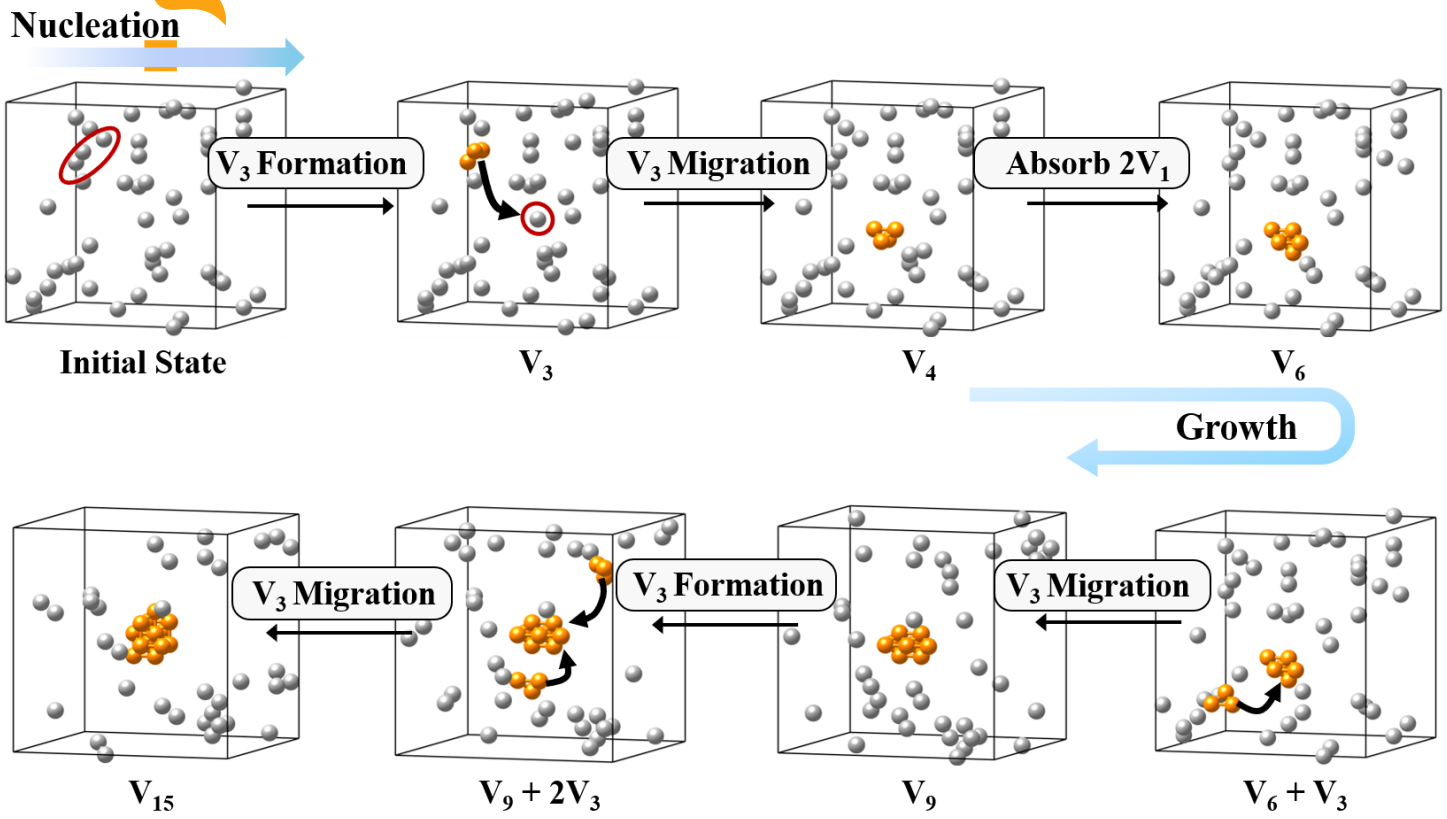
New state with time accumulated

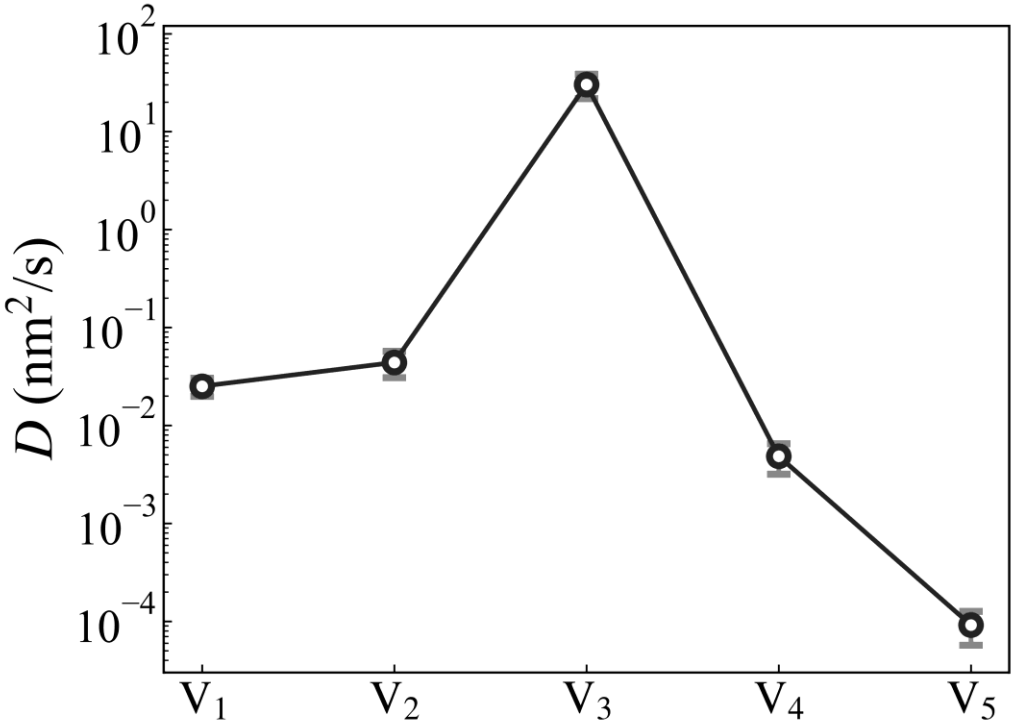
$$\Delta t = \left| \frac{\ln(\mu)}{\sum_{j=1}^{N_k} r_{k,i}} \right|$$

To accurately observe the evolution of vacancies on experimental time scales

Xu, L. & Henkelman, G. *J Chem Phys* **129**, 114104 (2008).

The importance of V_3 cluster



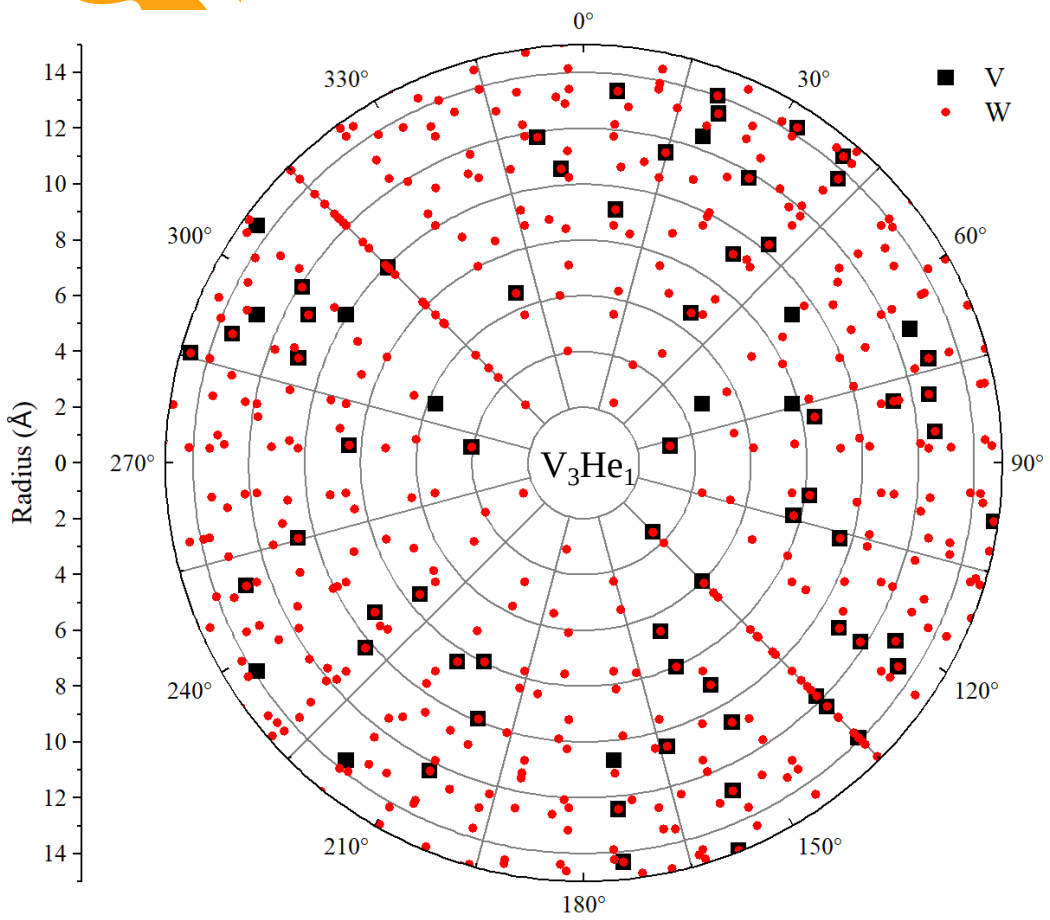


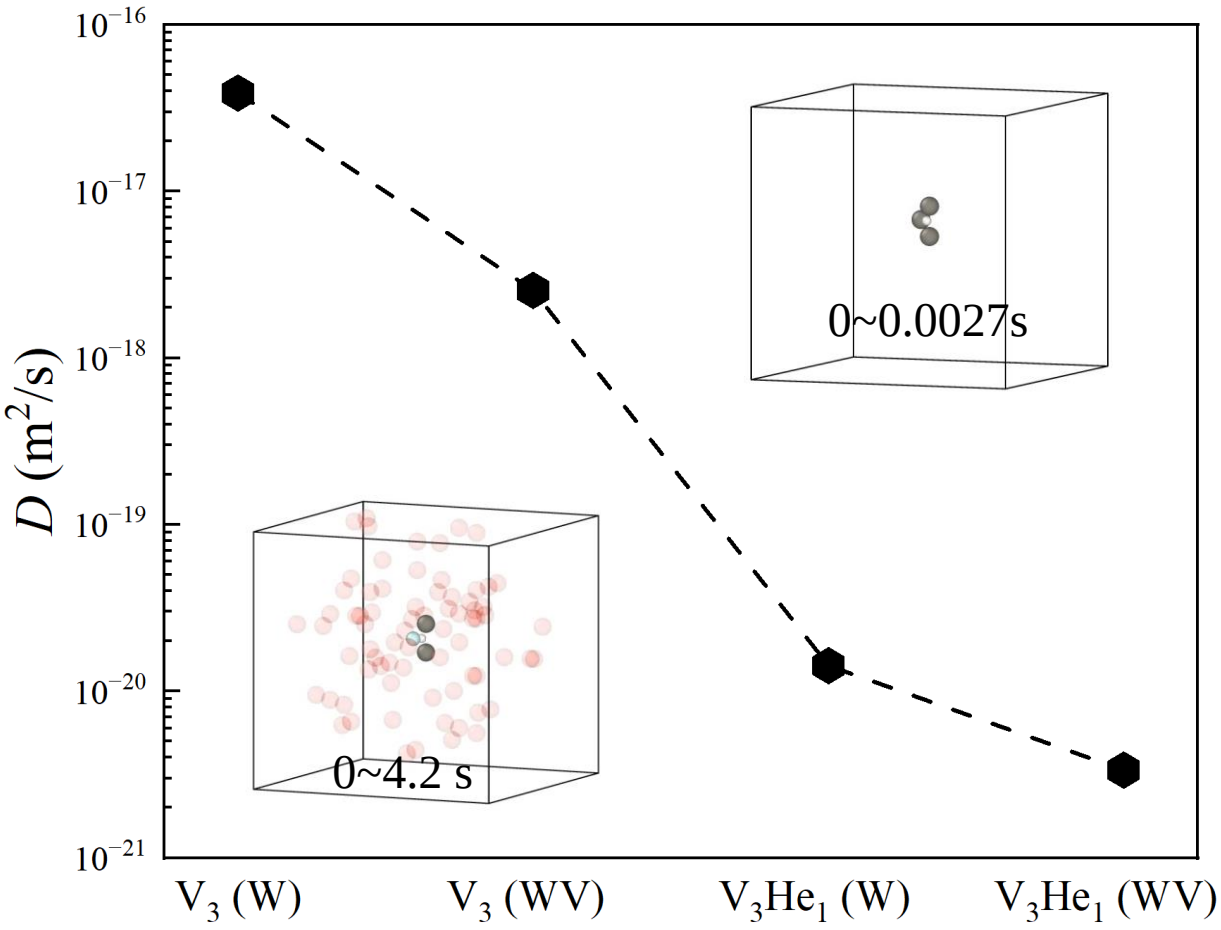
V_3 clusters exhibit extremely fast migration rates and serve as a key intermediate for vacancy-cluster nucleation and growth in W.

G. Wei, et al. Acta Materialia, 301 (2025) 121529.

The effect of V/He on the migration of V_3

5% V atoms are randomly and uniformly distributed in W





He and V effectively slow down V_3 migration and thus inhibit the nucleation and growth of vacancy clusters inside the W.

Summary

1. Simulation Validation

- The accurate tabGAP-pair potential for He-Mo-Nb-Ta-V-W proved effective for simulating irradiation damage and He diffusion.

2. The Critical Role of Vanadium (V)

- **Controls Radiation Damage:** The presence of V effectively controls radiation damage in refractory alloys.
- **Suppression Mechanism:** V suppresses He clustering at high temperatures (900-1500 K) and inhibits He self-trapping and the creation of vacancy traps (Frenkel pairs).
- **Trapping Sites:** V acts as a potent trapping site for mobile He atoms, creating stable, low-pressure "comfort sites" via elastic strain compensation.

3. Helium Diffusion & Defect Evolution

- **Inhibited Bubble Formation:** He atoms are less likely to form bubbles in V-containing alloys; diffusion is heavily influenced by lattice distortions.
- **He Release:** Unlike pure W where no release is detected, W-V binary alloys show significant He release (~20-30% at 1073K).
- **Cluster Inhibition:** He and V effectively slow down migration, inhibiting the nucleation and growth of vacancy clusters inside the W matrix.

Current published results

- G.Wei, J.Byggmästar, J.Cui,K.Nordlund, J.Ren, F.Djurabekova,Revelaing the critical role of vanadium in radiation damage of tungsten-based alloys, Acta materialia,V.274,(1) 2024,119991, DOI:10.1016/j.actamat.2024.119991
- G.Wei, J.Byggmästar, T.Sutinen, Z.Chen,F.Tuomisto, F.Djurabekova, Diffusion of helium in tungsten-basd refractory alloys by molecular dynamics simulations, Journal of Nuclear Materials,V.618,2026,156237, https://doi.org/10.1016/j.jnucmat.2025.156237
- Z.Chen, E.Lu, K.Mizohata, A.Liski, X.An, T.Suhonen, A.Laukkanen, J.Lagerbom, A.Pasanen, A.Vaajoki, F.Tuomisto, Journal of Nuclear Materials, V.599,2024,155238, https://doi.org/10.1016/j.jnucmat.2024.155238
- Z.Chen, G.Wei, K.Mizohata, E,Lu, , J.Byggmästar, F.Djurabekova, F.Tuomisto, Elemental diversity in high entropy alloy MoNbTaVW: complex He diffusion paths and improved radiation resistance, under review to Nature communications, https://doi.org/10.21203/rs.3.rs-7820411/v1 (pre-print)
- G.Wei, J.Byggmästar, Z.Chen, F.Tuomisto, F.Djurabekova, Suppression of helium clustering in tungsten across temperature via dilute vanadium alloying, to be submitted shortly.

Thank you for your attention!