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

EUROFUSION ENR-MAT.02.VTT-T001

01/01/2024 → 31/12/2025

PI: Prof. Flyura Djurabekova

Monitoring Enabling Research Activities for 2024, February 3, 2025

Partners of the HeRHEA project

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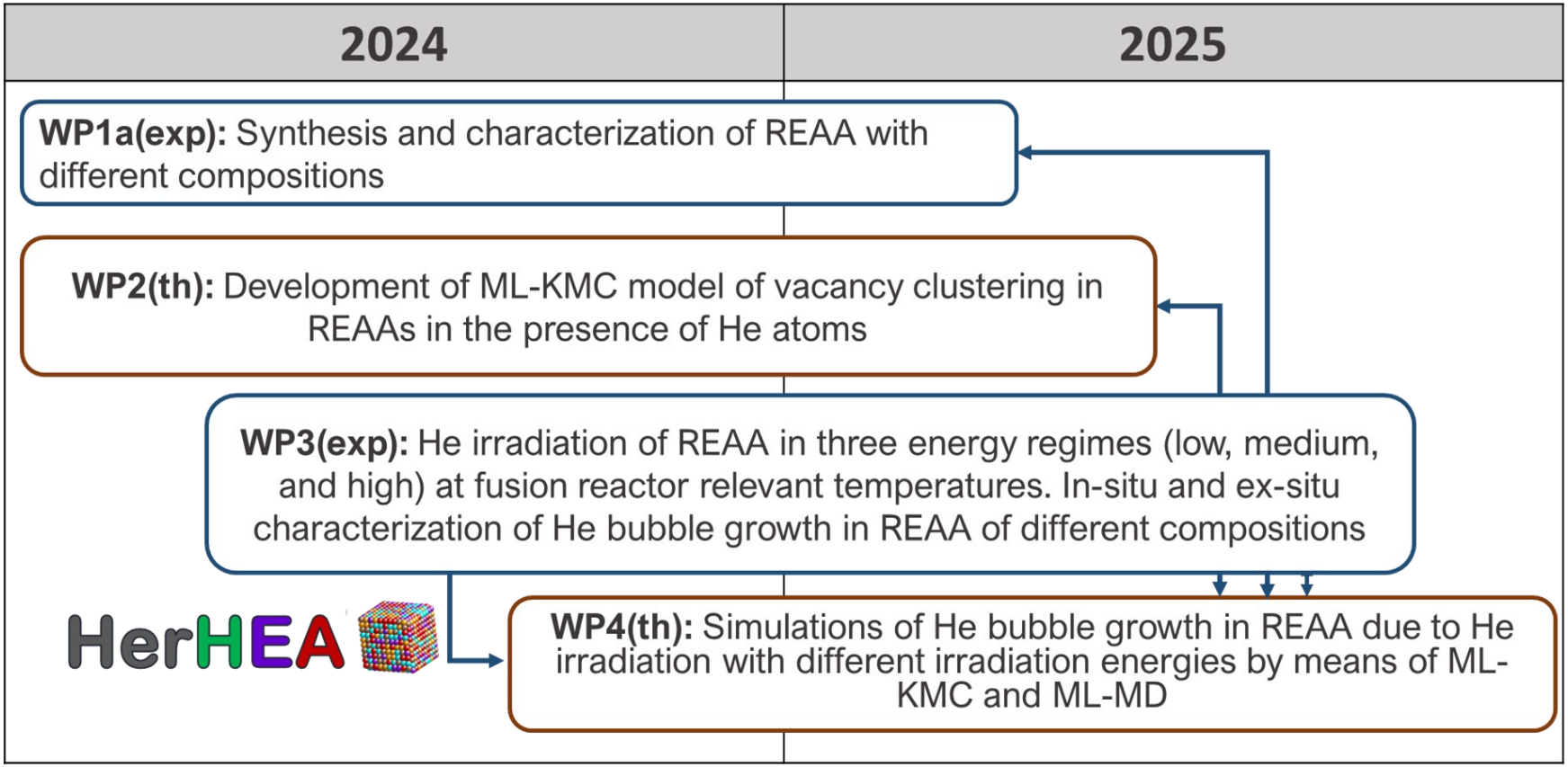
  - Dr. F. Foucher
  - Dr. C. Genevois
  - Dr. Aurélie Gentils
  - Dr. Stéphanie Jublot-Leclerc
  - Dr. Antoine Combrisson

Timeline of HeRHEA project



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

The diffusion of He in W-based refractory alloys by molecular dynamics

Potential He-refractory alloys

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

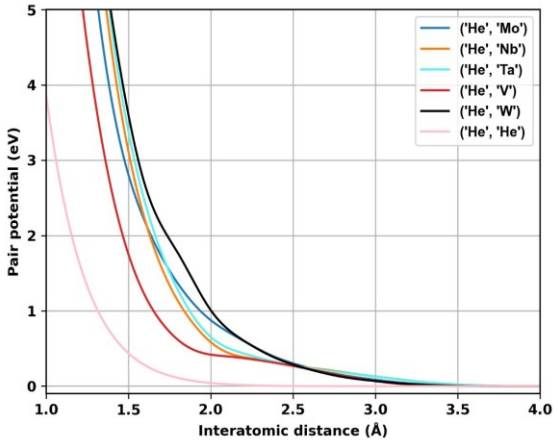


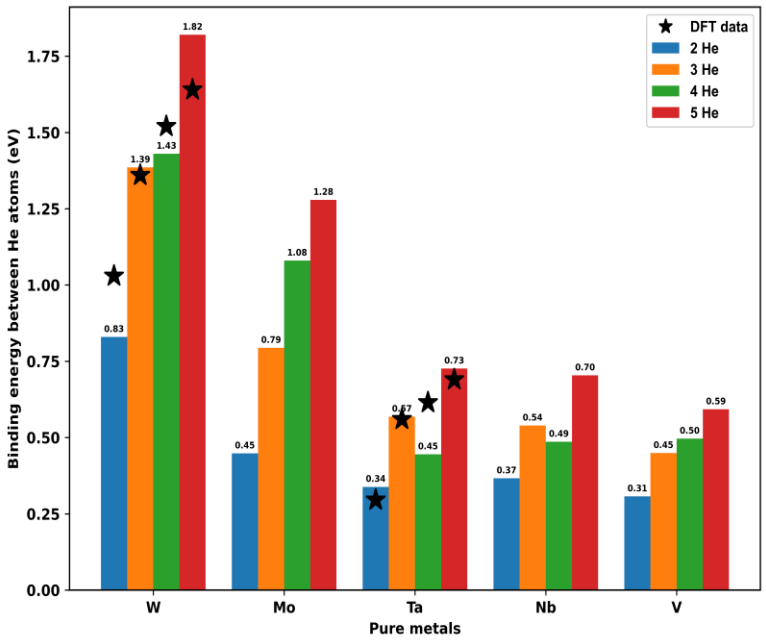
Table 2: Properties used for fitting and testing the interaction between refractory metals and He. Tetra. and Octa. means the formation energy of a He at the tetrahedral and octahedral positions. E_{binding} means the binding energy between an interstitial He with a vacancy. E_{mig} means the migration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

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

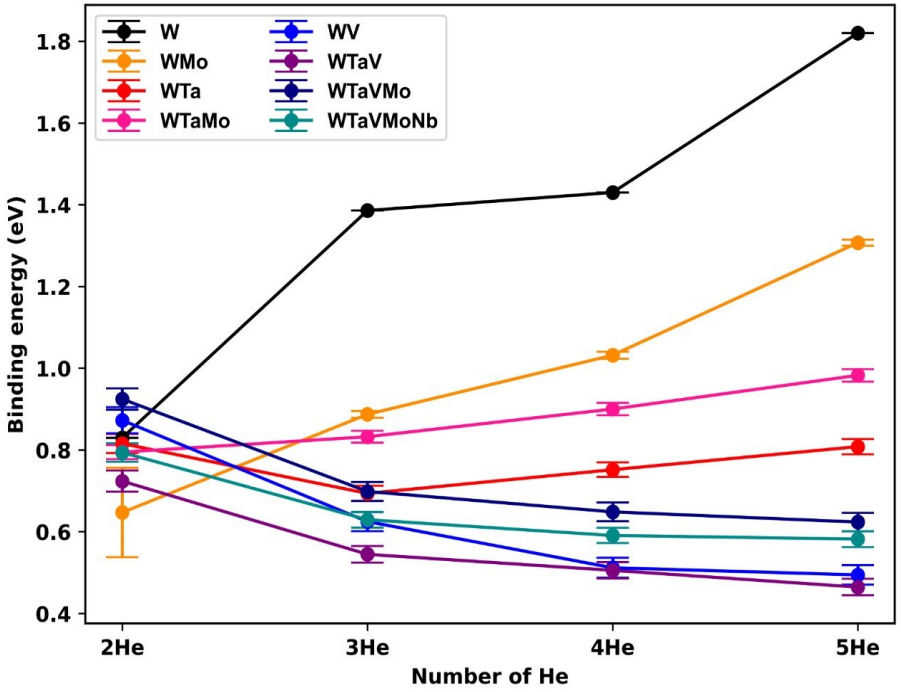
- We have developed the interatomic potential to describe the interaction of He atoms with all atoms in high-entropy alloy (HEA) composition. The interactions are purely repulsive, the HEA is described by previously developed tab-GAP potential [J. Byggmästar, K. Nordlund, F. Djurabekova, Simple machine-learned interatomic potentials for complex alloys, Phys. Rev. Materials 6 (8) (2022) 083801]
- Table 2 illustrates the comparison of formation, migration and binding energies for He atoms in monoelemental metals

Binding energy between He clusters

Pure metals



W and W-based alloys

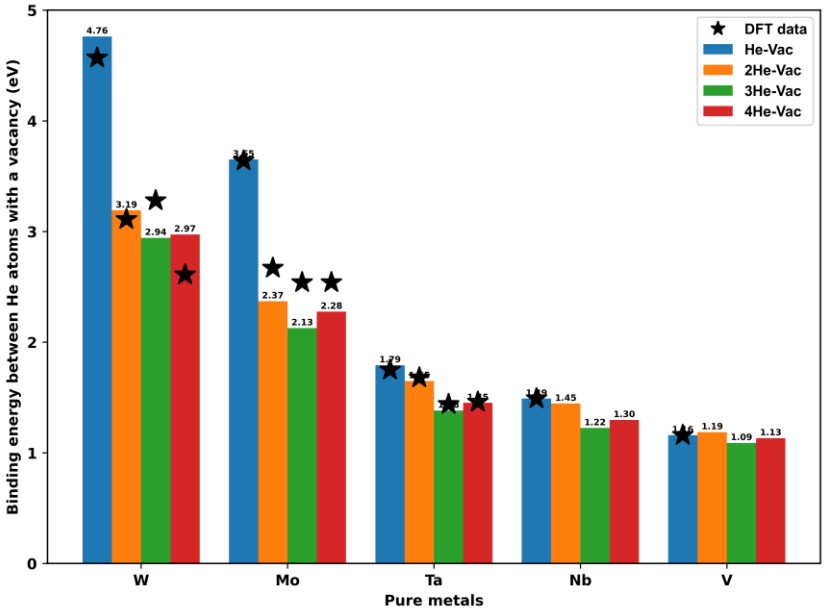


- References for DFT value:
- Ta: You et al, The behaviors of helium atoms in tantalum, rhenium and osmium, Journal of Nuclear Materials, 2018(499).
- W: Becquart et al, An object Kinetic Monte Carlo Simulation of the dynamics of helium and point defects in tungsten, Journal of Nuclear Materials, 2009(385).

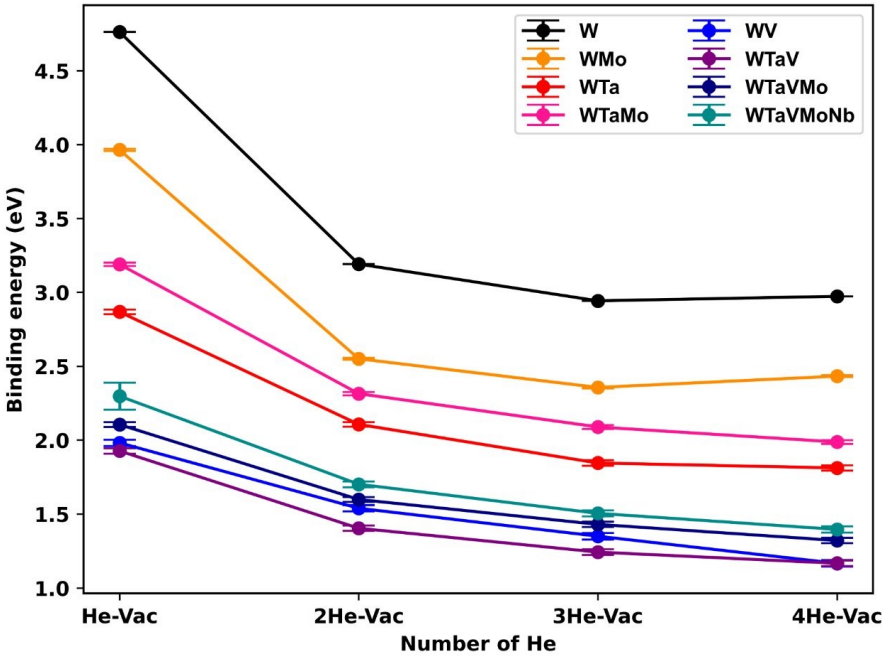
$$E_{\text{binding}}(D_1, D_2) = E(D_1) + E(D_2) - E(D_1 + D_2) - E_{ref}$$

Binding energies of He to vacancy

Pure metals



W and W-based alloys

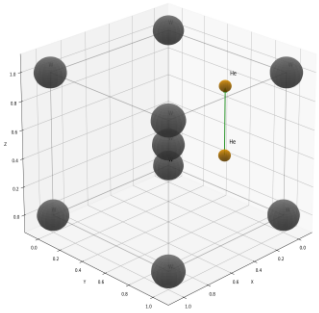


- References for the DFT values:
  - W: Becquart et al, An object Kinetic Monte Carlo Simulation of the dynamics of helium and point defects in tungsten, Journal of Nuclear Materials, 2009(385).
  - Mo: Runnevall et al, Helium cluster dissolution in molybdenum, Journal of Physics: Condensed Matter, 2009(21).
  - Ta: Omori et al, First principle calculations of energy of agglomerated helium in the period 6 elements, Nuclear Materials and Energy, 2018(16).
  - Nb & V: Jiang et al, Ab initio theory of noble gas atoms in bcc transition metals, Physical Chemistry Chemical Physics, 2018(25).

Average migration energy of a He atom

He position	WMo	WTa	WTaMo	WV	WTaV	WTaVMo	WTaVMoNb
(0,0.5,0.25)*a ↓ (0,0.5,0.75)*a (a: lattice constant)	0.13± 0.003	0.20± 0.004	0.196± 0.008	0.43± 0.007	0.34± 0.005	0.32± 0.005	0.29± 0.004

Migration path



Pure metals

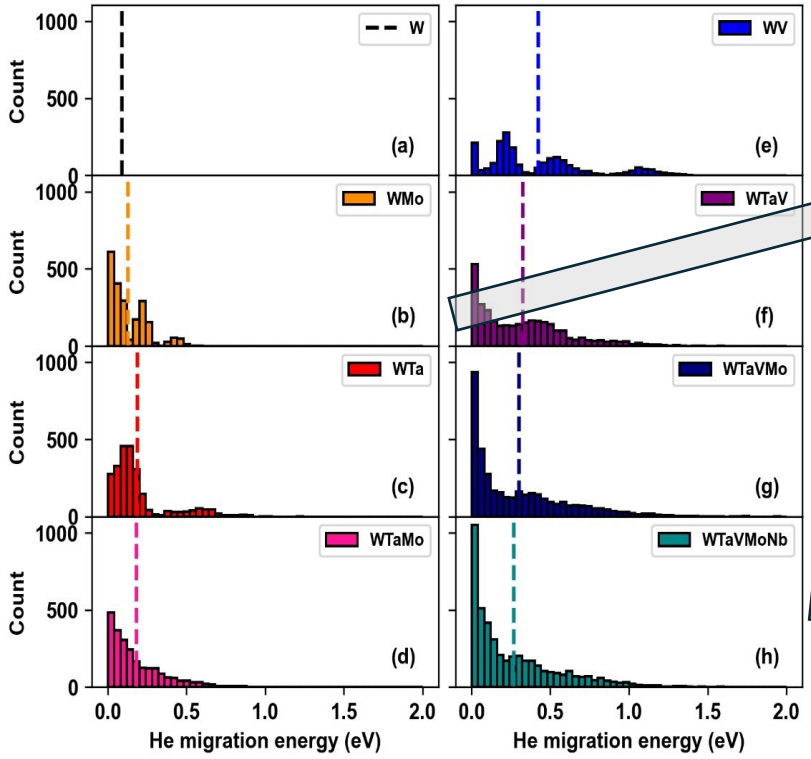
Migration energy	Mo	Nb	Ta	V	W
DFT data[1]	0.09	0.11	0.09	0.09	0.06
Our results	0.06	0.09	0.09	0.09	0.06

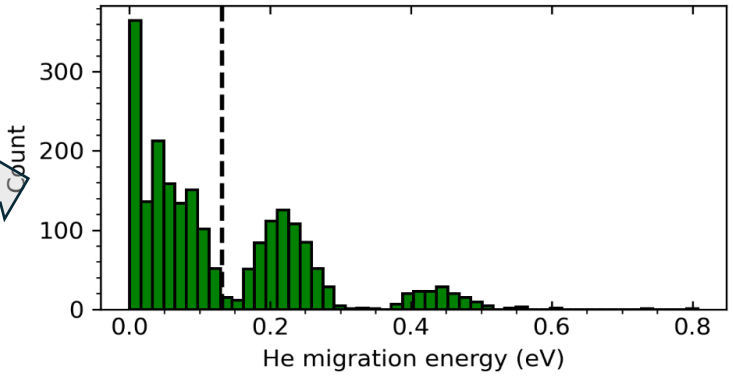
- [1]: Jiang et al, Ab initio theory of noble gas atoms in bcc transition metals, Physical Chemistry Chemical Physics, 2018(25).

Migration energy of a He atom

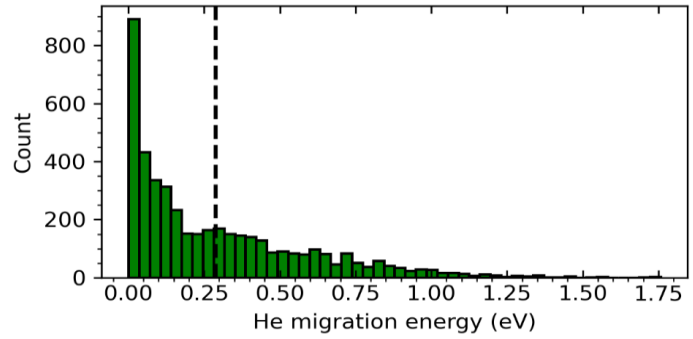
NEB results

- The effect of chemical environment on He migration





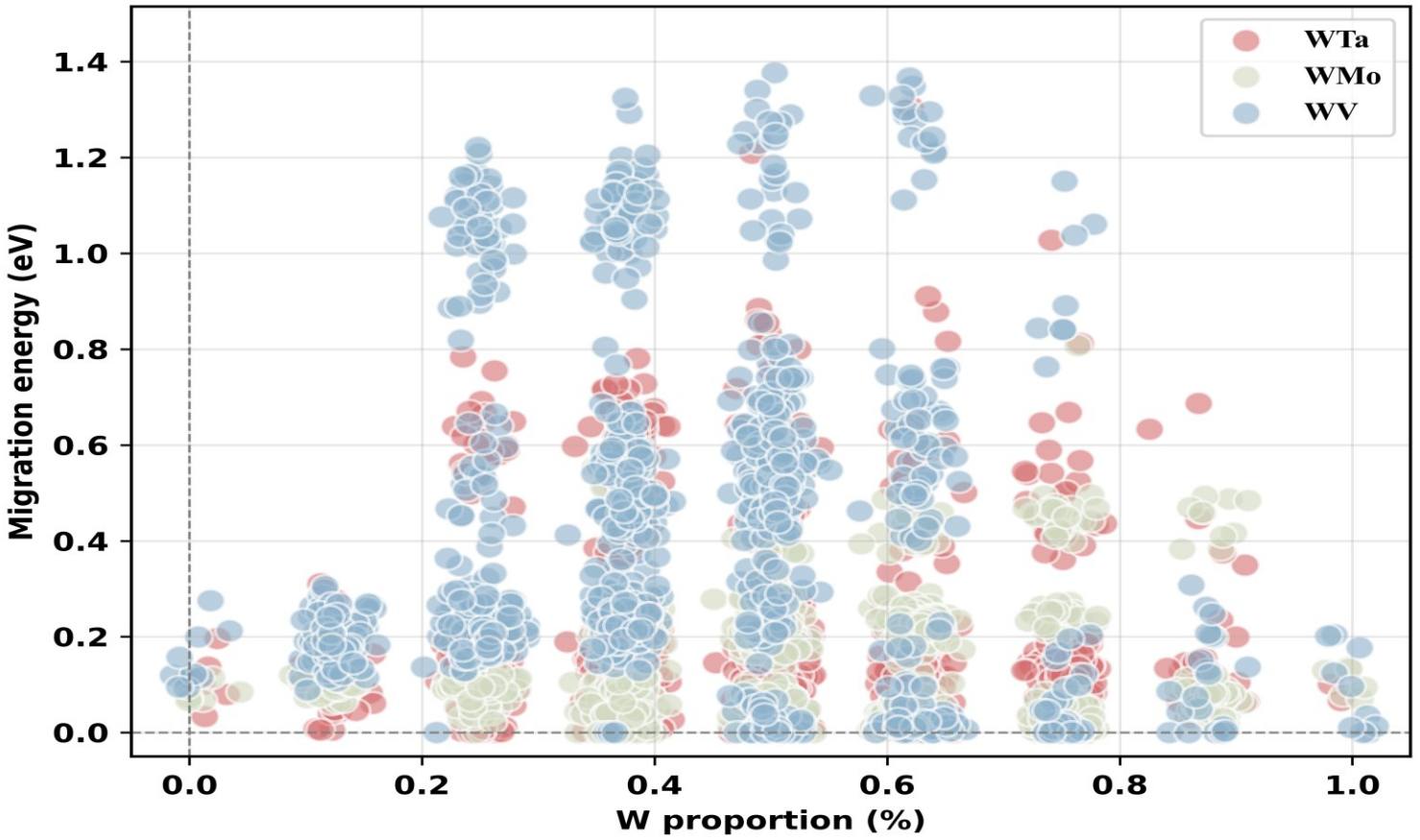
WMo



WTaVMoNb

The distribution of migration energies

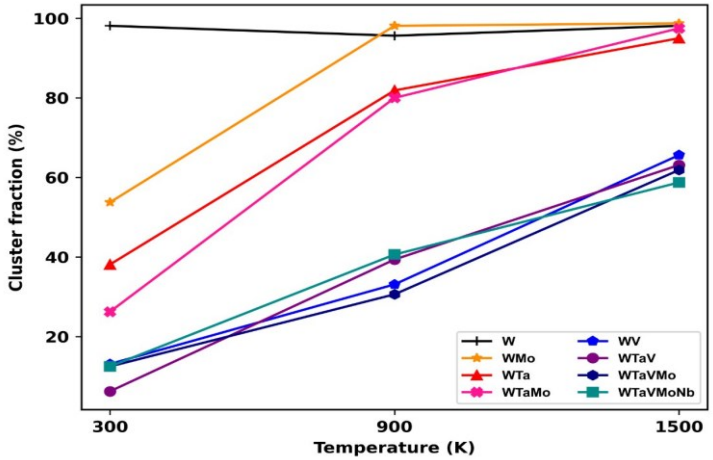
Migration energy of a He atom



- Effect of W coordination environment on the migration energy of He atoms

Diffusion of He (MD simulation)

- Simulation details:
  - Box size: $20 \times 20 \times 20 = 16000$ atoms with 0.1% Vacancies(16) and 1% He (160 atoms)
  - Relaxation runs in NPT ensemble for 5 ns at 300 K, 900 K and 1500 K



  - We observe a strong He clustering in W at all temperatures, while in the V-containing alloys, the growth is much slower. The He atoms prefer to remain dissolved in the lattice

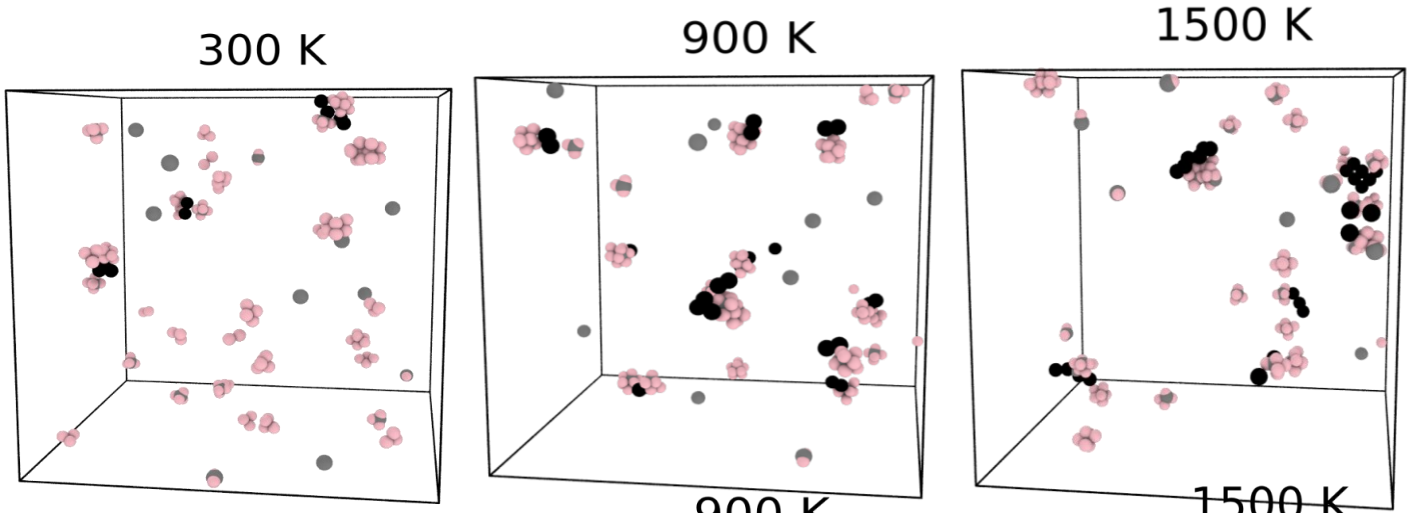
Final frames at all three temperatures for W and WV

W

Pink: He

Gray: Vacancies

Black: W interstitials



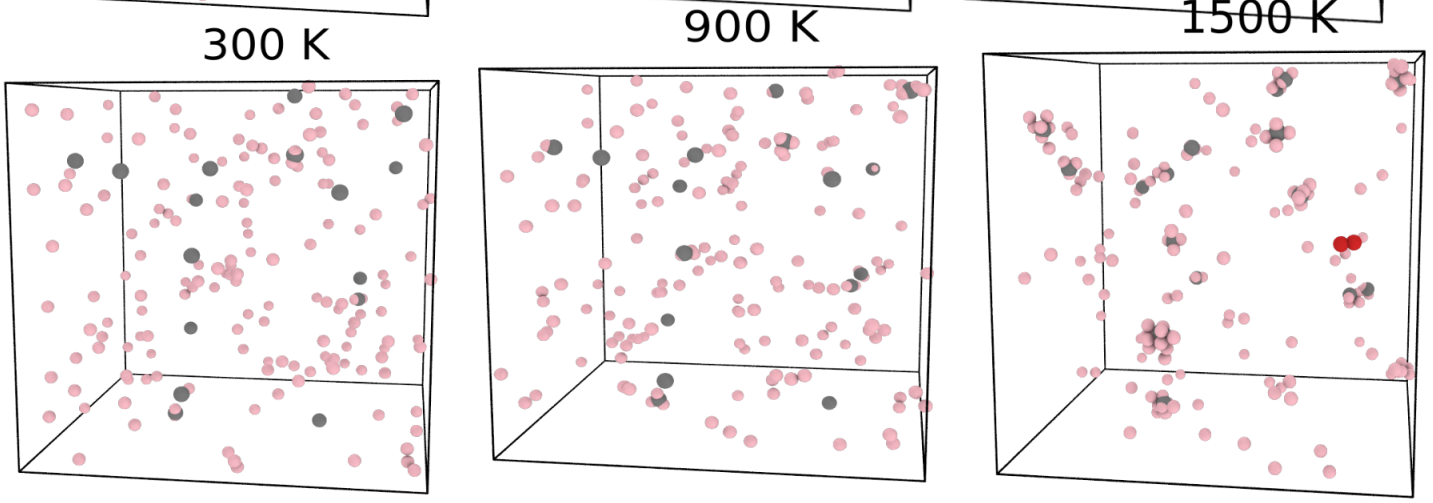
WV

Pink: He

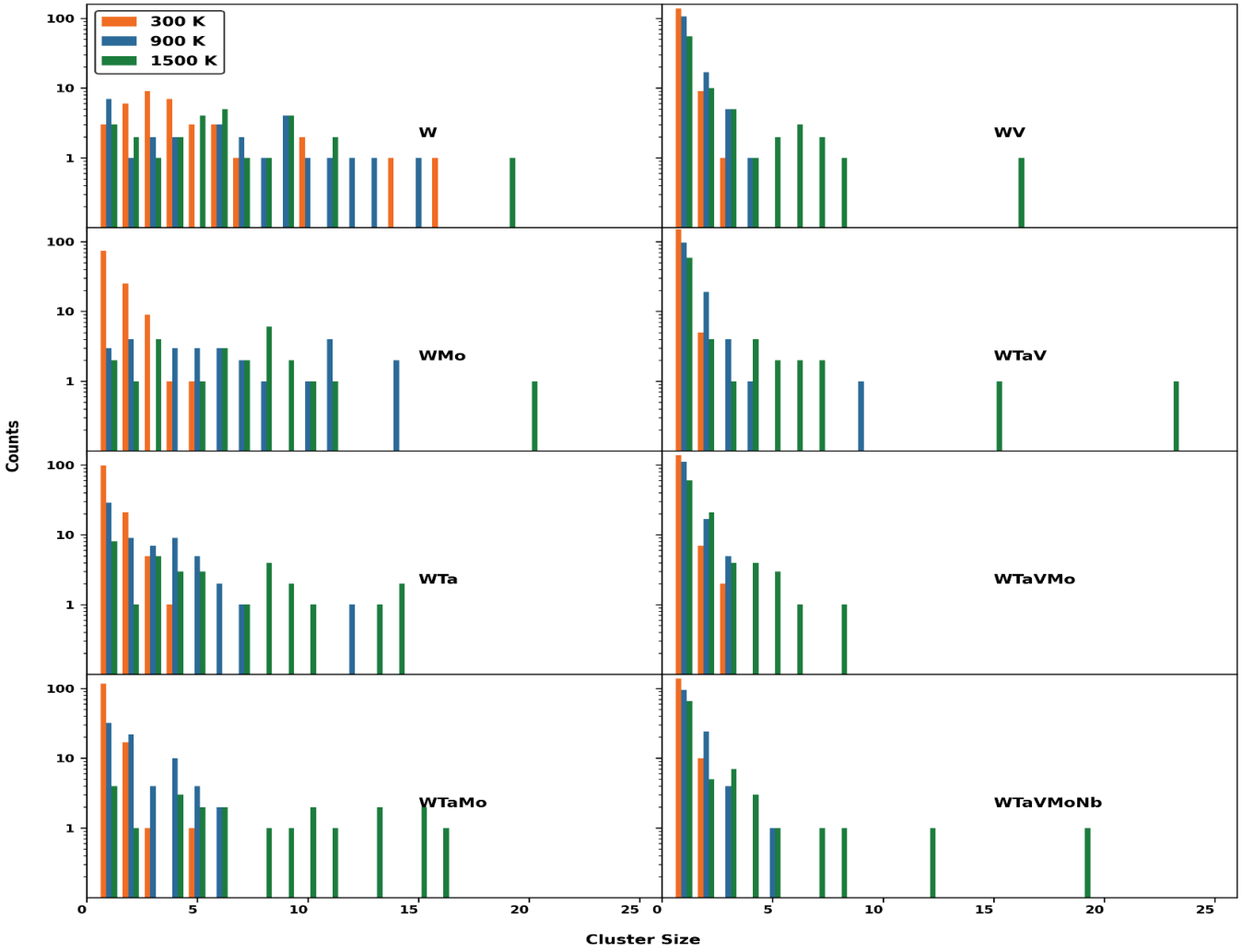
Gray: Vacancy

Black: W interstitials

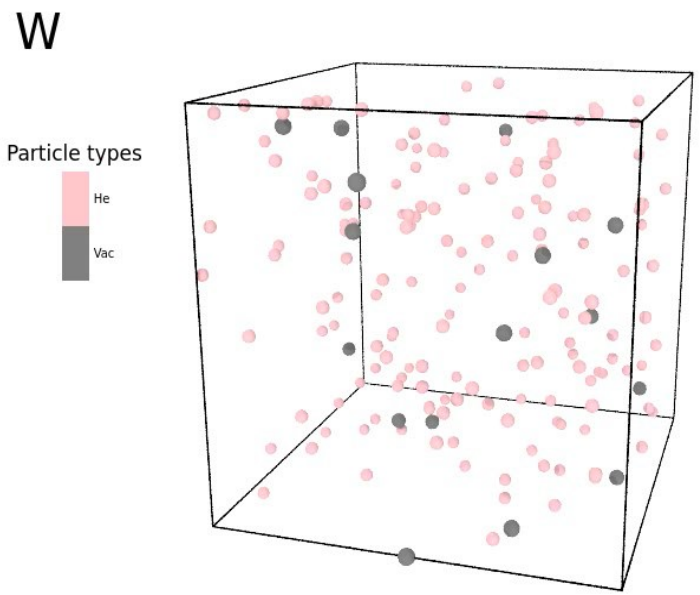
Red:V interstitials

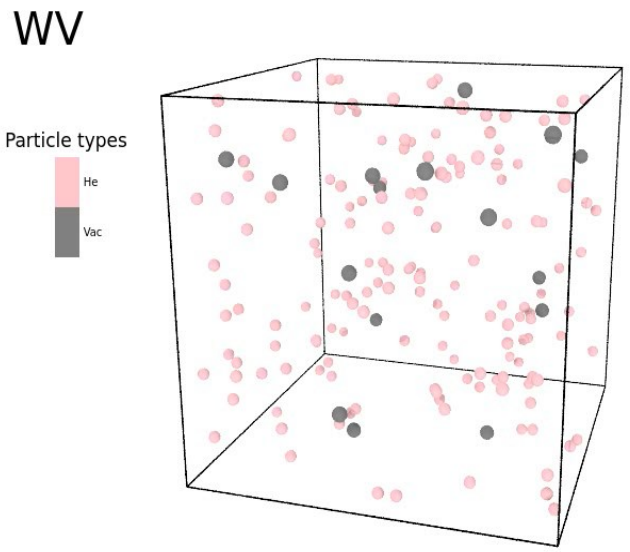


Distributions of He cluster size



Evolution of diffusion (1500 K)





- Dynamic evolution of He clustering at 1500 K in W and WV as an example of V-containing alloy

WP3(exp):

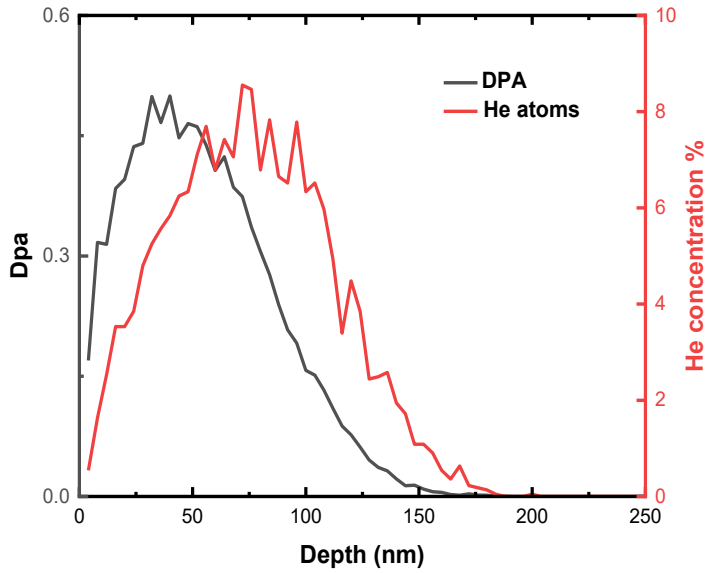
He irradiation of REAA in three energy regimes (low, medium, and high) at fusion reactor relevant temperatures.

In-situ and ex-situ characterization of He bubble growth in REAA of different compositions

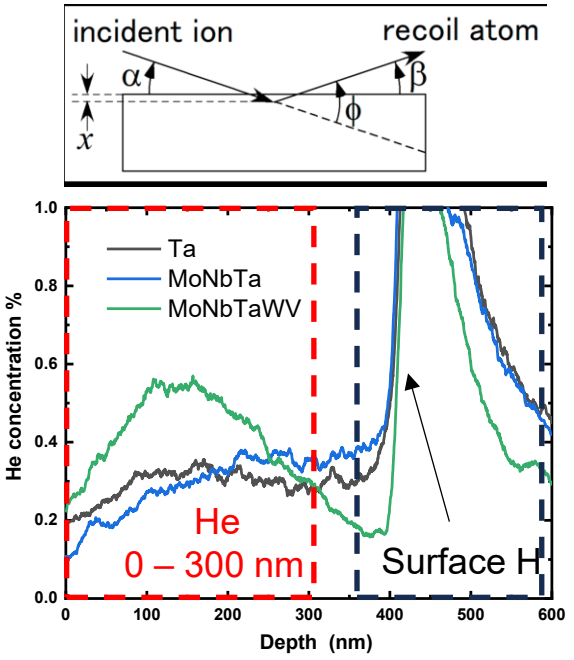
Experimental study: Suppression of long-range helium migration in HEAs

He in Ta series Refractory HEA (BCC)
(unpublished)

- Samples: Arc-melted Ta, MoNbTa, MoNbTaWV
- Irradiation: 5×10^{16}, 25 keV He (ions/cm^2) , room temperature (RT)
- Method: Elastic recoil detection (ERDA), direct measurement of helium concentration within 0-300 nm



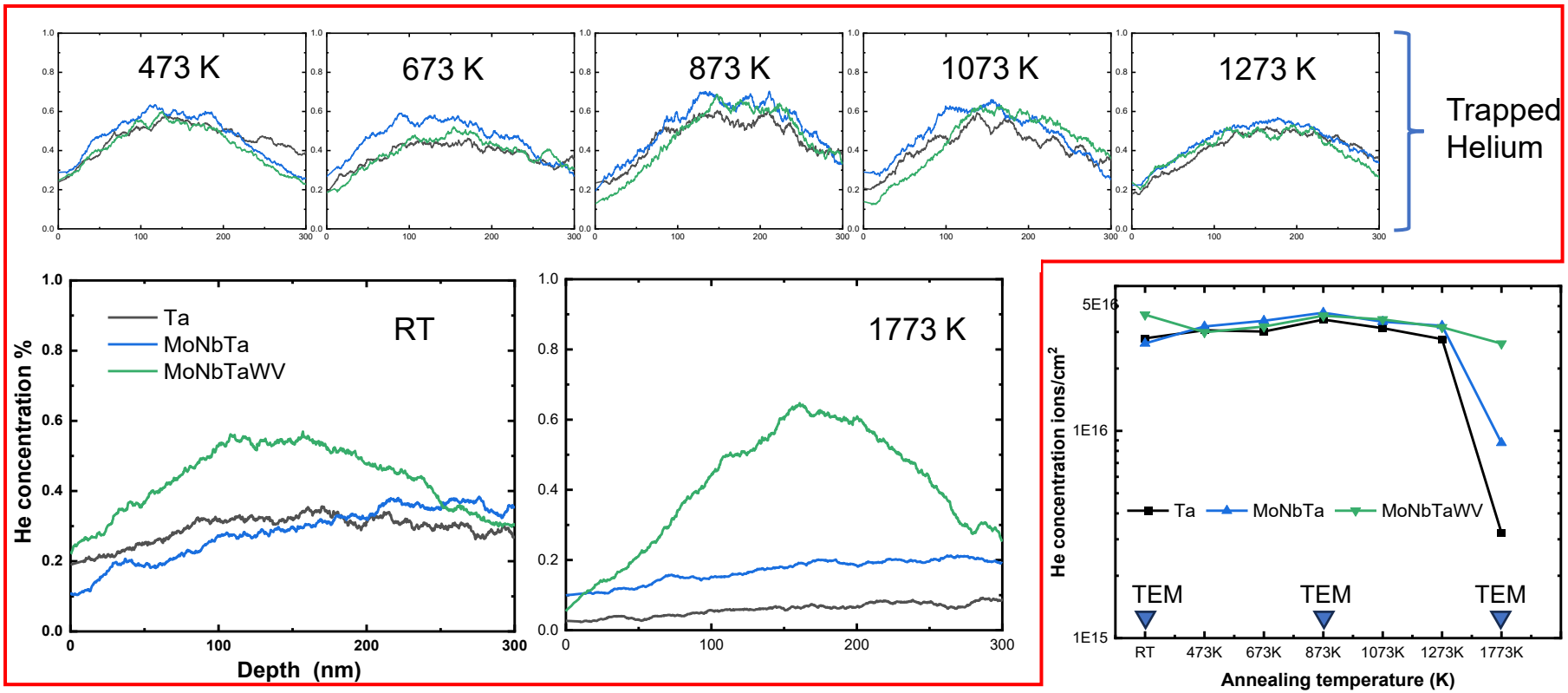
SRIM simulation of 25 keV He in Ta



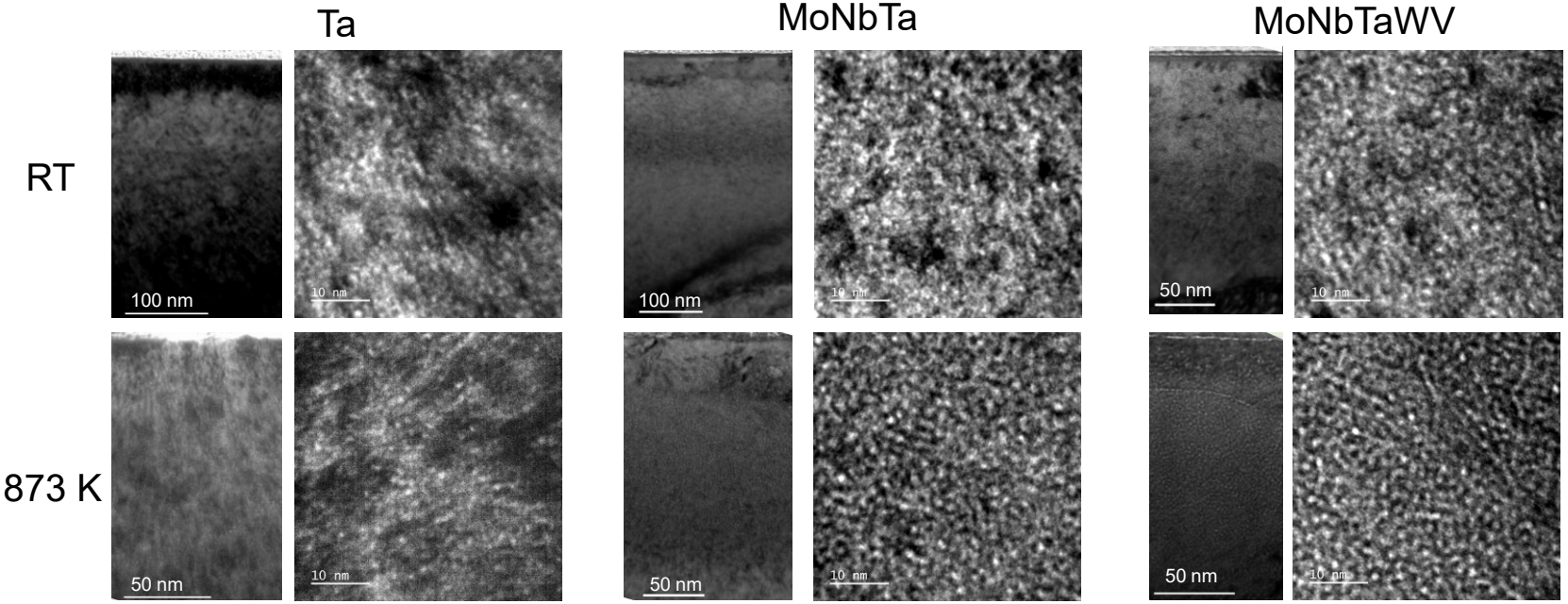
ERDA principle and spectrums after RT irradiation

Helium depth profile after annealing at RT -1773 K for 1h

- For reference, $0.5T_m$: Ta ~1645 K, MoNbTa ~1490 K, MoNbTaWV ~1482 K

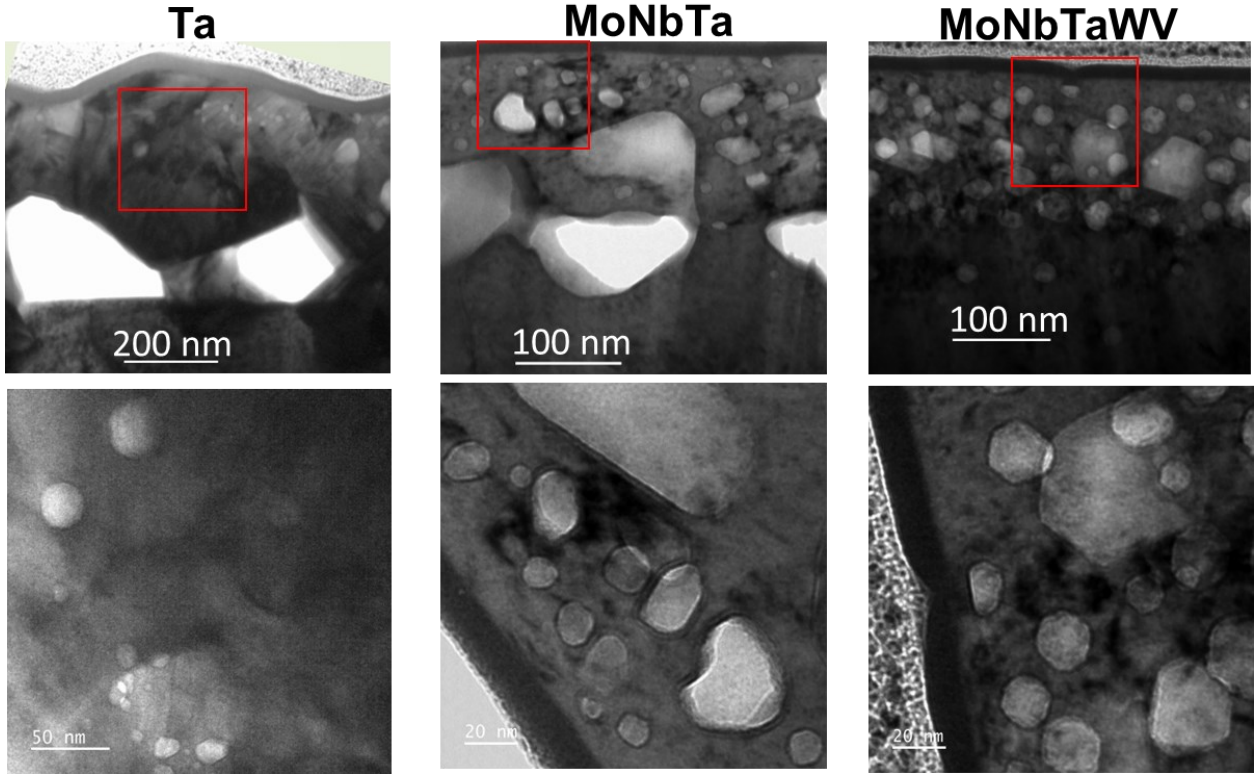


Helium Cavities: at RT and 873 K



- The damage peak is located at a depth of approximately 200 nm
- Helium cavities size: 1-2 nm
- No significant changes were observed between the measurements at room temperature to 873 K.

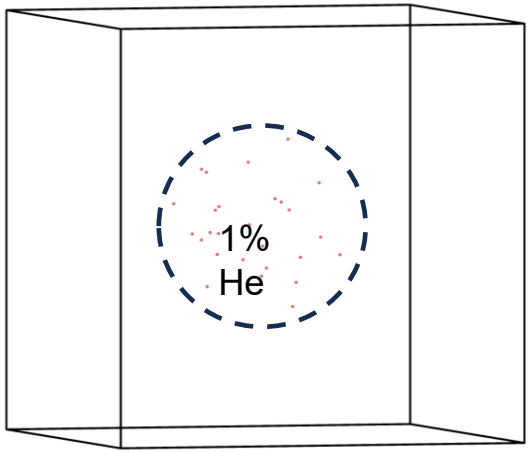
Helium Cavities: at 1773 K



- Helium cavities exhibited significant growth in all samples after reaching half of the melting temperature.
- Less large helium cavities were observed at grain boundaries as the number of principal elements increased, indicating that long-range helium migration was limited.
- In pure Ta, the sample surface was deformed by large cavities.

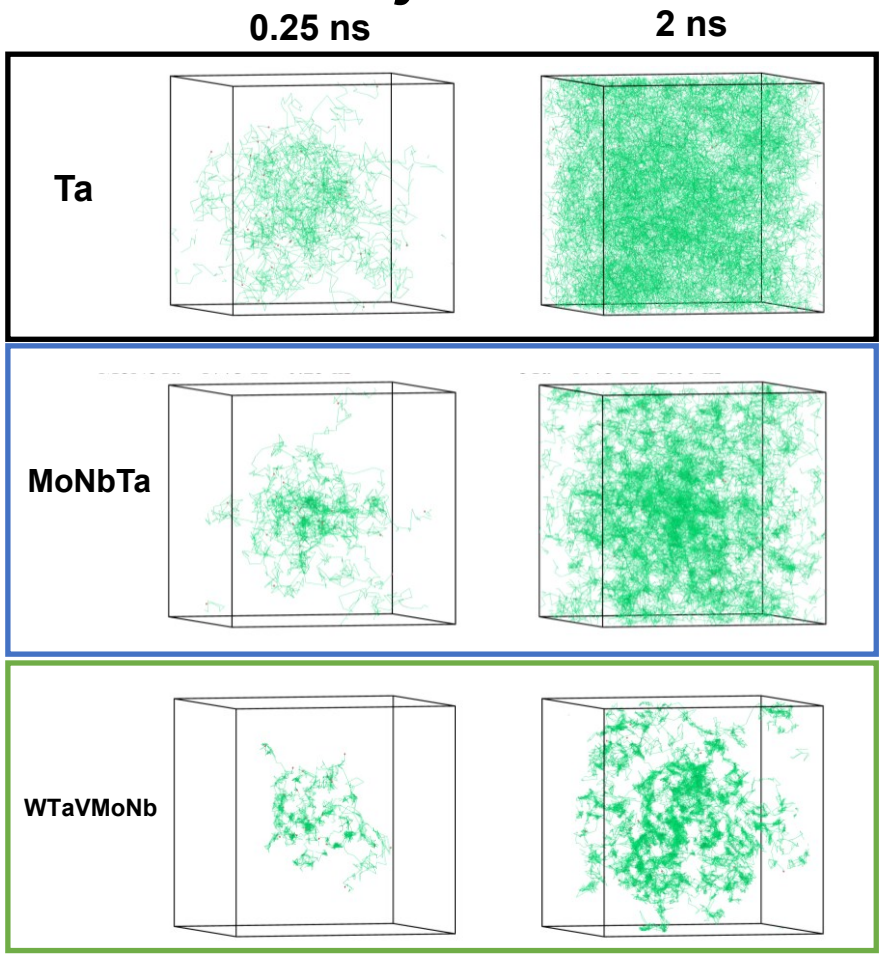
Molecular Dynamics simulation of He diffusion in Ta-based alloys

- Modeling parameters:
- Box size : 30*30*30 , (54000 atoms)
- Central spherical volume : 0.05 * box volume (~2700 atoms), where we Insert 1% He atoms (27 atoms)



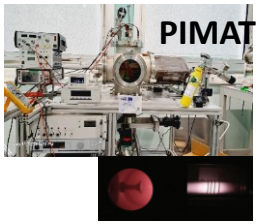
- He atom

— Diffusion path of helium atom



The approach and some first results

- At CEMHTI
  - Preparation of samples (polishing, annealing and preliminary characterization)
  - Two types of He exposure at RT and 500°C
    - Low energy (100-500 eV) using plasma reactor (**PIMAT**) closer to divertor conditions
    - Medium energy (500 keV) using Pelletron accelerator closer to “fast ions” escaping the fusion plasma + α particles (transmutation)



  - Characterization using
    - Nuclear Reaction Analysis (NRA) using deuteron beam and the ^{2}H (^{3}He, ^{4}He)^{1}H reaction for He inventory.
    - Positron annihilation spectroscopy (PAS, Doppler broadening spectrometer coupled to a slow positron beam- DBS-SPB) and *ex situ* transmission electron microscopy (TEM) -in some specific samples- for microstructure defects and bubbles
    - Atomic Force Microscopy (AFM) for surface topography

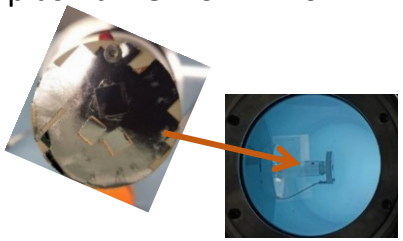
  - Samples : pure W and REAA alloys (arc-melted W-Ta, W-Mo and W-V binaries and ternaries) massive samples prepared by VTT

PIMAT : Plasma Irradiation in Materials

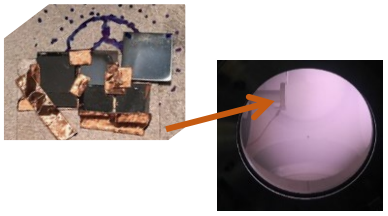
- ^{3}He exposure in PIMAT

(300 eV)

Flux estimated for homogeneous plasma ~ 8x10^{15} $m^{-2}.s^{-1}$

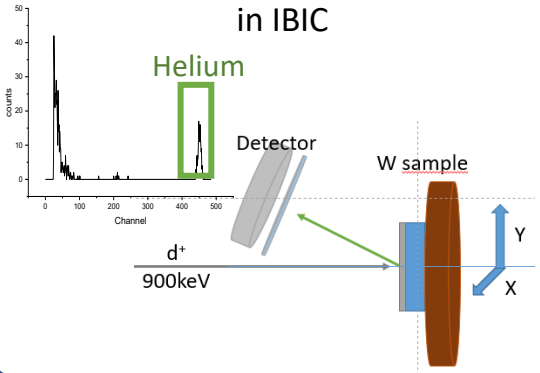


(100) W Single crystal
+ W polycrystals (polished & annealed)

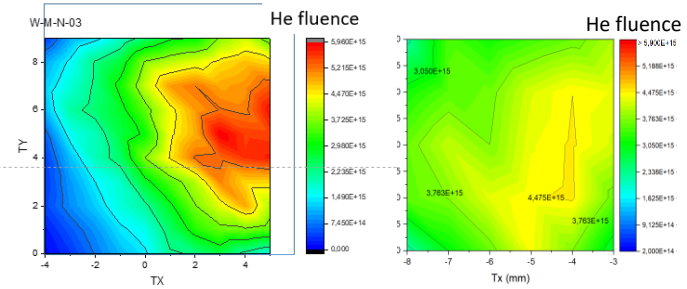


(100) W Single cristal (pol. & ann.) +
W based REA thin layers W, WV & WNbV

^{3}He mapping
(NRA, ^{2}H (^{3}He, ^{4}He)^{1}H)
in IBIC



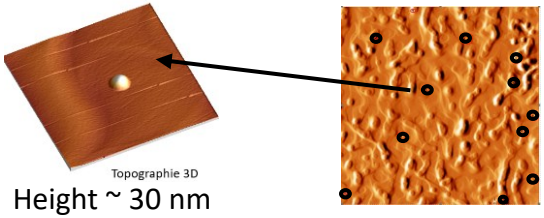
Optimisation of plasma conditions
Before & After



0.2–6×10^{19} m^{-2} 2–5×10^{19} m^{-2}

in (100) W single crystal

AFM in (100) W single crystal
after exposure ~4x10^{19} m^{-2}



Height ~ 30 nm

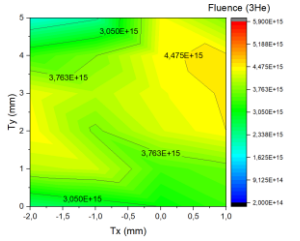
in 40x40 µm

He Bubbles ?

Comparison between W single crystal and REA thin layers : first results

In W epitaxial layer

2–5×10^{19} m^{-2}



Work plan

- Initial work plan for 2024

No	Description	Expected date
M1.1	1st generation (batch) of binary alloys samples, incl. basic charac. (WP1)	June 2024
M2.1	Extension of ML-IAP to include He interactions with HEA is ready (WP2)	May 2024
M3.1	He irradiation and implantation profiles (WP3)	Sep 2024
M3.2	High energy He ion irradiation of HEA (1st batch) (WP3)	Dec 2024
M2.2	ML-KMC model for vacancy migration in REAA with different composition including vacancy clusters is ready (WP2)). Links to D2.1	July 2024
M4.1	ML-MD simulations of plastic deformations around He nanobubbles in binary (WTa, WMo, WV)). Links to D4.1	Oct 2024
M2.3	Cascade simulations with recoils from high energy He irraidiation to deduce the vacancy cluster size distribution in REAAs with increasing complexity are completed (WP2). Links to D2.1	Dec 2024

- Delivery of samples from VTT was postponed to 2025
- In the meantime in 2024
- Optimisation of Exposure conditions in PIMAT
- Modification of the NRA configuration for He mapping
- Tests of 3He exposure in W and in W, WV and WNbV thin layers epitaxially grown on MgO substrates (11-20/12/2024)
- Work plan for 2025
- Reception of VTT samples (next week)
- Cutting of samples and preparation
- Preliminary characterizations
- He introduction
- Characterizations NRA, PAS, ex-situ TEM, AFM

Observing the bubbles nucleation and growth by *in situ* ion TEM at IJCLab

- The tasks completed in 2024 :

- Thin foil preparation dev. / optimization
  - ✓ Literature review
  - ✓ Waiting for the materials (1st test will be done by FIB)

In situ TEM coupled to 190 kV IRMA ion implanter and 2 MV ARAMIS accelerator

- Preliminary choice of ions parameters (comparable with ex situ experiments + using results obtained by simulation)
  - Helium, 10 to 20 keV, up to the maximum fluence in one day
  - Temperature : RT and 500°C

Future work

Material fabrication at VTT

Cutting of the bulk as-fabricated material

(subcontractor found in France for EDM cutting – not initially in our task ; cost to be validated)

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

Select the material(s) to be studied (depending on availability + inputs from literature + modelling + *ex situ* He implantations)

Most likely: W, W-Ta, W-Mo, W-V

TEM thin foils preparation and optimization

Preliminary TEM characterization of the initial microstructure

Selection of the He ion implantation conditions

Energy, T°C, range of fluence (with the help of simulations)

Follow the nucleation and growth of He bubbles

Transmission Electron Microscopy (*ex situ* + *in situ*)

Analyse the experimental data

Interpretation / Comparison with other HerHEA results / Publication

M3.1 *In situ* TEM experiments performed (Links to D3.1) June 2025 → may be delayed to October

Current published results

- G. Wei, J. Byggmästar, J. Cui., K. Nordlund, J. Ren, F. Djurabekova, Revealing the critical role of vanadium in radiation damage of tungsten-based alloys, V. 274, (1) 2024, 119991; doi.org/10.1016/j.actamat.2024.119991
- Zh. Chen, E. Lu, K. Mizohata, A.Liski, Xu. An, T. Suhonen, A. Laukkanen, J. Lagerbom, A. Pasanen, A. Vaajoki, F. Tuomisto Journal of Nuclear Materials, V. 599, 2024, 155238; doi.org/10.1016/j.jnucmat.2024.155238
- G. Wei, J. Byggmästar, F. Djurabekova, Diffusion of helium in tungsten-based refractory alloys by molecular dynamics, in preparation

Milestones and deliverables

No	Description	Expected date
M1.1	1st generation (batch) of binary alloys samples, incl. basic charac. (WP1)	June 2024
M2.1	Extension of ML-IAP to include He interactions with HEA is ready (WP2)	May 2024
M3.1	He irradiation and implantation profiles (WP3)	Sep 2024
M3.2	High energy He ion irradiation of HEA (1st batch) (WP3)	Dec 2024
M2.2	ML-KMC model for vacancy migration in REAA with different composition including vacancy clusters is ready (WP2)). Links to D2.1	July 2024
M4.1	ML-MD simulations of plastic deformations around He nanobubbles in binary (WTa, WMo, WV)). Links to D4.1	Oct 2024
M2.3	Cascade simulations with recoils from high energy He irraidiation to deduce the vacancy cluster size distribution in REAAs with increasing complexity are completed (WP2). Links to D2.1	Dec 2024
M3.1	He irradiation and implantation profiles, 2nd batch damage build up (WP3)	Sep 2025
M1.5	2nd generation (batch) of ternary WTaV an basic characterisation (WP1). Links to D1.3	
M4.2	Analysis of He self-trapping mechanism in R	
M3.1	*In situ* TEM experiments performed (Links t	
M4.3	ML-KMC model for migration of vacancie He atoms in REAA with different compos ready (WP2). Links to D2.1	
M4.4	ML-MD simulations of plastic deformations WTaV alloy and RHEA WTaMoNbV (WP4	

Title	WP	Due date	Description
D1.1	WP1	Sep 2024	Report on 1st batch sample synthesis and mechanical properties characterization
D1.3	WP1	June 2025	Report on 2nd batch sample synthesis and characterization
D2.1	WP2	Jan 2025	Report and submitted publication on parameterization of the KMC model for vacancy diffusion with and without He load
D4.1	WP4	Oct 2025	Report and submitted publications on possible He bubble growth via plastic deformations in REAA with increased complexity
D3.1	WP3	Dec 2025	Report and submitted publication on *in situ* TEM analysis of He bubbles
D4.2	WP4	Dec 2025	Report and submitted publication on He bubble growth via vacancy clustering and agglomeration of vacancy clusters
DD	All	Jan 2026	Submission of materials data to Eurofusion materials database (foreseen to be in one of ETASC Advanced Computing Hubs).
DF	All	Jan 2026	Final report on project including outlook for further work.

Outlook for 2025

- In 2025 we will focus on WP4, where the KMC model to describe the bubble agglomeration in V-containing HEA will be developed
- Meanwhile, we will investigate the He bubble growth mechanisms in several alloys (ongoing work)
- Initial experimental results agree with the experimental observations, clearly showing more localized diffusion of He in V-containing concentrated alloys
- While the sample preparation appears to be an issue (some bureaucratic delay at VTT-VTT site with opening of the project), we are looking for other sources of HEA.
- As risk mitigation, we will explore the thin-film grown alloys, which will help us to reveal the effect of chemical composition on He self-trapping and long-range migration