Using Ion Irradiation *In situ* TEM to Support Tritium Science

SAND2017-11664C

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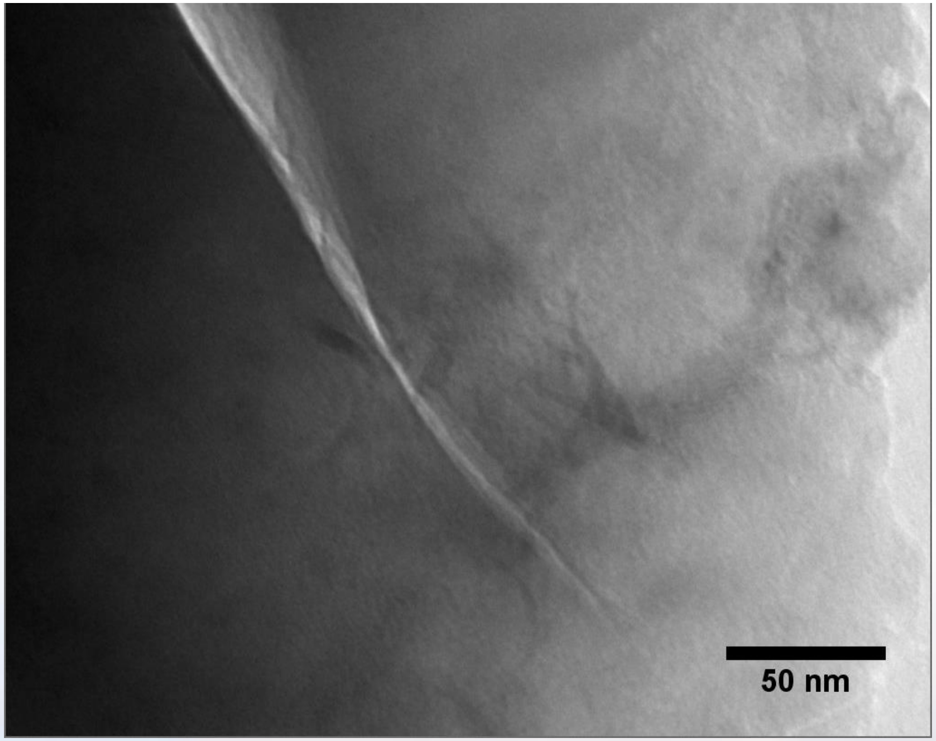
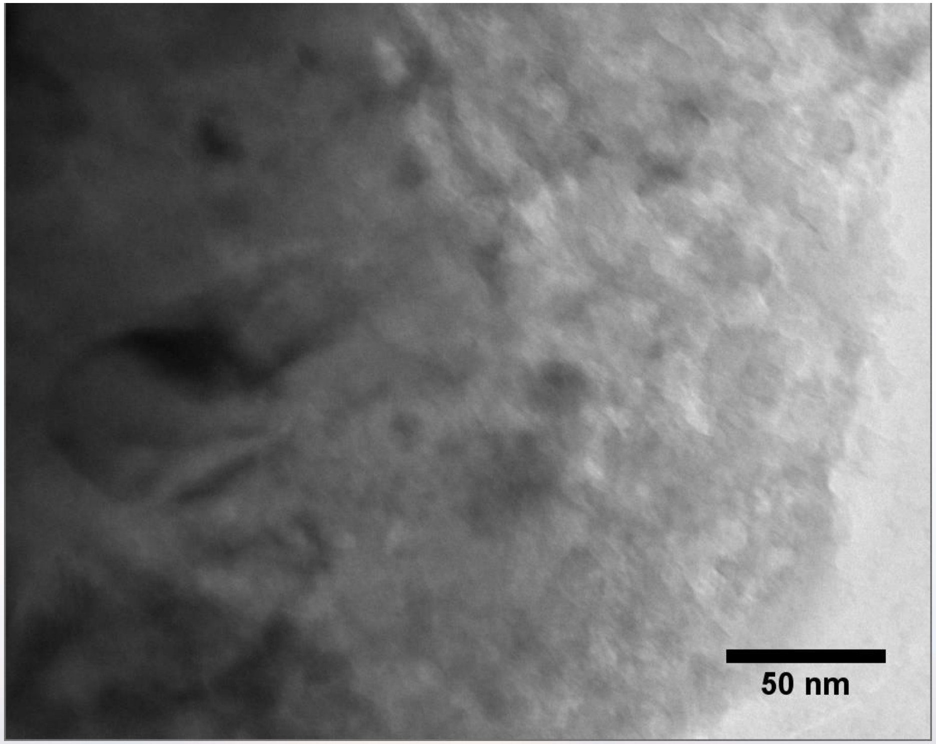
Sandia National Laboratories

September 13, 2017





Utilizing *In situ* TEM microscopy to deconvolute governing environments and elucidate the underlying mechanisms.

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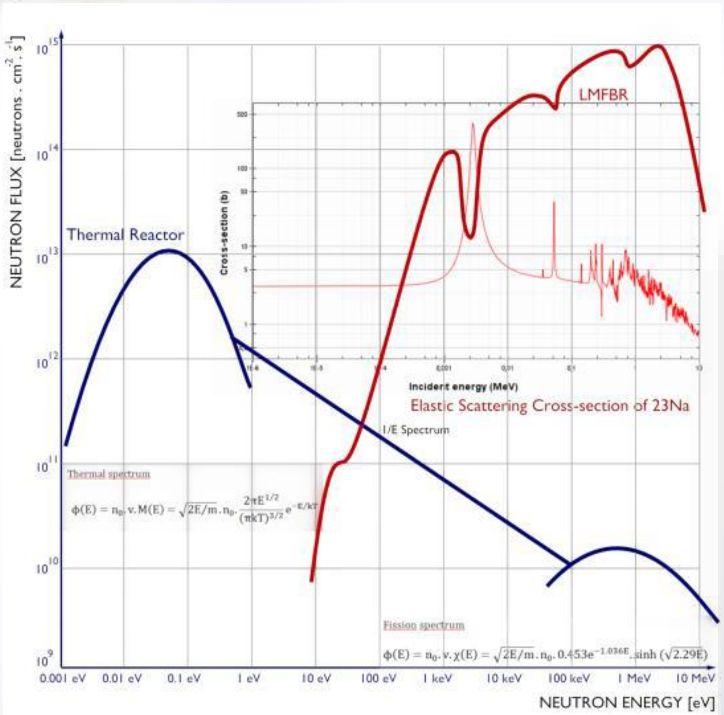
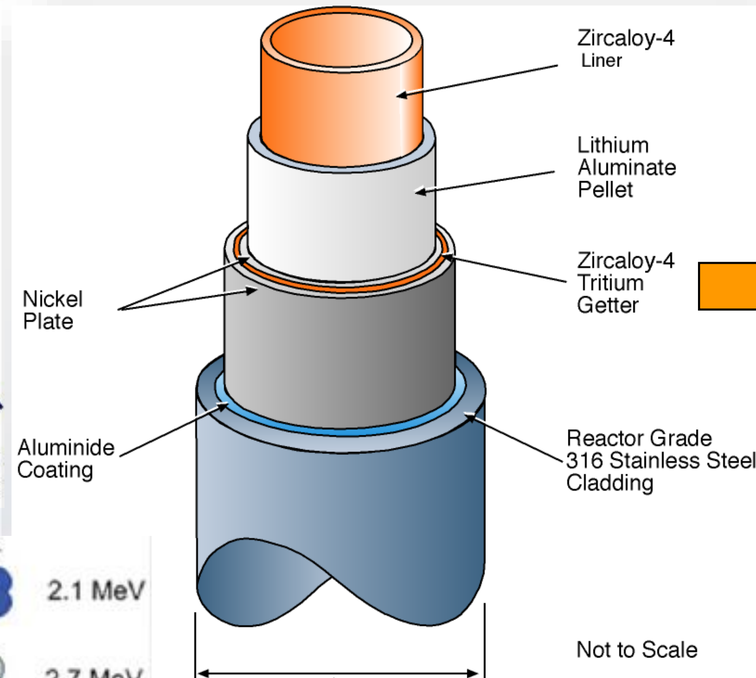
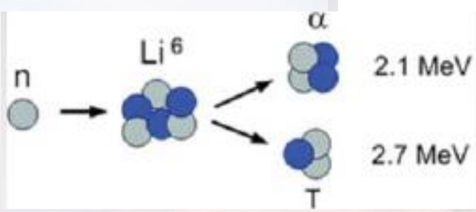
TPBAR Design & Reactor Environment



Tritium Producing Burnable Absorber Rod (TPBAR)





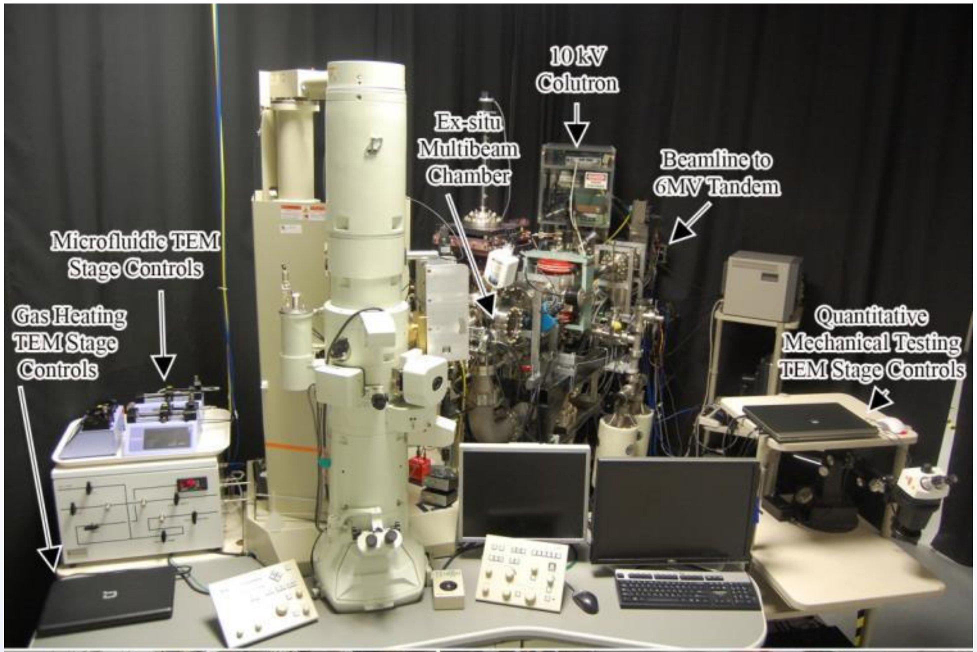
- **Displacement Damage**
- **Helium Implantation**
- **Tritium Implantation**
- **Elevated Temperatures**

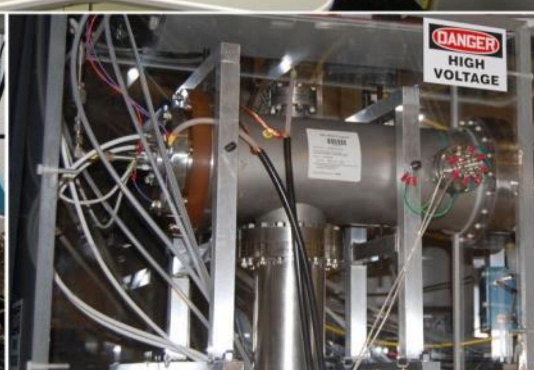
Simulating neutron irradiation in a reactor is complicated, and TPBAR adds the additional complication of ^{3}H production

Sandia's Concurrent *In situ* Ion Irradiation TEM Facility

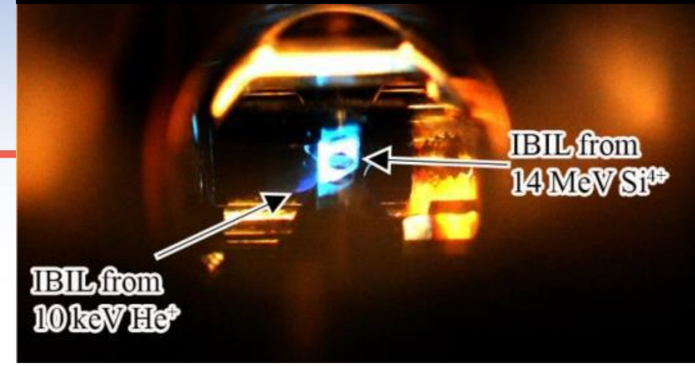
Collaborator: D.L. Buller

10 kV Colutron - 200 kV TEM - 6 MV Tandem



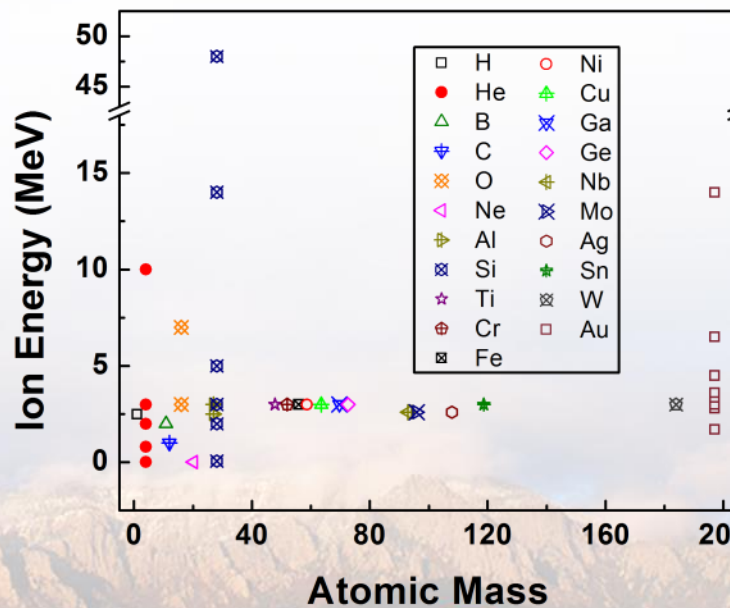


IBIL from a quartz stage inside the TEM



Direct real time observation of ion irradiation, ion implantation, or both with nanometer resolution

Ion species & energy introduced into the TEM



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Benefits & Limitations of *in situ* TEM

Benefits

1. **Real-time nanoscale resolution observations of microstructural dynamics**

Limitations

1. **Predominantly limited to microstructural characterization**
   - Some work in thermal, optical, and mechanical properties
2. **Limited to electron transparent films**
   - Can often prefer surface mechanisms to bulk mechanisms
   - Local stresses state in the sample is difficult to predict
3. **Electron beam effects**
   - Radiolysis and Knock-on Damage
4. **Vacuum conditions**
   - 10^{-7} Torr limits gas and liquid experiments feasibility
5. **Local probing**
   - Portions of the world study is small

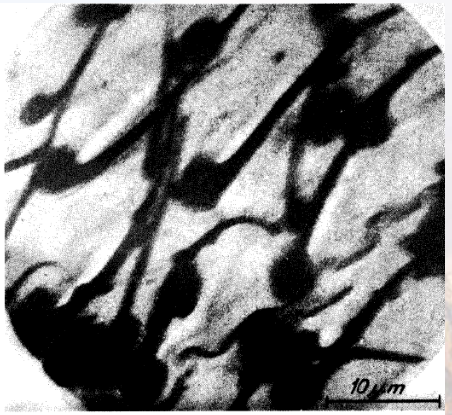


Fig. 6: Wing surface of the house fly.
(First internal photography, U = 60 kV, M_{el} = 2200)
(Driest, E., and Müller, H.O.: Z. Wiss. Mikroskopie 52, 53-57 (1935)

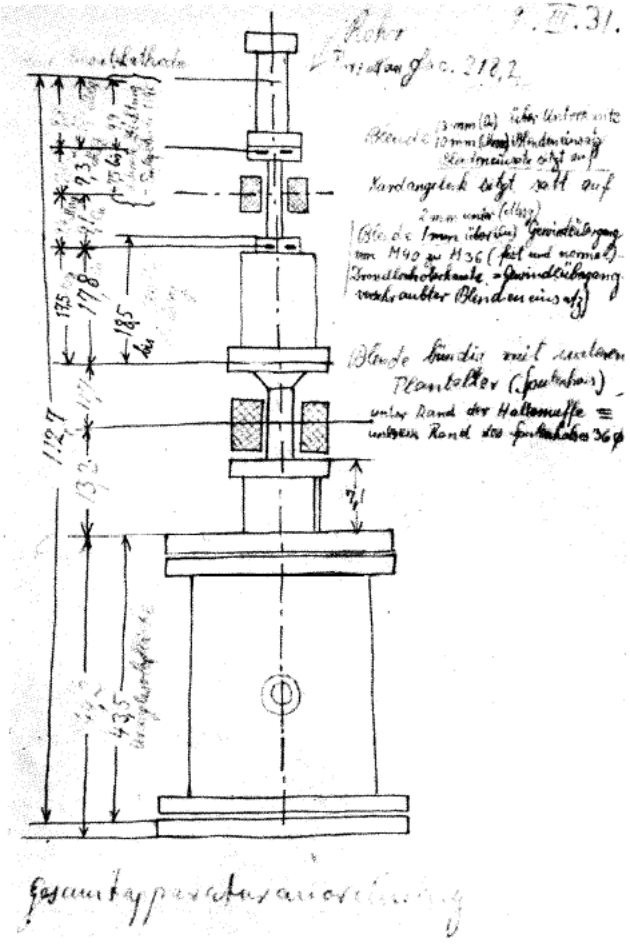
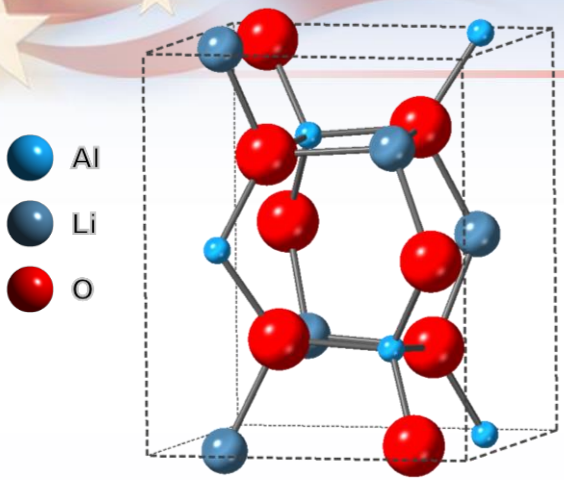


Fig. 2: Sketch by the author (9 March 1931) of the cathode ray tube for testing one-stage and two-stage electron-optical imaging by means of two magnetic electron lenses (electron microscope) [8].

E. Ruska Nobel lecture (1986)

$LiAlO_2$ Background

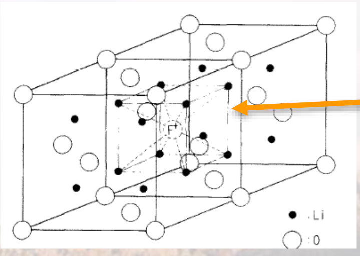


γ–$LiAlO_2$ is tetragonal (space group: P 41 21 2)

Previous Work

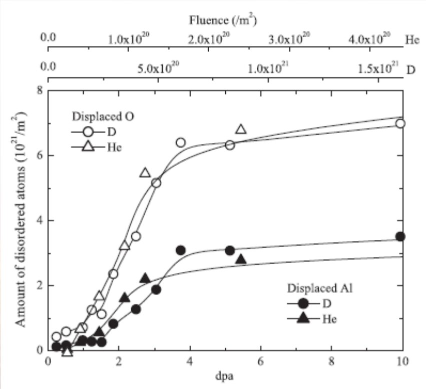
- Structural defects
  - Luo *et al* JNM 372 (2008) 53-58
- Volume swelling
  - Noda JNM 179-181 (1991) 37-41
- ^3H detrapping
  - Oyaidzu *et al* JNM 375 (2008) 1-7
- Gas diffusion and release
  - Raffray *et al* JNM 210 (1994) 143-160

- H isotopes are thought to trap in oxygen vacancies
  - ^2H release occurs at the same temperature as defect annealing in implanted $LiAlO_2$



Can be determined with luminescence

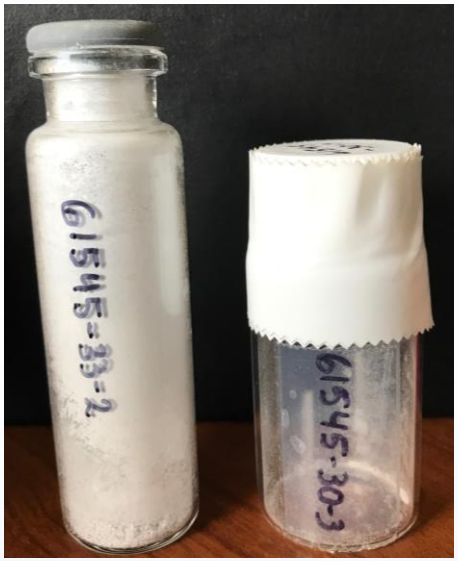
Noda JNM 179-181 (1991) 37-41

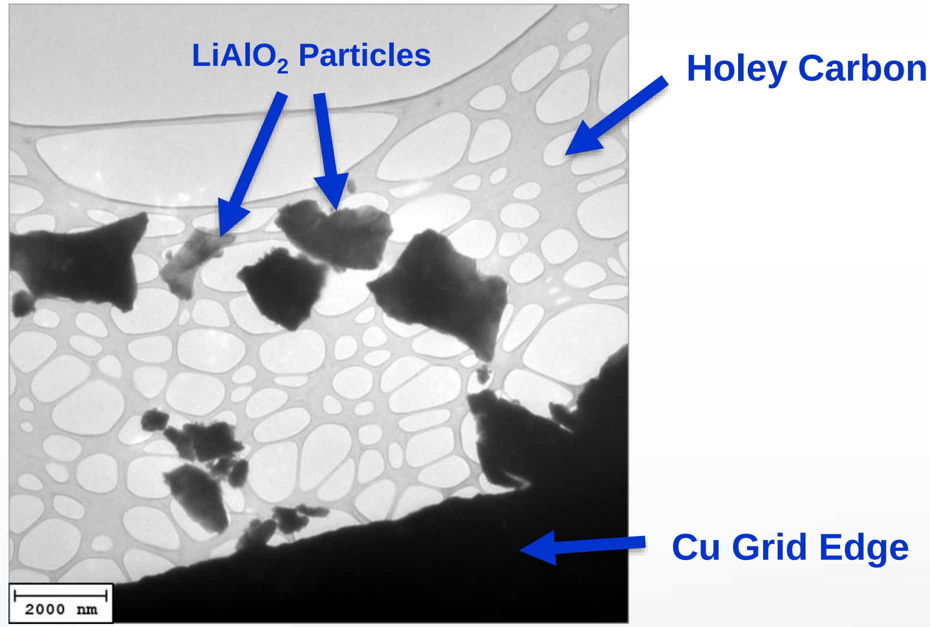


Katsui *et al.* NIMB 268 (2010) 2735-2739

$LiAlO_2$ in-situ ion irradiation parameters

- **Powders were drop-cast onto TEM grids**



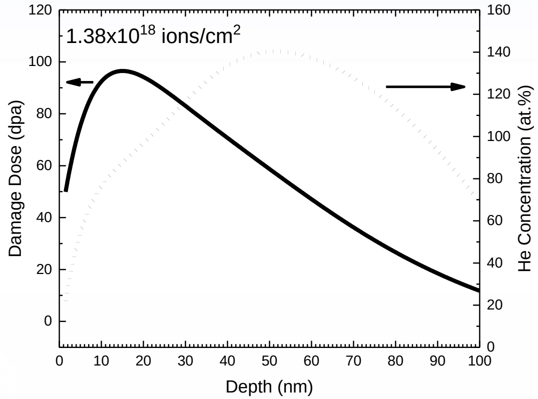


- **Samples were heated to 310°C using Hummingbird HT stage**
- **Three sets of irradiations:**
  - 10 keV He → simulates He accumulation from ^{6}Li transmutation and ^{3}H decay
  - 10 keV He + 5 keV D → simulates He and ^{3}H interaction
  - 10 keV He + 5 keV D + **1.7 MeV Au**→ simulates gas build-up + displacement cascades

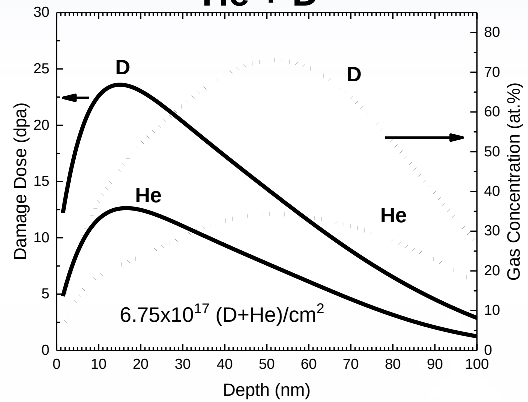
$LiAlO_2$ in-situ ion irradiation parameters

Most He/D diffuses out of thin film immediately

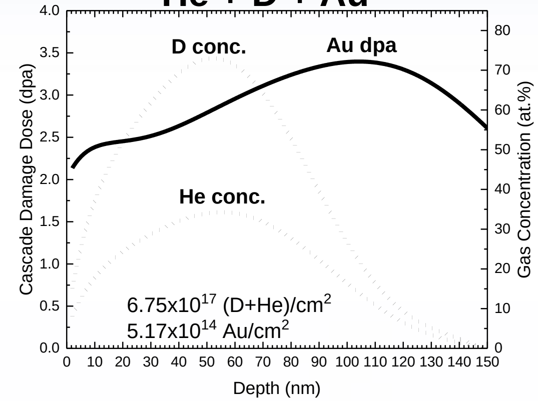
10 keV He



He + D



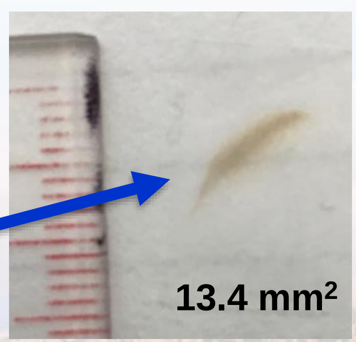
He + D + Au



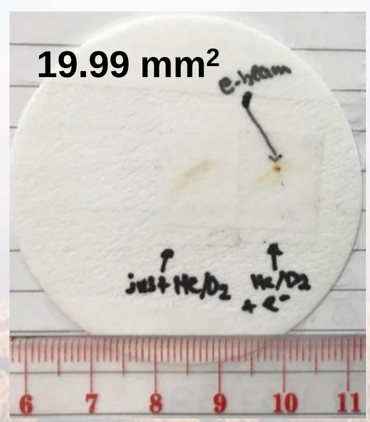
- **Burn spots were used (1) to confirm that electron beam spot overlaps ion beam spot and (2) to determine the ion beam irradiation area.**

He & D beams are shaped like a comet due to TEM objective lens

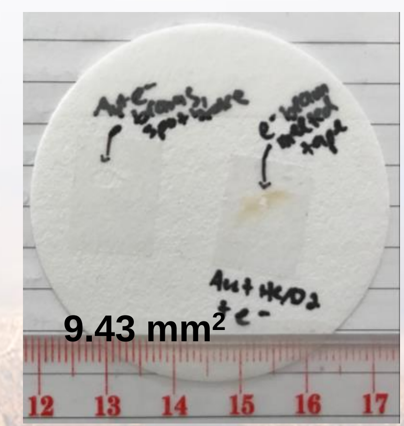
He



He + D

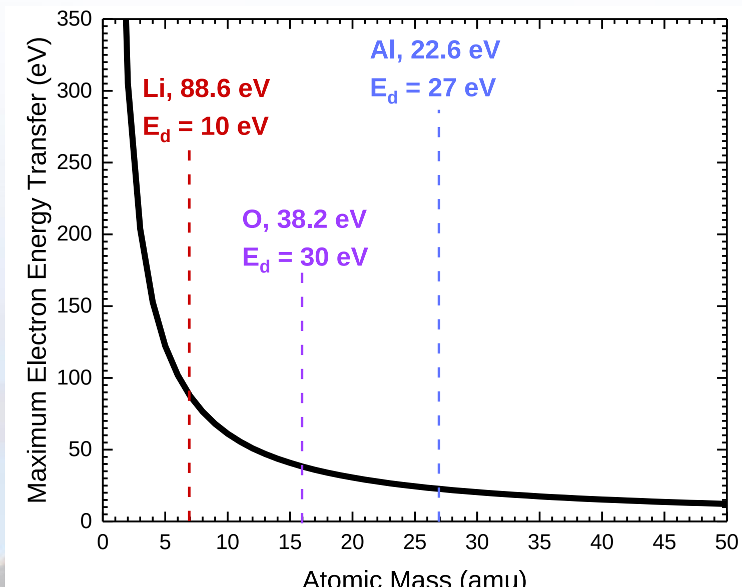


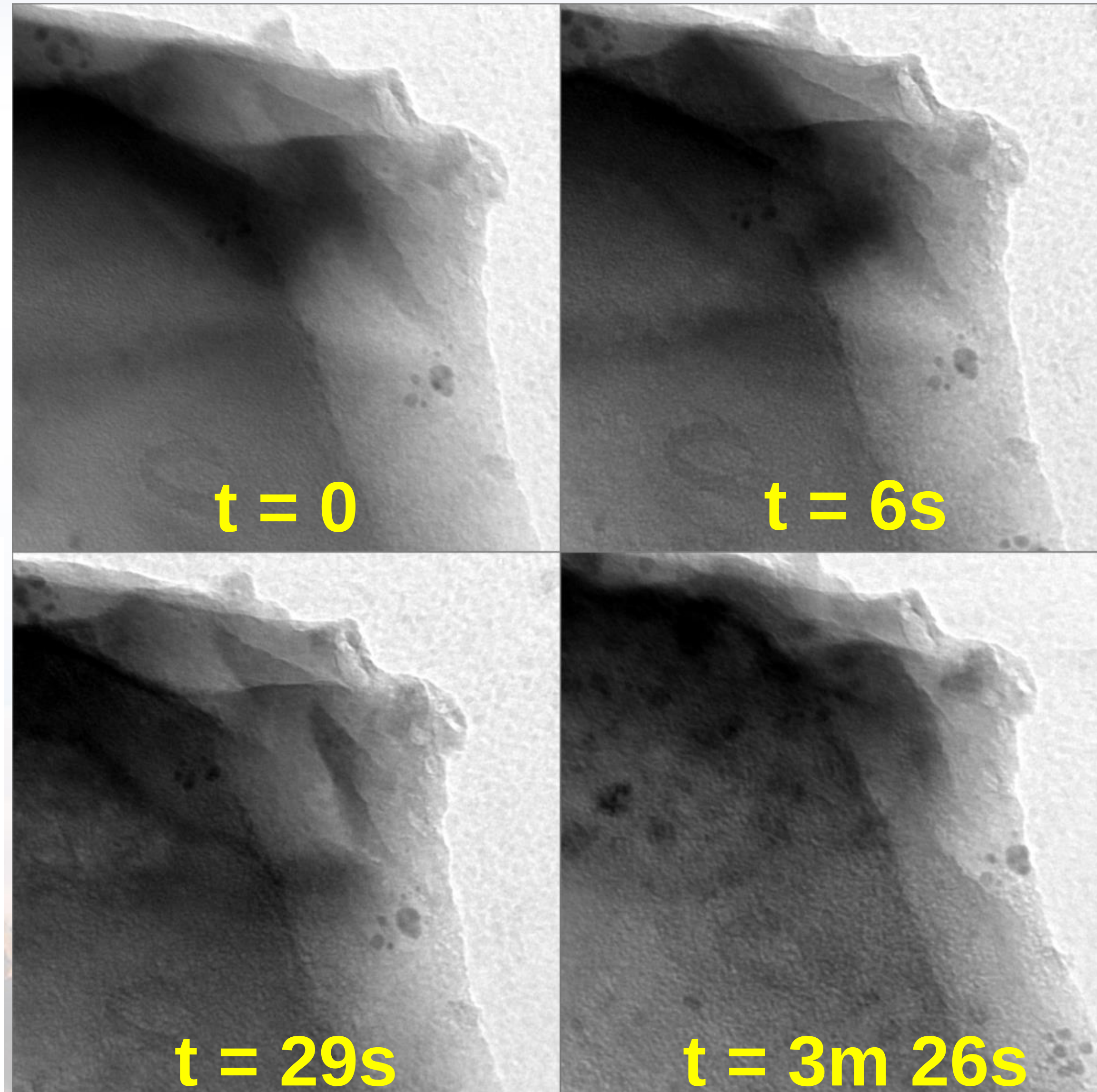
He + D + Au



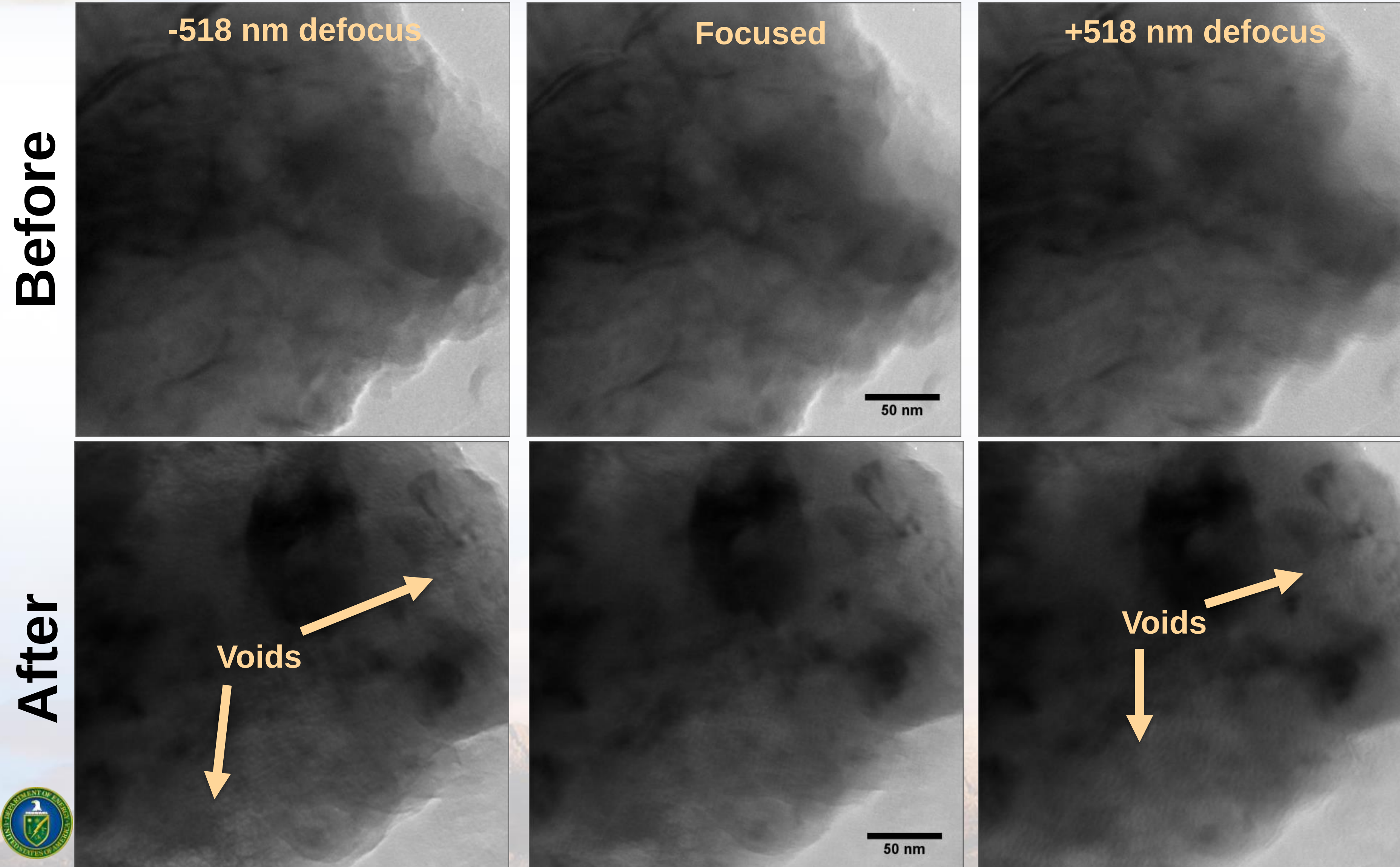
Electron beam induced void growth

- Voids were observed to form under the electron beam in several particles
- Rate of void formation is not consistent between particles
- Possibly due to electron beam displacing Li and O atoms





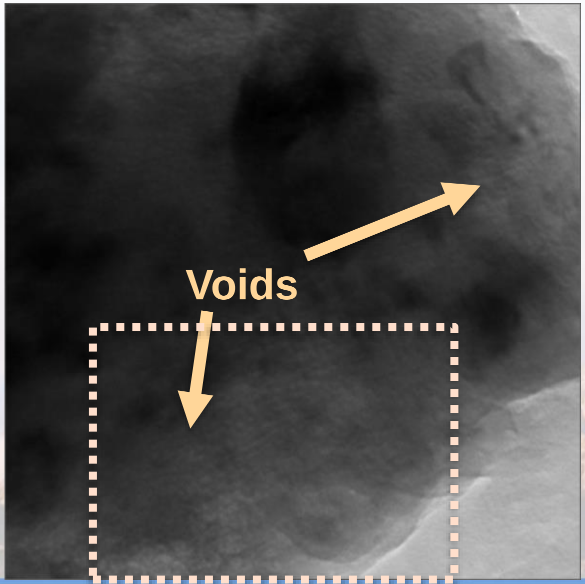
In-situ He implantation @ 310°C



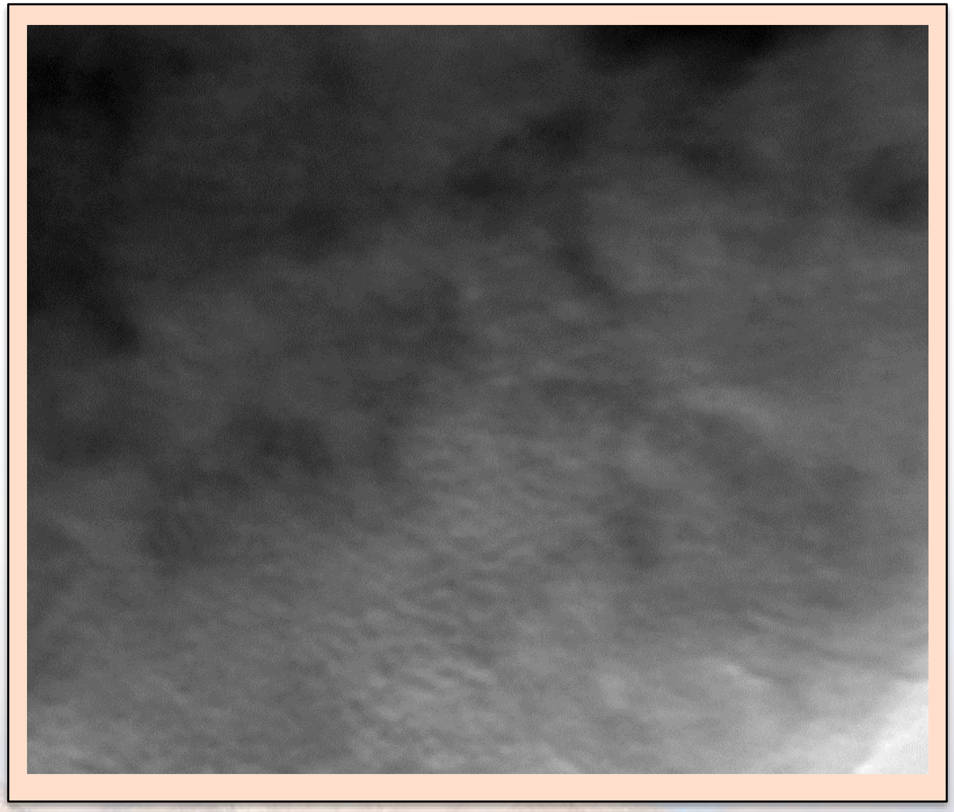
In-situ He implantation @ 310°C

- Each frame = 1 min of irradiation
- Because the voids are difficult to see in powders, I paused the video at a few points to show overfocus images
- Electron beam on for most of experiment
- Bubbles formed after ~13 min (1.5×10^{17} He/cm^2)

After Irradiation



In-situ Video



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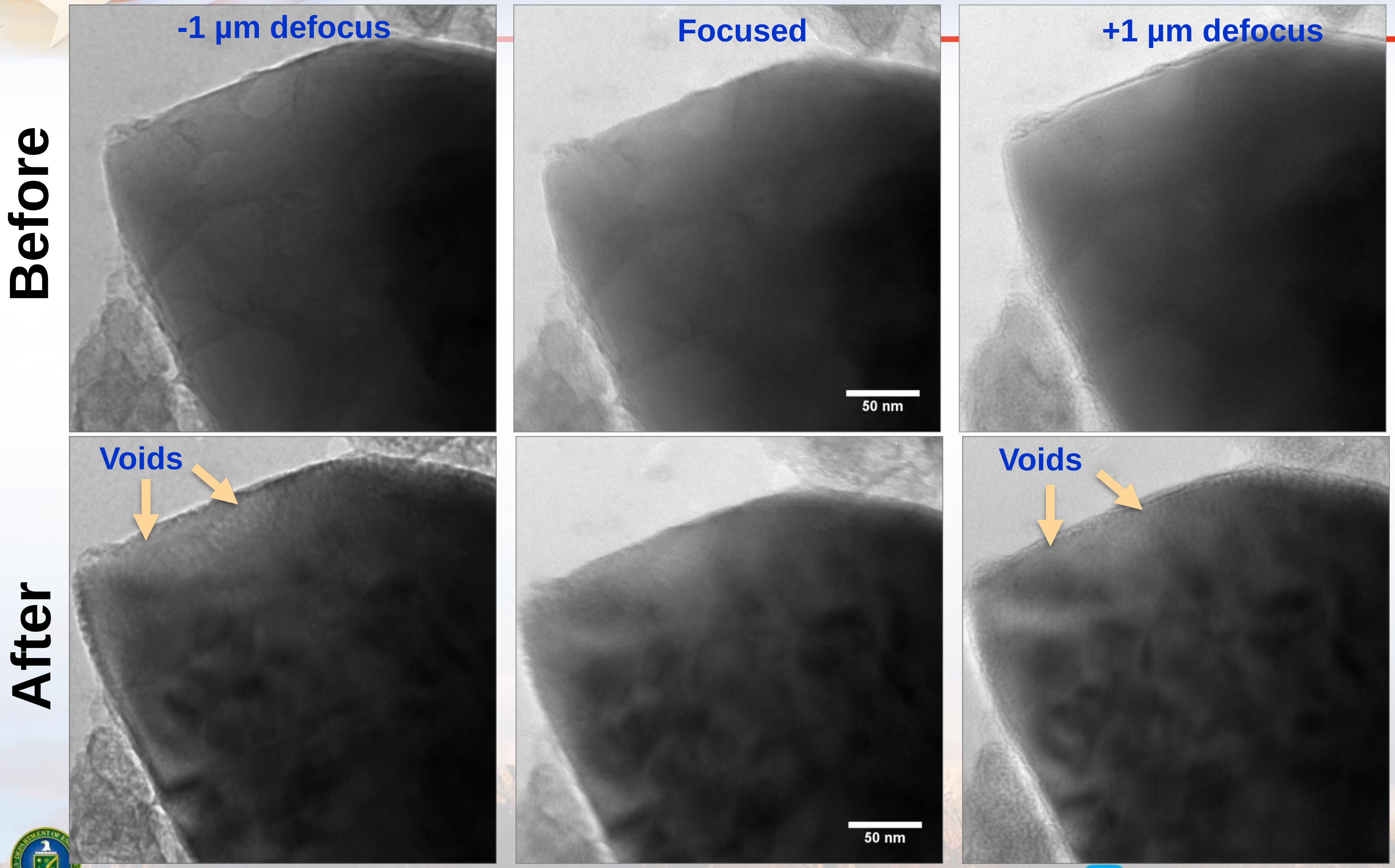
In-situ He + D irradiation @ 310°C



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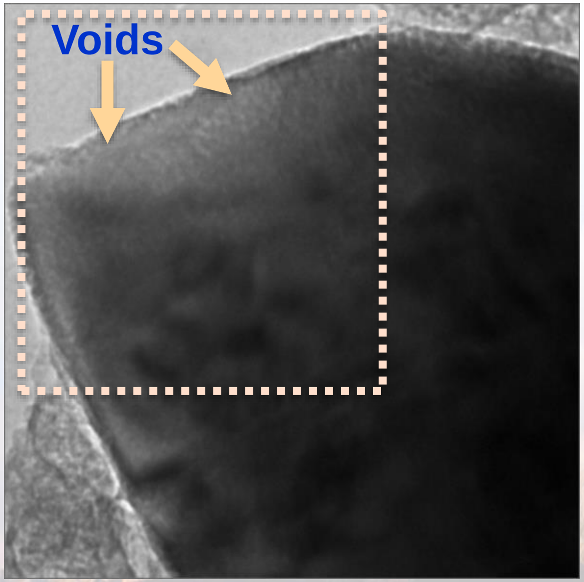
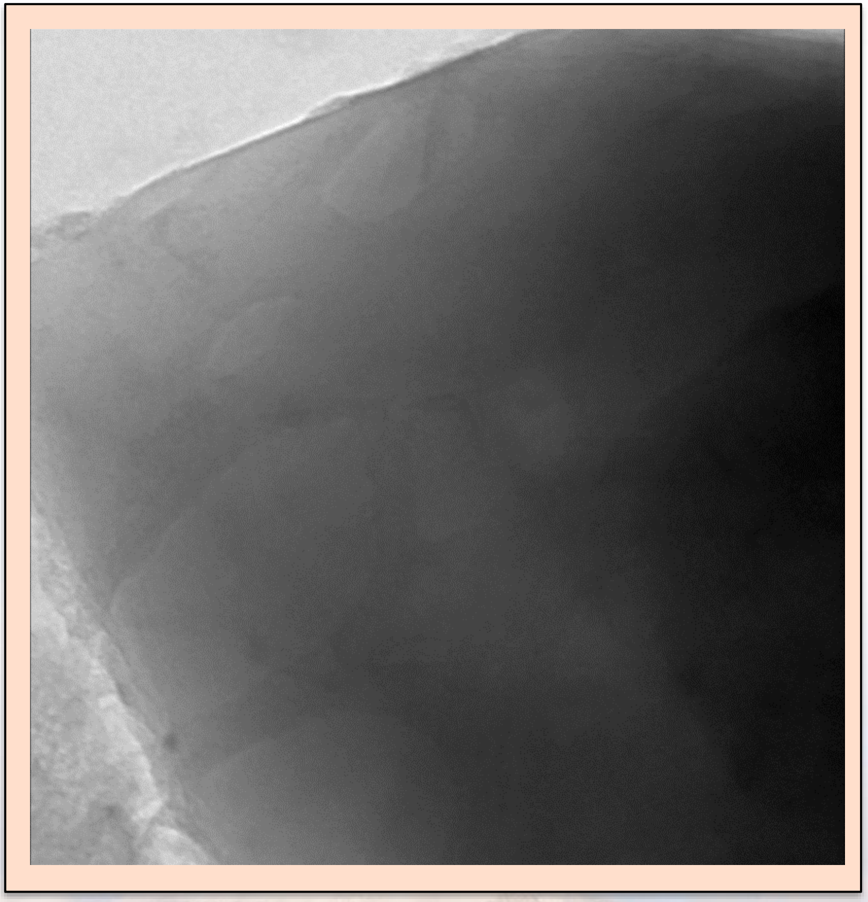
In-situ He + D irradiation @ 310°C

- Each frame = 5 min of irradiation
- All underfocus images
- Electron beam was off except for imaging
- Bubbles formed after ~60 min (1.7×10^{17} He/cm^2, 3.4×10^{17} D/cm^2)

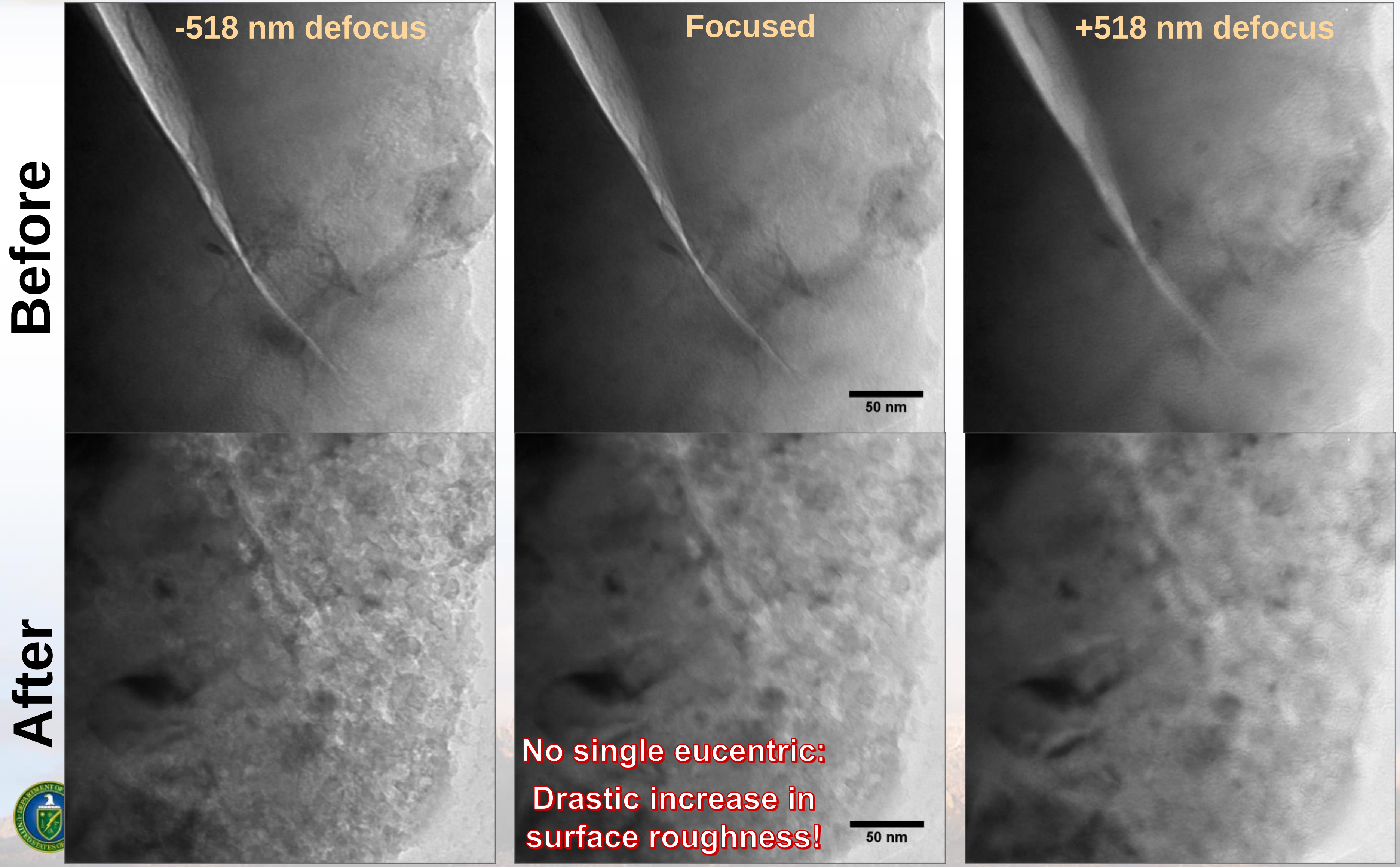
After Irradiation



In-situ Video



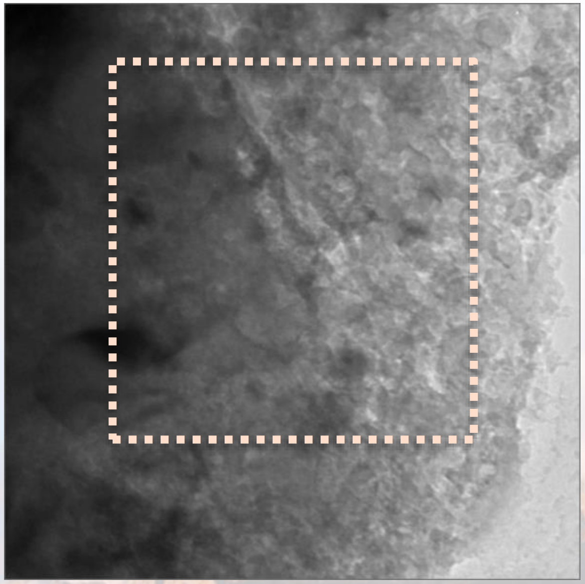
In-situ He + D + Au @ 310°C



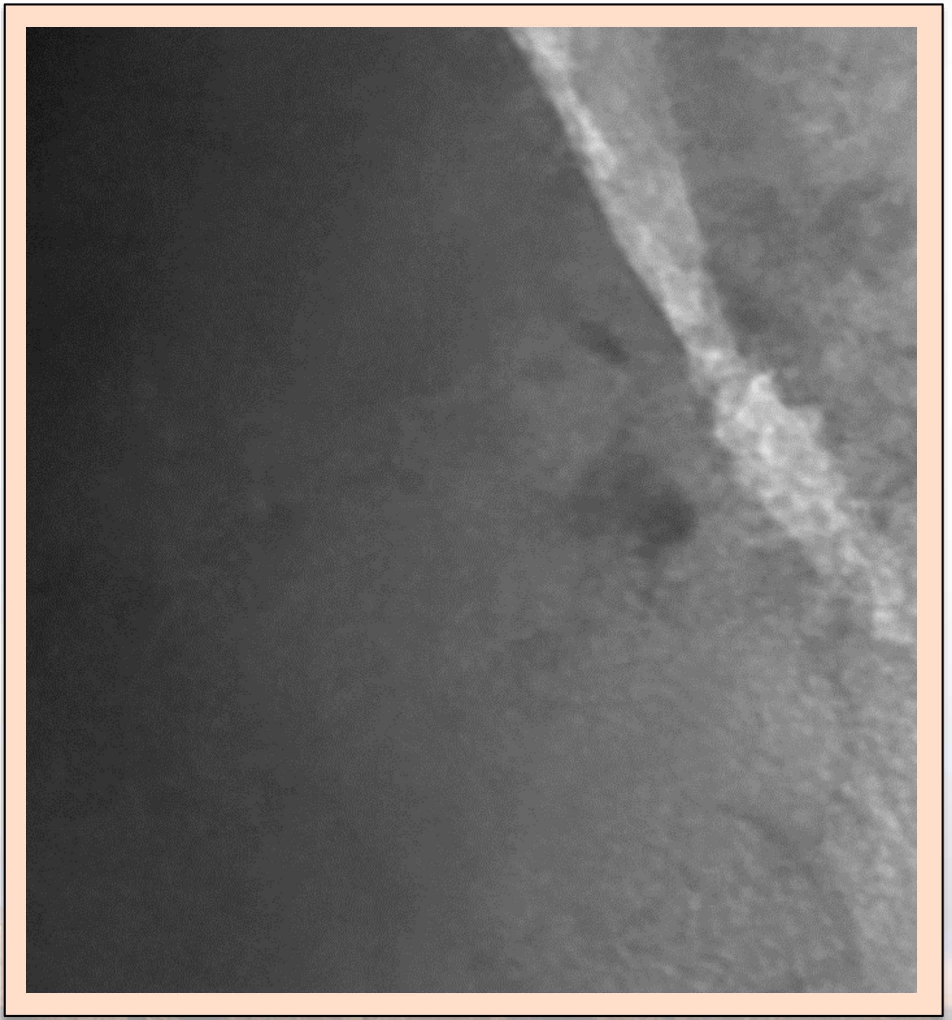
In-situ He + D + Au @ 310°C

- Each frame = 5 min of irradiation
- Pre-existing voids could have an effect on this final microstructure
- Electron beam was on for most of the experiment

After Irradiation



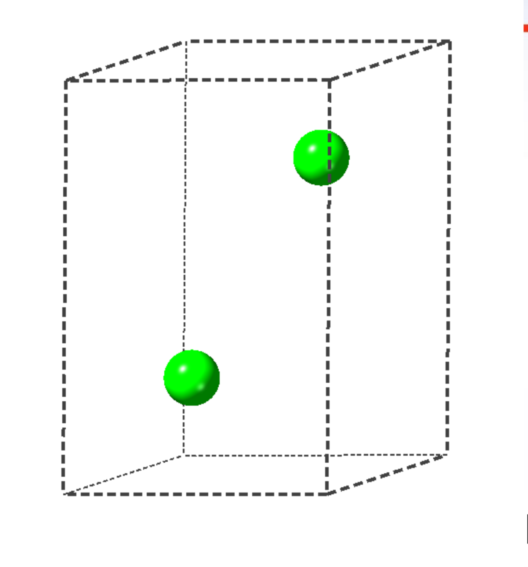
In-situ Video



Zircaloy Background

<u>What is Zircaloy?</u>

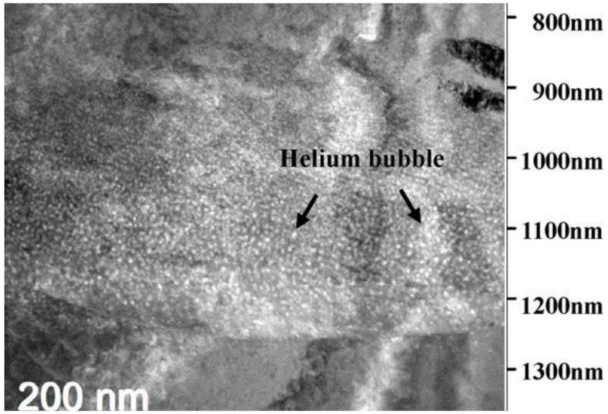
- Zircaloy-2: predominantly used as fuel cladding for BWRs
  - α-Zr, 1.5% Sn, 0.15% Fe, 0.1% Cr, 0.05% Ni
- Zircaloy-4: Removed the Ni and increased Fe content for less H uptake in certain reactor conditions
  - α-Zr, 1.5% Sn, 0.2% Fe, 0.1% Cr
- Zr-Nb alloys (e.g. Zirlo) are also common
- α-Zr has a hexagonal close-packed (HCP) crystal structure up to 810^{o}C



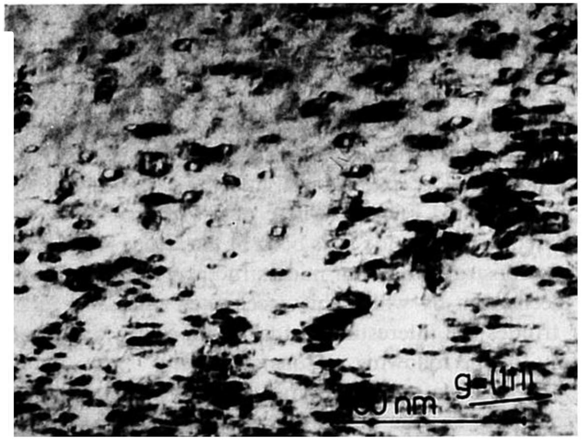
Cr **P)**

<u>Gas and defect behavior in Zr/Zr alloys</u>

- ^{3}H, H, and He diffusion and release
- Bubble formation
- Irradiation induced metallic precipitate formation



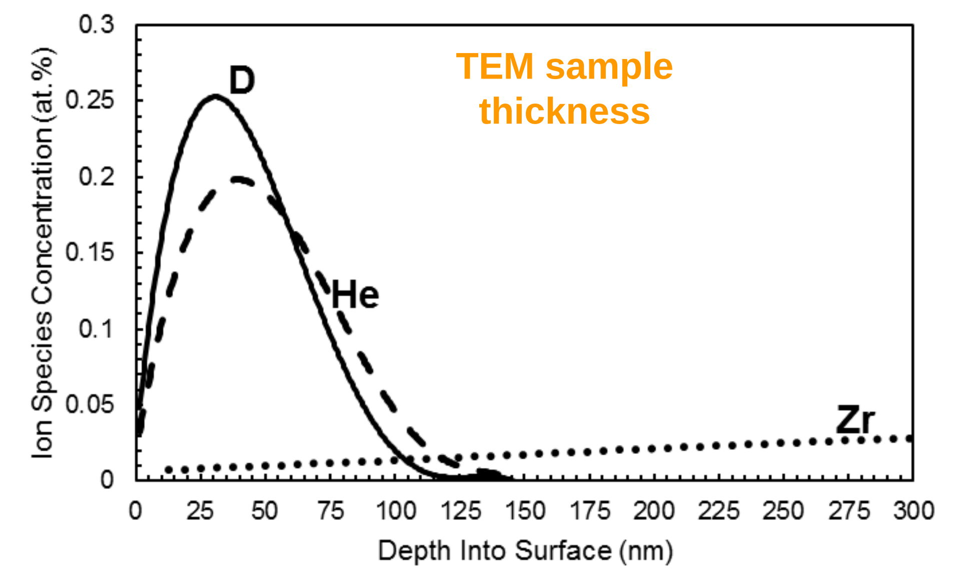
He bubbles in Zr-Nb alloy
Shen et al Mat Char 107 (2015) 309-316



TEM of Zr tritide after 325d
Schober et al JNM 141-143 (1986) 453-457

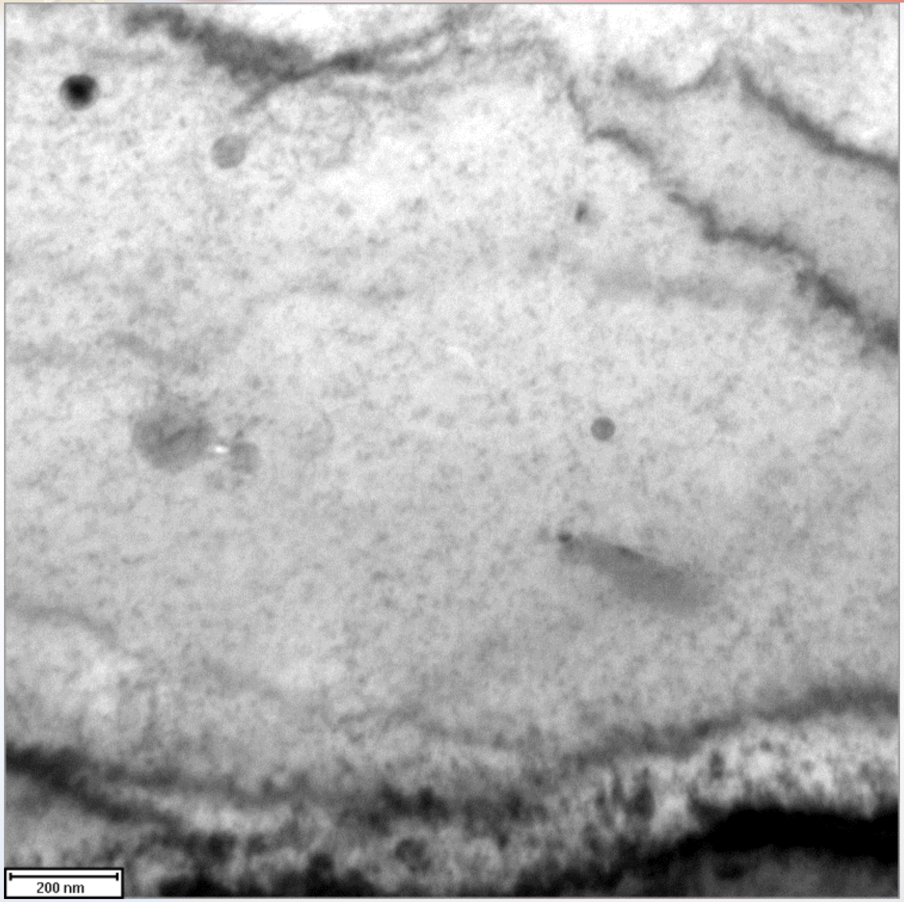
Zr alloy in-situ ion irradiation parameters

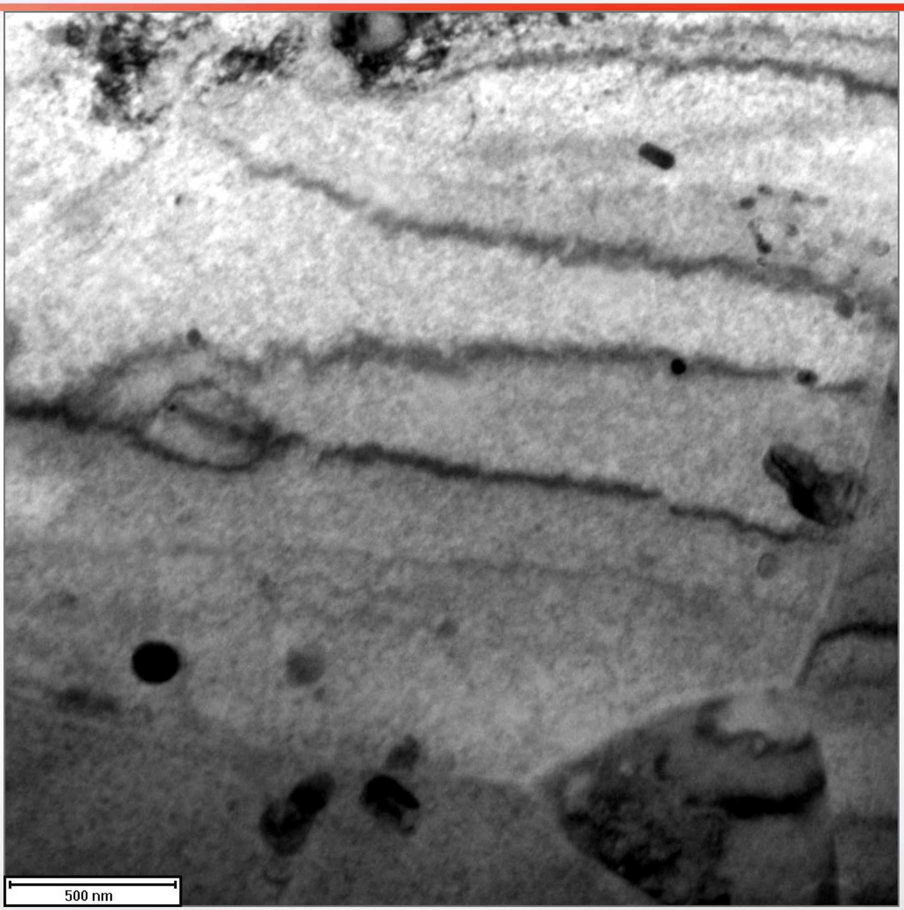
- **Samples were prepared by electropolishing zirconium alloy samples (mostly ZIRLO)**
- **Several sets of irradiations done at 310°C, including:**
  - 10 keV He → simulates He accumulation from ^{6}Li transmutation and ^{3}H decay
  - 10 keV He + 5 keV D + **3 MeV Zr**→ simulates gas build-up + displacement cascades
- **SRIM, a Monte Carlo based program for simulating the number of displacements produced by an ion, was used to predict damage dose and concentration profiles.**
- **These preliminary experiments were run overnight and the exact gas concentrations/damage doses are not all known**



He and D profiles are implanted within the TEM sample, while most Zr passes through the sample, leaving only cascade damage.

10 keV He^+ Implantation at 310°C





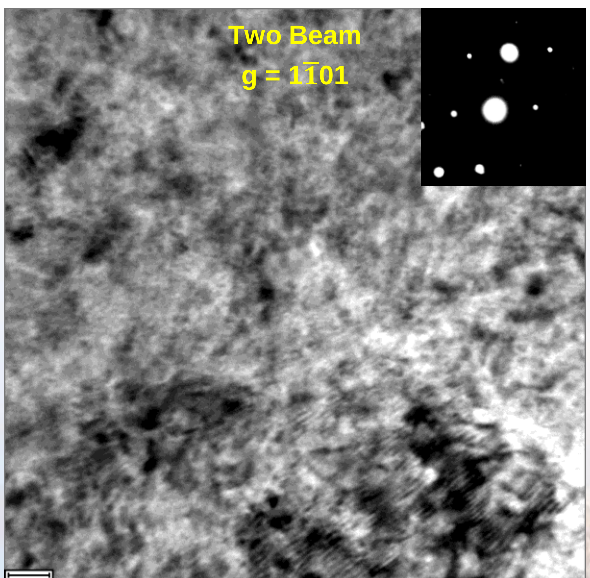
After Implantation.
Damage, No Cavities.

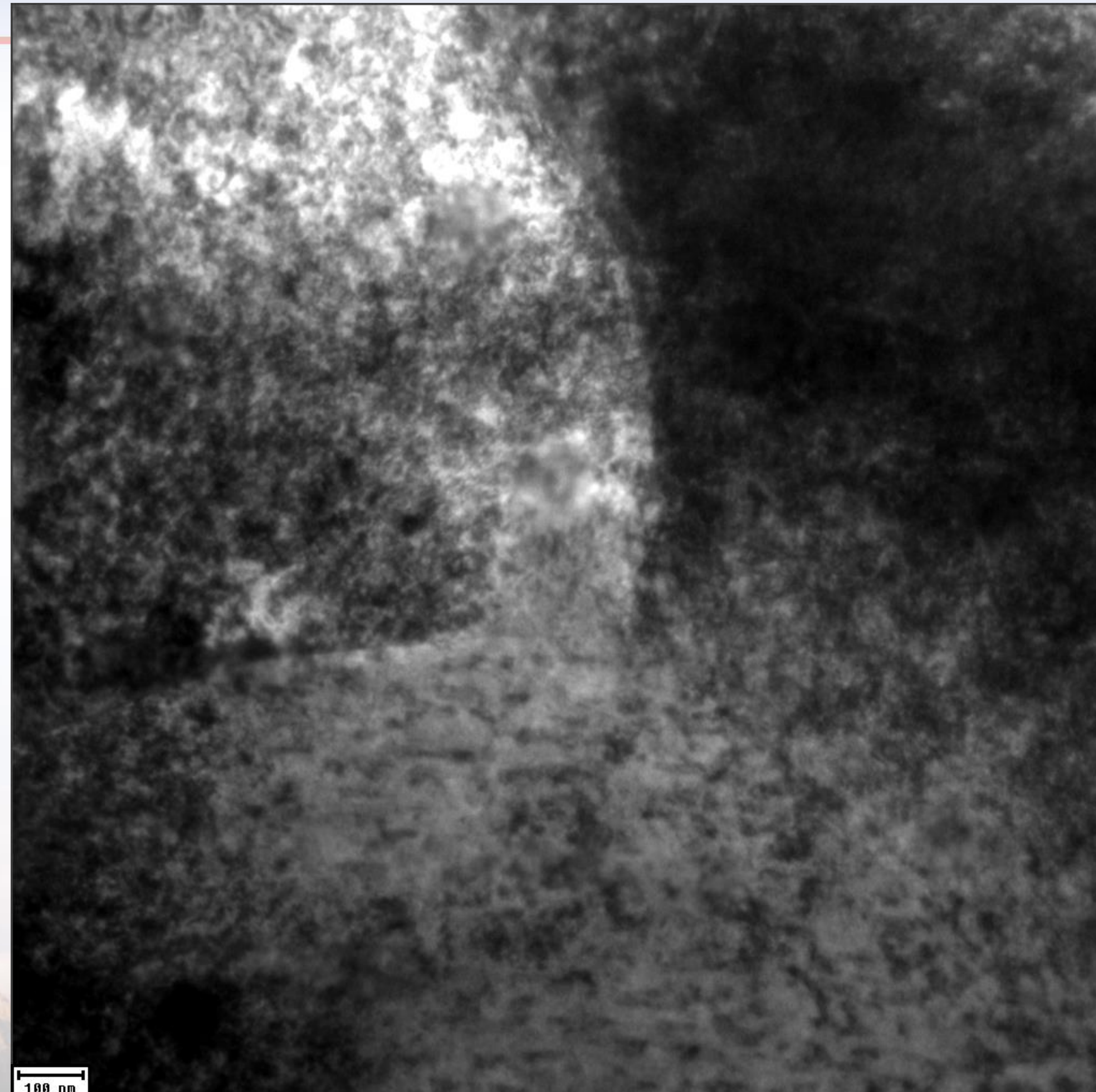
Still no cavities after subsequent irradiation with 3 MeV Zr.

Concurrent D & He Implantation & Zr Irradiation

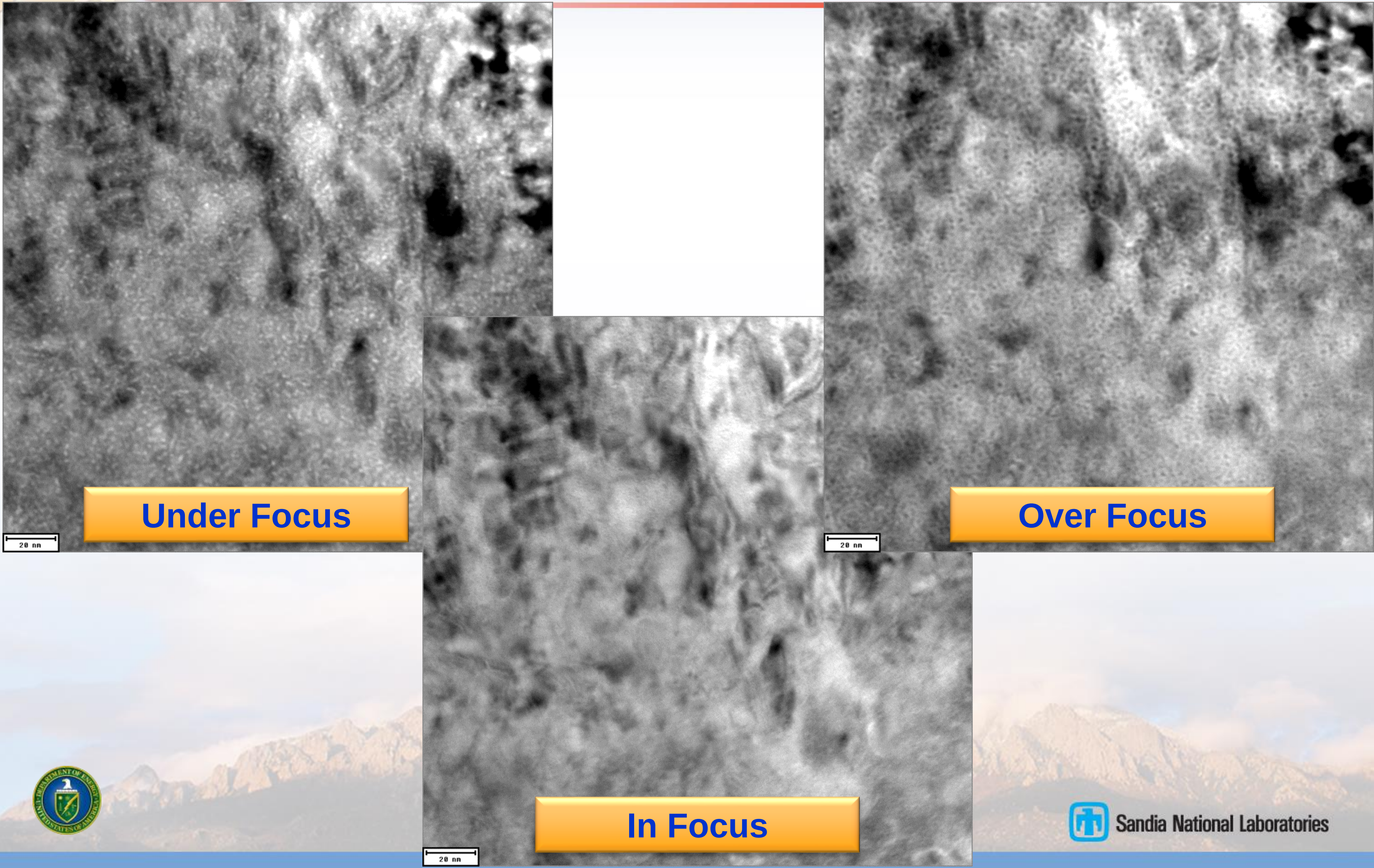
After triple beam irradiation

- Very dense, complex defect structure
- No visible cavities
- Fuzzy defects difficult to characterize





Cavities were observed in He implanted Zr alloy samples 30 days after irradiation



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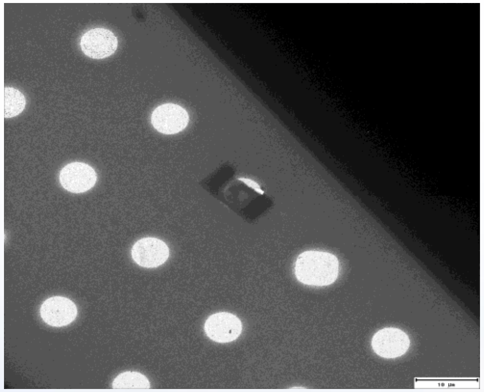
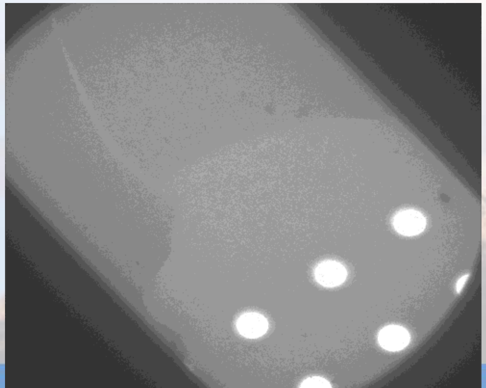
Feasibility of Studying Zircaloy 2 at Nominally 1 atm

Collaborators: S. Rajasekhara and B.G. Clark

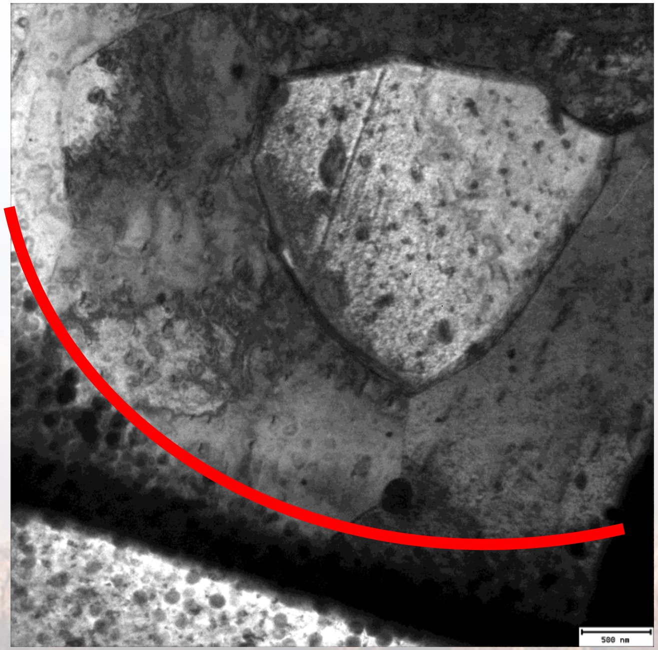
Vapor-Phase Heating TEM Stage

- Compatible with a range of gases
- *In situ* resistive heating
- Continuous observation of the reaction channel
- Chamber dimensions are controllable
- Compatible with MS and other analytical tools

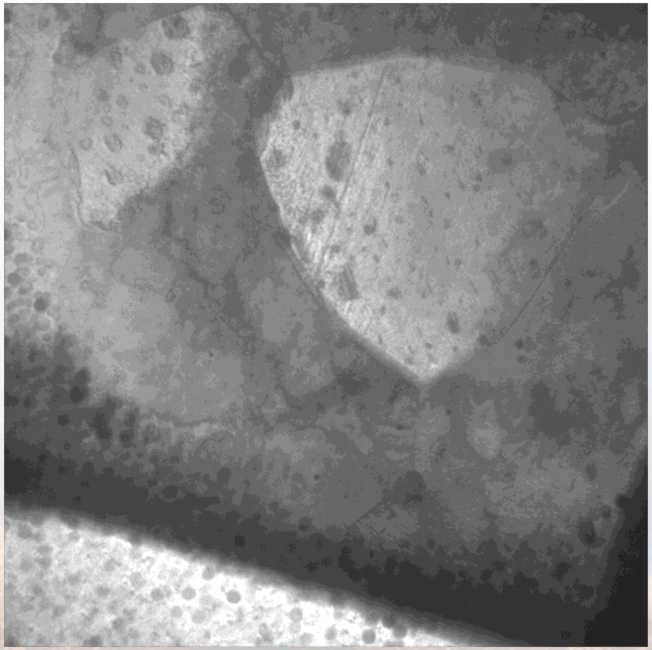




Vacuum & Single Window



Nominally 1 atm H_2 & Two Windows



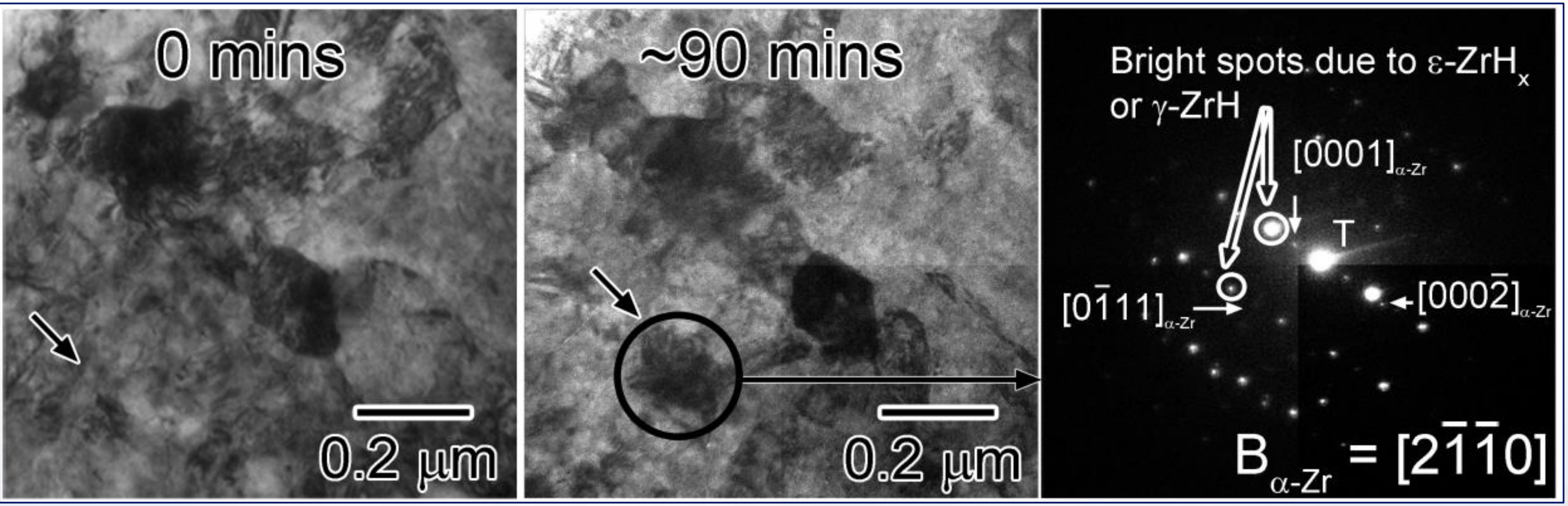
Most features are observed in both despite the decreased resolution resulting from the additional SiN window and 5 μm of air

In situ Observation of Hydride Formation in Zirlo

Collaborators: S. Rajasekhara and B.G. Clark

Absolute hydrogen pressure: 327 torr (~ 0.5 atm),

Ramp rate: 1 ^{o}C/s, Final temperature: ~ 400 C, Dwell time: ~ 90 mins



Hydride formation shown, for the first time by use of a novel TEM gas-cell stage, at elevated temperature and hydrogen pressure

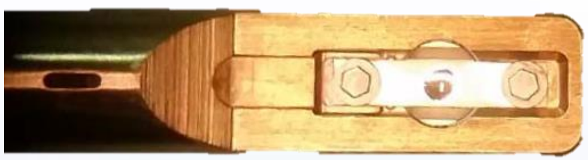
In situ Mechanical Testing

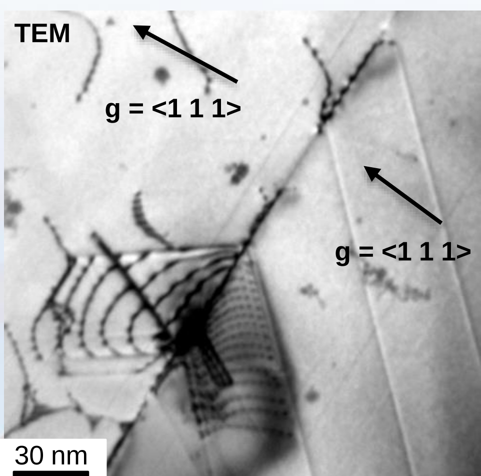
Qualitative "Bulk" Mechanical Testing

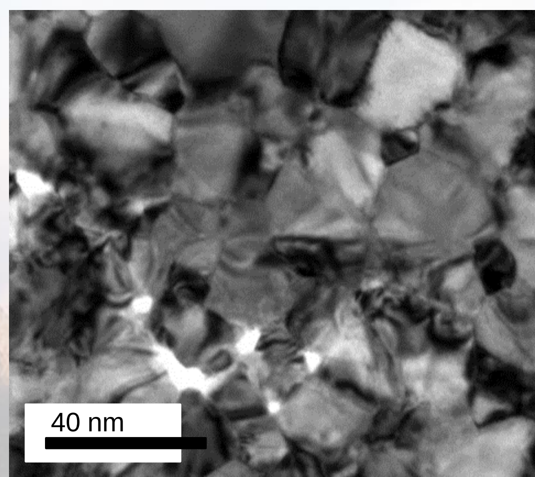
Minimal control over displacement and no "out-of-box" force information

- **Successful in studies in observing dislocation-GB interactions/mechanisms**
- **Ideally both grains have kinematic BF 2-beam conditions: challenging in ST holder**

Traditional Gatan Heating and Straining Holder







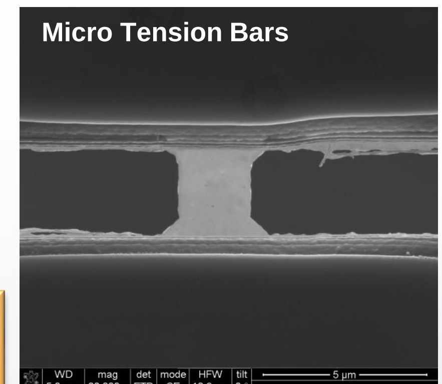
Quantitative Mechanical Testing

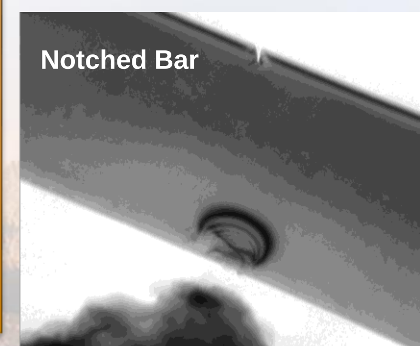
Minimal control over displacement and no "out-of-box" force information

- **Sub nanometer displacement resolution**
- **Quantitative force information with μN resolution**

Hysitron PI-95 Holder

1) Indentation
2) Tension
3) Fatigue
4) Creep
5) Compression
6) Bend



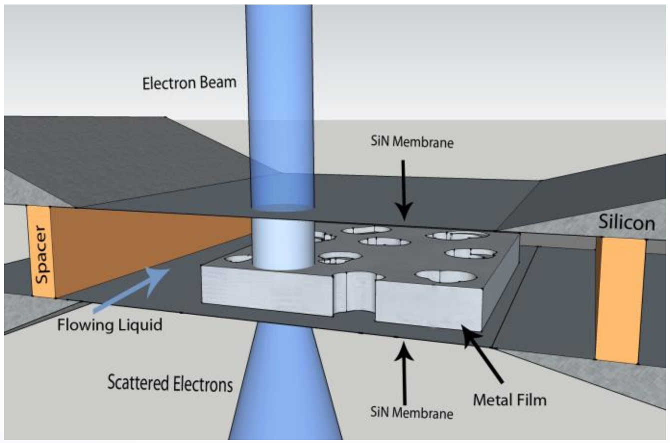


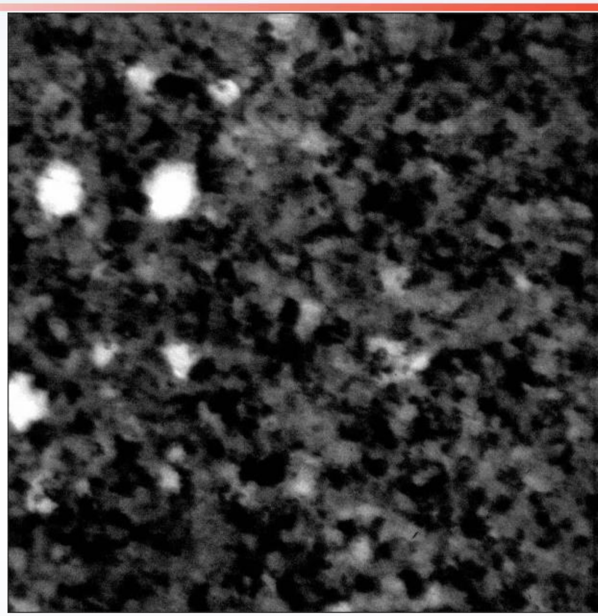
Can We Gain Insight into the Corrosion Process through *In situ* TEM?

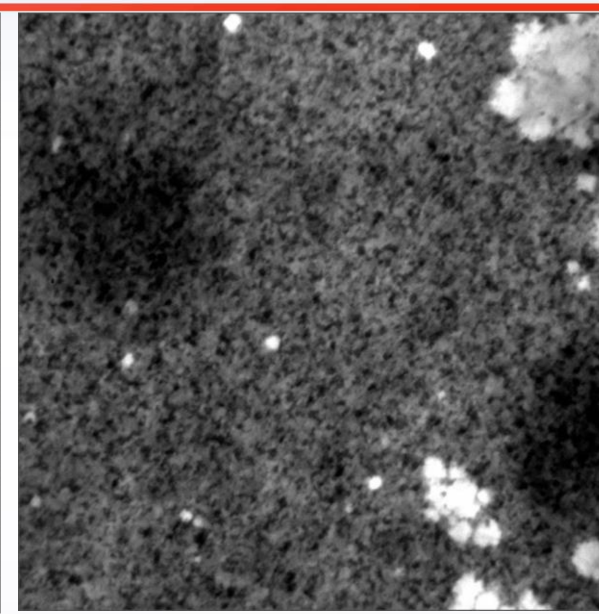
Contributors: D. Gross, J. Kacher, I.M. Robertson & Protochips, Inc.

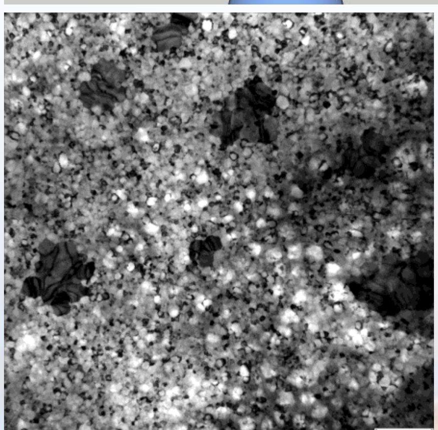
Microfluidic Stage

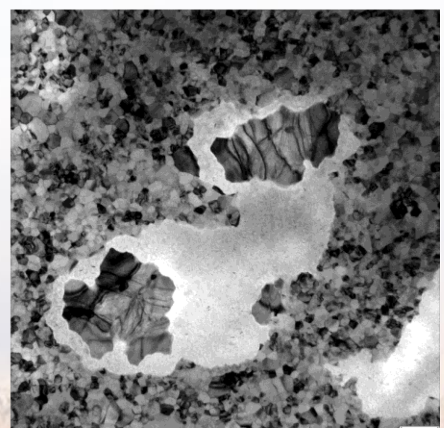
- **Mixing of two or more channels**
- **Continuous observation of the reaction channel**

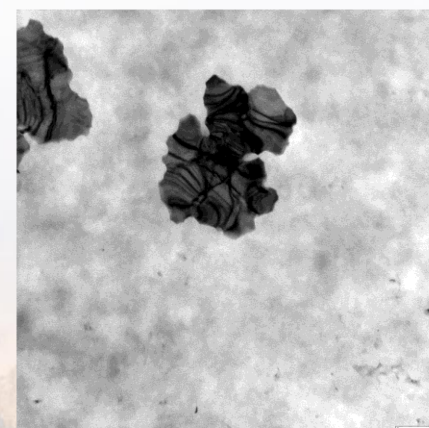










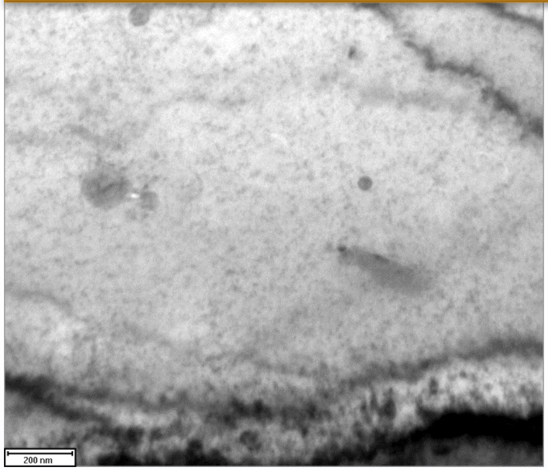


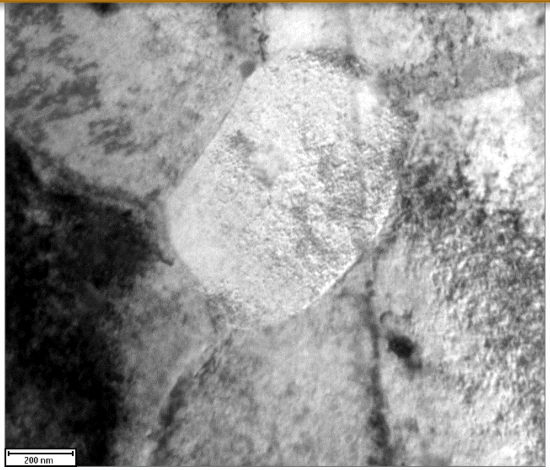
Pitting mechanisms during dilute flow of acetic acid over 99.95% nc-PLD Fe involves many grains.
Large grains resulting from annealing appear more corrosion tolerant

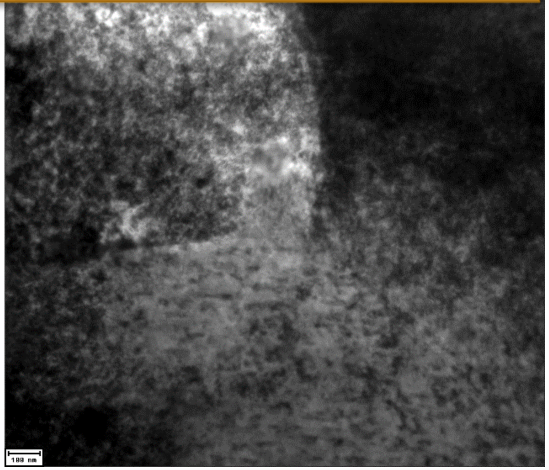
Summary

Zr Alloys

He accumulation → Damage + He → Damage + He + ^{3}H

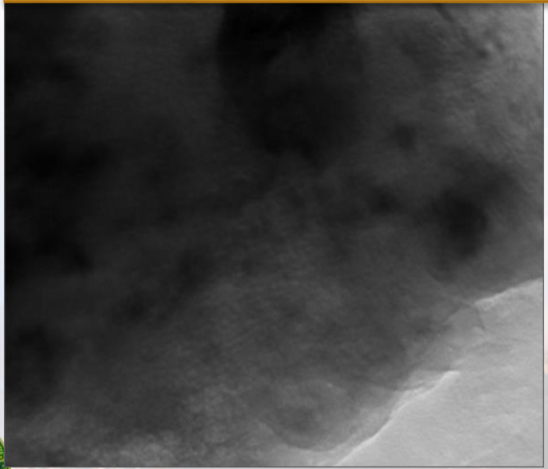


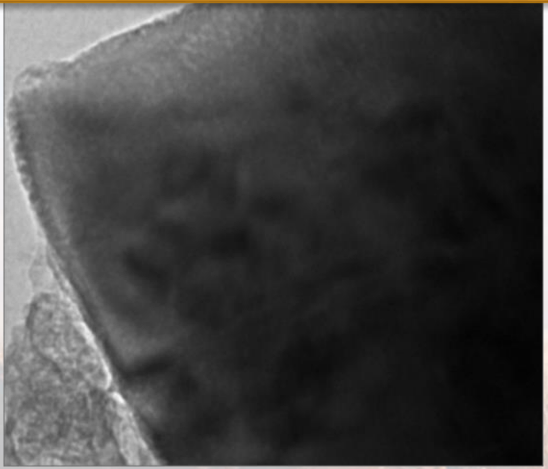


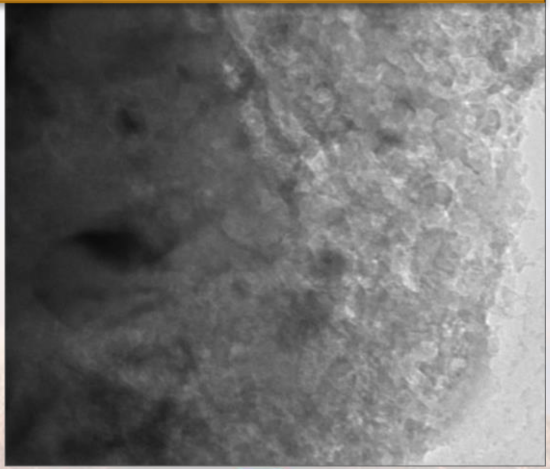


$LiAlO_2$

He accumulation → ^{3}H + He → Damage + He + ^{3}H







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