Nucleation and Growth of Helium Nanobubbles in Palladium Alloy Tritides

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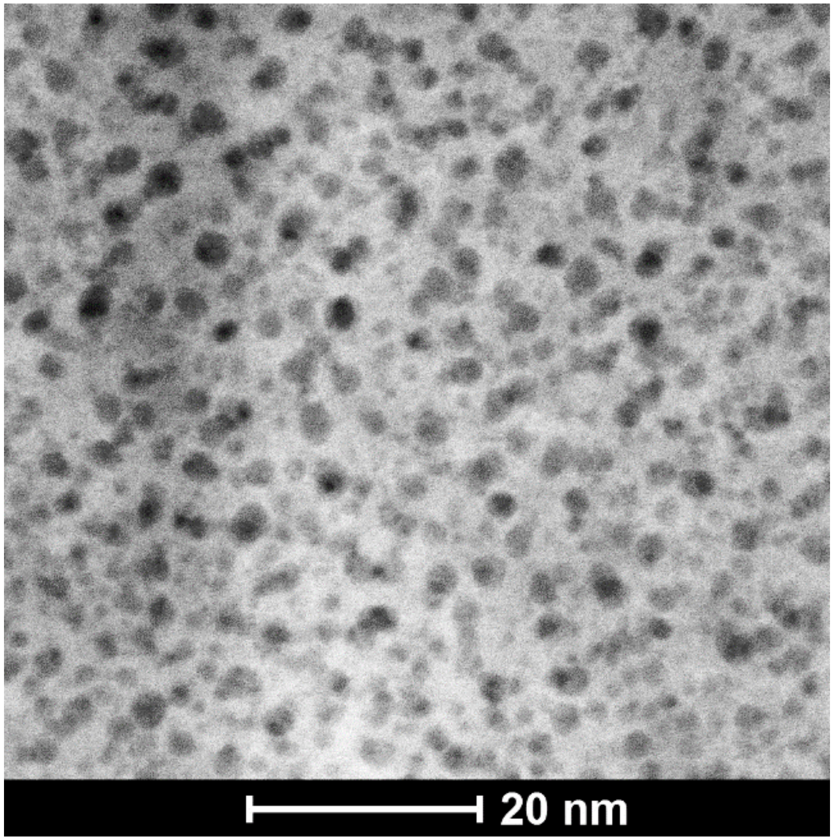
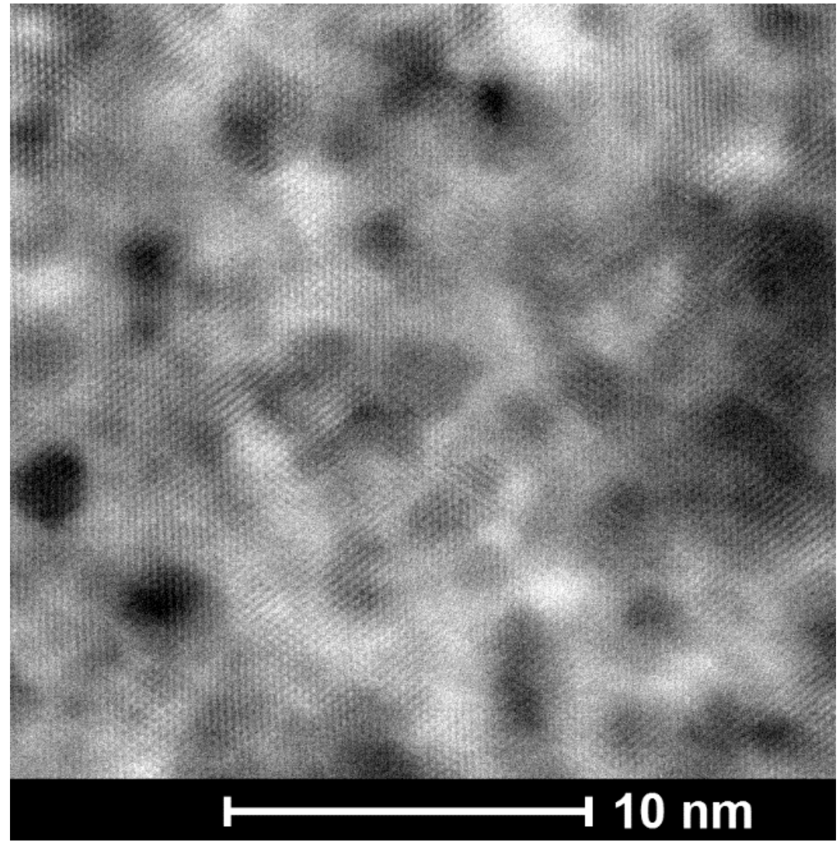
Helium nanobubbles were found in a PdNi tritide





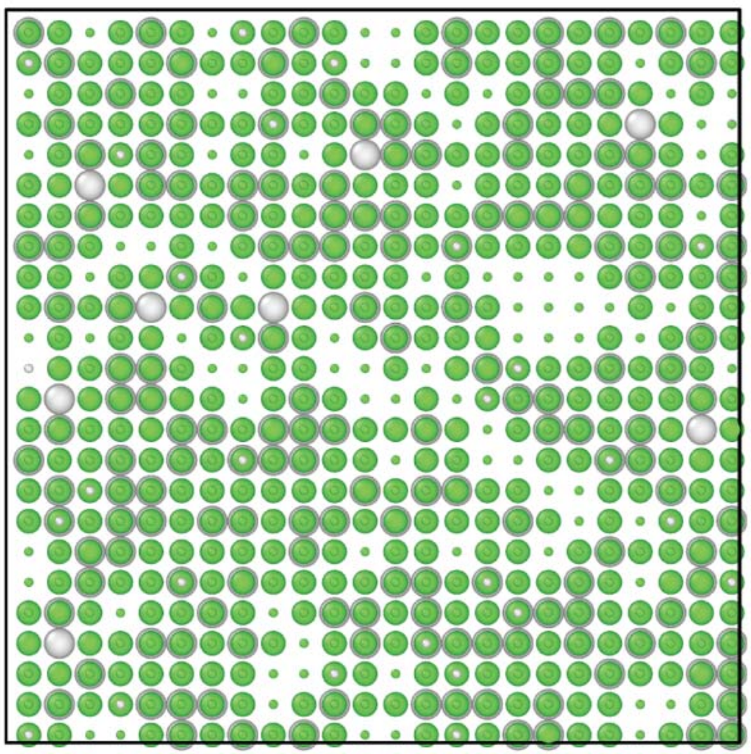
High-angle annular dark field STEM images

Thinned section of a PdNi alloy previously exposed to tritium

Bubbles appear dark

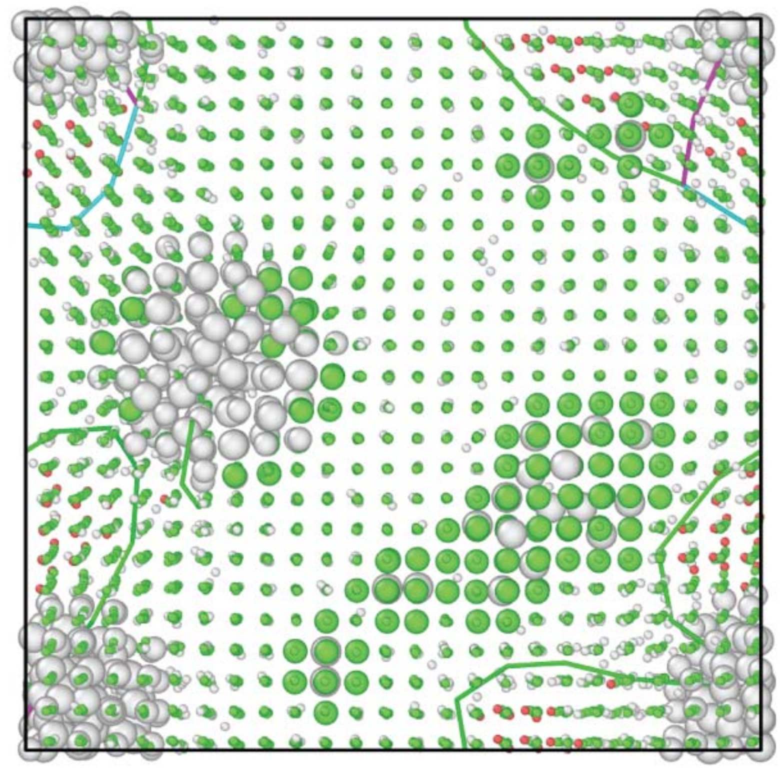
Bubbles are a few nm in diameter and spaced a few nm apart

Tritium decays to insoluble helium-3 within metal lattices



^{3}H decays to ^{3}He without damage to lattice

^{3}He occupies interstices

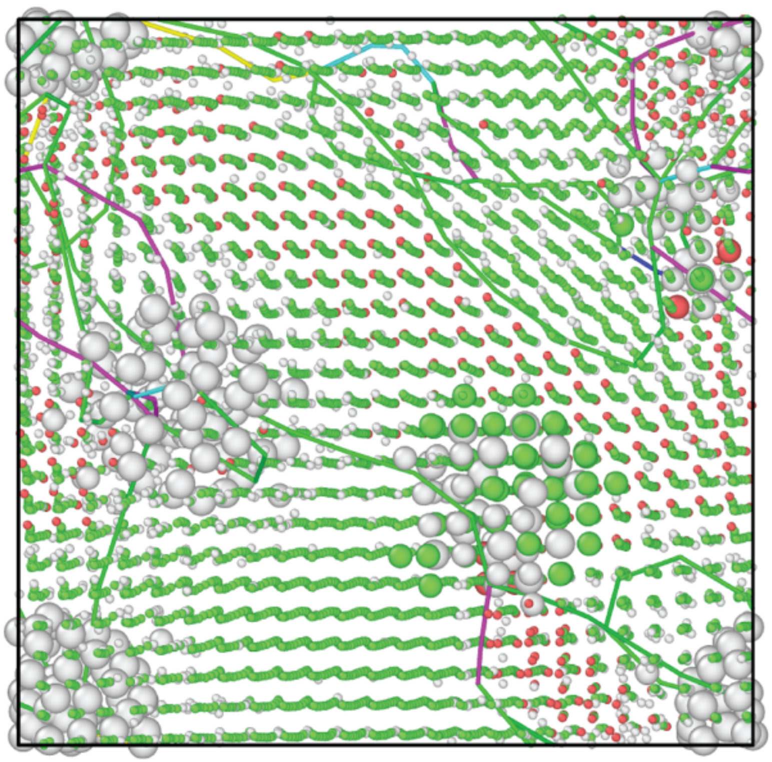


Interstitial ^{3}He diffuses rapidly

^{3}He becomes trapped at point defects

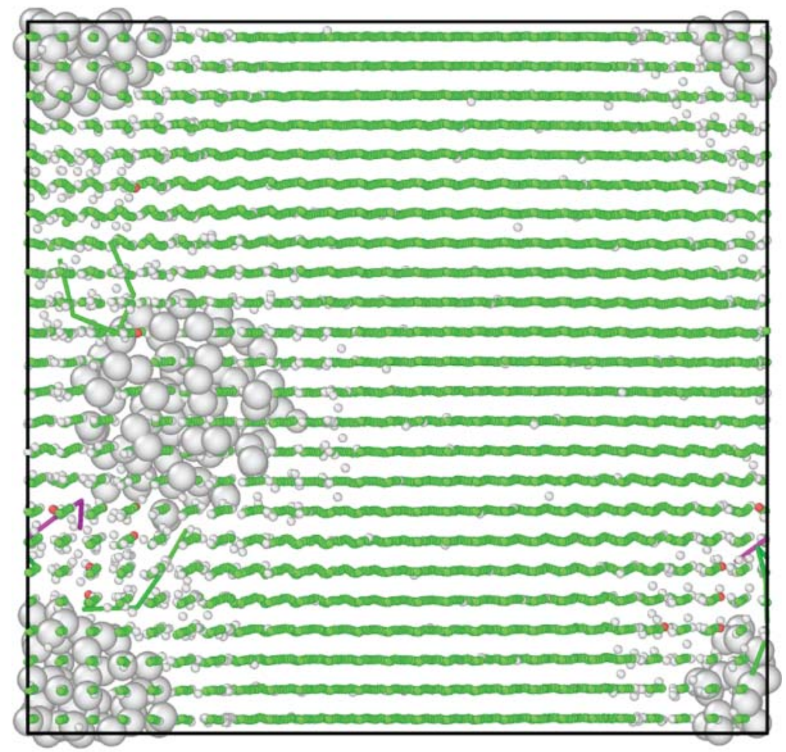
- Pd
- Pd with ^{3}He in O_h hole
- ^{3}He at lattice site
- ^{1}H

Helium-3 forms nanobubbles that cause defects in metal



^{3}He forms clusters

Clusters displace metal atoms and cause dislocations



Clusters diffuse within lattice

Clusters form bubbles that grow in volume

- Pd
- Pd with ^{3}He in O_h hole
- ^{3}He at lattice site
- ^{1}H

Open questions of helium bubble nucleation and growth

Questions

- What determines helium bubble size and spatial distribution?
- Do all helium bubbles nucleate within a narrow time range?
- What mediates bubble nucleation?

Goals

- To develop a model for helium bubble formation and evolution
- To validate model with experimental observations

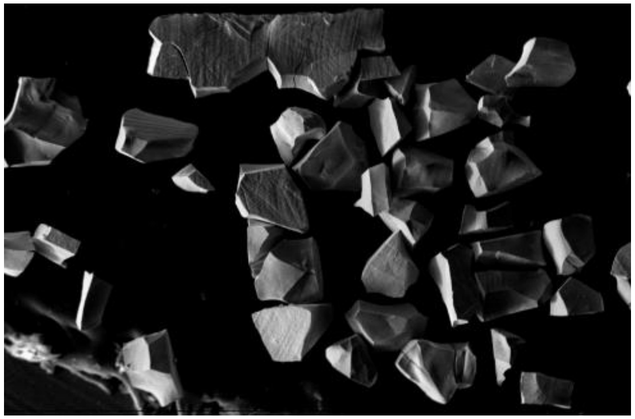
Approach

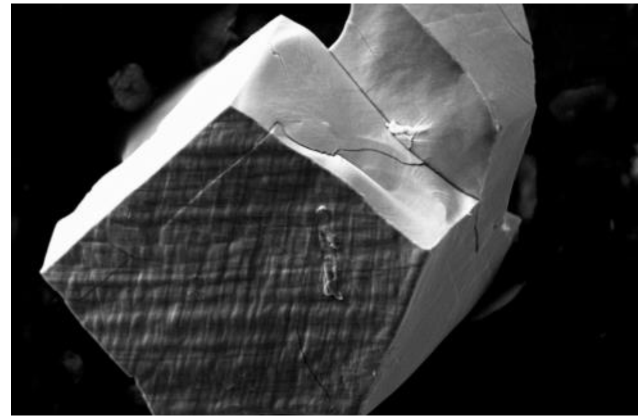
- Generate three-dimensional maps of helium bubbles trapped in metals by electron tomography
- Detect helium and measure pressure by electron energy loss spectroscopy (EELS)

Overarching aim is to develop a well-validated, comprehensive model for the nucleation, growth, and release of helium bubbles in metals

Recent prior work: (a) Cowgill, D. F. *Fusion Sci. Tech.* **2005**, *48,* 539. (b) Fabre, A.; Decamps. B.; Finot, E.; Penisson, J. M.; Demoment, J.; Thiébaut, S.; Contreras, S.; Percheron-Guegan, A. *J. Nuc. Mater.* **2005**, *342,* 101. (c) Montheillet, F.; Delaplanche, D.; Fabre, A.; Munier, E.; Thiébaut, S. *Mat. Sci. Eng. A* **2008**, *494*, 407.

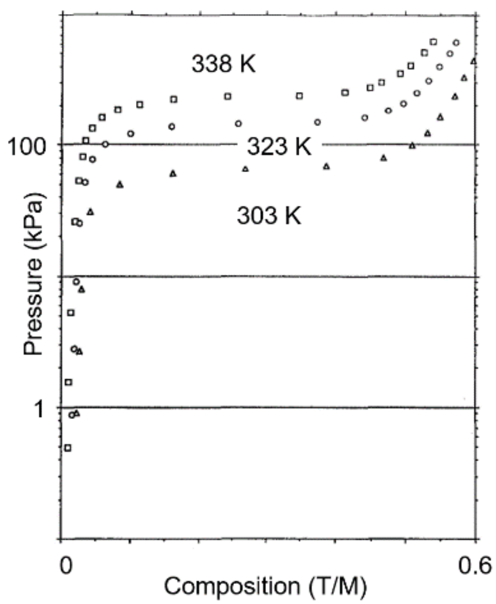
PdNi foil was exposed to tritium, aged, and decontaminated





SEM images

Tritium desorption isotherms



Sample characteristics

5 atom % Ni solid solution in Pd

Aged 3.8 years under tritium

He/Pd ratio: 0.12

Tritium removed for analysis by cycling D_2 and vacuum near room temperature

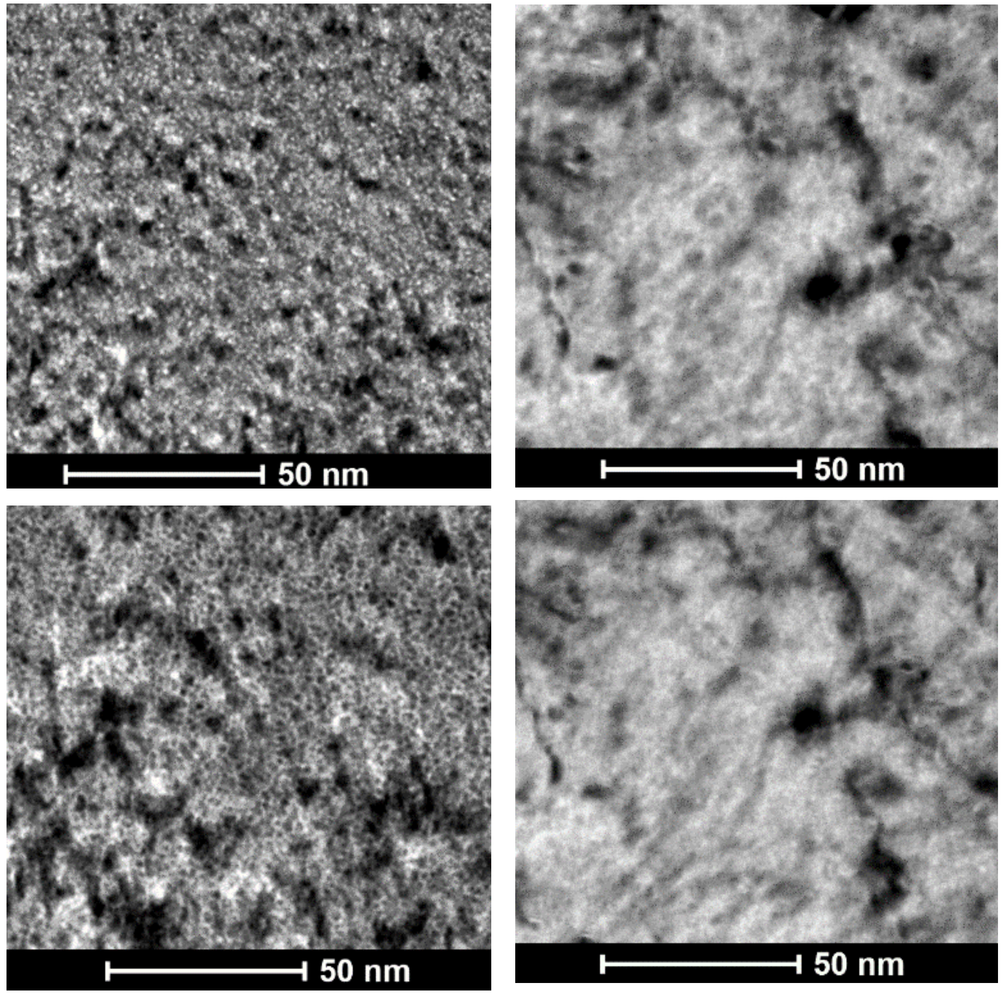
40 μCi / g by dissolution followed by liquid scintillation counting

(a) Hölder, J. S.; Wermer, J. R. *J. Alloys Compounds* **1995**, *231*, 773. (b) Shanahan, K. L. *Fusion Sci. Tech.* **2017**, *71*, 555.

Fresnel contrast seen in tritium-exposed sample but not in control

Under-focused images

Over-focused images



Tritium-exposed sample

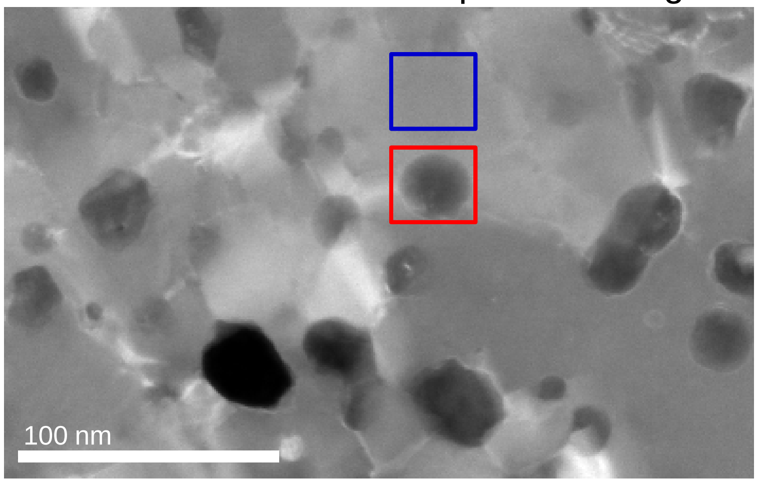
Control sample

Change in contrast with focus indicates round features (bubbles) are regions of lower density

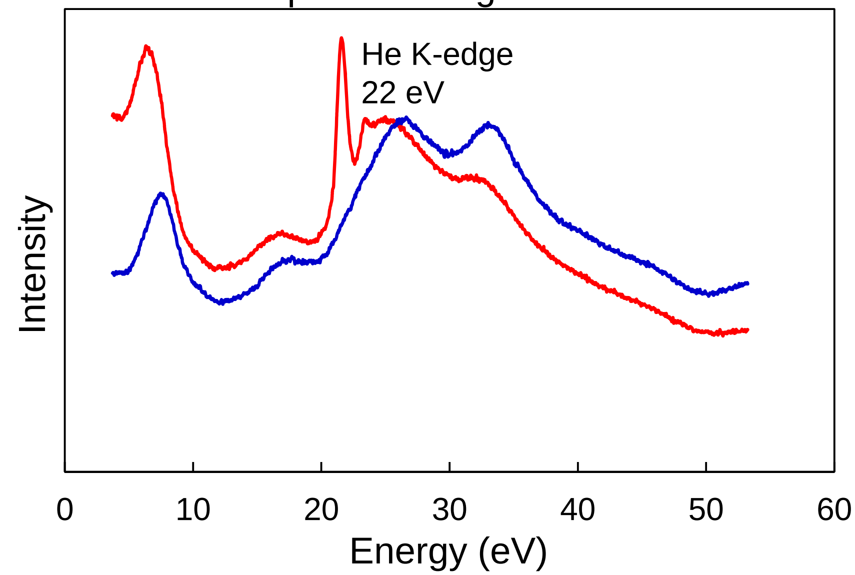
No contrast reversal occurs in the PdNi control sample that was never exposed to tritium

Electron energy loss spectroscopy detects He in He^{+} implanted Pd

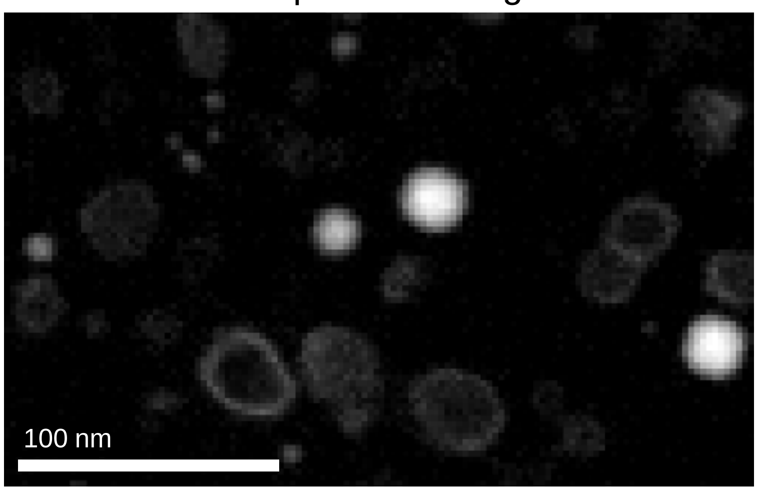
Annular dark-field STEM spectrum image



EELS spectra of regions of interest



Map of He K-edge



Pd implanted with 1 x 10^{17} helium ions / cm^2

Annealed at 600°C for 2 hours

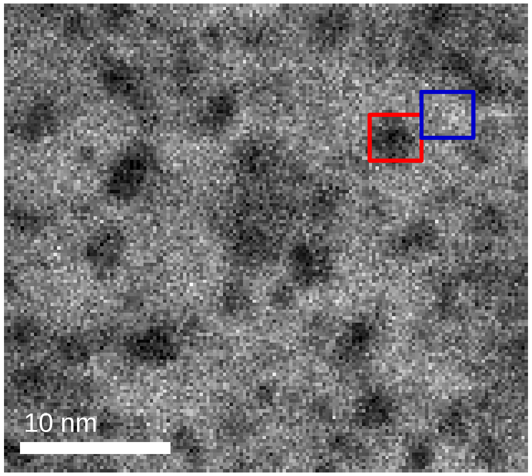
Large, sparse, low-pressure bubbles

He signal maps on to bubble locations

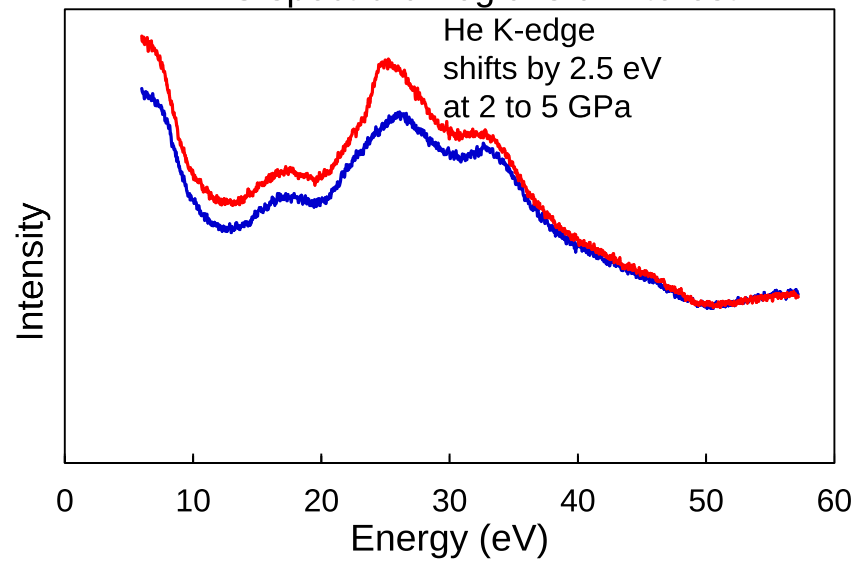
Taverna, D.; Kociak, M.; Stéphan, O.; Fabre, A.; Finot, E.; Décamps, B.; Colliex, C. *Phys. Rev. Lett.* **2008**, *100* 035301.

Electron energy loss spectroscopy detects He in tritium-exposed PdNi

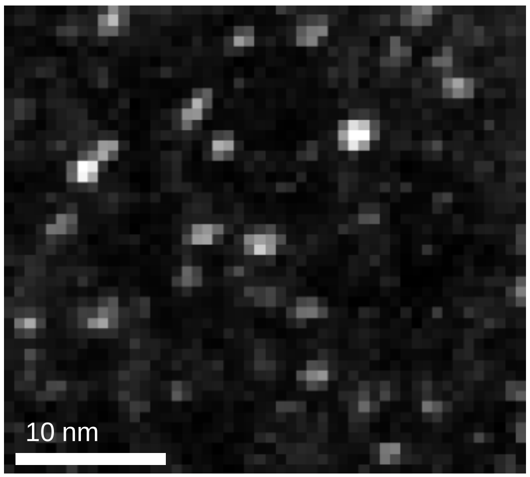
Annular dark-field STEM spectrum image



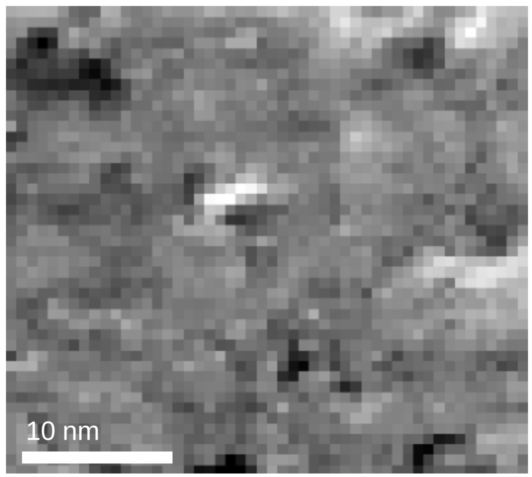
EELS spectra of regions of interest



Map of shifted He K-edge

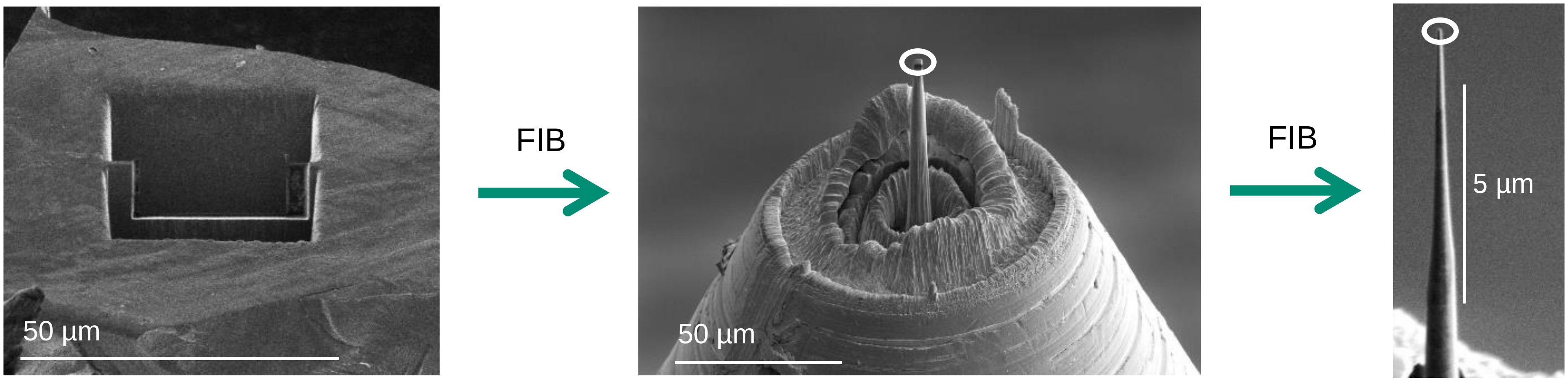


Map of Pd spectrum



Walsh C. A.; Yuan, J.; Brown. L. M. *Phil. Mag. A* **2000**, *80*, 1507.

PdNi was thinned to a tip for collection of tomography data set

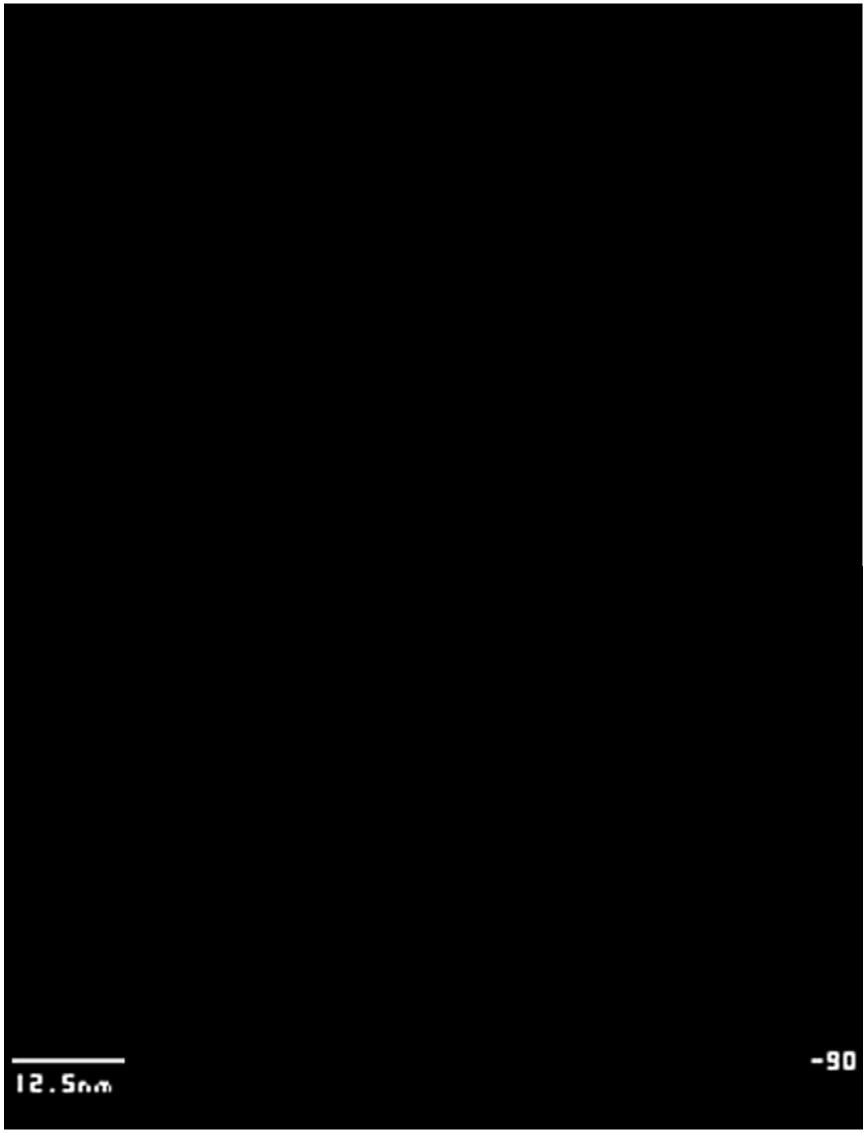


SEM images

Measurement of 3D bubble volumes and locations are needed for validation of He transport models

Specimen from PdNi particle was extracted and thinned with a focused ion beam to acquire a series of images at various angles by tilting sample

Set of images for tomographic reconstruction



Series of images in 1° increments through 140°

First set of images:

- 2D high-angle annular dark-field STEM images
- Raw images from microscope
- Helium bubbles appear dark

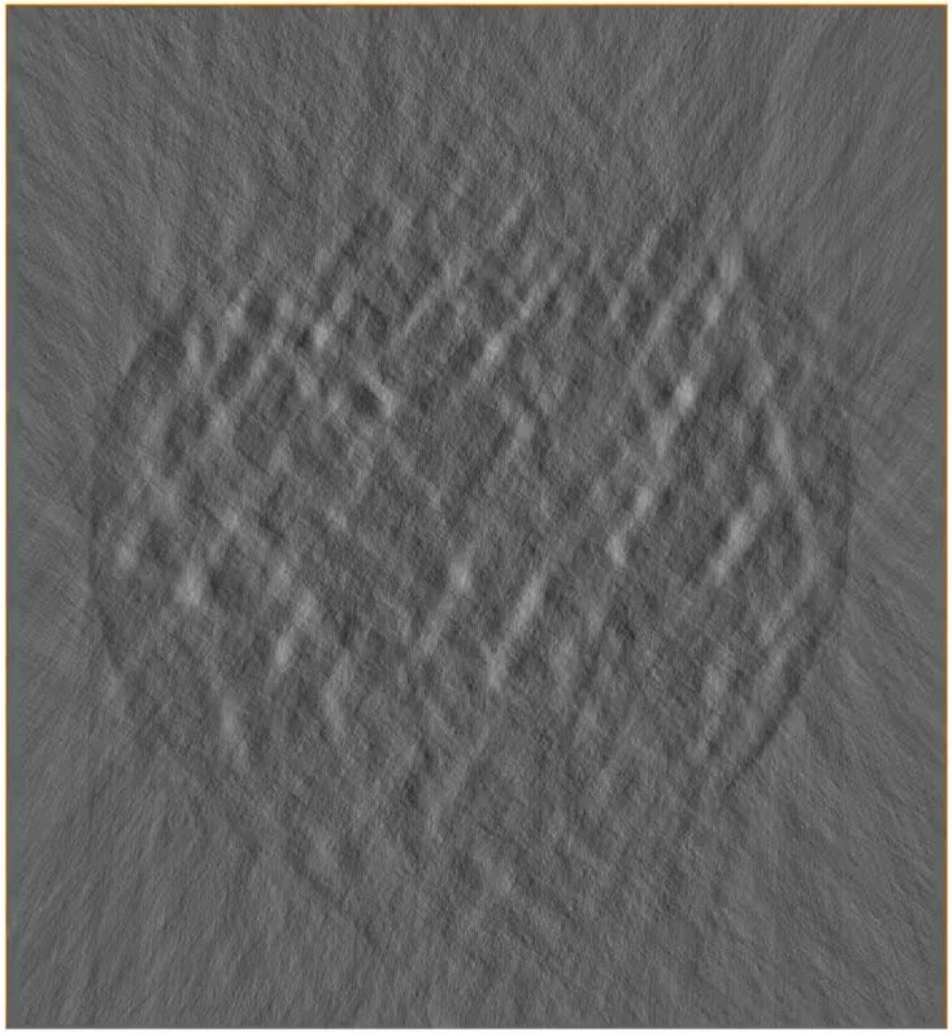
Second set of images:

- Filtered, contrast-inverted images
- Low-frequency background removed
- Basis for Simultaneous Iterative Reconstruction Technique (SIRT) algorithm

3D reconstruction of TEM tomography images

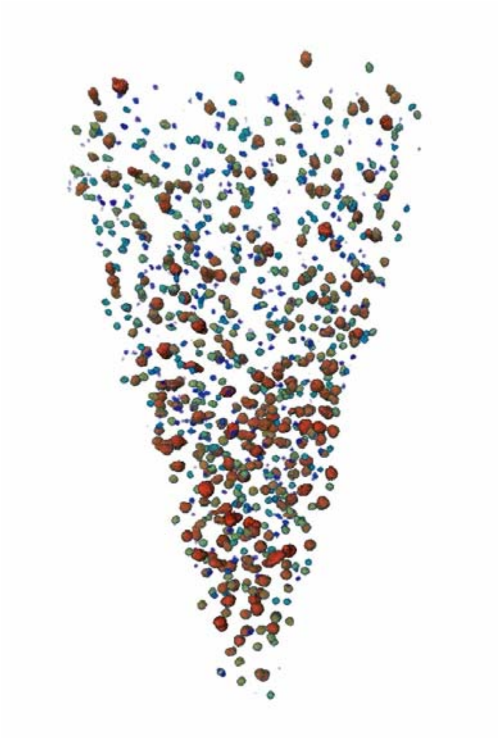
Visualization of helium bubble-impregnated PdNi tip parallel to tip axis

3D reconstruction of TEM tomography images

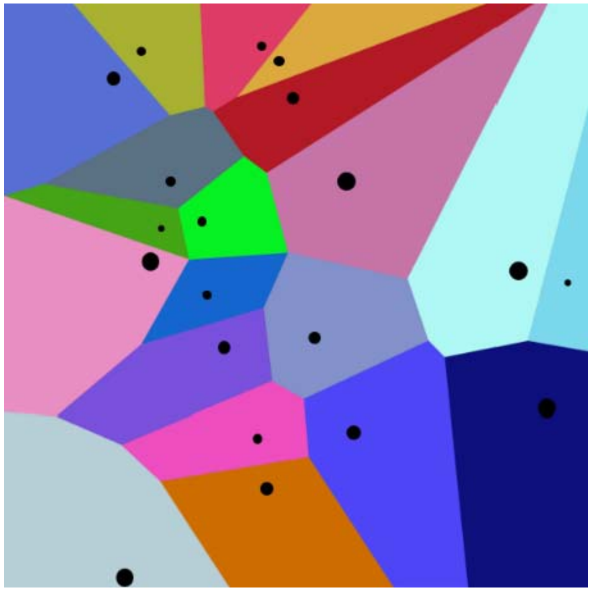


Visualization of helium bubble-impregnated PdNi tip along tip axis

Thresholding of reconstruction yields discrete bubbles of differing sizes



3D map of bubbles within PdNi tip



2D Voronoi diagram

1248 bubbles

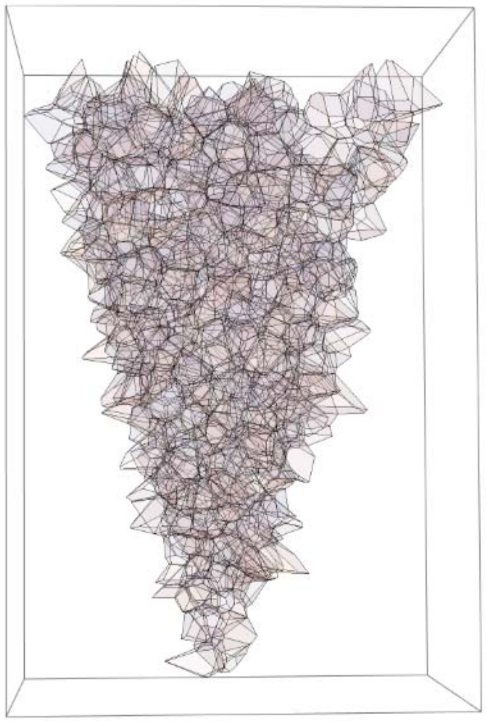
Colored from largest (red) to smallest (blue)

Capture volume is described by Voronoi tessellation

Larger capture volume → larger bubble?

Fortune, S. *Handbook of Discrete and Computational Geometry,* 2nd ed.; Goodman, J. E.; O'Rourke, J., Eds.; Chapman & Hall/CRC: Boca Raton, FL, 2004; pp 514.

Spacing of bubbles yields capture volumes of various sizes



Outlines of Voronoi polyhedra formed by bubbles

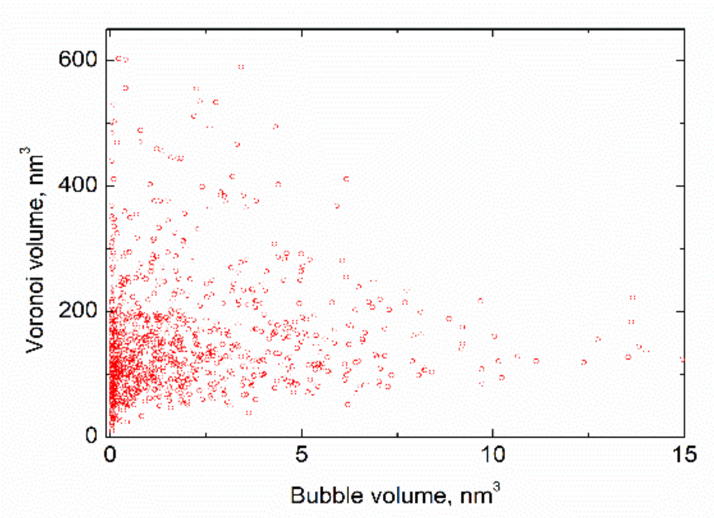
Voronoi polyhedra expanded for visualization

PdNi tip was divided into polyhedra based on distribution of bubbles

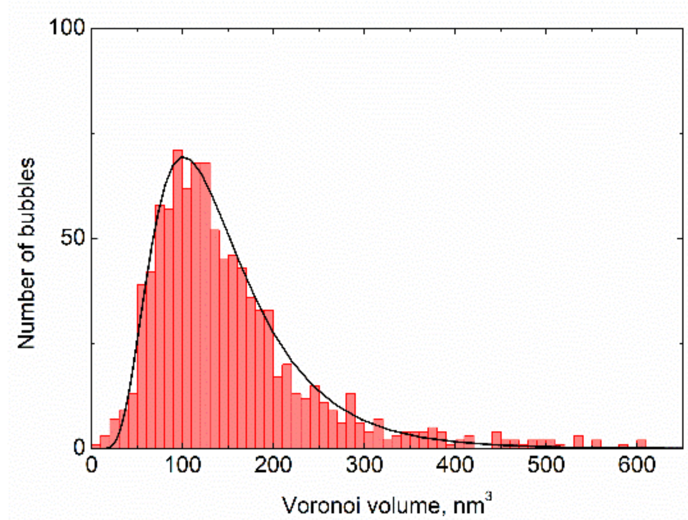
Each bubble has a corresponding polyhedron representing its capture volume

Experimental results differ from predictions of capture volume theory

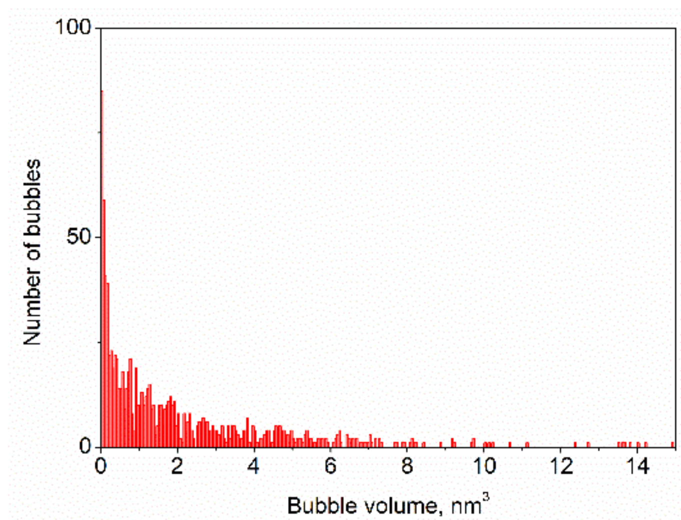
Capture volume and bubble volume: no correlation



Voronoi volume distribution: log-normal



Bubble volume distribution: not log-normal



Theory suggests:

- Capture volume and bubble volume adhere to log-normal distributions
- Capture volume determines bubble volume

Conclusions

What determines helium bubble size distribution?

No correlation between capture volume and bubble volume → Bubble size is not primarily determined by proximity to other bubbles

What determines helium bubble spatial distribution?

Capture volume distribution is log-normal → Nucleation is spatially random and homogeneous

Do all helium bubbles nucleate within a narrow time range?

Bubble size distribution is not log-normal → Raises possibility of late nucleation of bubbles

Acknowledgements

Sandia National Lab, CA team

Dave Robinson | Norm Bartelt | Josh Sugar | Xiaowang Zhou | Warren York | Suzy Vitale

Sandia National Lab, NM collaborators

Savannah River National Lab collaborators

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Work at Savannah River National Laboratory was performed under contract number DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).