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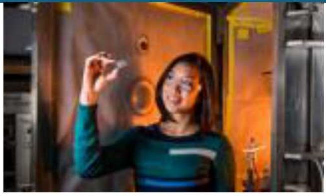
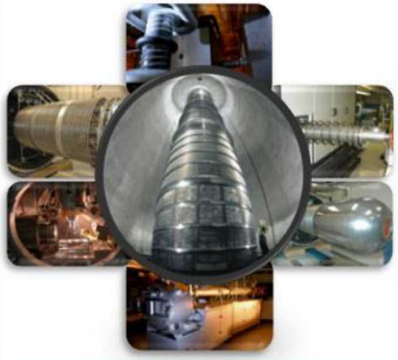
Sandia National Laboratories

SAND2018-9093C

Direct Comparison of Helium Aging in Ion Implanted and Tritium Loaded Materials





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CAARI

25th International Conference on the Application of Accelerators in Research and Industry
August 12th - 17th, 2018
Grapevine, Texas

U.S. DEPARTMENT OF ENERGY NNSA

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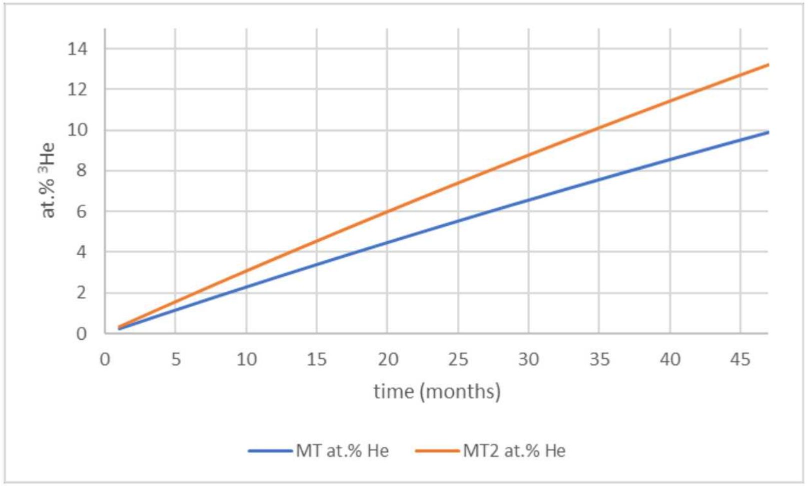
Outline

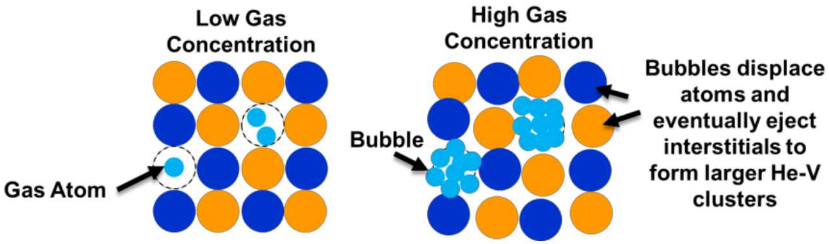
- Background
- Thermal aging of He implanted Pd
- Thermal aging of tritium aged PdNi
- He implantation into Er
- Thermal aging of aged ErT_2

Solid-State Tritium Storage Materials

- Typically metal hydrides
- Tritium β-decays with a half-life of 12.3 years, releasing ^{3}He into the lattice.
- Plot of at.% He in MT and MT_2 vs. time



- He accumulates into bubbles in the lattice

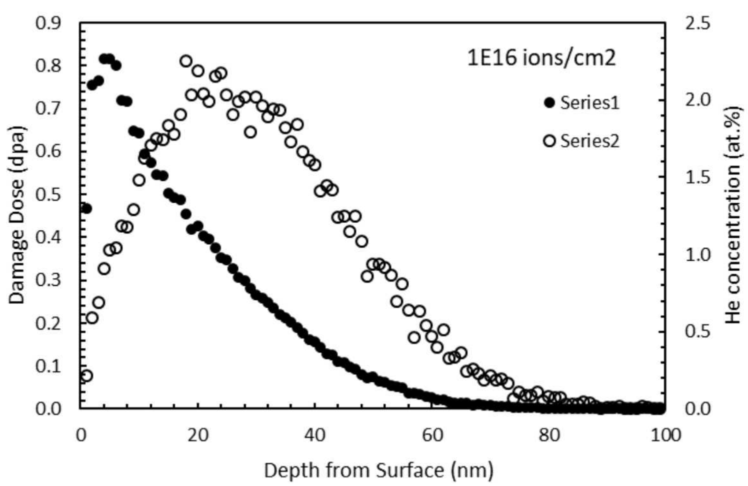


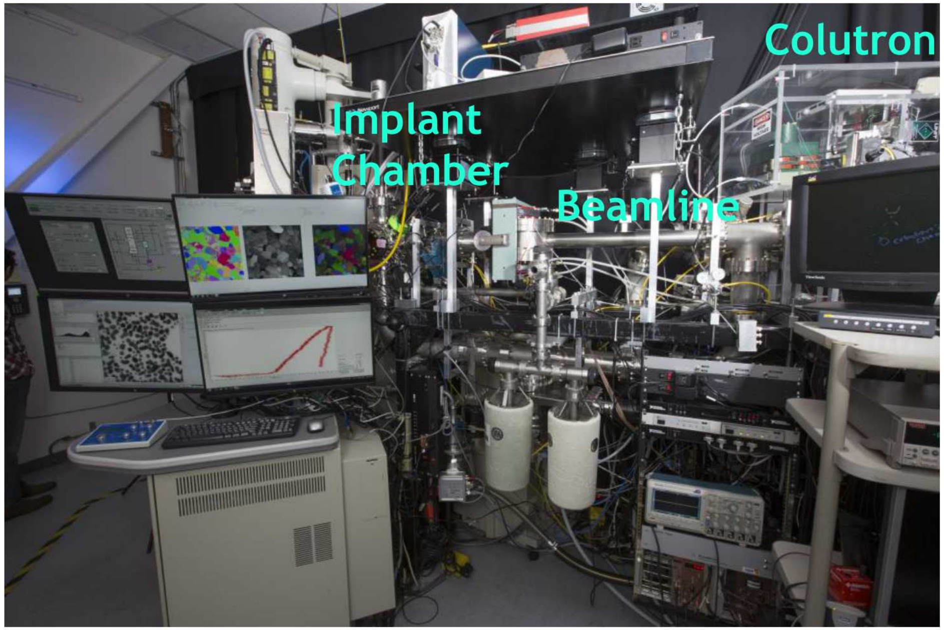
- Knowledge of bubble nucleation, growth, and He release mechanisms are required for predictive aging models. Most of these mechanisms are not well understood.

Different Microstructures are Expected from He Accumulation from to ^3H Decay vs. He Implantation into Metals

- Tritium β-decay induces no displacement damage; the ^3He is released with a maximum energy of 3.4 eV and the β-particle has a maximum energy of 18.6 keV.
- Palladium or Erbium tritide samples were aged either at SRNL or SNL. FIB lift-outs of aged samples were prepared at either SNL or PNNL.
- Helium implantation results in displacement damage except at very low energies:
  - <280 eV for Pd
  - <430 eV for Er
- Helium implantations in this work were done in-situ inside a TEM using 10 keV He, which implants entirely within a 100 nm thick TEM sample.

SRIM profile for Pd

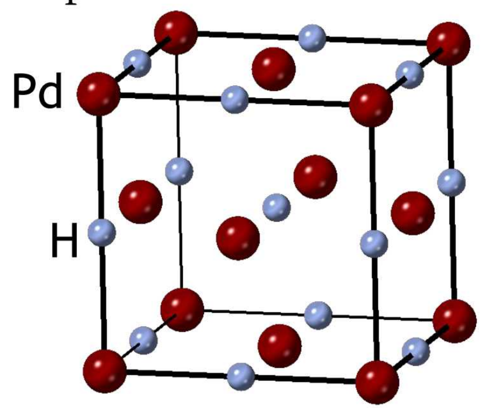


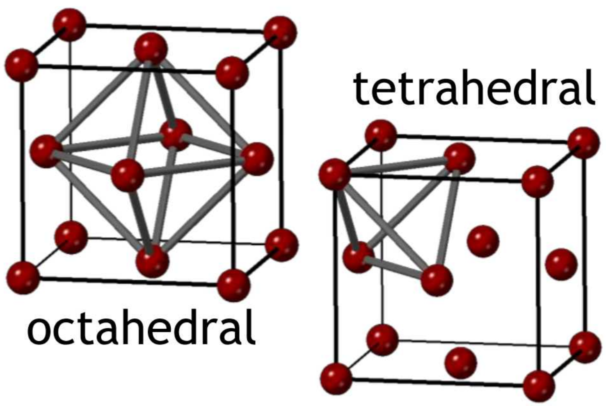


Palladium and palladium hydride both have a face-centered cubic crystal structure

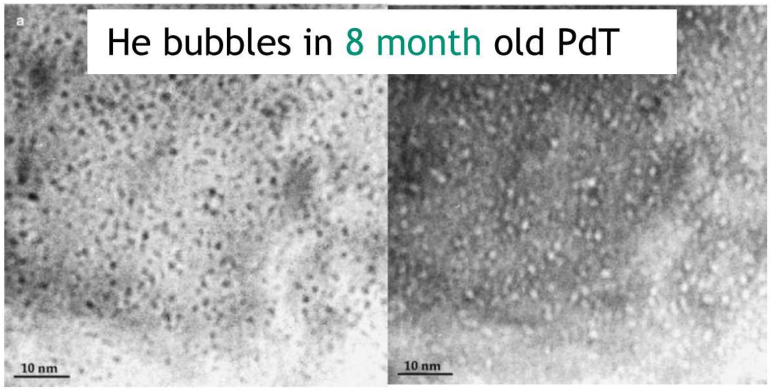
- Hydrogen resides in the octahedral sites in PdH, causing no phase transformation but a slight lattice expansion

PdH is not fully stoichiometric. Hydrides close to $PdH_{0.6}$.





- Tritium β-decays to ^{3}He, which likely either remains in the octahedral site, or moves to the tetrahedral site
- Models predict that ^{3}He remains in the octahedral interstitial site and diffuses by octahedral → tetrahedral → octahedral diffusion
- Previous work:



Fabre et al, JNM 342 (2005) 101-107

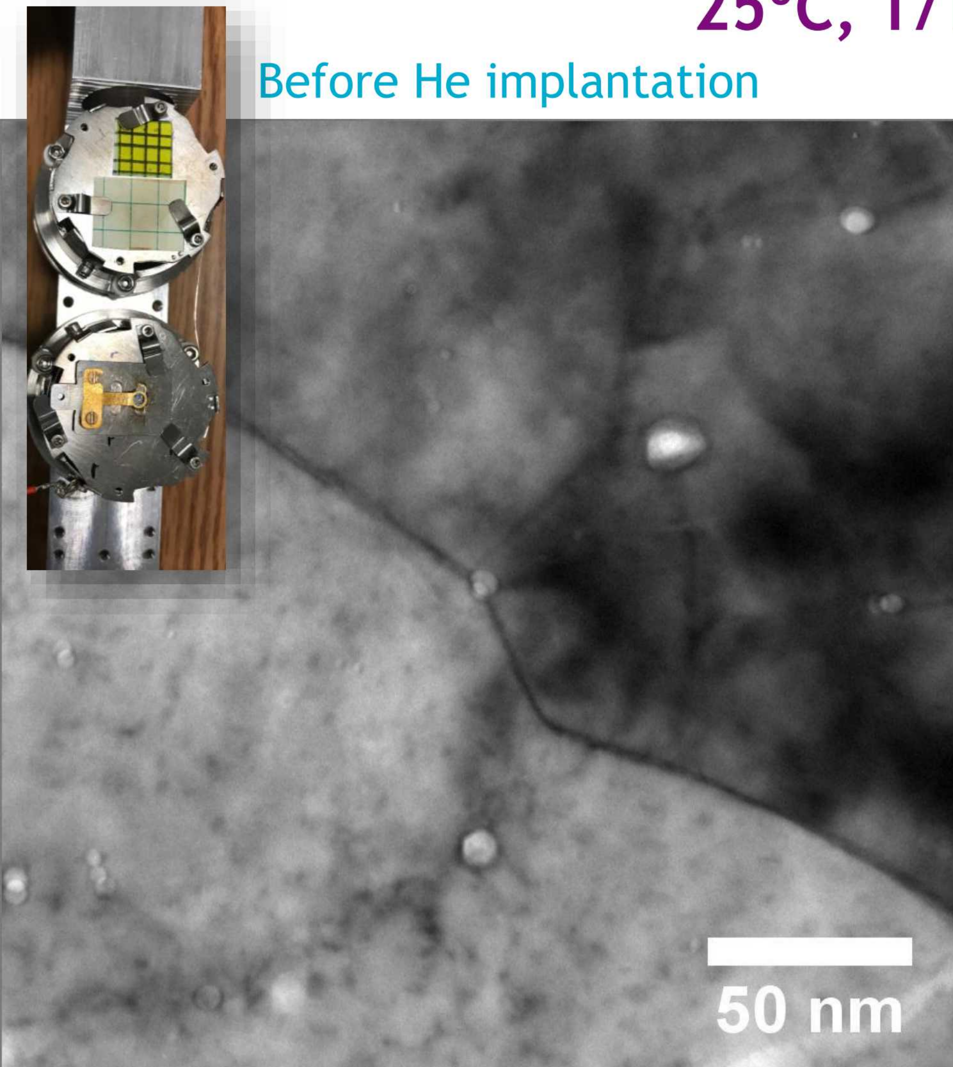
Outline

- Thermal aging of He implanted Pd
- Thermal aging of tritium aged PdNi
- He implantation into Er
- Thermal aging of aged ErT_2

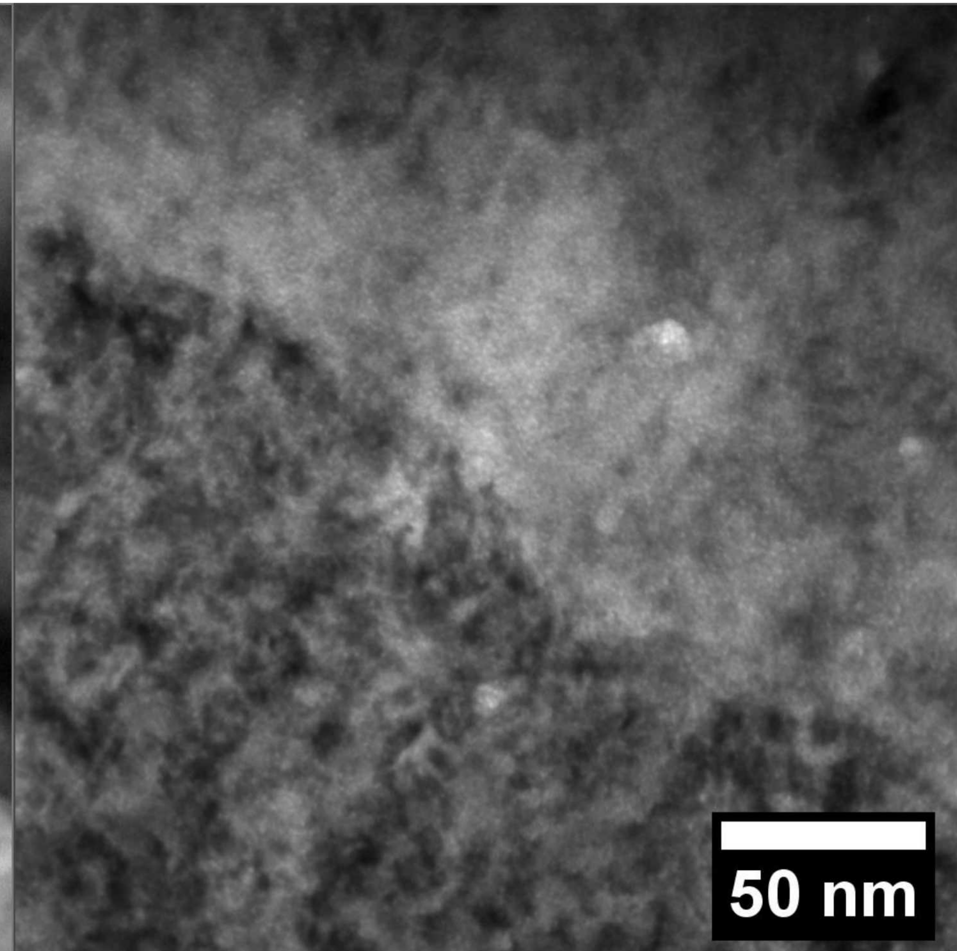
Helium implantation into palladium resulted in temperature dependent microstructures

25°C, $T/T_m = 0.16$

Before He implantation



After He implantation to ~6.9×10^{16} He/cm^2

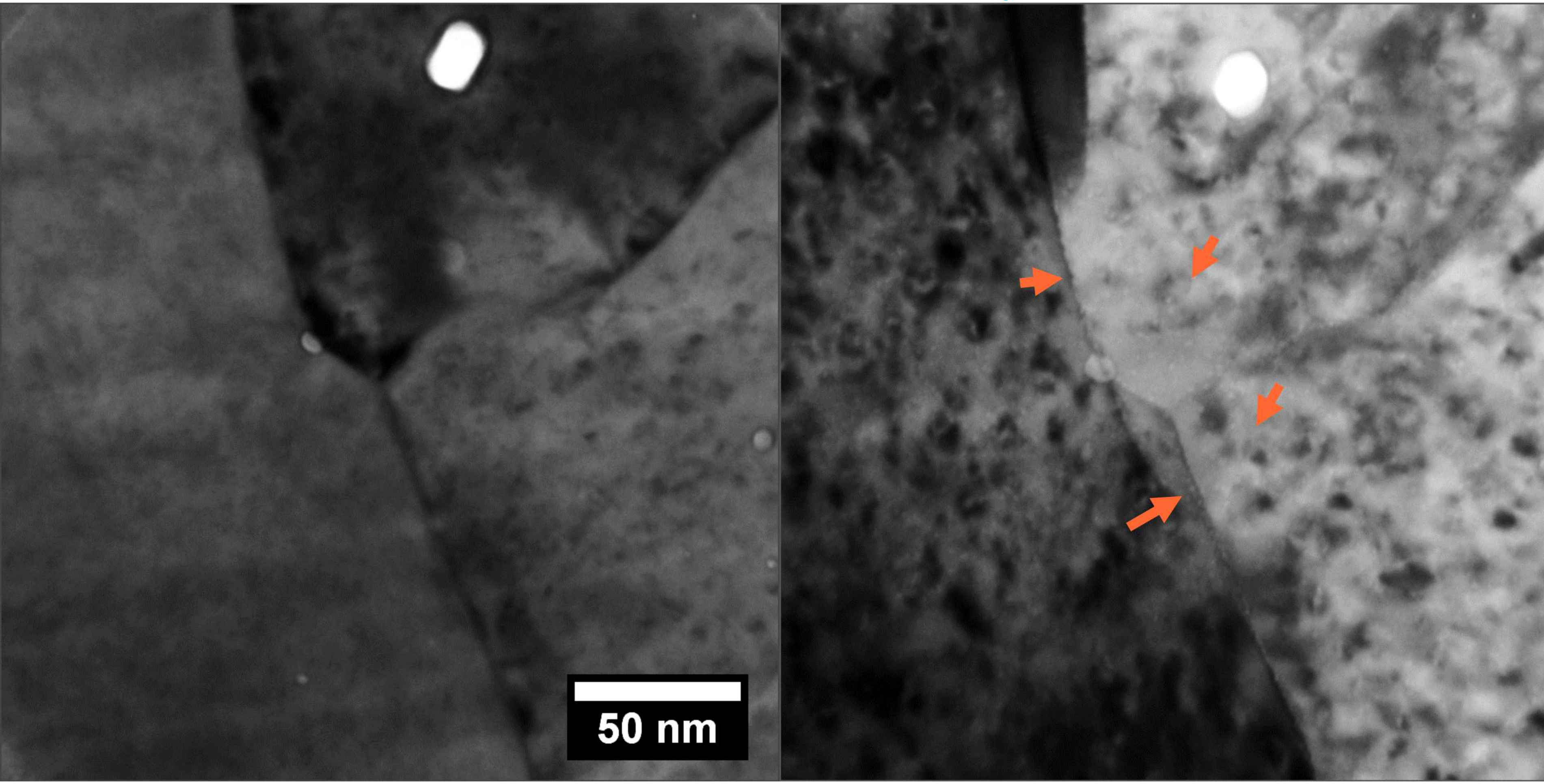


- Indicates very little He diffusion before trapping in lattice
- 5.6 dpa, 14 at.% He

Helium implantation into palladium resulted in temperature dependent microstructures

250°C, $T/T_m = 0.29$

Pristine Material | After He implantation to ~3.3×10^{18} He/cm^2

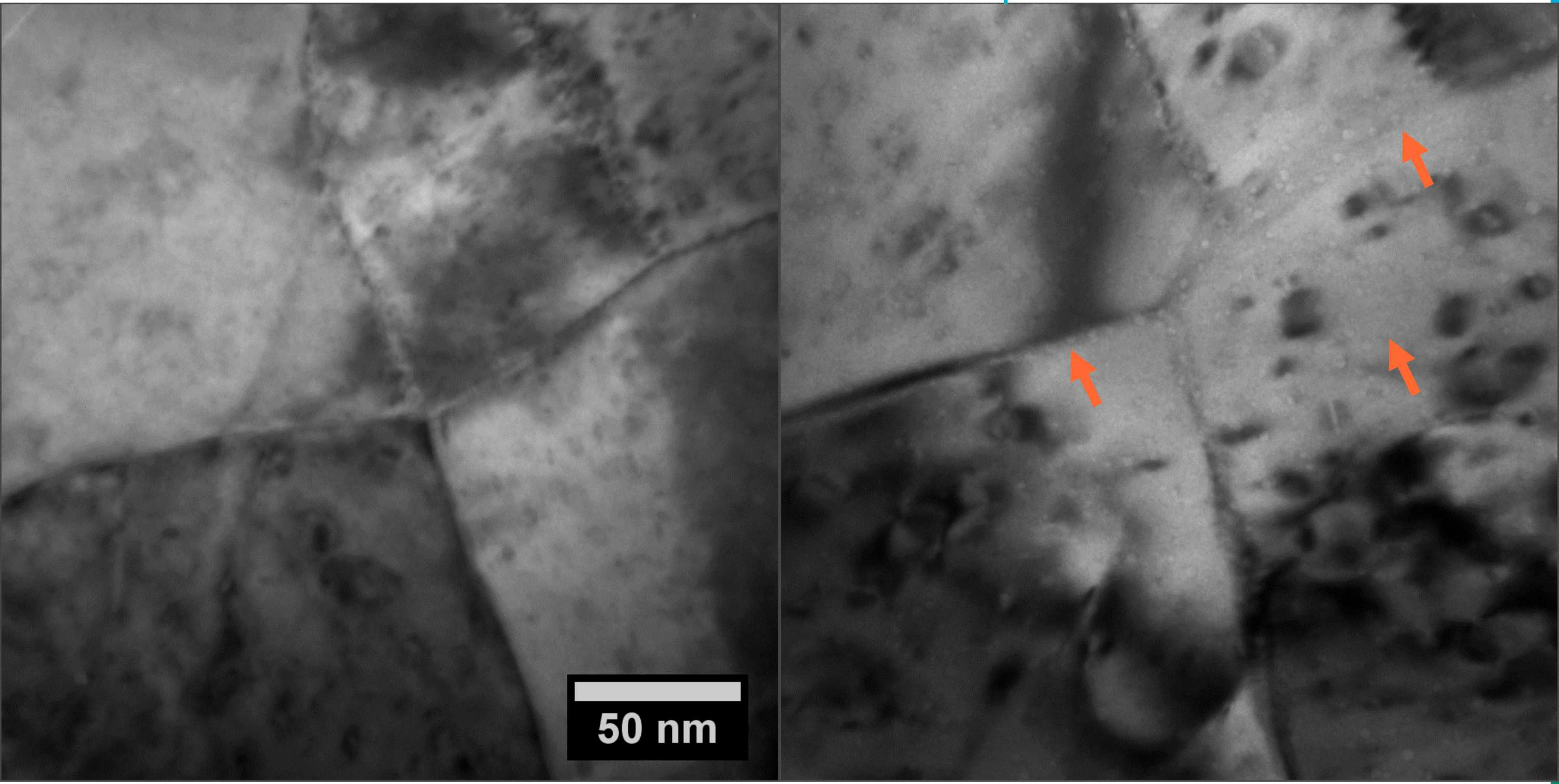


- Cannot observe early nucleation stages in the TEM because bubbles are < 1 nm in diameter
- Preferential GB nucleation → diffusion before trapping/bubble nucleation

Helium implantation into palladium resulted in temperature dependent microstructures

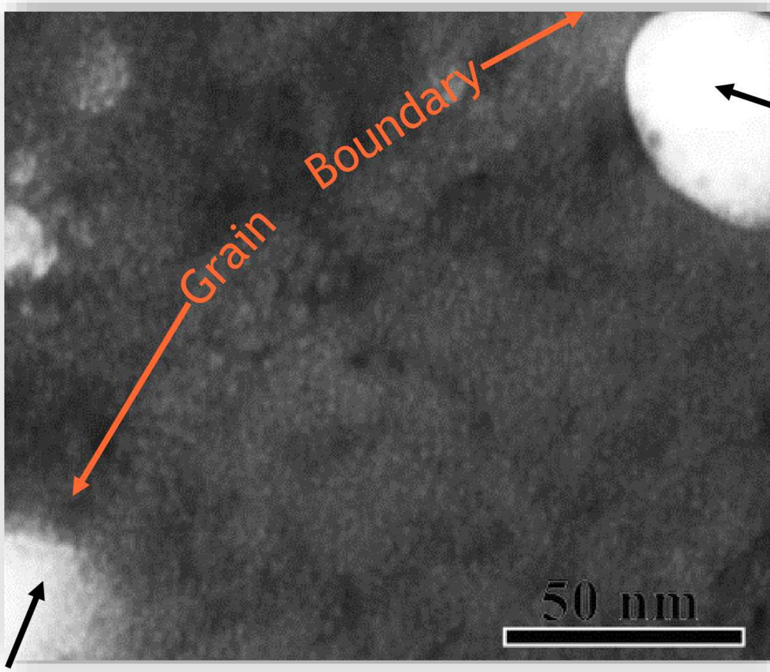
400°C, $T/T_m = 0.37$

Pristine Material | After He implantation to ~3.6×10^{18} He/cm^2



Cavities evolved into faceted structures during in-situ annealing of the sample implanted at room temperature

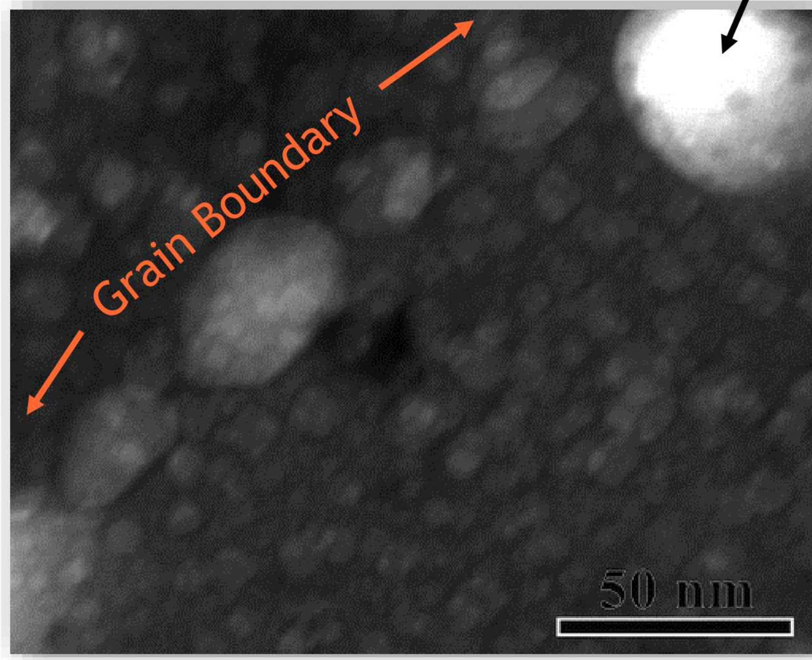
In-situ anneal @ 350°C



Pre-existing void

Pre-existing void

Pre-existing void

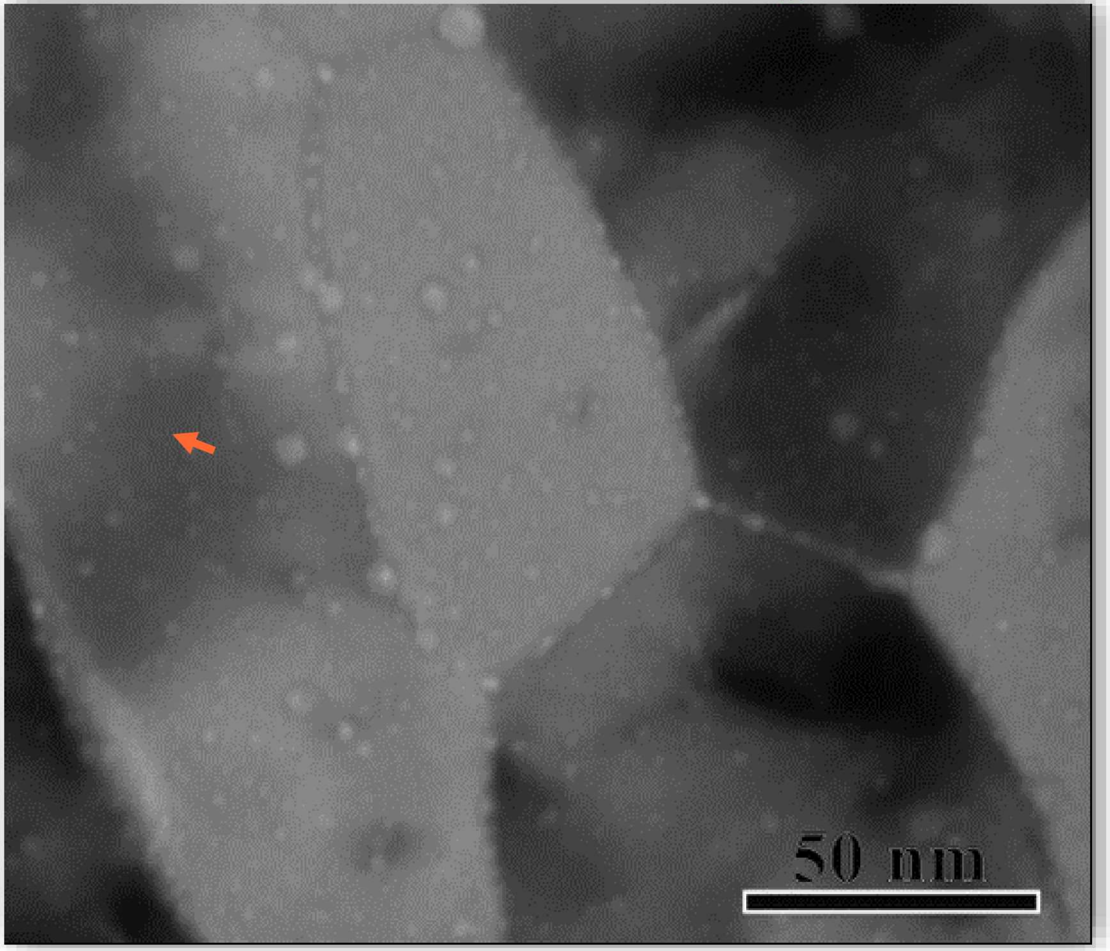


In-situ anneal @ 450°C

- Blisters form at boundaries by absorbing nearby cavities
- Large faceted cavities form inside the grains by absorbing smaller bubbles and possibly He from the matrix
- Blisters eventually burst, leaving behind a denuded zone at the boundary. Material remains in-tact.

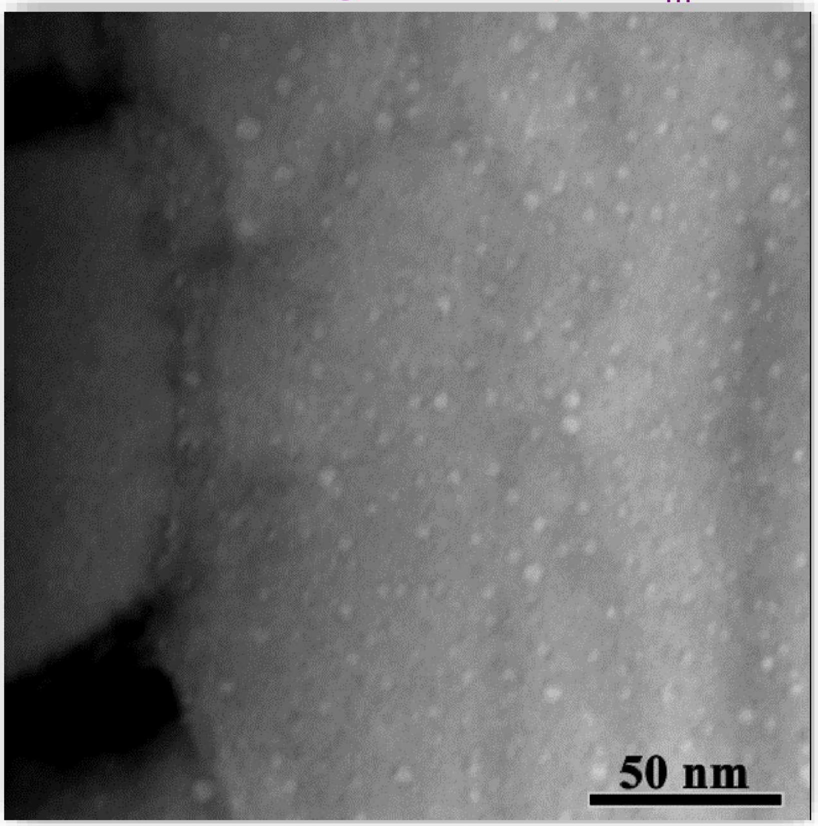
After 250°C implantation with a low fluence of helium, growth occurred due to bubble coalescence under annealing

In-situ annealing at 500°C, T/T_m = 0.42

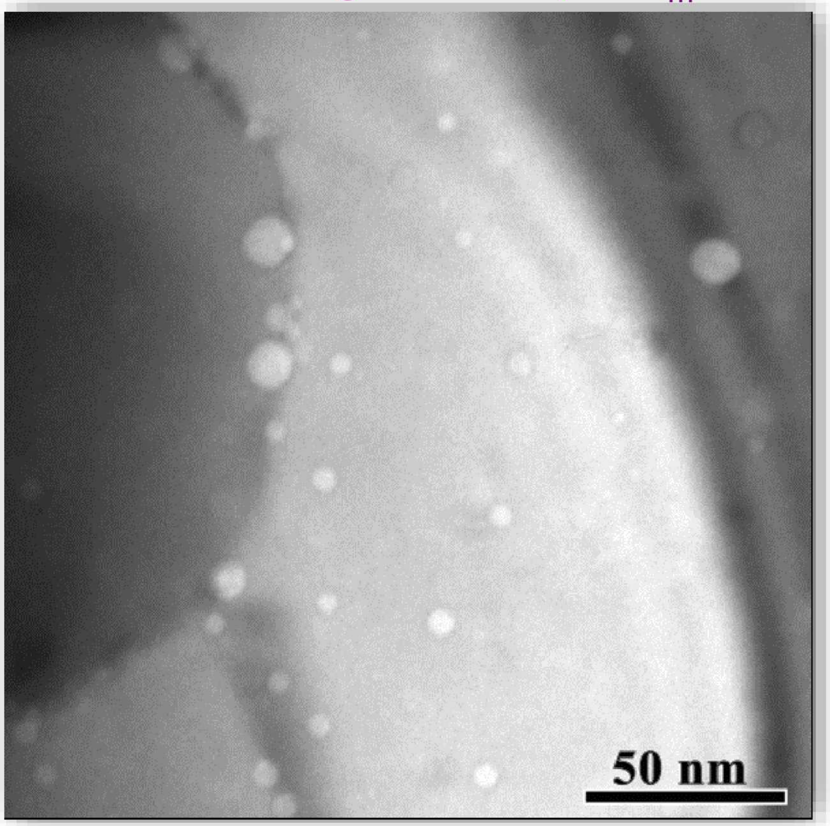


After 400°C implantation with a low dose of helium, growth occurred due to bubble coalescence under annealing

In-situ annealing at 550ºC, $T/T_m = 0.45$



In-situ annealing at 700ºC, $T/T_m = 0.53$



- Bubble growth by bubble migration and coalescence
- Bubbles remain tied to boundaries during grain growth and appear to pin boundaries in some cases
- Some bubbles appear to be strongly trapped inside grains (e.g. at defects)

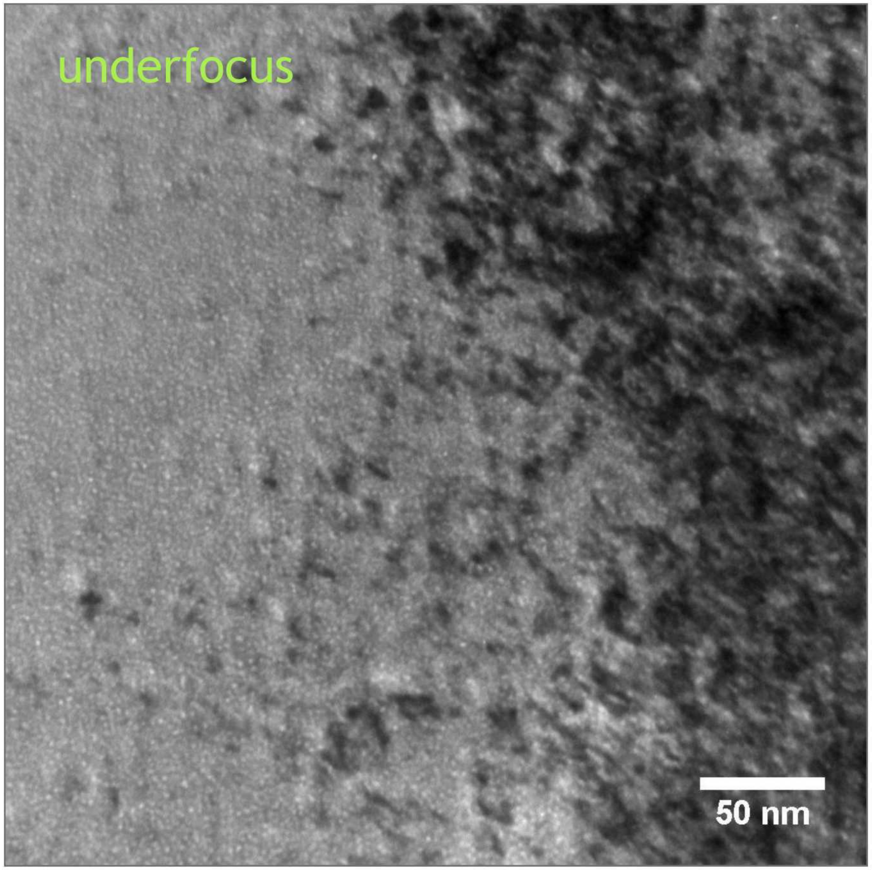
Outline

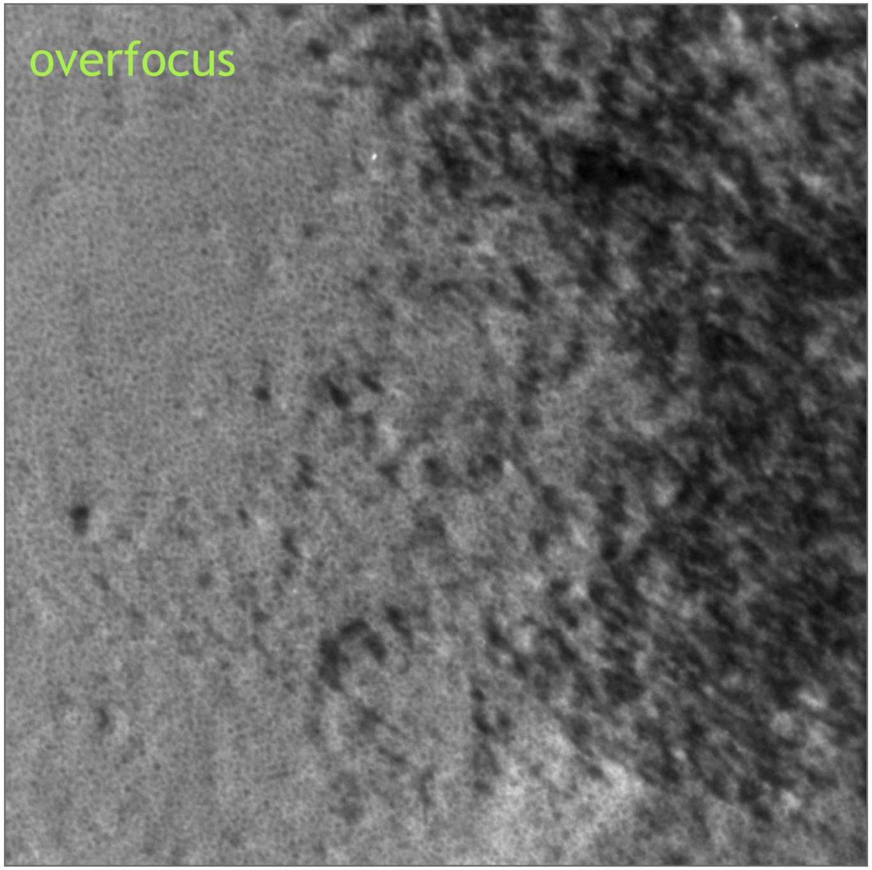
- Thermal aging of He implanted Pd
- Thermal aging of tritium aged PdNi
- He implantation into Er
- Thermal aging of aged ErT_2

A palladium-nickel alloy was aged under tritium for 3.8 years

- Palladium-5% Nickel alloy was tritiated and aged for 3.8 years at SRNL
- Estimated 12 at.% ^{3}He

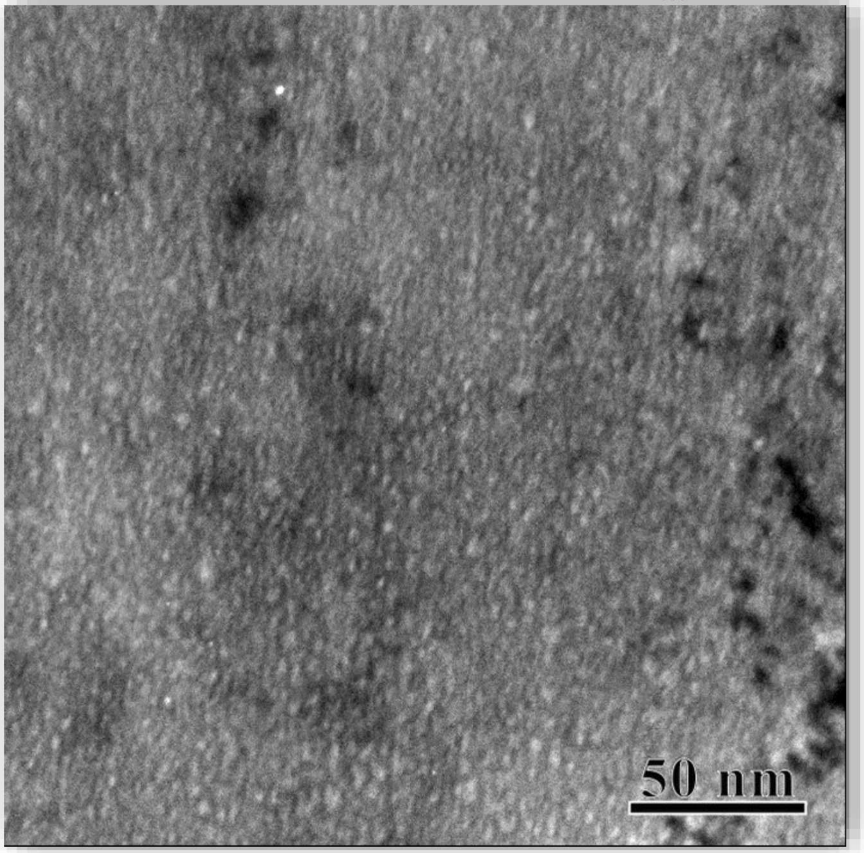
A high density of small, uniformly distributed ^{3}He bubbles (~1.5 nm in diameter) were present in the aged material



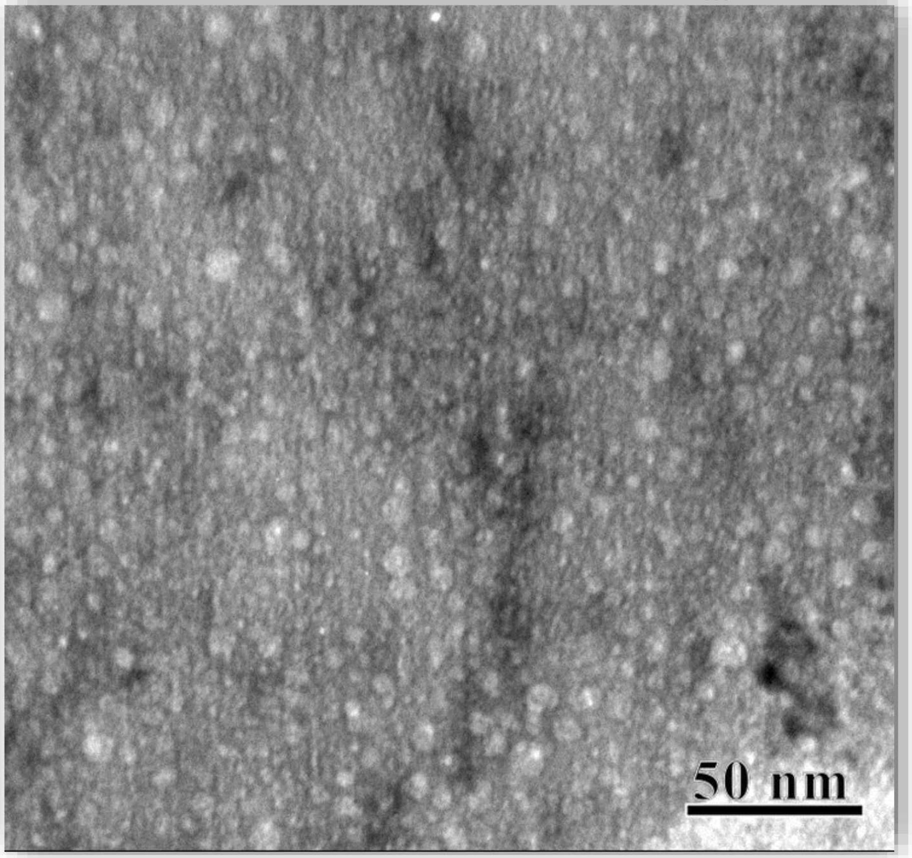


Bubbles began to grow @ 350°C during in-situ annealing aged PdNi sample, and became faceted @ 400°C

In-situ annealing at 350ºC, $T/T_m = 0.34$



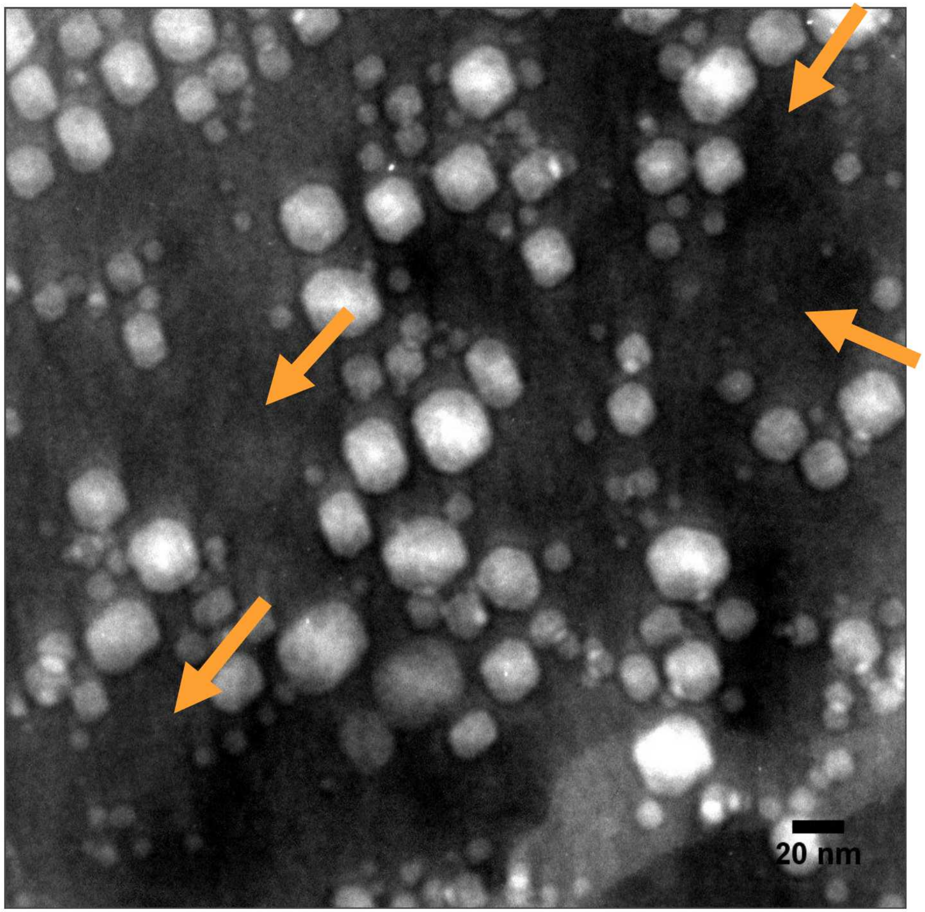
In-situ annealing at 400ºC , $T/T_m = 0.37$

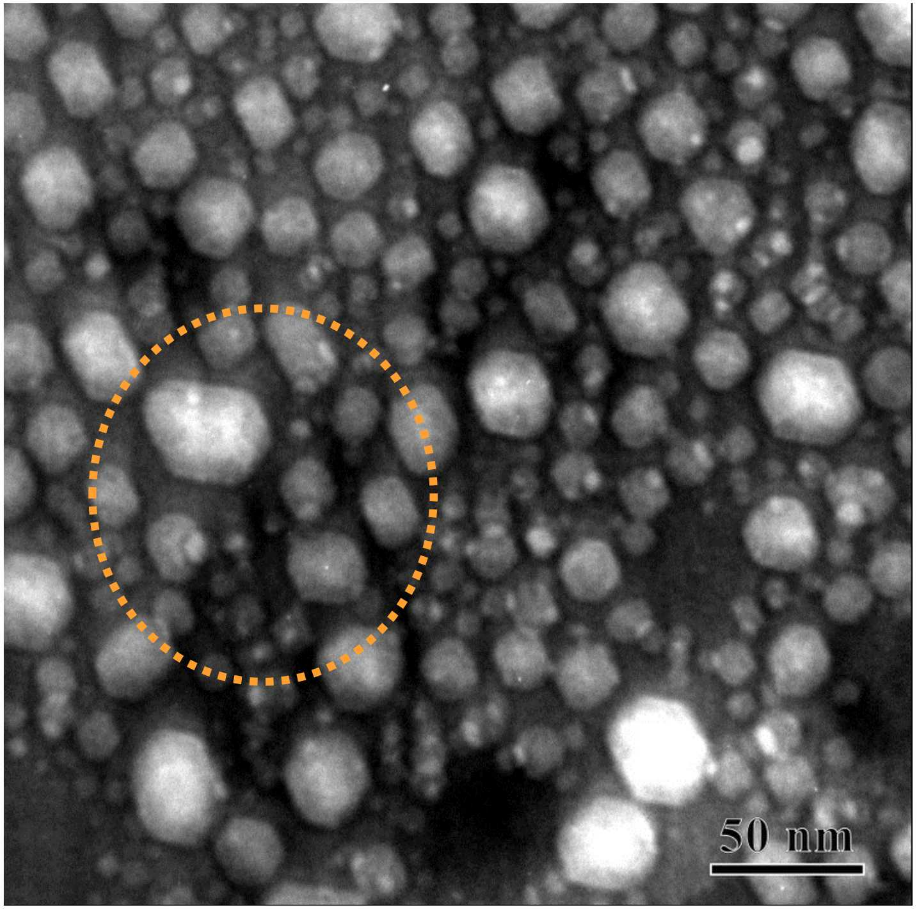


- Faceted cavities continued to grow with increasing temperature
- Facets indicate that cavities are near equilibrium by $T/T_m = 0.37$

Cavities grew by absorbing nearby smaller bubbles in aged PdNi

In-situ annealing at 900°C , $T/T_m = 0.64$





- At high temperature, cavities coalesced or reached the surface, leaving behind denuded zones

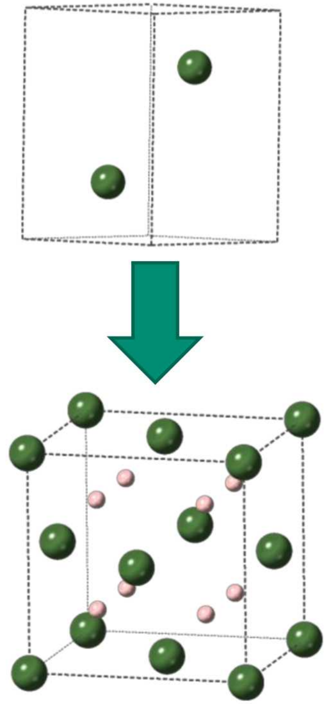
Comparison of bubble microstructure in helium implanted and tritium aged palladium before and after annealing

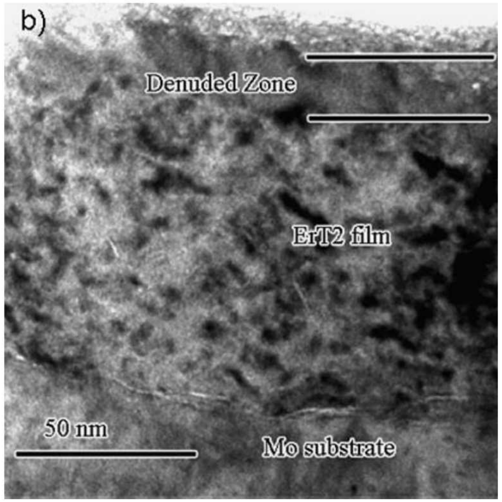
- Bubble microstructure before annealing:
  - Tritium aged sample had a uniform distribution of ~1.5 nm He bubbles → similar to RT implantation
  - High temperature implantation increased He and defect mobility, resulting in preferential nucleation at grain boundaries and heterogeneous nucleation within grains.
- Bubble growth as a function of temperature:
  - Faceted bubbles began to form in tritium aged sample at ~400ºC → same as RT implantation
    - Cavities inside the grains appeared to grow in both samples at 350ºC
  - High temperature implantations were done to a much lower fluence, so large blisters did not form during annealing. Individual bubbles began to migrate in both samples at 500ºC under annealing.
- Growth mechanisms:
  - Cavities in tritium aged and RT implanted samples grew by absorption of nearby cavities.
  - In HT implanted samples, migration of individual cavities.
- Microstructure after annealing:
  - Large faceted cavities were present in both tritium aged and RT implanted samples after annealing
  - Large spherical cavities were present in HT implanted samples after annealing.

Tritium aged and RT He implanted samples had similar bubble microstructures before and during annealing, suggesting that RT He implantation may be a reasonable method of accelerated He aging in Pd.

Hexagonal erbium metal transforms to an fcc fluorite structure after hydriding

- Unlike Pd, Er undergoes a phase transformation from a hexagonal to a fcc structure under hydriding, forming ErH_2
- Tritium β-decays to ^3He, which models predict to remain in the tetrahedral site. Diffusion may occur through the octahedral site.
- Previous work showed that ErH_2 usually contains some oxide, Er_2O_3.
- ^3He in ErT_2 tends to form platelet structures along the {111} planes instead of bubbles.





Snow et al JNM 374 (2008)

- One paper suggests that defects or cracks form along the {111} planes during the hydriding process in ErD_2.


Shen et al Materials Letters 106 (2013)

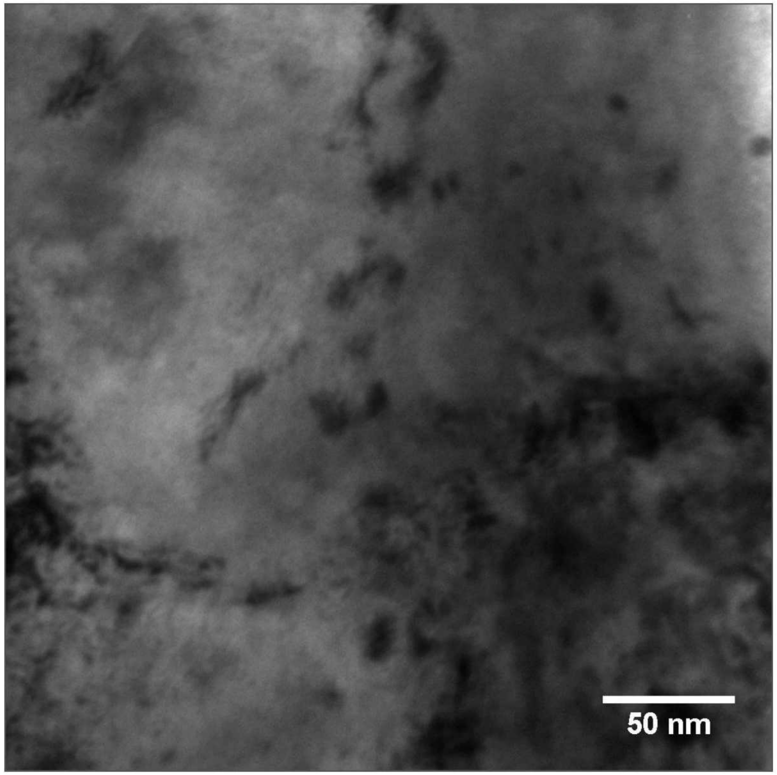
Outline

- Thermal aging of He implanted Pd
- Thermal aging of tritium aged PdNi
- He implantation into Er
- Thermal aging of aged ErT_2

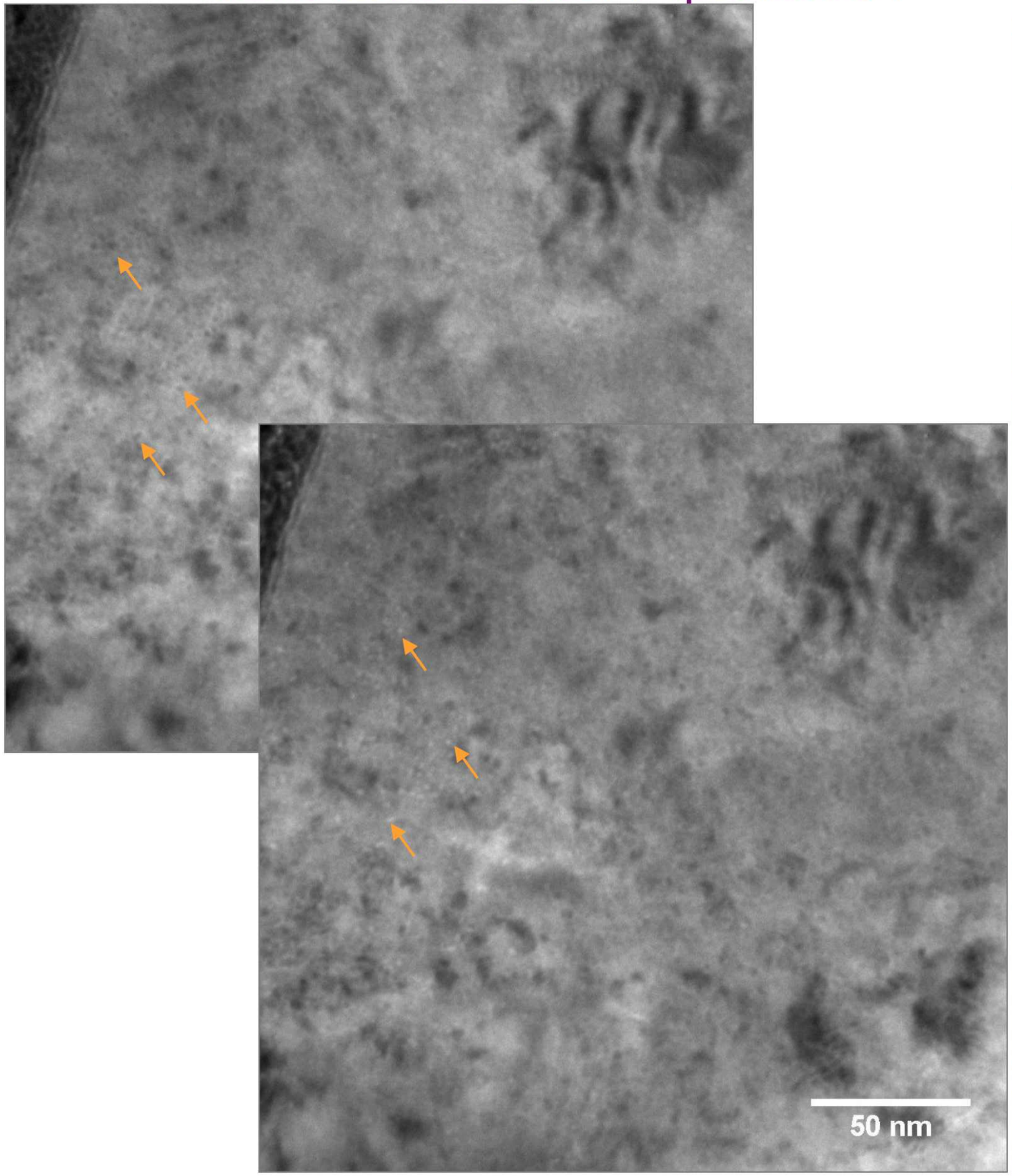
Initial results showed a distribution of nano-sized helium bubbles in ErD_2 after helium implantation @ 450°C

- A thin (~200 nm) layer of ErD_2 was deposited on a rolled Mo substrate.
- He was implanted into a TEM sample in-situ at 450ºC, $T/T_m = 0.40$, to a fluence of $\sim 2.9 \times 10^{18}$ ions/cm^2

No bubbles before implantation



Round bubbles after implantation



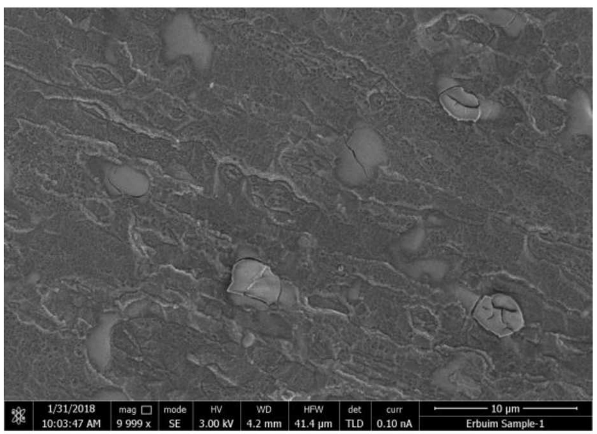
Outline

- Thermal aging of He implanted Pd
- Thermal aging of tritium aged PdNi
- He implantation into Er
- Thermal aging of aged ErT_2

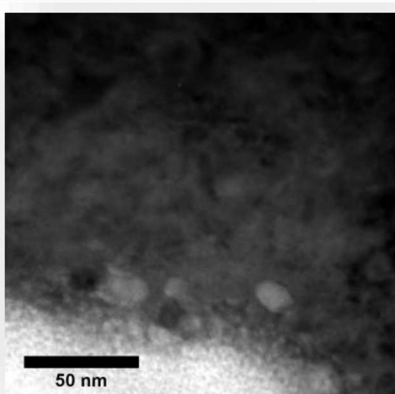
As expected, ^{3}He formed platelets along the {111} crystallographic planes in the aged erbium tritide

- A thin (~200 nm) film of Er metal was deposited on a rolled Mo substrate and loaded with tritium to form ErT_2.
- Sample was aged for ~6 months prior to TEM sample preparation by FIB at PNNL
- Annealing experiment was performed ~11 months after FIB sample preparation.
  - Total amount of ^{3}He in the sample is estimated to be ~3.4 at.% at the time of annealing.

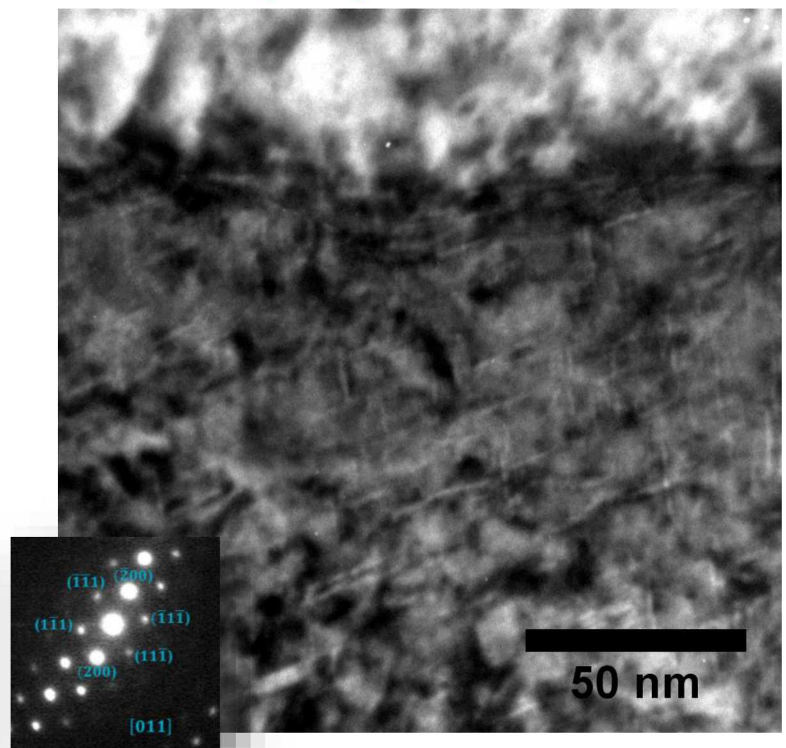
SEM showed blisters on the surface



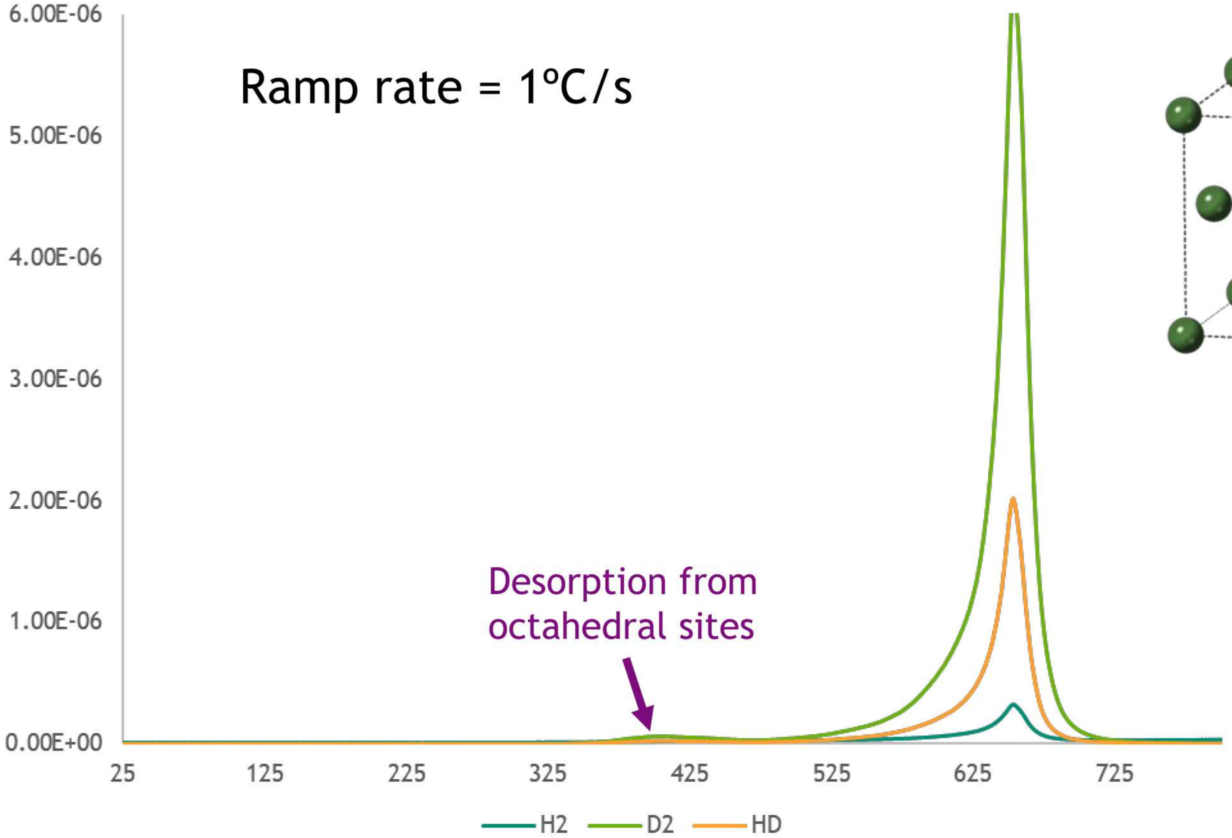
TEM showed large, circular bubbles at the surface

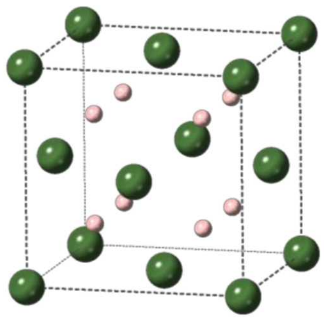


^{3}He platelets oriented in the {111} direction



Hydrogen desorption profile indicates two release mechanisms

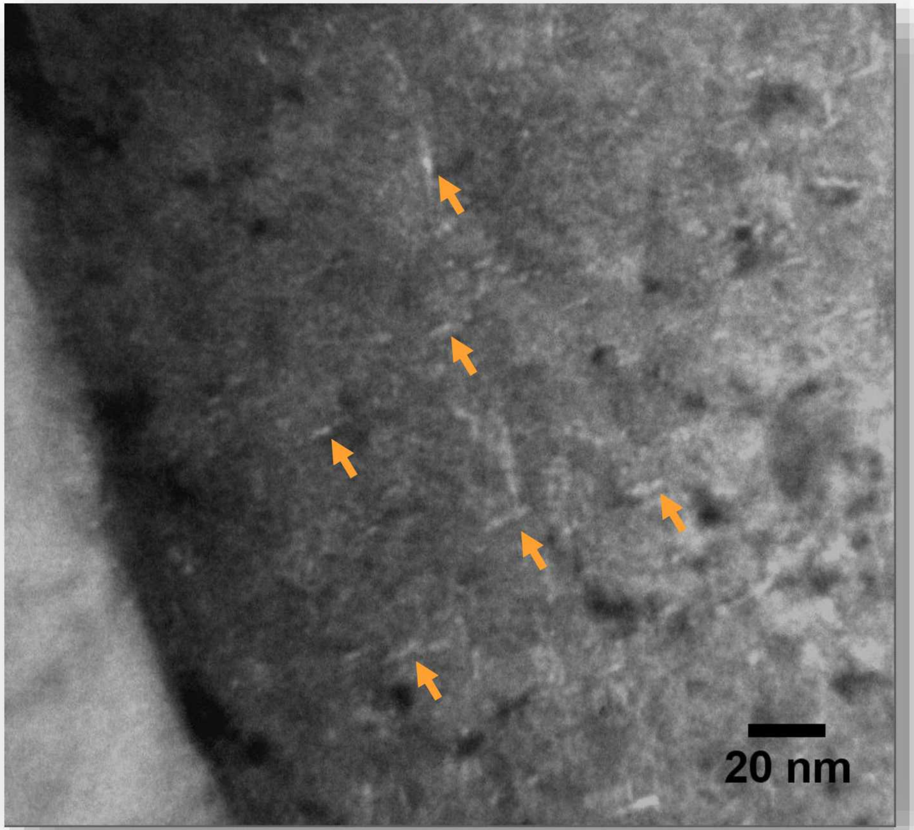




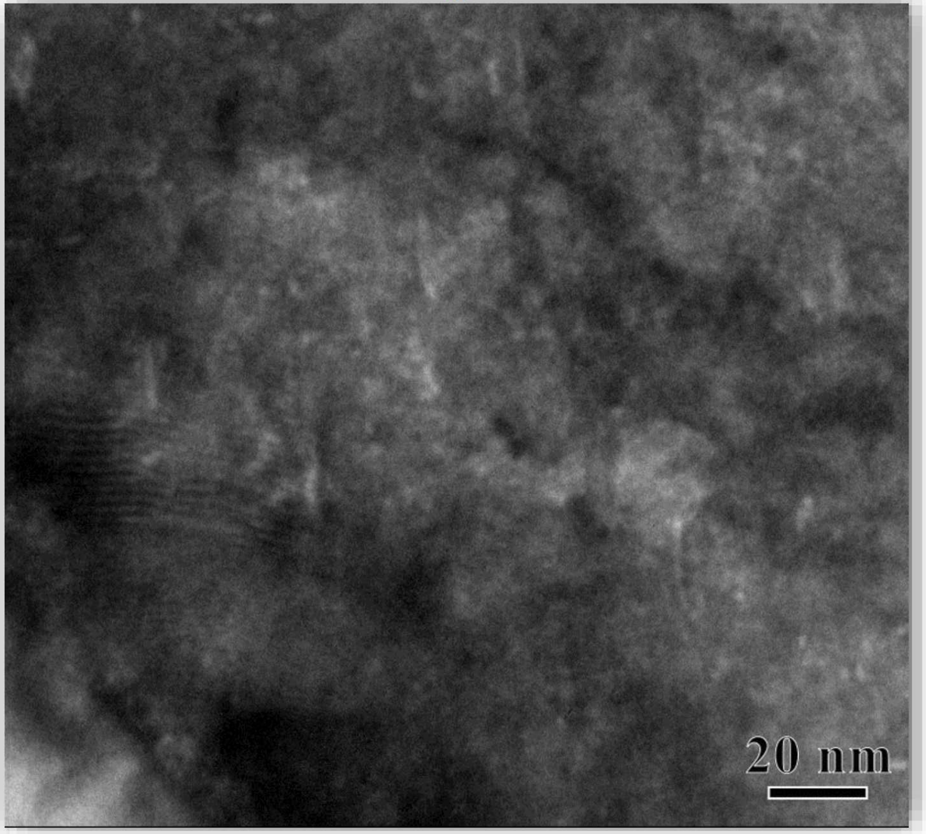
- ➢Desorption at ~400ºC is from super stoichiometric hydrogen located in octahedral sites
- ➢Hydrogen desorption could be expected at any temperature >525ºC

Minor changes were observed after in-situ annealing up to 575°C, but major changes occurred at 600°C.

After in-situ annealing at 575ºC , $T/T_m = 0.46$



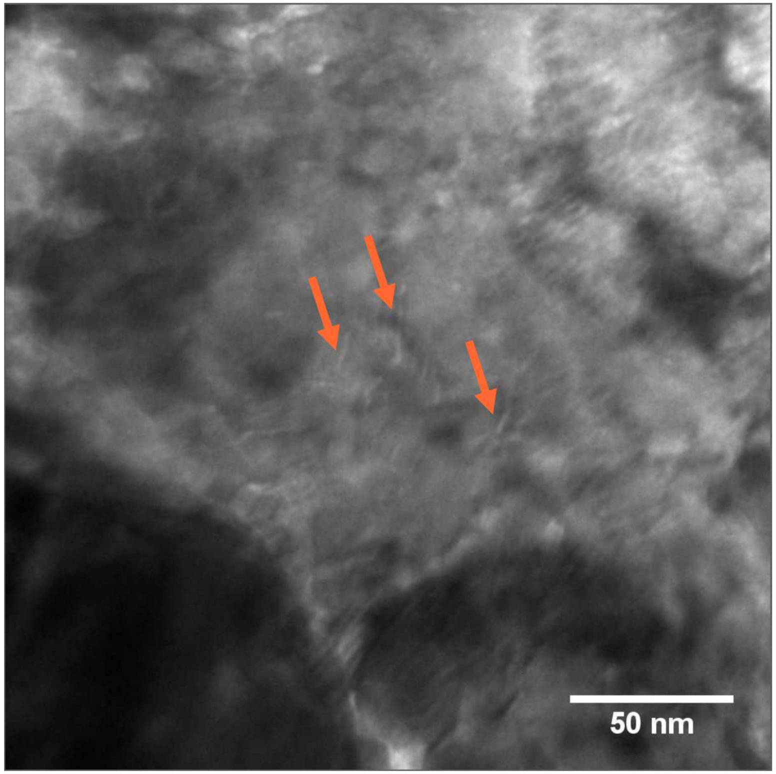
After in-situ annealing at 600ºC , $T/T_m = 0.48$



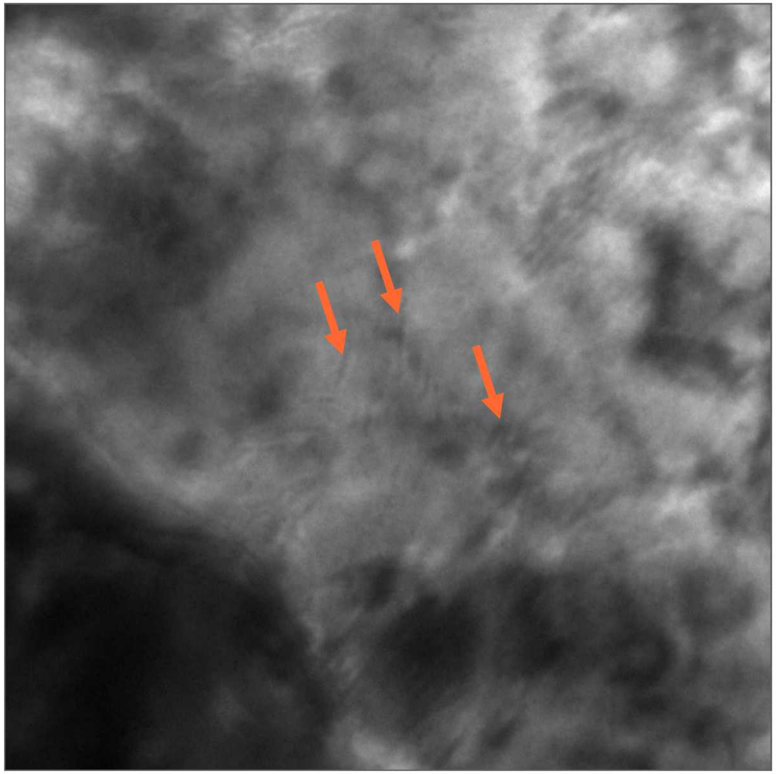
- Possibly slight platelet growth by 575ºC
- Platelets seem to have disappeared after annealing at 600ºC, near the TDS peak measured in ErD_2. ^3He was possibly released during a phase transformation from fluorite to hexagonal Er.

Post-characterization of the erbium tritide sample annealed up to 600°C indicated that helium platelets remained in some regions

underfocus



overfocus



- Possible retention in portions where 1) Er_2O_3 was present or 2) where tritium did not desorb.

Comparison of bubble microstructure in helium implanted and tritium aged erbium before and after annealing

- He implantation at 450°C resulted in mostly spherical bubbles
- ^{3}He platelets formed along the {111} planes in the aged ErT_2
- Unknown microstructural changes were observed during annealing of aged ErT_2
- ^{3}He platelets were stable up to 600°C, and did not transform into groups of spherical bubbles, as has occurred in literature studies of Mo
- In some regions, the platelets appeared to disappear entirely.
- Several mechanisms are not understood, including:
  - Crack formation during the tritium or deuterium loading process
  - Microstructural changes during tritium or deuterium desorption
  - Role of oxide in platelet formation

Conclusions

- In Pd, room temperature ^{4}He and subsequent in-situ annealing resulted in very similar initial bubble microstructure and cavity evolution compared to tritium aged material containing ^{3}He.
  - Preferential nucleation at GBs was observed in the HT implanted samples, and has not been observed in aged PdT.
- In ErD_2, ^{4}He implantation at 450ºC resulted in a distribution of spherical bubbles, in stark contrast to the platelets that appeared in aged ErT_2.
  - ^{3}He platelets were stable under annealing up to 600ºC, and did not dissociate into bubbles.
- Future work: He implantation at RT and annealing in ErD_2, low energy helium ion gun implantations, characterization of metal tritides as a function of age with tritium FIB, annealing experiments of pure metal hydrides to characterize phase transformations.