The life story of a helium bubble in a metal tritide: a rough draft

PRESENTED BY

David B. Robinson

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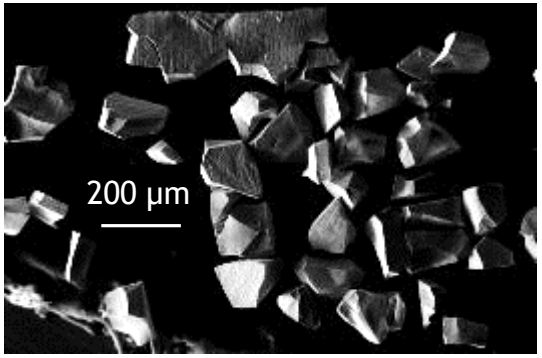
Main points of presentation

We currently cannot reliably predict properties of aged metal tritides.

We have a good but rough outline of the phases of the life of helium in a metal tritide.

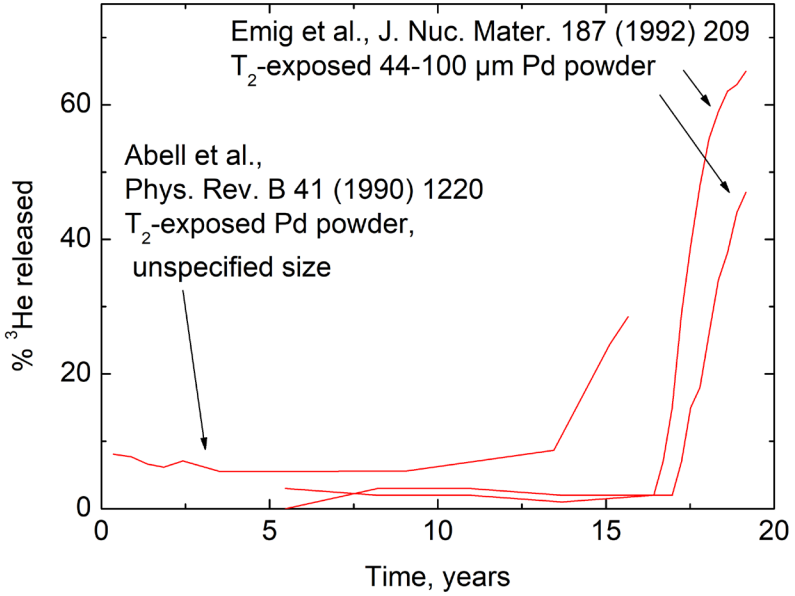
- Atomic transport, trapping, and clustering
- Bubble nucleation
- Bubble growth, migration, and coalescence
- Blistering, popping, and fracture



Crumbled Pd-5 at. % Ni foil aged 3.8 years
Shanahan, Fusion Sci. Tech. 71 (2017) 555

Remaining questions about the details are tractable by modern methods.

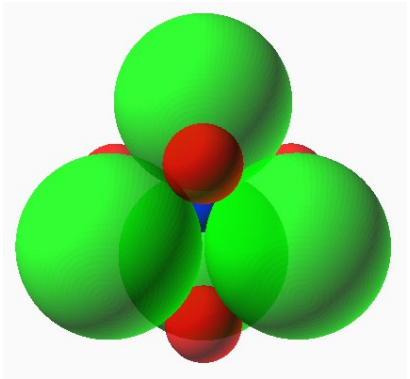
A model allowing reliable and general prediction of metal tritide properties is within reach.



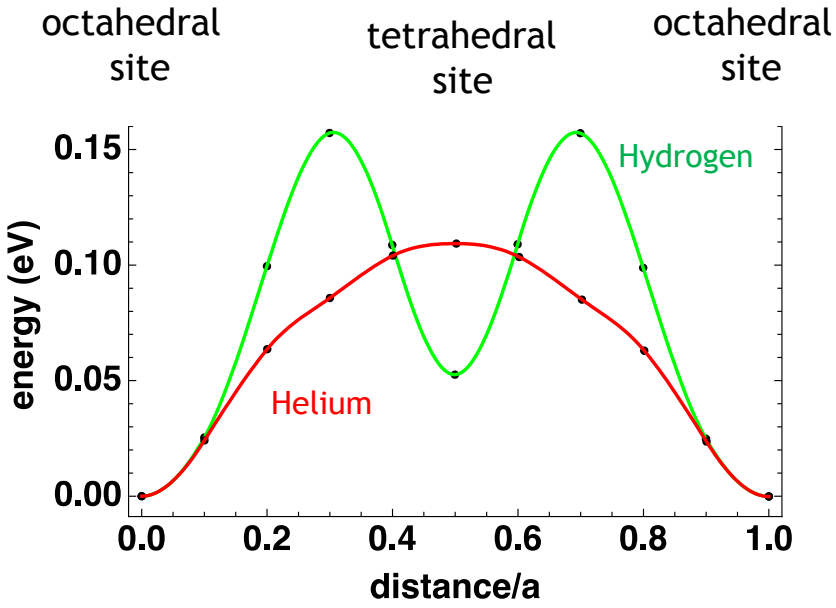
Helium should escape from a perfect, finite metal tritide crystal

Considering ^3H and ^3He in palladium

- Face-centered cubic lattice of metal atoms (green)
- Tritium resides in ~2/3 of octahedral sites (red), hopping through tetrahedral sites (blue, obscured) at a rate of $D \approx 10^{-5}$ cm^2/s at room temperature (James et al., Chem. Eng. Sci. 2012, 68, 250)
- Helium is generated at $S \approx 10^{-10}$ mol/cm^3 s
- Density functional theory predicts similar diffusion constants for ^3He, T (Bartelt)
- Recent ion implantation experiments validate activation energy; prefactor may be lower (Cowgill)
- Maximum concentration in R=0.8 cm sphere:
- $SR^2/6D \sim 10^{-6}$ mol/cm^3
- 100,000x lower than T concentration



DFT-PBE calculation
32 Pd atom cell



Not much helium escapes from real samples

Experiment by G. Thomas, SNL/CA, 1980s

Thin Pd TEM sample exposed to tritium

Aged until 1 in 10^{-4} T decayed to He

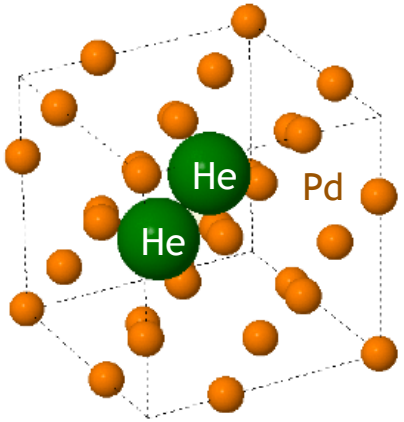
He more than 5 nm from surface forms nanobubbles

Presumably most black dots in TEM image are He bubbles

Hypotheses:

- He atoms trap at impurities
- He traps at other He to form clusters

Homogeneous bubble distribution suggests homogeneous trap distribution



Donnelly and Evans, ed., "Fundamental Aspects of Inert Gases in Solids", Plenum Press, NATO ASI Ser. B 279 (1991) 98

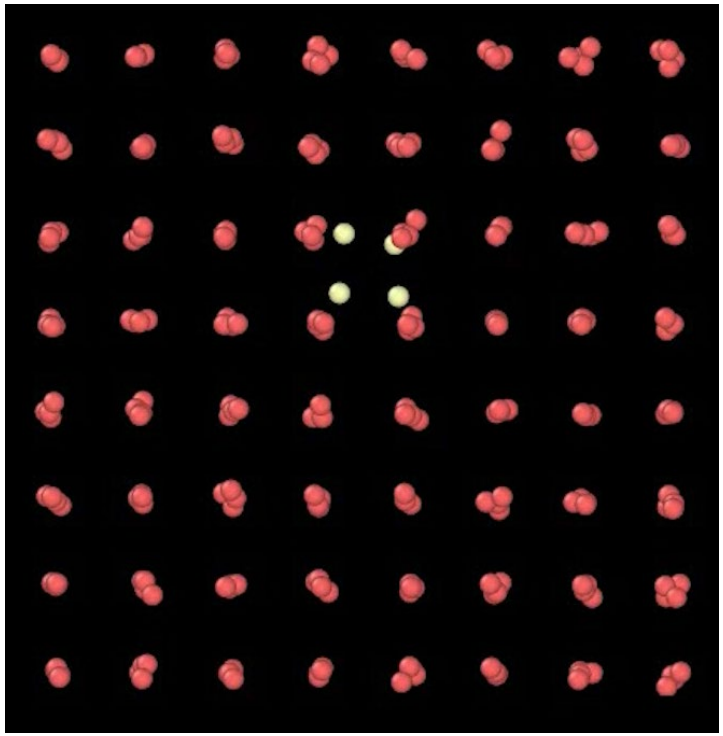
He clusters are mobile in a perfect crystal

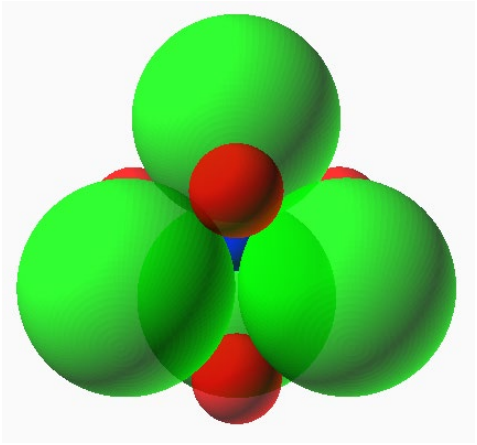
Helium atoms strongly dimerize (0.8 eV binding energy)

Density functional theory by us (Bartelt) and others:

- Dimers, trimers, and tetramers diffuse about as quickly as He atoms
- Cao and Geng, J. Nucl. Mater 478 (2016) 13

Molecular dynamics simulations suggest mobility of larger clusters (Zhou, Alvarado)





300 K
3 ps timescale

What impurities can trap?

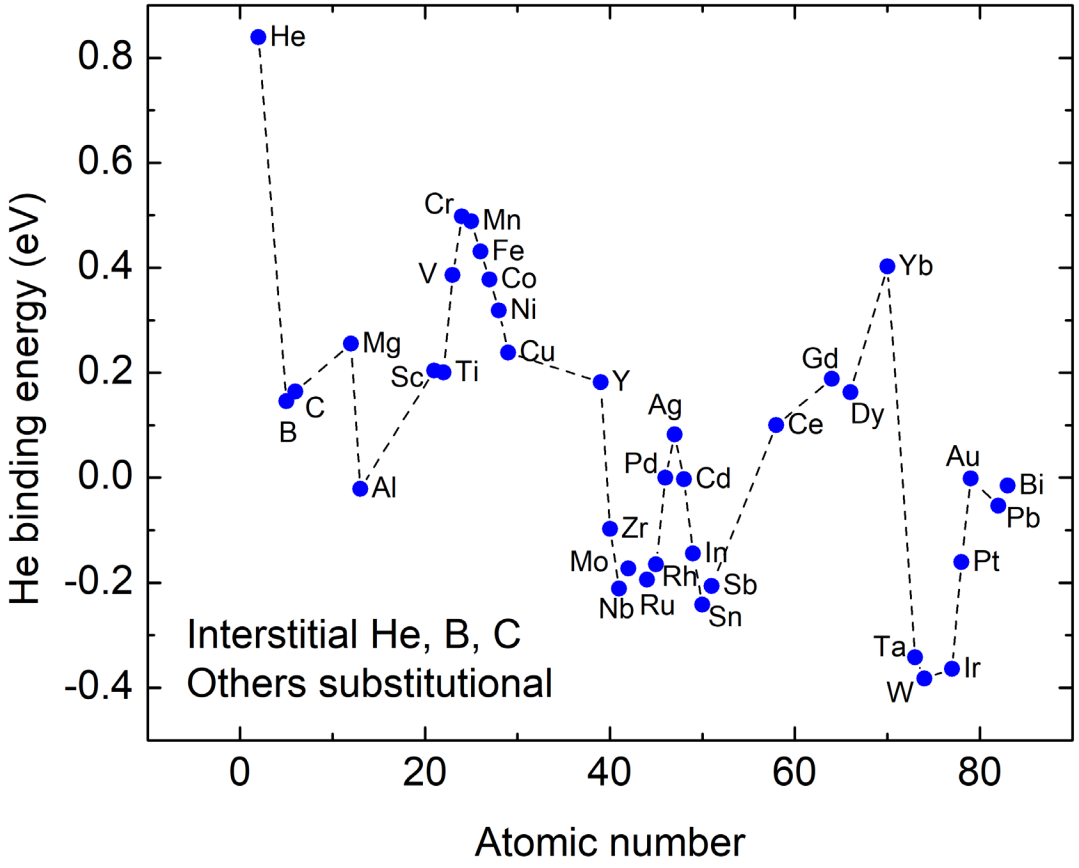
Density functional theory by us (Bartelt) and others (P. Lin, GA Tech) suggests that impurities in Pd can bind or repel He

Binding can slow diffusion of atomic He, maybe stop it for clusters

Impurity concentration presumably must exceed bubble concentration, about 10^{-6} per Pd atom

Testable by preparing dilute solid solutions, measuring bubble nucleation latency and initial density.

Electron energy loss imaging can help us find He in the lattice.



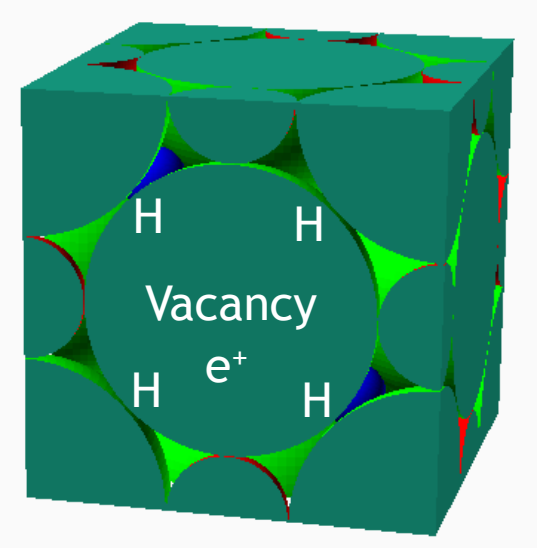
Vacancies; substitutional H and He

Vacancies strongly bind He (4 eV) and are much less mobile.

Thermal vacancies in room-temperature Pd are negligible at equilibrium

Hydrogen stabilizes vacancy concentrations of 10 ppm at room temperature

- Theory predicts 100 ppm at 100 °C, 1000 ppm at 200 °C
- Positron annihilation studies by Cizek et al., J. Alloys Compounds 2015
- Positrons trapped in vacancies survive 200 ps, longer than in other environments
- Can vacancies be generated and transported as quickly as helium?



Testable by preparing samples with thermal treatments in presence of T_2, measuring bubble nucleation latency and initial density (and positron studies)

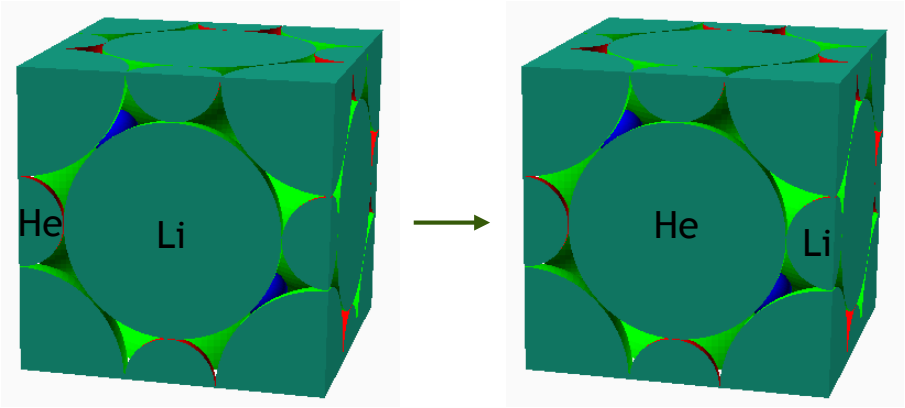
More complex hypothetical traps

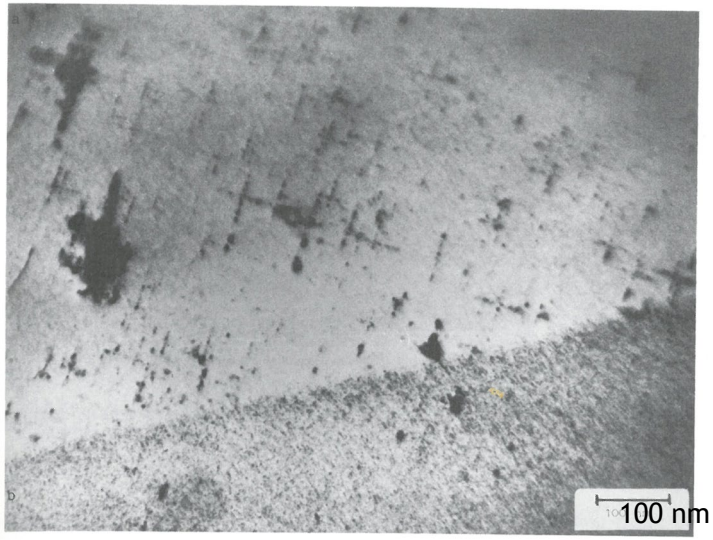
Interstitial He could hypothetically displace some substitutional impurities (Li, B, C) so they would trap He almost as strongly as a vacancy.

Stacking faults create unusually close octahedral sites that could stabilize atomic He or dimers.

Dislocations, including those created by bubbles, could trap He, so bubbles could seed other bubbles.

These are more difficult but tractable questions for density functional theory.





Defects near bubbles in dilute V hydride; dense bubbles in concentrated hydride
Donnelly and Evans, ed., "Fundamental Aspects of Inert Gases in Solids", Plenum Press, NATO ASI Ser. B 279 (1991) 97

Bubble nucleation

Bubbles form by accumulation of vacancies or ejection of metal atoms by a He cluster, as dislocation loops

- Probably not self-interstitials, even as intermediates (Wolfer, Phil. Mag. A 1988).

Without vacancies, how many He atoms in a trapped cluster are needed to eject metal atoms?

Is there a minimum stable bubble size, such as one that creates a certain sized dislocation loop?

Is nucleation suppressed after an initial burst?

How much He goes to bubbles vs. staying in lattice?

To address these questions:

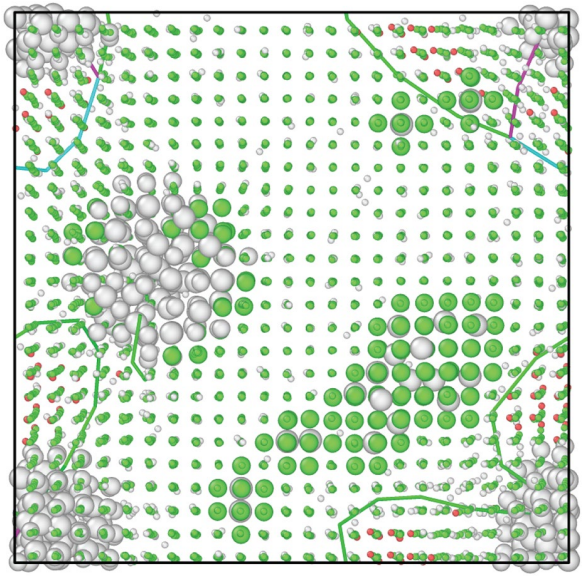
- Age-dependent microscopy
- Measure He content by EELS
- Molecular dynamics simulations
- Continuum diffusion models

Pd

Pd with ^{3}He in O_h hole

^{3}He at lattice site

^{3}H



Xiaowang Zhou

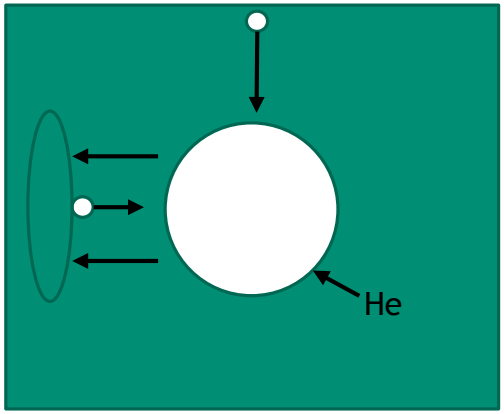
Growth and pressurization of stationary bubbles

Mechanisms:

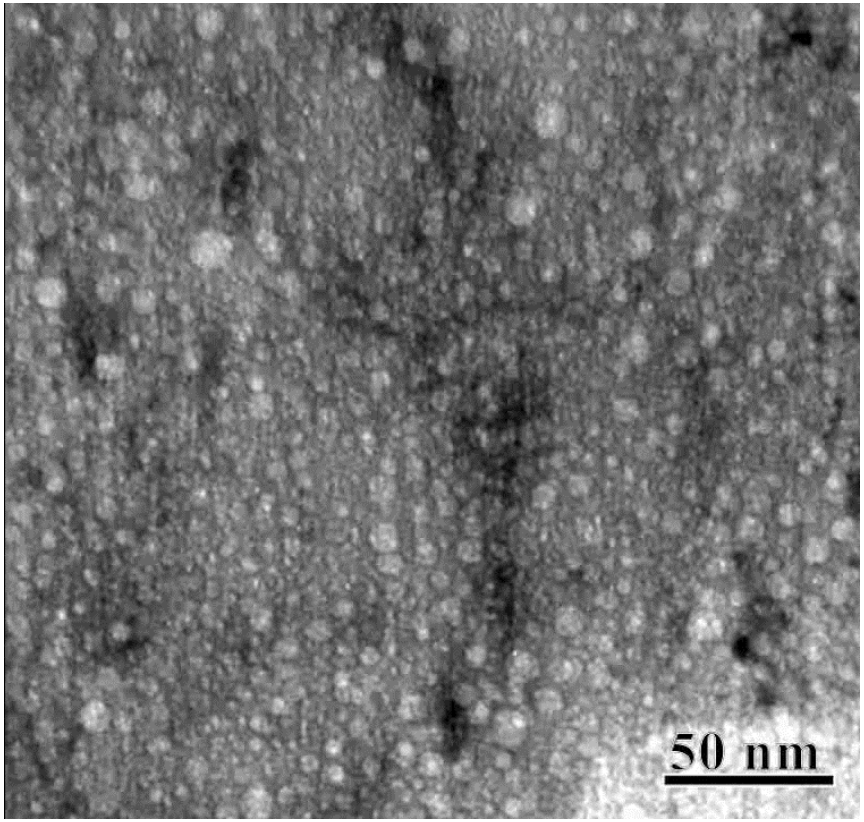
- Accumulation of lattice He (atoms or clusters)
- Accumulation of vacancies (gradual growth)
- Displacement of metal atoms as dislocation loops or interstitials (more abrupt growth)

Heated-stage TEM can help distinguish these mechanisms (Taylor).

Electron tomography can help distinguish overlapping bubbles (Catarineu, Sugar).



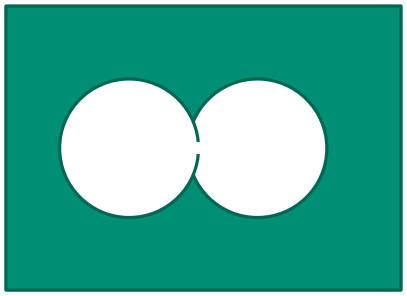
PdNi heated to 400 °C

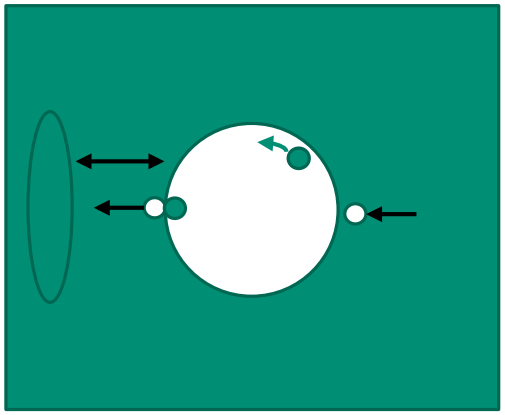


Migration and coalescence of bubbles

Migration mechanisms:

- Diffusion of bubble surface metal atoms
- Vacancies entering one side, exiting the other
- Directional creation of dislocation loops
- Field-driven directional transport vs. random walk





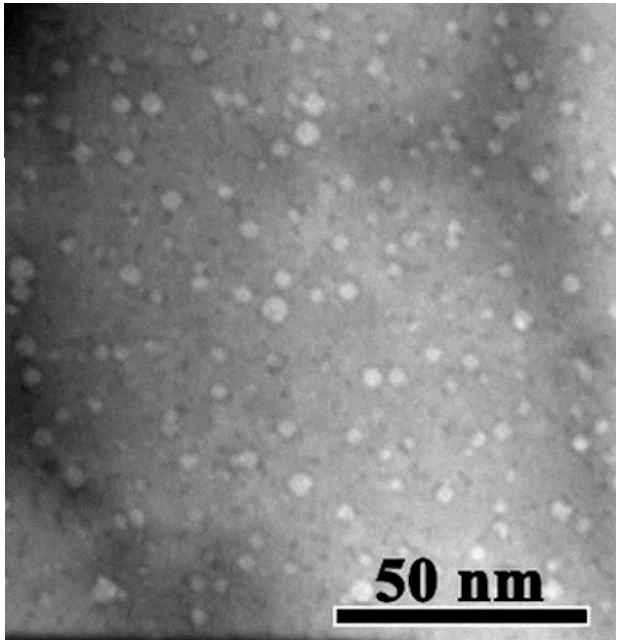
Coalescence mechanisms:

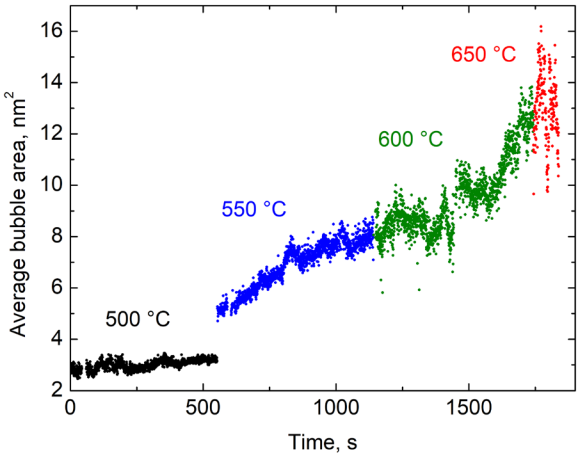
- When does fracture play a role?
- Is there a barrier to formation of a thin wall between bubbles?
- Can products be dumbbells or tubes, or just spheres?
- Can timescale of coalescence be resolved?

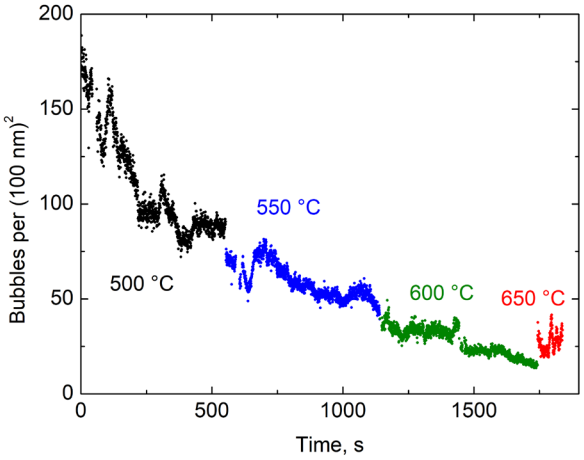
^{3}H interaction with surface atoms and vacancies could strongly affect these.

Addressable by heated-stage TEM (Taylor) and our analysis (Gibson) and modeling methods

Pd implanted with 10 keV He ions at 400 °C then heated at 550 °C







Helium release mechanisms

Coalescence with surface

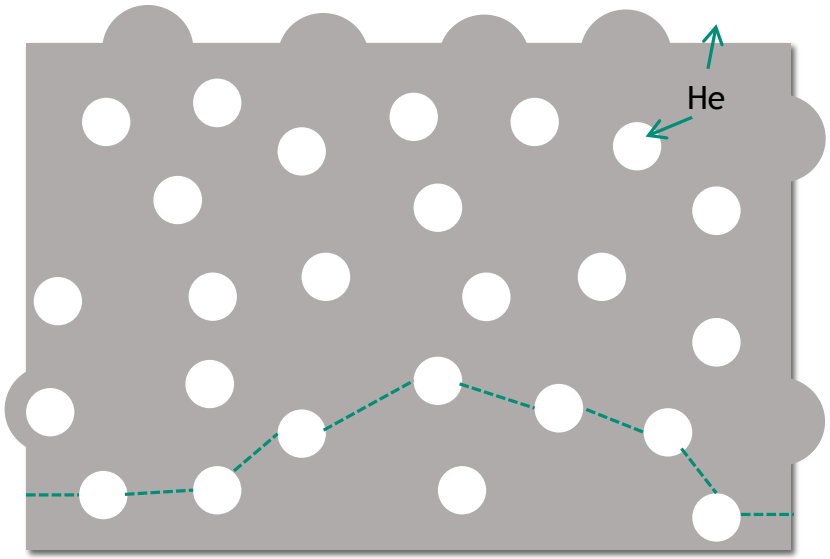
- Surface blistering may be apparent by scanning electron microscopy
- Mechanism may relate to inter-bubble coalescence

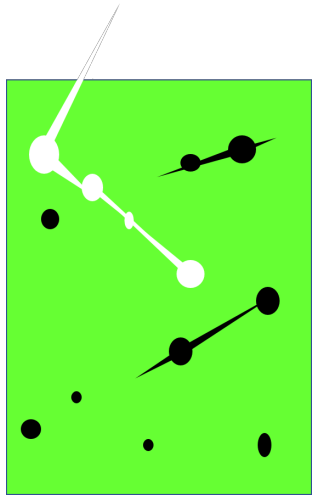
Interbubble crack propagation could cause fracture and release

- Not observed by us yet
- Relevant at lower temperatures, higher pressures?

In situ TEM mechanical tests are challenging but feasible (Hattar)

Finite element modeling can describe stress state





Summary

We have a bounded list of hypotheses for the life cycle of helium in metal tritides.

All can be addressed by current experimental and modeling capabilities.

A general and predictive model of aged metal tritide properties appears feasible.

Such a model could ultimately improve the safety and efficiency of tritium handling operations.

Acknowledgements

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