SAND2020-7357C

Sandia National Laboratories

Three-Dimensional Analysis of Materials at Multiple Length Scales

M&M 2020 MICROSCOPY & MICROANALYSIS VIRTUAL MEETING

Presentation # 654
P07.5 –FIB-SEM Technology and Electron Tomography for Materials Science and Engineering

PRESENTED BY

Josh Sugar

U.S. DEPARTMENT OF ENERGY NNSA

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.

Acknowledgements

He Bubbles in PdNi alloys aged in Tritium

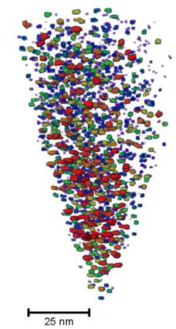
- Dave Robinson (SNL)
- Norm Bartelt (SNL)
- Noelle Catarineu (LLNL)
- Suzy Vitale (Carnegie Institute of Washington)

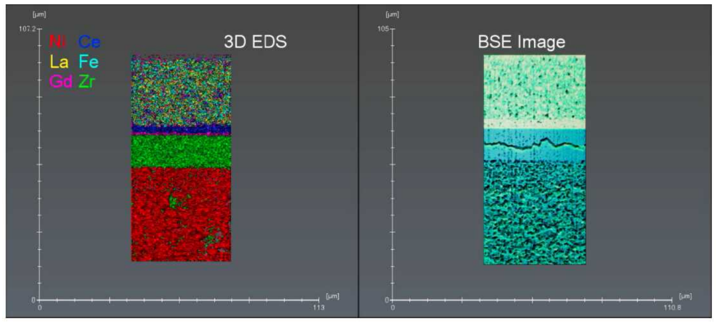
Aging and Degradation in High Temperature electrolysis materials

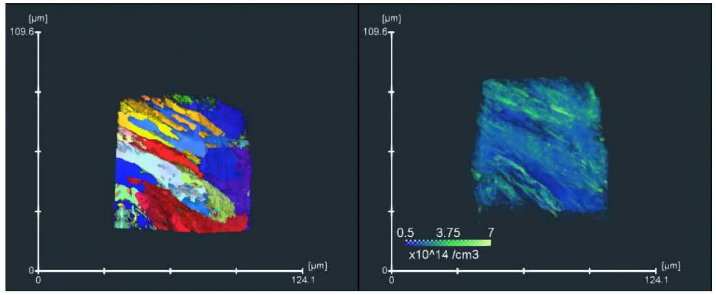
- Dong Ding (INL)
- Hanping Ding (INL)
- Heidy Vega (SNL)
- Warren York (SNL)

3D EBSD of Additively Manufactured Stainless Steels

- Bonnie Antoun (SNL)
- Coleman Alleman (SNL)
- Thale Smith (Mantle, Inc.)
- Heidy Vega (SNL)
- Warren York (SNL)
- Suzy Vitale (Carnegie Institute of Washington)







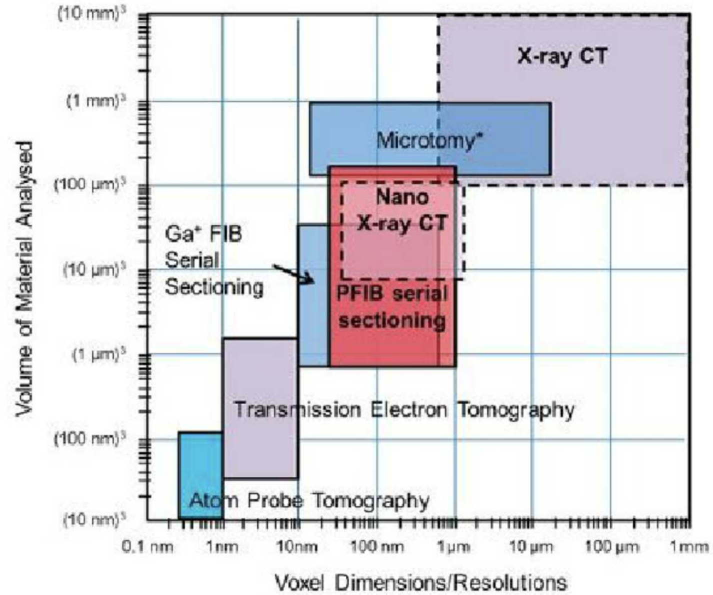
3D Experiments with Electrons are Complex and Time Consuming (Expensive)

Electrons do not penetrate very deep in most materials at typical operating voltages (20 – 300 kV)
- Limited to viewing approximately 1 μm deep in the SEM
- Thin, electron transparent samples needed in TEM (<100 nm)

Electron-based characterization techniques may have the best spatial resolution but field-of-view may be limited
- In the TEM, cubed microns
- In the FIB/SEM tens – hundreds of cubed microns

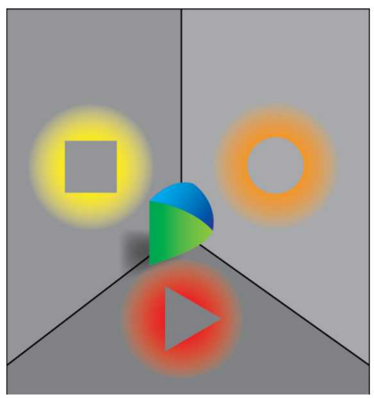
Alternative techniques are available to address gaps in scale
- Mechanical serial sectioning/microtomy
- X-Ray Computed Tomography
- Atom-Probe Tomography

When the analysis capabilities or spatial resolution of electrons makes sense, 3D analysis can be significant for understanding the nature of materials and answering scientific questions

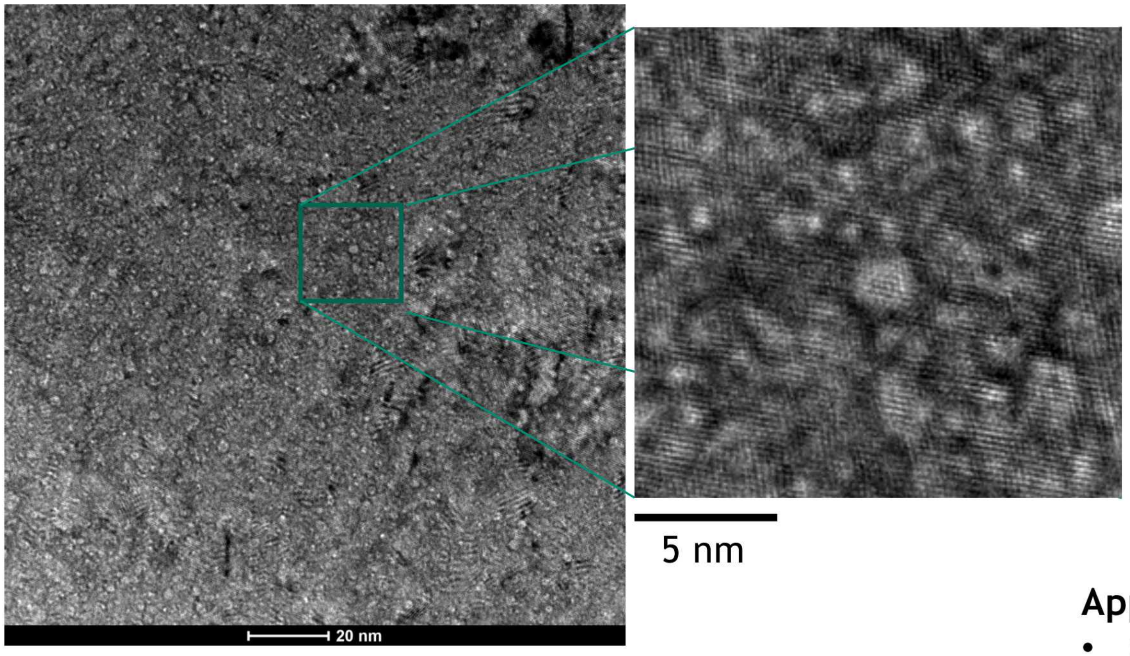


Burnett, T. *et al.* Xe Plasma FIB: 3D Microstructures from Nanometers to Hundreds of Micrometers. *Microscopy Today* **24**, 32-39

The projection problem exists for both single cross section SEM and TEM imaging



Helium Bubbles in Metals



^3H Decays into ^3He and forms bubbles in tritium storage materials

Bubbles are a few nm diameter, tens of nm apart.

Questions

- When did bubbles form?
  - Early nucleation or continual
- Where did the He come from?
  - Surrounding volume, coalescence, or ripening
- How much He is in each bubble?
  - Pressure

Approach

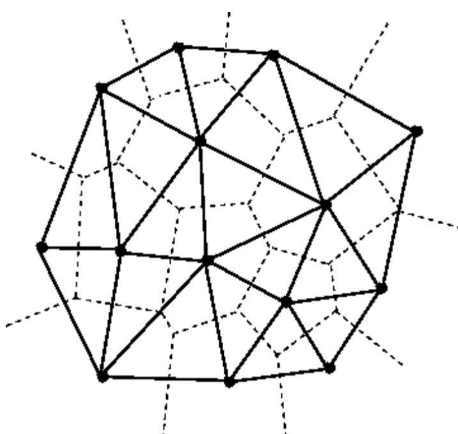
- Map bubbles in 3D using electron tomography
  - Eliminates 2D projection issues
- Use EELS to measure the pressure of He and to understand growth mechanisms

Goal: To develop improved models of helium bubble nucleation and growth, and better predict swelling, fracture, and ^3He release.

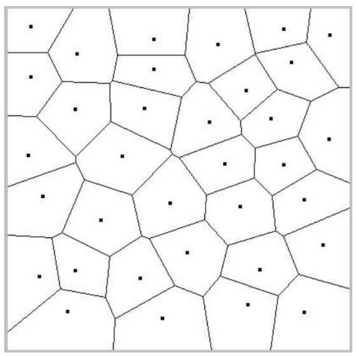
Capture Volume Theory

- If all bubbles nucleate at a same early time and their growth is diffusion limited, then they should contain the He generated in a capture region geometrically nearest each bubble.

- Capture volume is described by Voronoi tessellation.



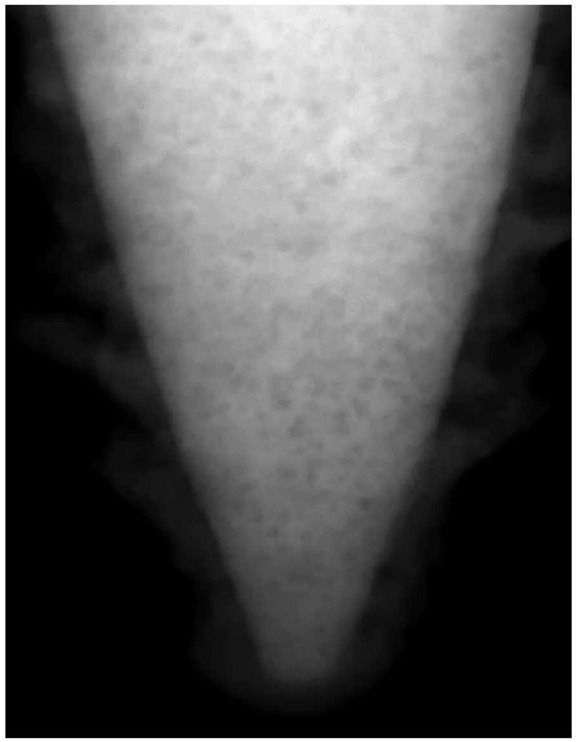
2D Voronoi tessellation

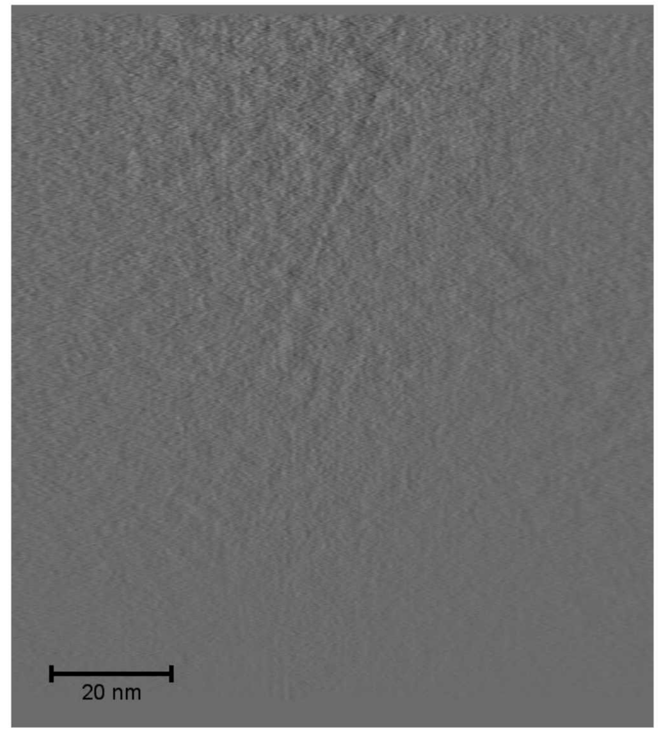


small capture area ⇒ small bubble?

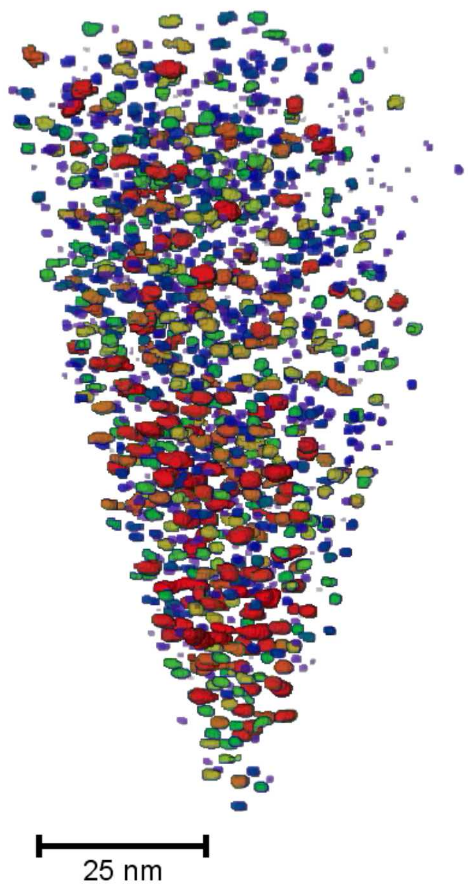
Dark field (HAADF) STEM Electron Tomogram

- Tritiated for 3.8 years (from a SRNL Pd-5 at.% Ni ribbon).
- No Grain Boundaries
- Estimated He/Pd = 0.12
- Bubbles are dark, ~2 nm diameters.
- Images taken from -70^{o} to 70^{o} (increment 1^{o}).



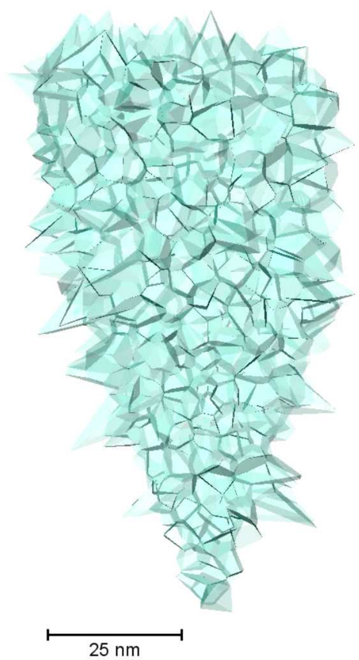


Reconstruction of the 3D Bubbles

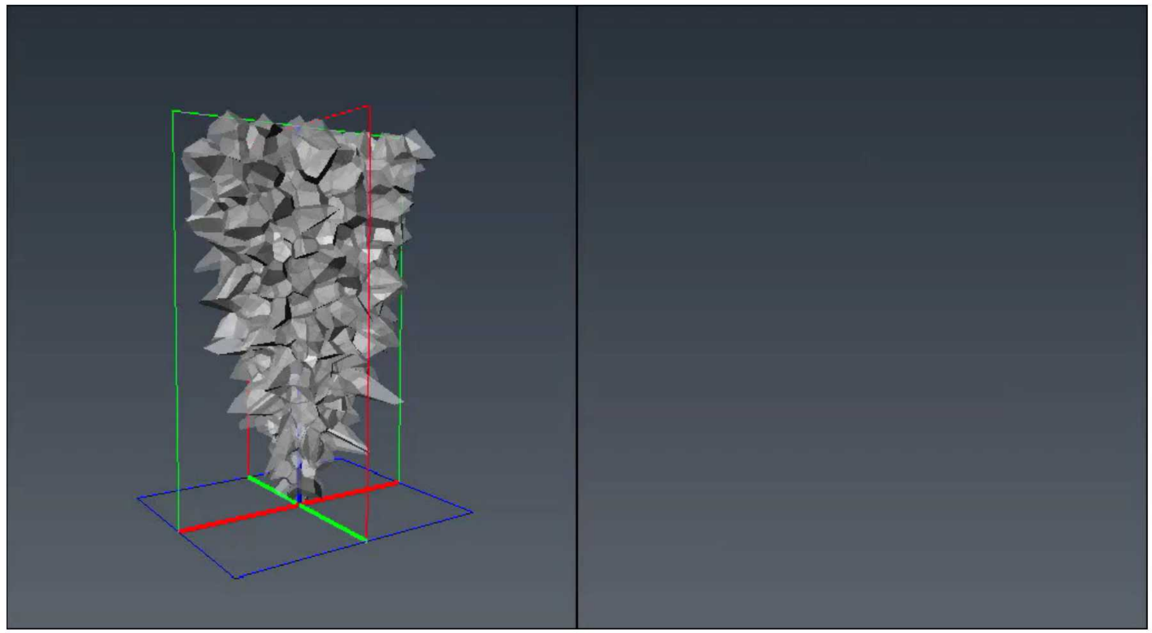


- 3D bubbles are reconstructed from images using the "*Weighted Back Projection*"
- ~1500 bubbles with average diameter 2 nm
- Bubbles can be elongated due to reconstruction artifacts
- Red bubbles are large, blue bubbles are small.

Reconstruction of Capture Volumes



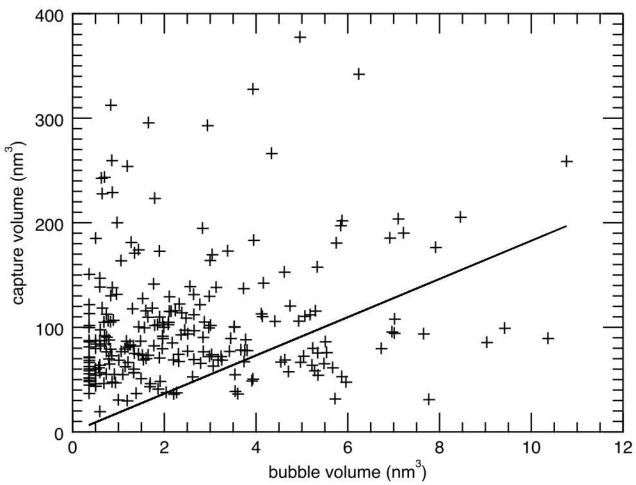
2D voronoi tessellation



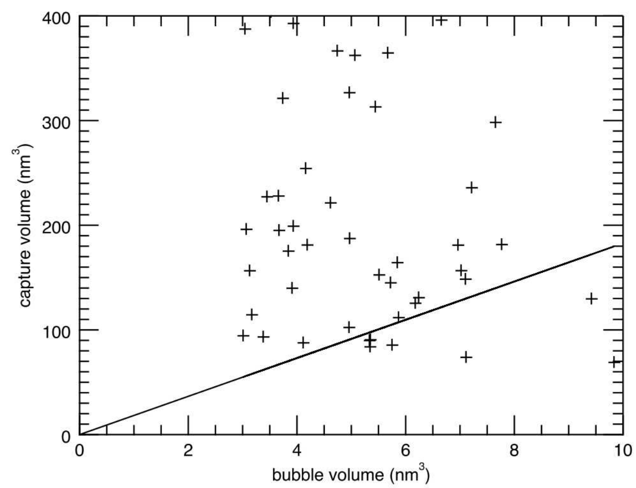
- Determined by 3D Voronoi tessellation of bubbles
- Outer layer of surface-crossing volumes is omitted from further analysis

Bubble and Capture Volume Correlation

Individual Capture Volume



Individual Capture Volume



Exclude bubbles smaller than 3 nm^3

Solid line: expected for 3.8 year of tritium decay (He/Pd = 1.2) if bubbles have 5GPa pressure based on the loop punching growth

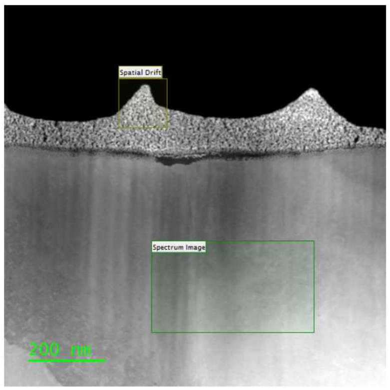
Still no correlation!

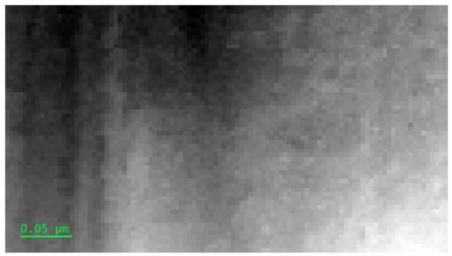
No bubble and capture volume correlation is found!

EELS measurements of pressure will help determine which bubbles grow

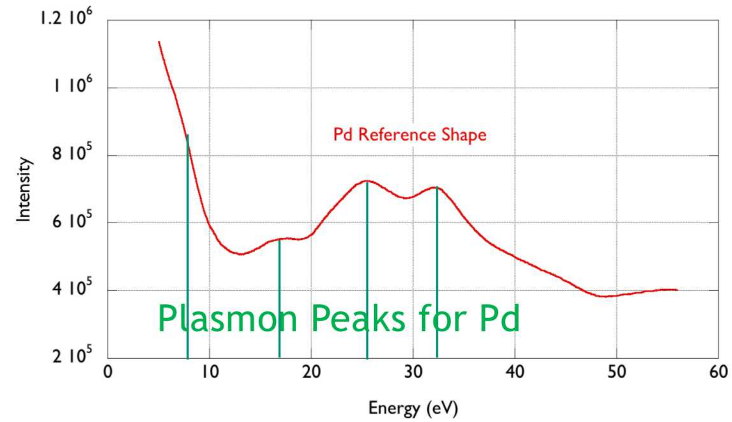
2 Step Fitting with Pure Pd Reference and Gaussians

Step 1: Get Residual Signal After MLLS fit with Pd ref

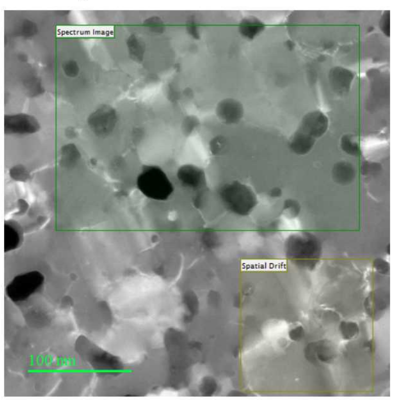


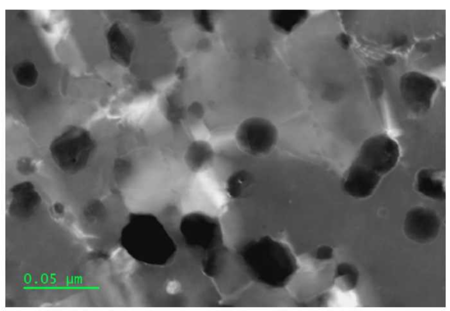


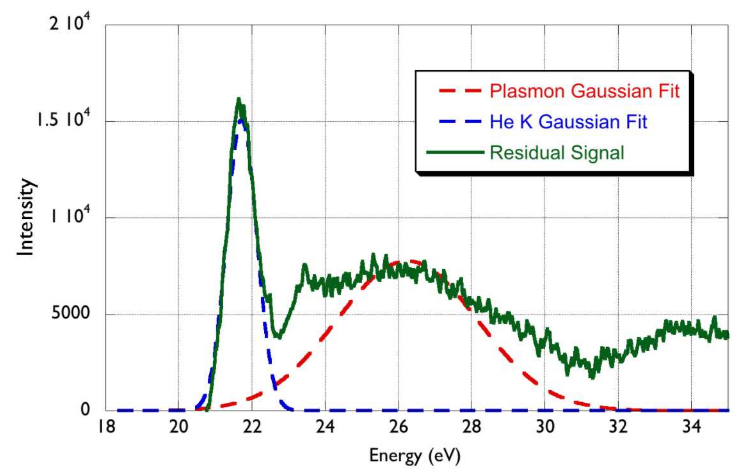
Annealed Pd Wire



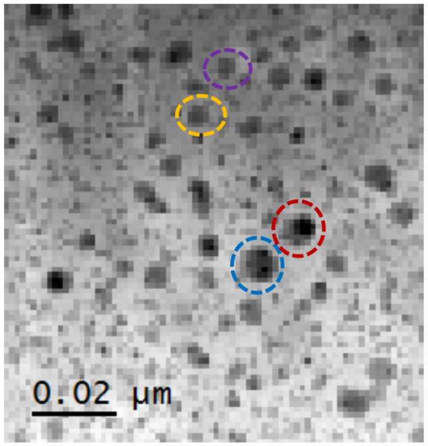
Step 2: Fit Residual with 2 Gaussians

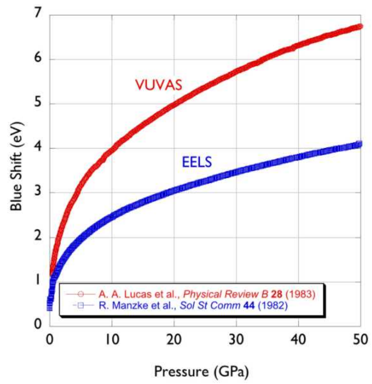




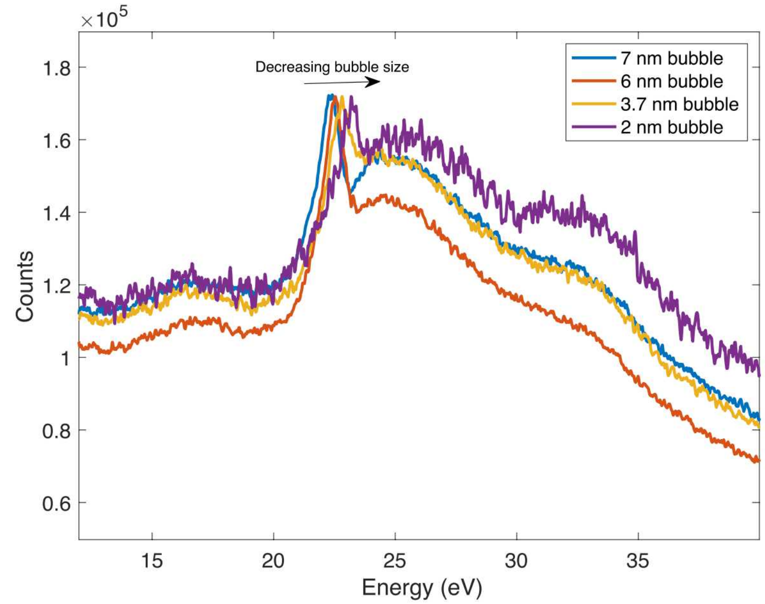


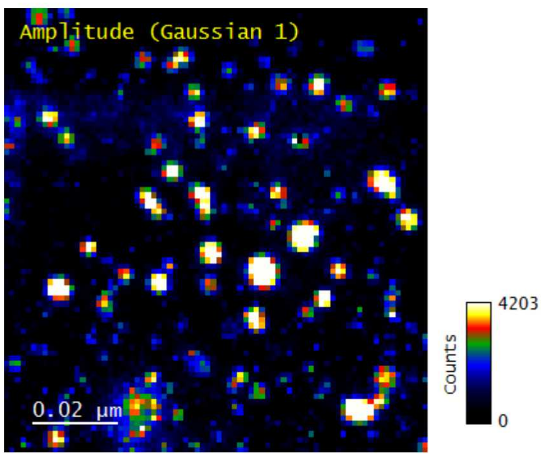
Correlation With Size and HeK Peak Energy

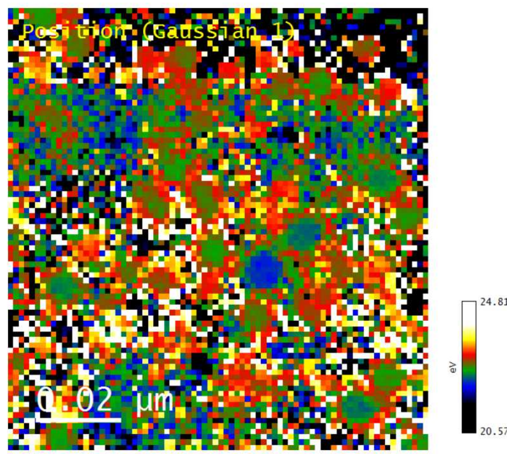




S.E. Donnelly, *Radiation Effects* **90** (1985)



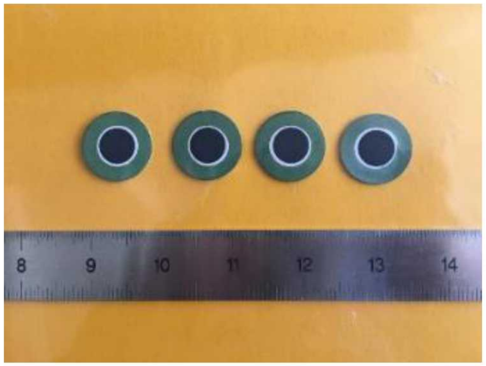




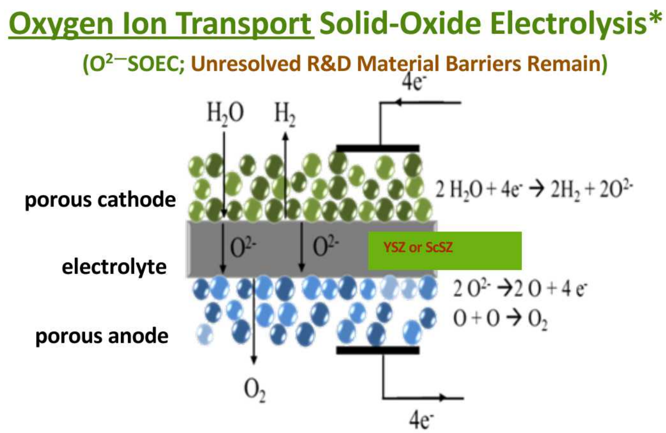
He K gaussian position and amplitude

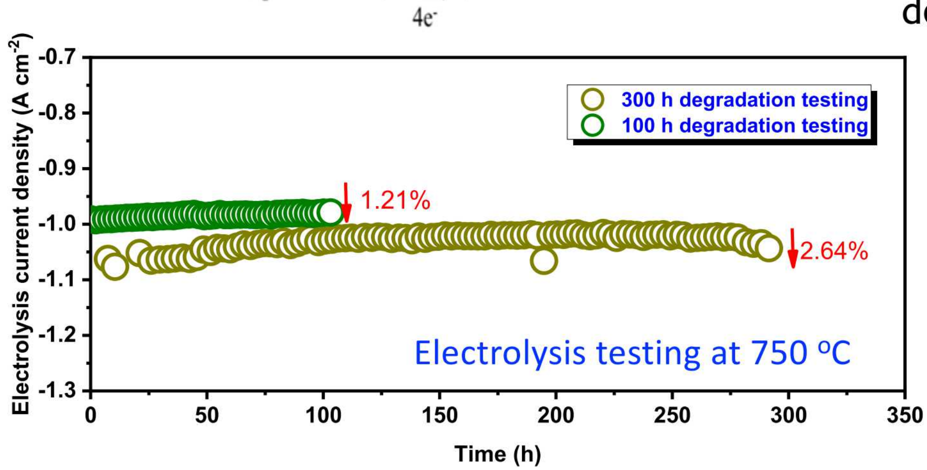
- We can combine the other techniques in the TEM to understand how much He is in each bubble
- We measure pressures ~5 Gpa, which is expected for these size bubbles with $P=2\gamma/r$
- 3D analysis helped us identify gaps in nucleation theory for tritium decay

Degradation in High-Temperature Electrolyzers



YSZ-based reference cells





The Critical questions are:

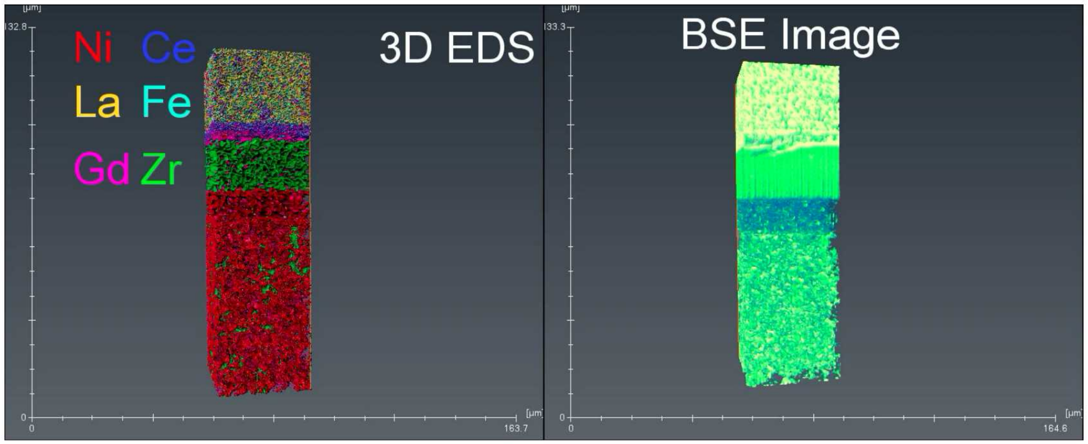
- How reproducible and reliable are the manufacturing processes?
- What are the critical degradation mechanisms that lead to decreased performance over time?
  - How can we slow them down or prevent them

The complex microstructural details are better represented by 3D microstructural measurements

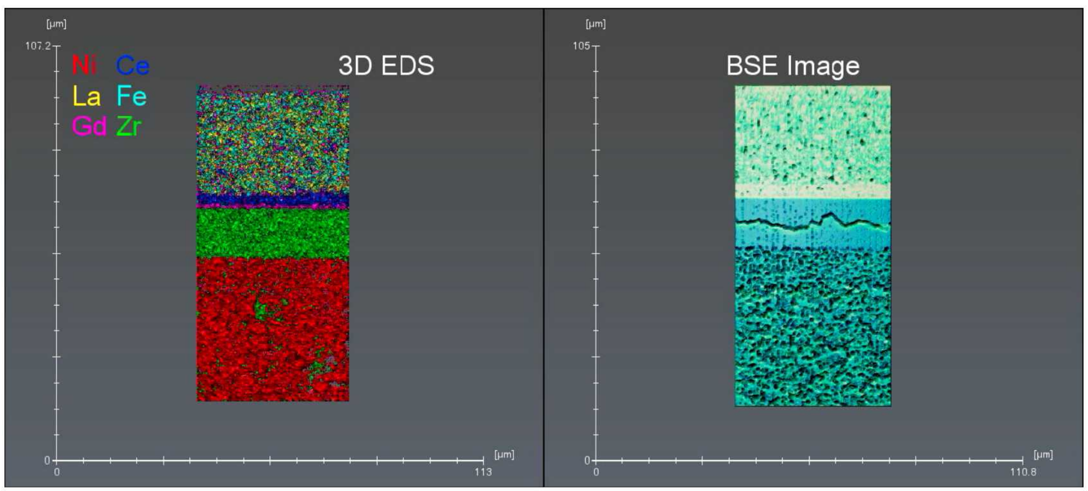
3D FIB-SEM Serial Sectioning of the Entire Cell Stack

We can learn where we need to look in more detail.

As-received



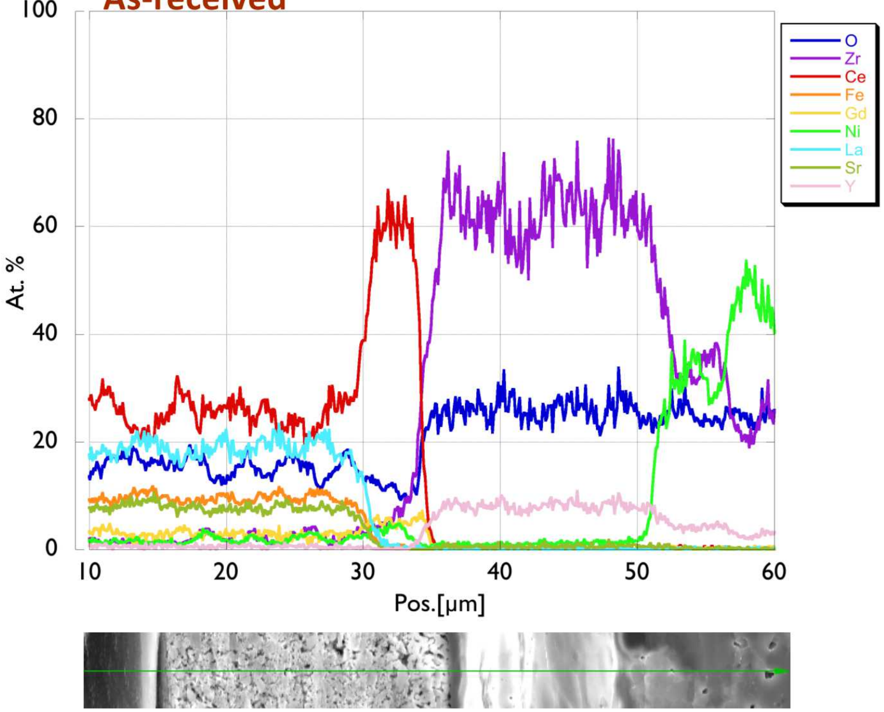
750°C
50 hours
Electrolysis mode



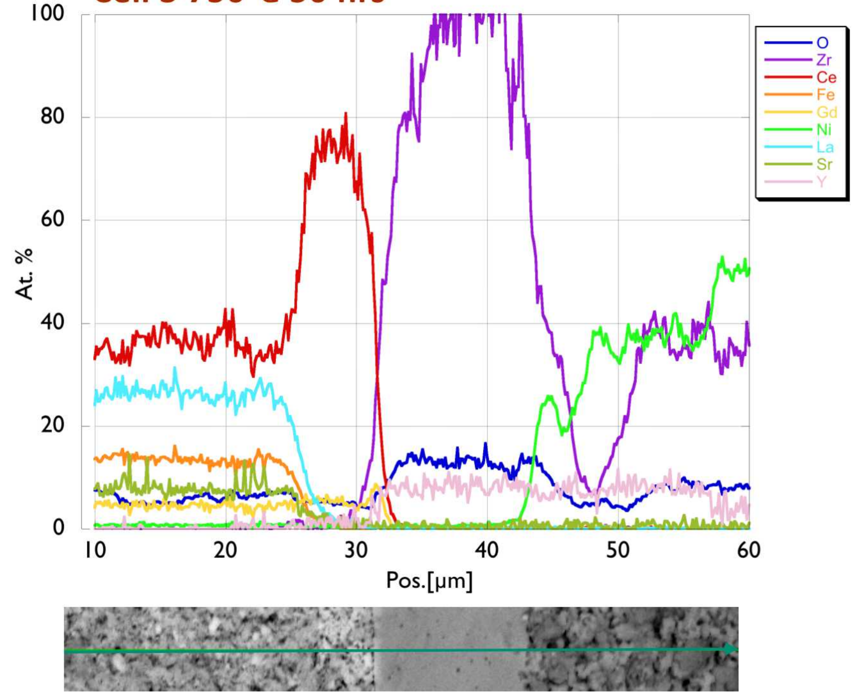
- **Large crack in the YSZ layer**
- **Change in Gd distribution**

Singe Slice Data Confirms the 3D EDS Observation for Gd Segregation

As-received

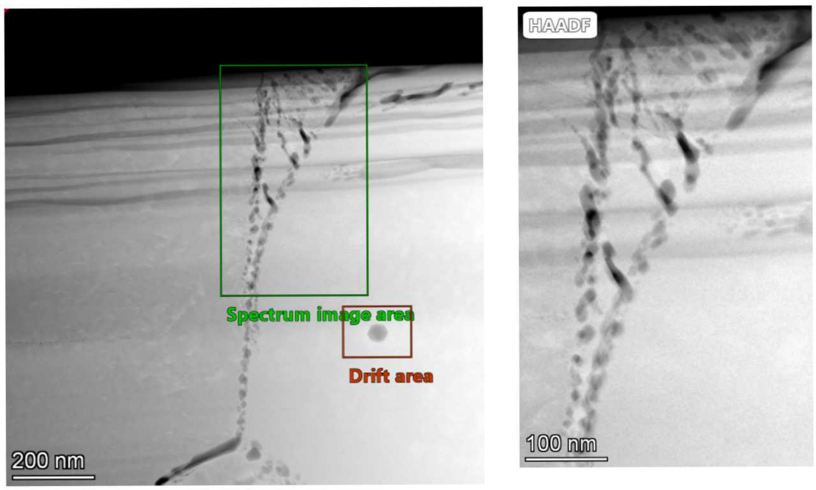


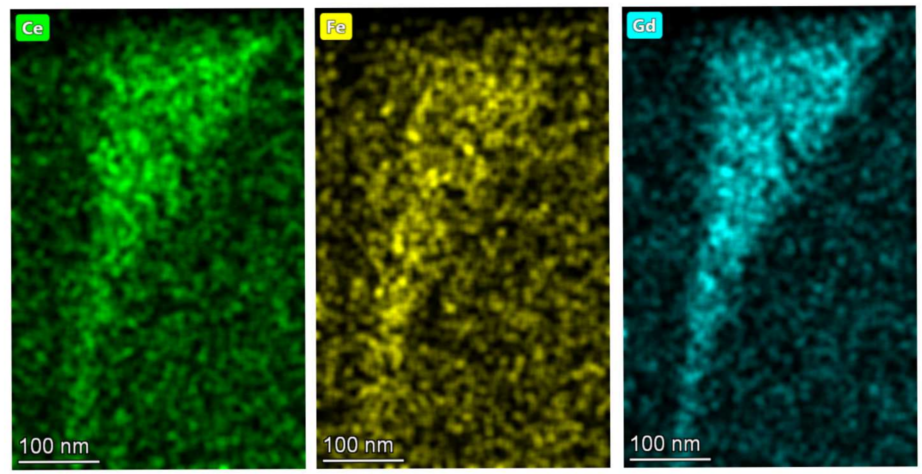
Cell 3 750°C 50 hrs



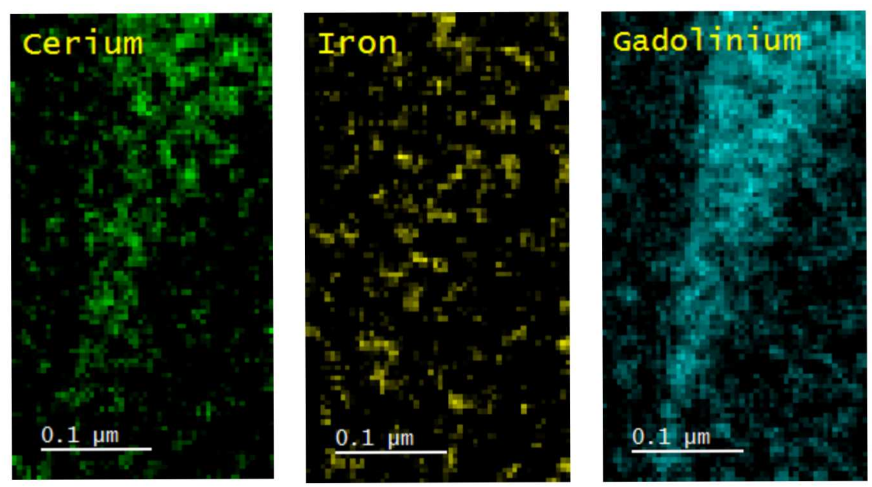
- **Distribution of elements is relatively unchanged after cycling**
- **Gd is still at LCSF/YSZ interface and perhaps is sharper in the after cycling condition**
- **Ce is still more concentrated at LCSF/YSZ Interface and is relatively sharp**
  - **Any differences in the thickness of the Ce-rich layer could be attributed to differences in the manufacturing process**
- **Is this capturing the elemental redistribution at the correct scale?**

Subtle Compositional Rearrangement Could Explain the Cracking





EDS maps

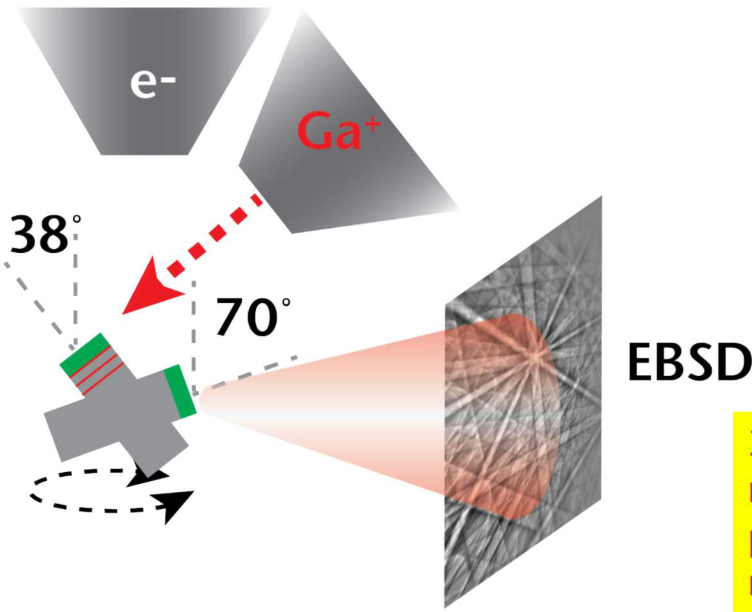


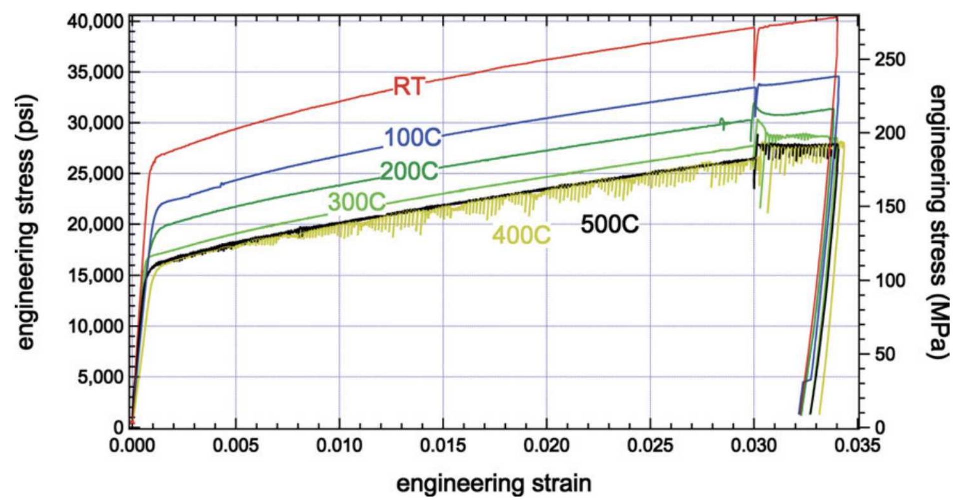
EELS maps

EDS and EELS maps confirm that Ce, Fe, and Gd has segregated to the grain boundary of YSZ, which could explain the cracking

Dynamic Strain Aging of Stainless Steels

- A phenomenon where dislocations interact with solute atoms
  - Is sensitive to temperature
  - Causes reversal of expected trends with temperature and strain rate
- Accurate prediction of properties at elevated temperature requires that we can predict this behavior



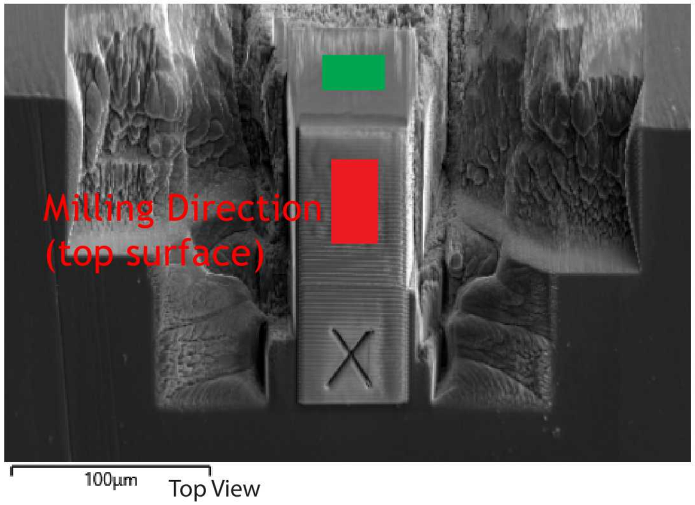


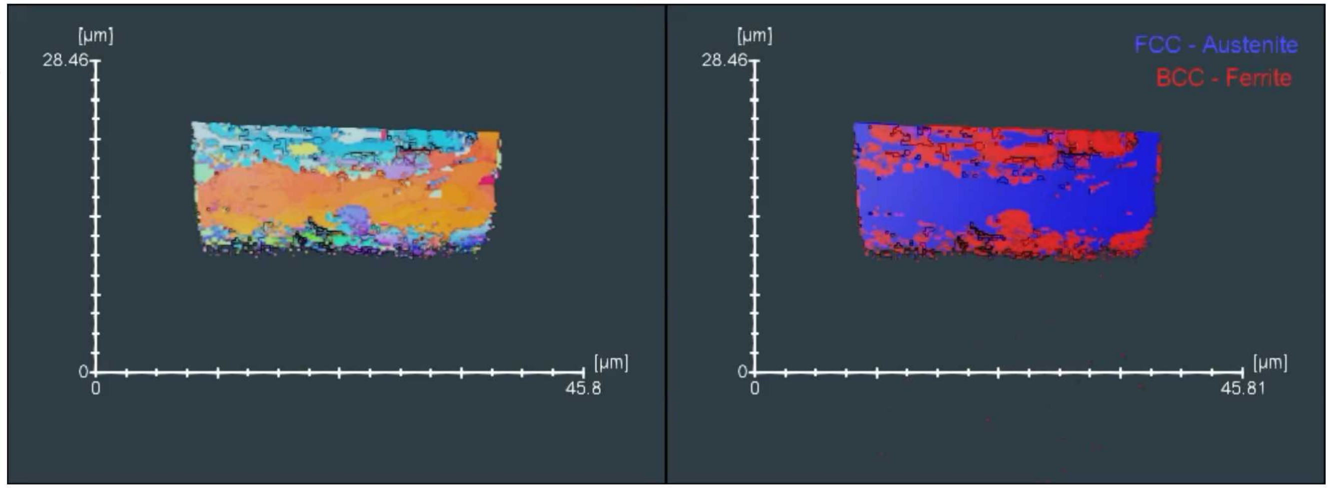
Antoun, B. R., Chambers, R. S., Emery, J. M. & Brown, A. A. in *Challenges in Mechanics of Time Dependent Materials, Vol 2 Conference Proceedings of the Society for Experimental Mechanics Series* (eds B. Antoun *et al.*) 141-148 (Springer, 2017).

3D measurements of dislocation structures in deformed metals can help us validate models (e.g. crystal plasticity) that will predict deformation behaviors in metals

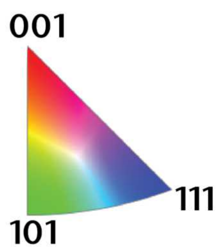
Stainless Steels of Interest Had Unexpected Phase Transformations

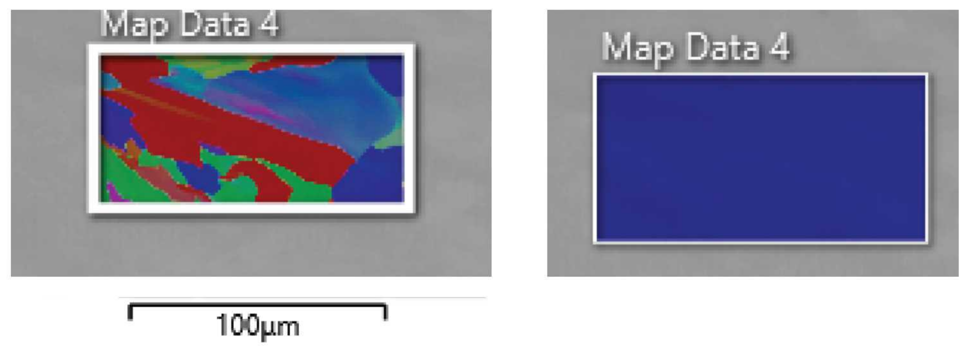
EBSD analysis surface





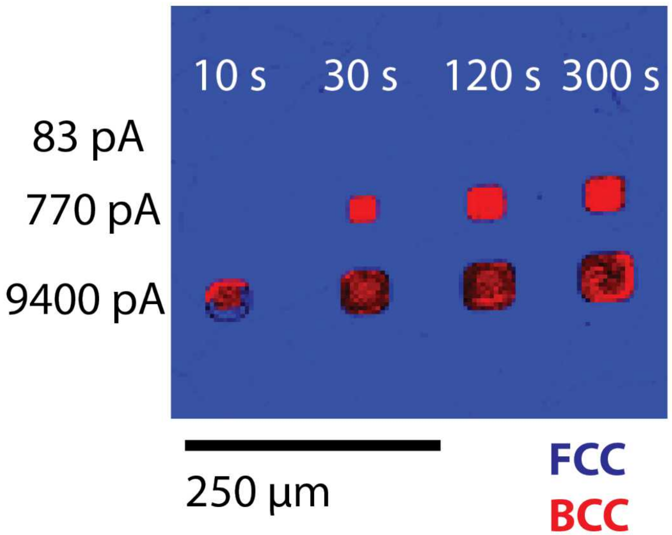
EBSD from top surface showed ferrite fraction=0 so something was not correct





What Can we Do to Prevent the Transformation?

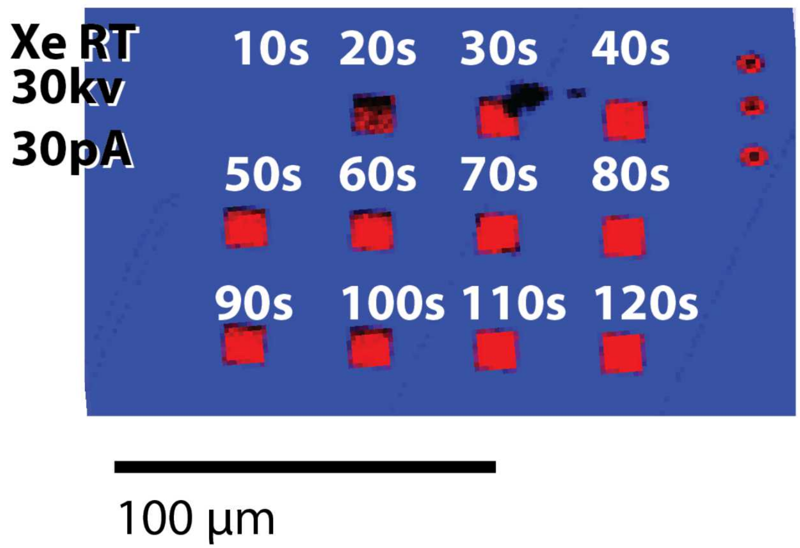
Ga ions; Different Doses



More Dose, more transformation

A lower current takes longer to cut the same volume as a higher current

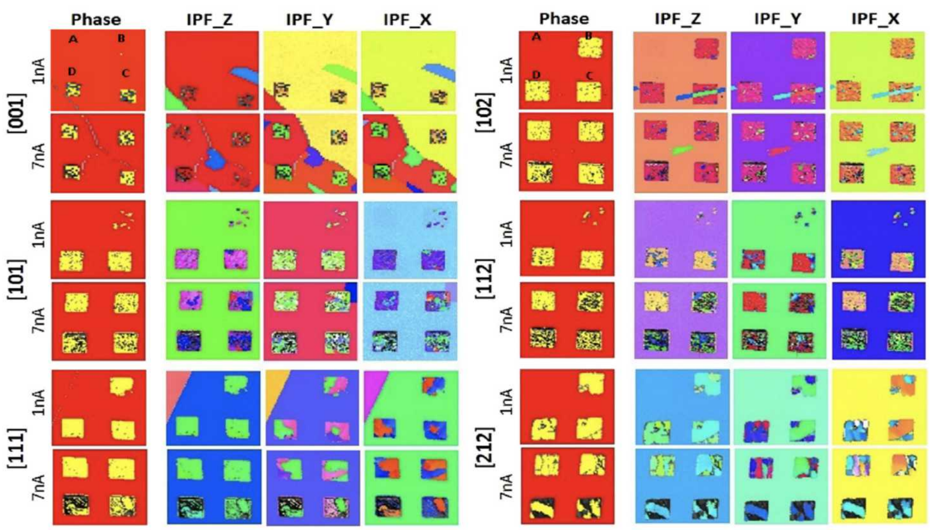
Xe ions; Different Doses



Xe ions, transformation occurs, not just Ga alloying!

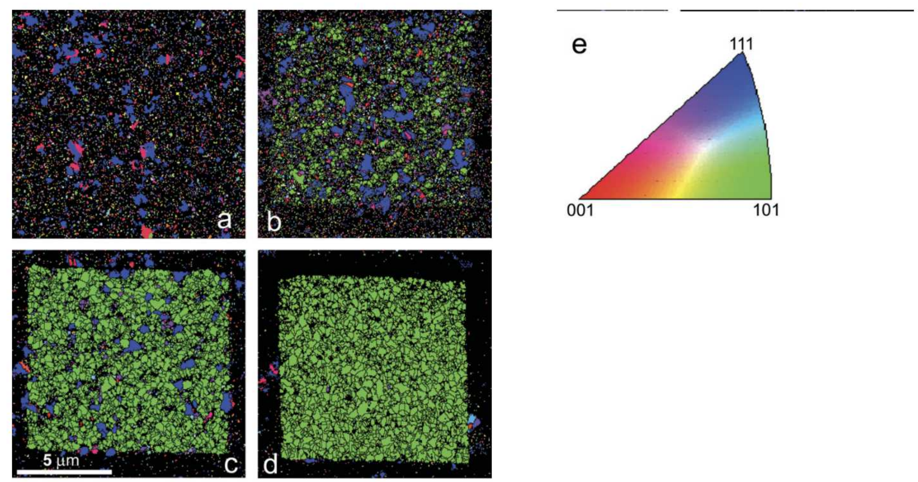
Xe operates at higher currents generally, and still transforms the metal

These Transformations Have Been Observed Before



Babu, R. P.; Irukuvarghula, S.; Harte, A.; Preuss, M. *Acta Mater* **2016,** 120, 391-402.

Orientation dependence of austenite → ferrite in 316

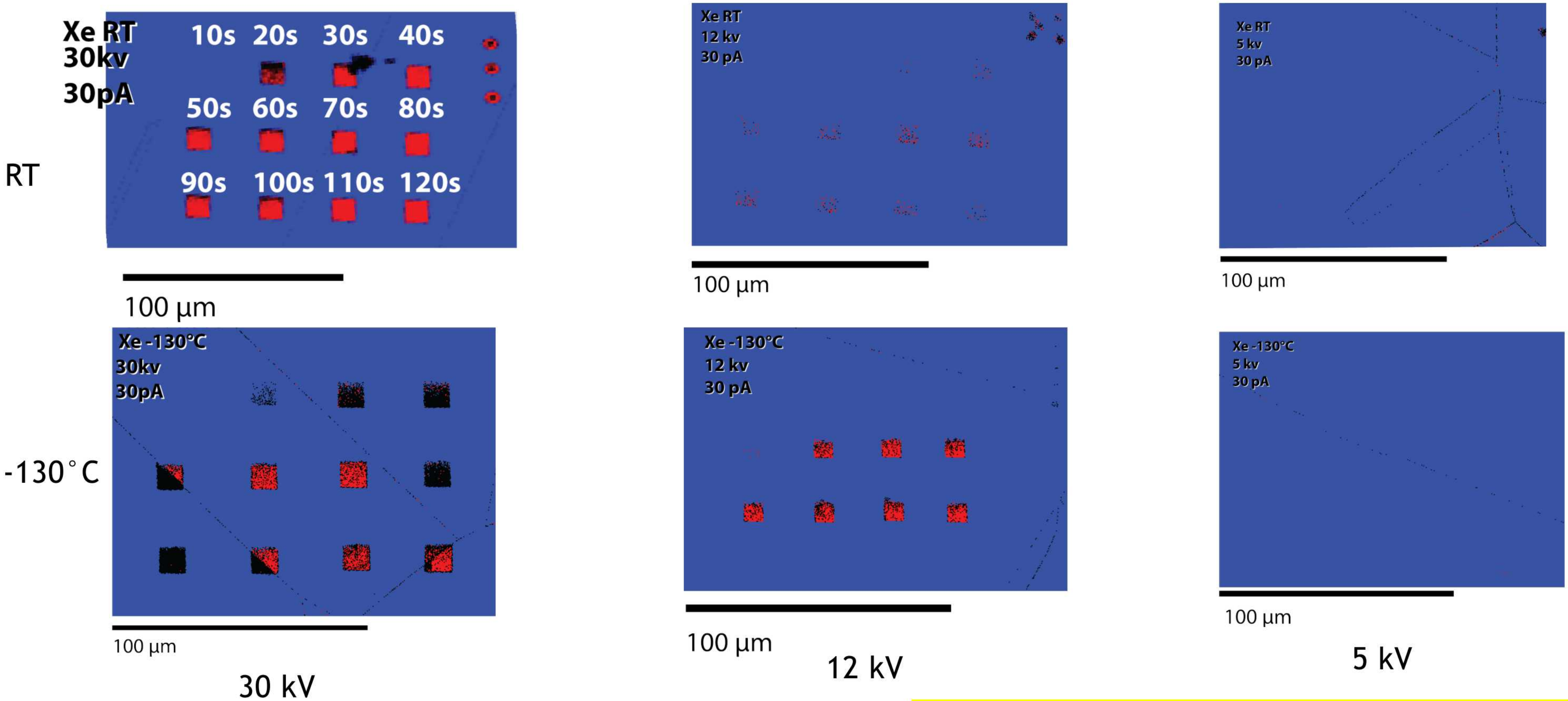


Michael, J. R. *Microsc Microanal* **2011,** 17, (3), 386-397.

Ga implantation can change the orientation of grains in Cu

Ion implantation creates an environment for stainless steels that could have a high propensity for an artificial transformation

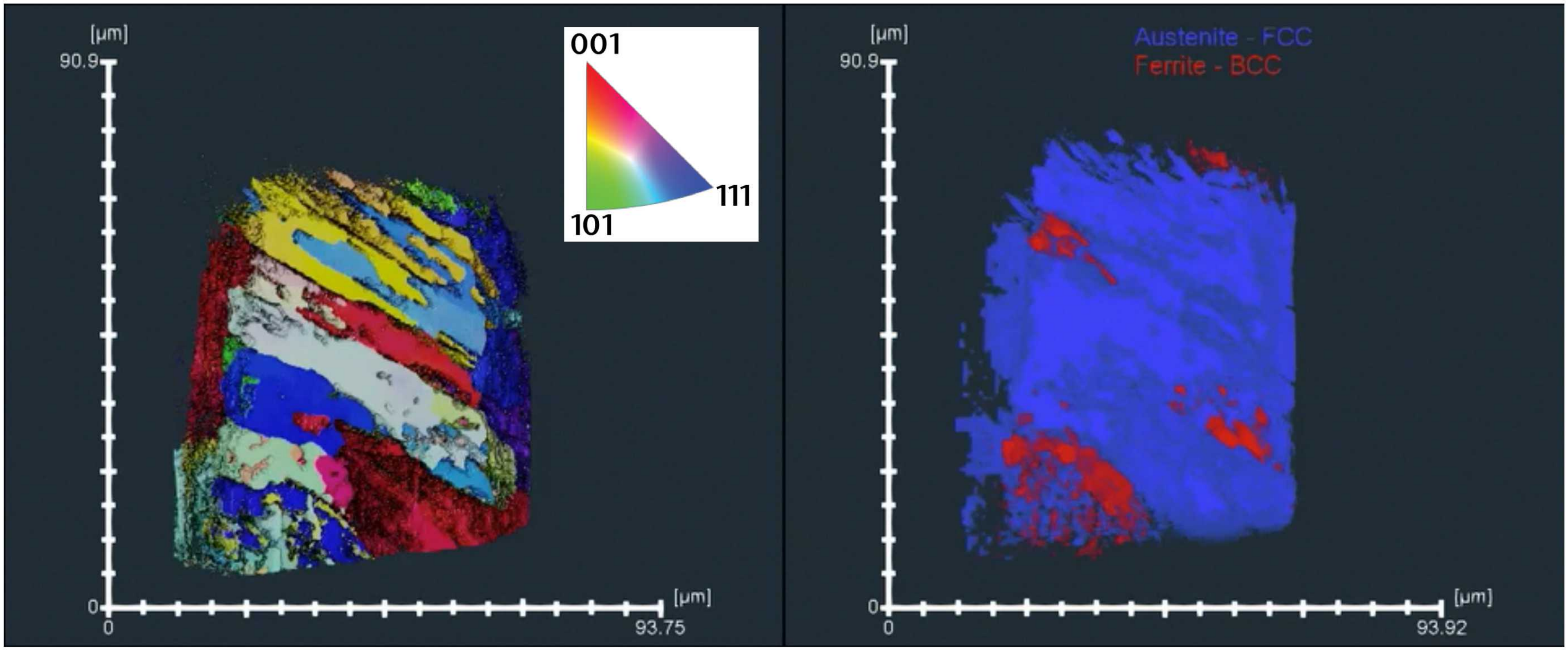
What Approaches Are Available to Reduce this Artifact?



- Cryotemperatures don't help much
- Lower kV looks promising, but it will take longer

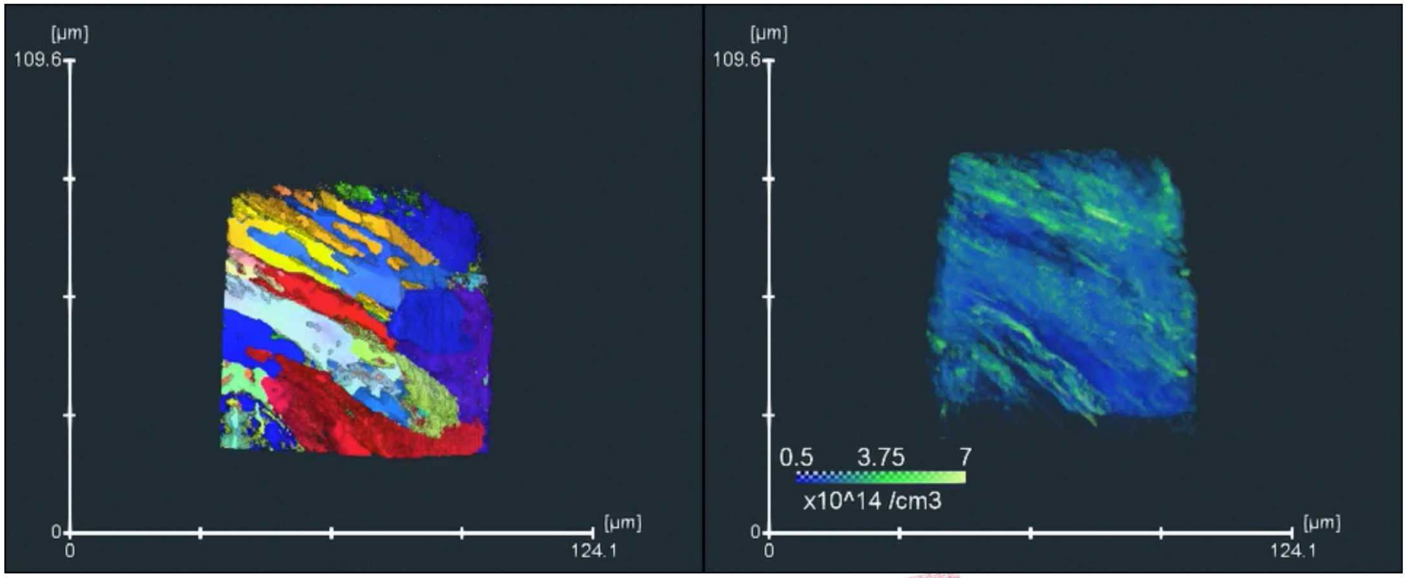
A10.3 8/6 2-3:15 *308-Ion Induced Transformations in Metastable Phases* by Lucille Giannuzzi et al.

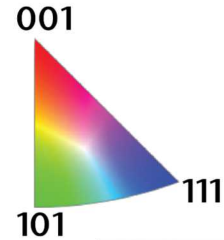
Successful Data From Composition with More Stable Austenite

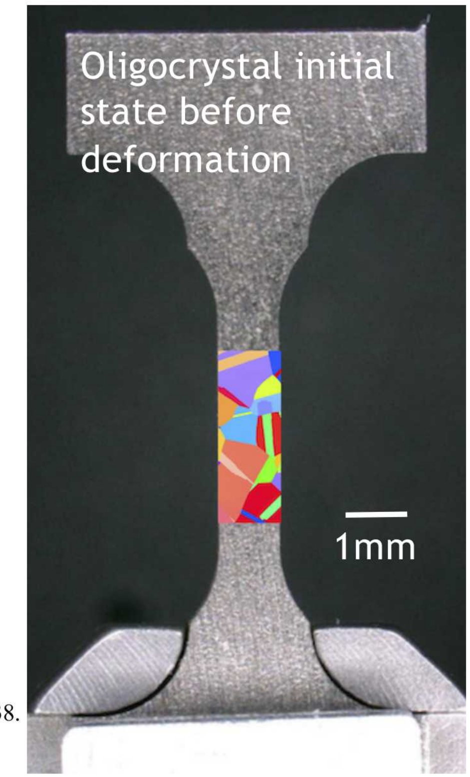


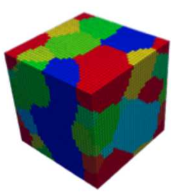
Wt%	Cr	Ni	Mn	Si	S	P	N	C	O	Fe
Good	19.3	10	1.5	.005	.007	.008	.082	.011	.018	Bal.
Bad	18	9.8	1.4	.6	.004	.013	.05	.01	.04	Bal.

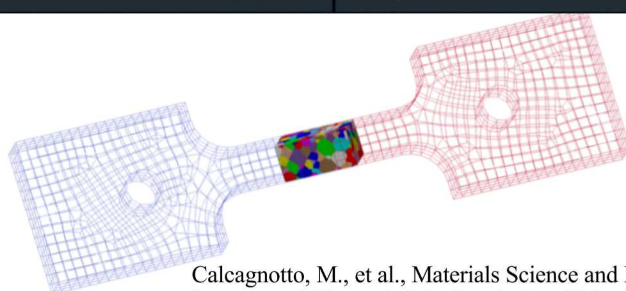
Can Calculate the GND Density in the Volume for Modeling Validation Experiments







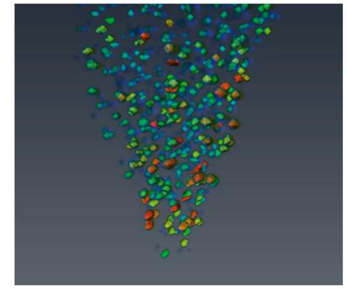


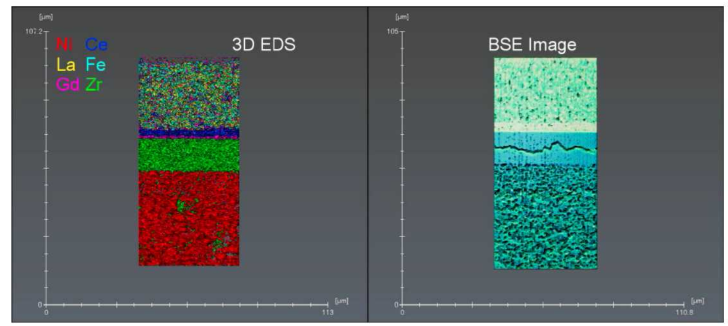


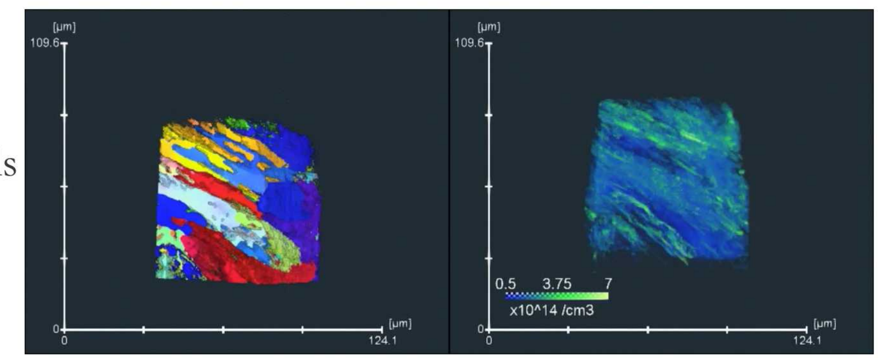
Calcagnotto, M., et al., Materials Science and Engineering: A, 2010. **527**(10–11): p. 2738-2746.
Lawrence, S.K., et al., Metallurgical and Materials Transactions A, 2014. **45**(10): p. 4307-4315.
Moussa, C., et al., IOP Conference Series: Materials Science and Engineering, 2015. **89**(1): p. 012038.
Kubin, L.P. and A. Mortensen, Scripta Materialia, 2003. **48**(2): p. 119-125.
Gao, H., et al., Journal of the Mechanics and Physics of Solids, 1999. **47**(6): p. 1239-1263.
Kamaya, M., Ultramicroscopy, 2011. **111**(8): p. 1189-1199.

Summary

- 3D Electron Tomography and EELS provides critical information for understanding and refining models of gaseous bubble formation in metals
  - The three dimensional size and location distribution of He bubbles in aged Pd-Ni after tritium decay shows no correlation between bubble size and capture volume size
  - Bubble nucleation occurs throughout aging process
- Finally we can detect He atoms in nanoscale bubbles and quantitatively check classic theories of radiation damage in materials
- Combined 3D analysis and conventional cross-sectional analysis provide insight into degradation mechanisms in high-temperature electrolyzers
- 3D EBSD allows us to have 3D representations of dislocation structures that can be used for validation in crystal plasticity models







Conclusions

3D electron microscopy experiments have the potential to provide materials information with fidelity that may not be available by other techniques

- Morphological information
- Crystallographic Information
- Compositional Information

The experiments are challenging and time consuming, and it is important to be mindful of potential artifacts that result from the experimental technique

- Automation, detection limits, and speed are constantly improving and providing more access to these experiments