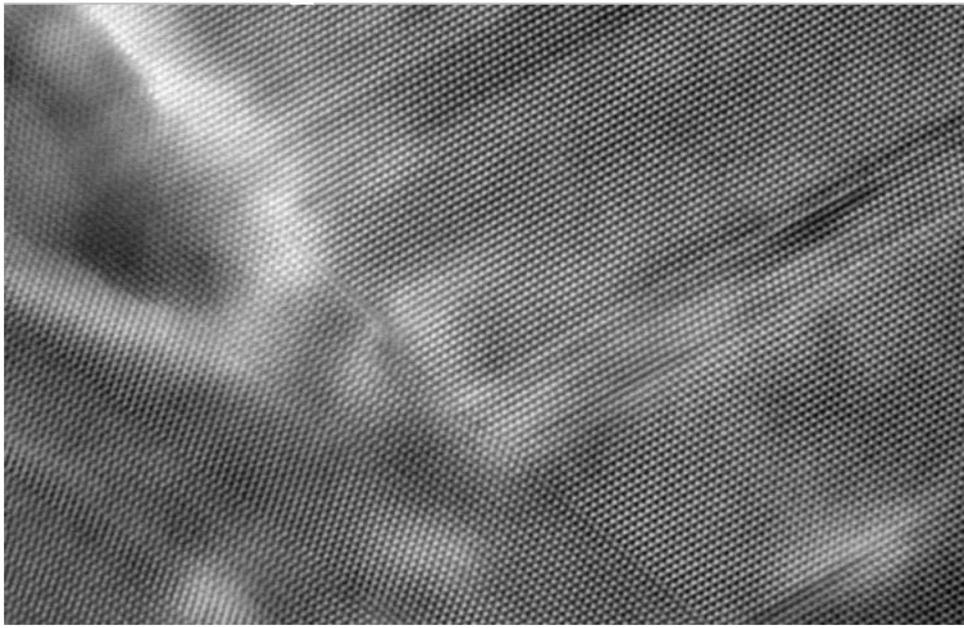
Interrogating atomic- and nanoscaled defects of structural metals using advanced microscopy techniques

SAND2020-0536PE



Presented by:

Julian E.C. Sabisch

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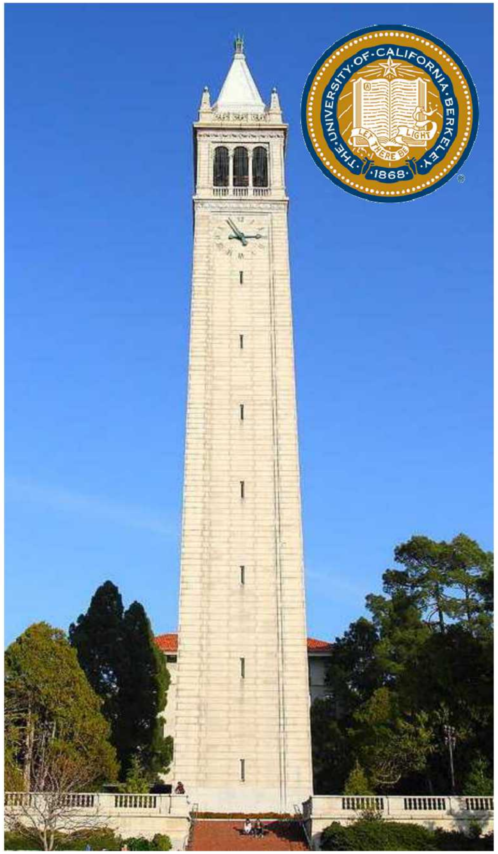
Personal Background

Sandia National Laboratories

- BS in Materials Science from UC Berkeley.
- MS in Materials Science from UC Berkeley.
  - Masters thesis developed a methodology for recycling end-of-life commercial lithium-ion batteries and re-casting them into new battery cells.
- PhD in Materials Science from UC Berkeley.
  - Advised by Prof. Andrew M. Minor. Dissertation investigated microstructural evolution of pure Re metal for the development of chemically complex replacement alloys.
- Post-Doctoral Work was performed at Sandia National Laboratories, Livermore.
  - Mentored by Douglas L. Medlin. Postdoctoral work will comprise this presentation.

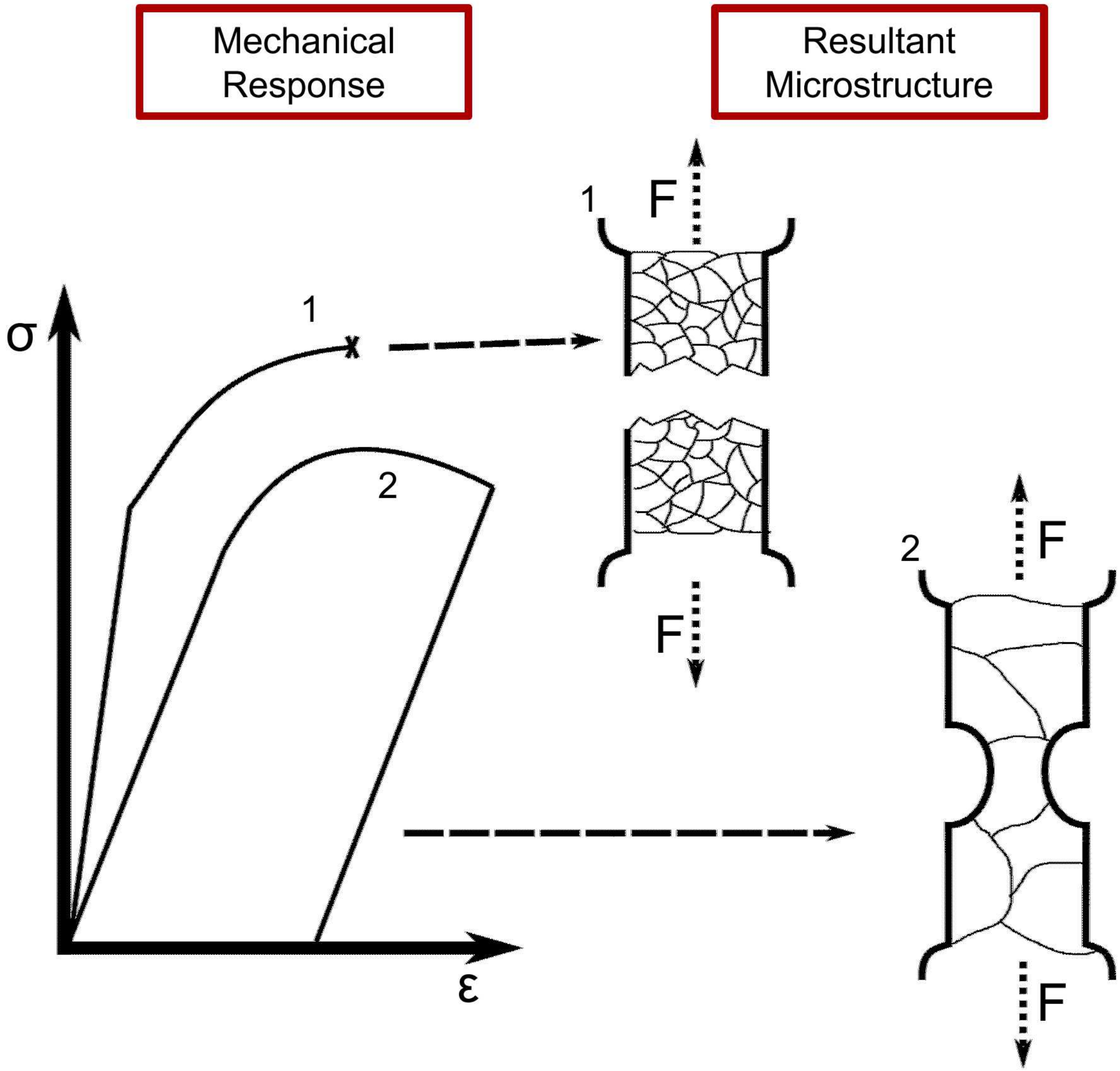


Outline

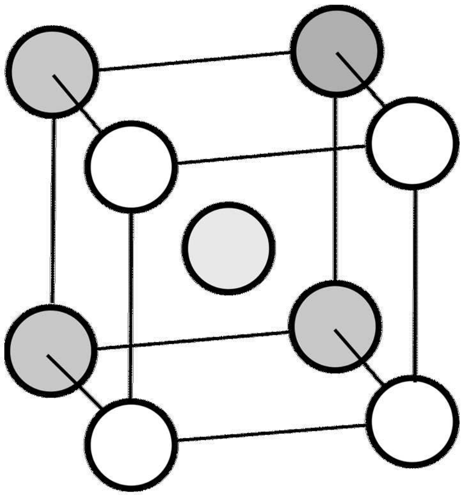
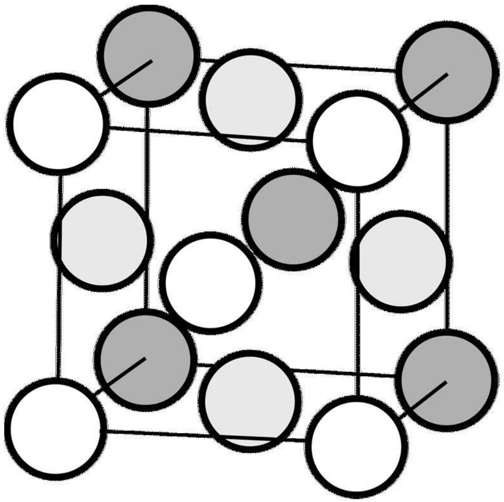
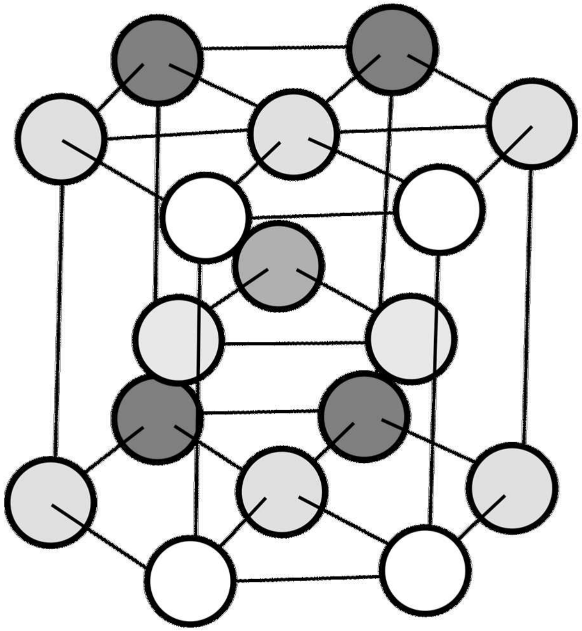
- **General information on defects, microscopy, and materials.**
- Microstructural effect of hydrogen on 304L stainless steel.
  - Observations of the microstructural evolution between hydrogen charged (HC) and non-charged (NC) samples below 5% strain.
  - High strain samples (20% strain) were investigated with HRSTEM images showing the nucleus of secondary phases.
- Investigation of ductile rupture in pure copper using high resolution STEM.
  - Observations of void nucleation at inclusions within the copper matrix.
  - High resolution and mass-thickness contrast STEM imaging of nanoscaled voids within the deformation shear bands within the necked region.
- Continuing work and conclusion.

Microscopy for Understanding Metals

- Materials have mechanical responses dependent on the material character and microstructure.
- As microscopists, we bridge the gap from mechanical response to the micro- and nano-scale microstructural features within materials.
- Large variety of defects can influence the mechanical response including grains, twins, shear bands, secondary phases, dislocations, ect.

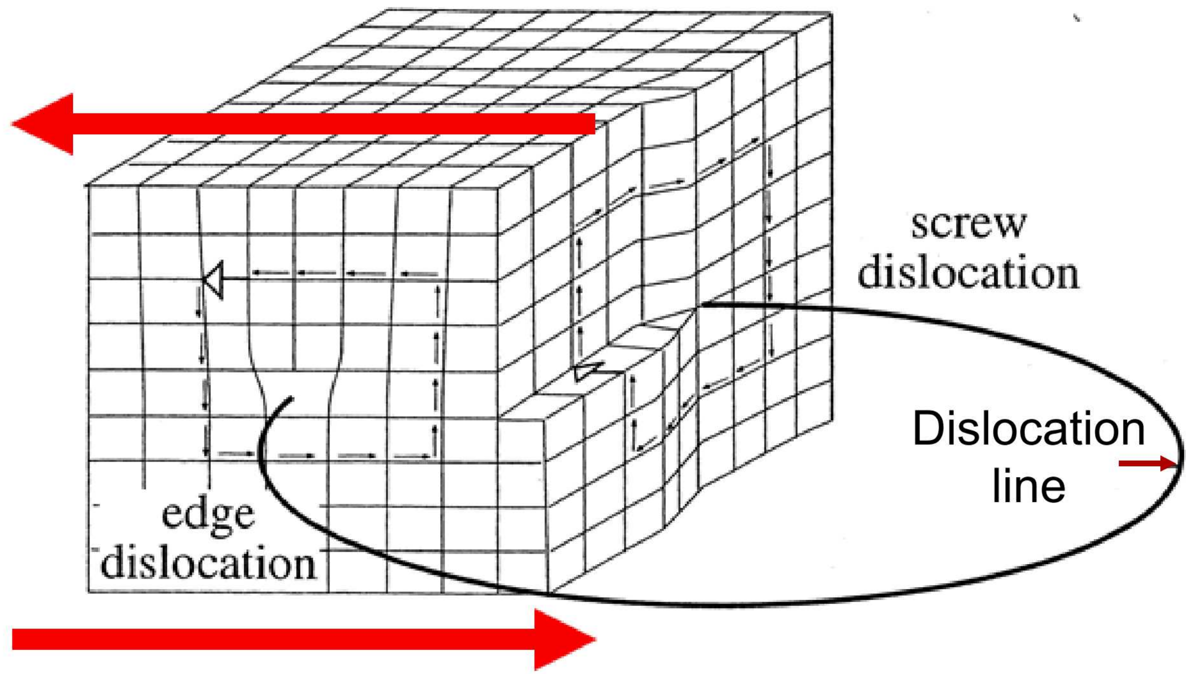


Relevant Crystals Structures

Body Centered Cubic: (BCC)	Face Centered Cubic: (FCC)	Hexagonal Close-Packed: (HCP)
		
Pure Iron, W, Cr	Cu, Au, Ag, Stainless Steels	Re, Mg, Ti
α-Martensite	γ-Austenite	ε-Martensite

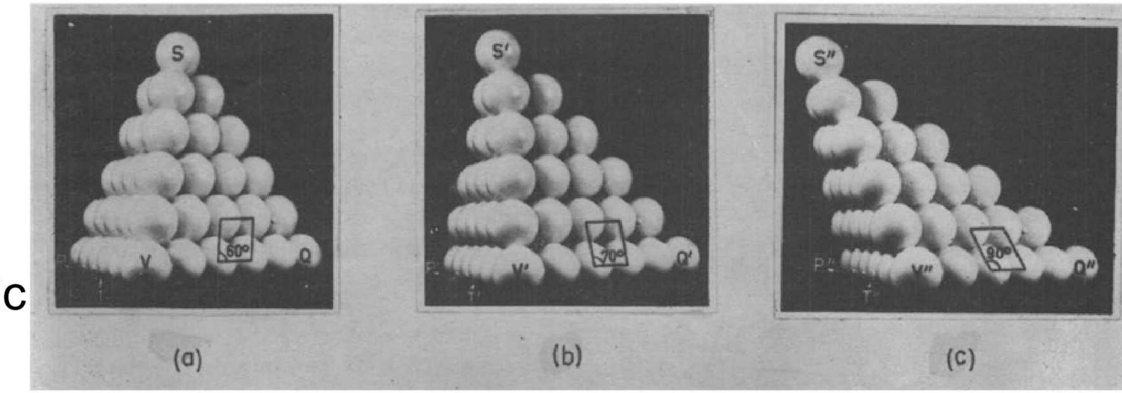
Dislocations in Metals

- Plastic deformation in metals is largely accommodated through dislocations.
- Deformation characteristics can change based on dislocation character.
- Dislocations can have edge, screw, or mixed type.



FCC Deformation Twinning

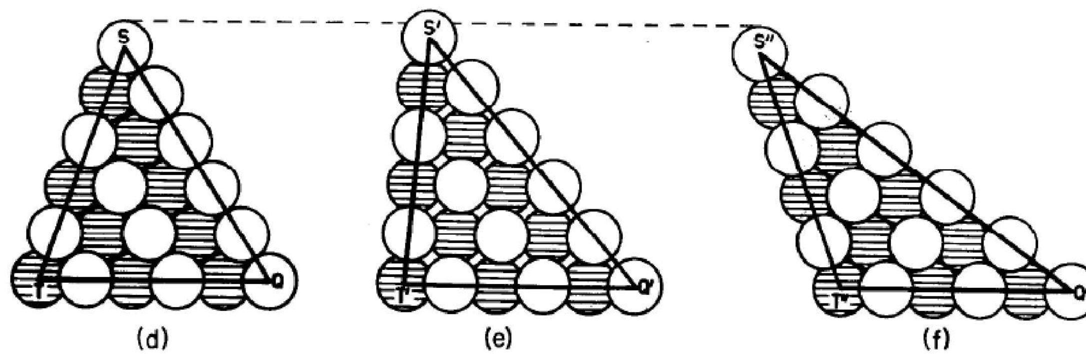
- Many metals can also deform through twinning.
- Twinning is when one part of a crystal is oriented with respect to another through a crystallographic symmetry operation.
- In the case of Austenitic Steels twinning is induced through Deformation and produces a Mirror symmetry along $\{111\}$ planes.
- A $\langle 112 \rangle$ shear along every $\{111\}$ plane produces a twin, the shear spread to every other $\{111\}$ plane produces an HCP structure



(a) Original tetrahedral arrangement with four {111} planes.

(b) Intermediate position after 1/3 of normal twin shear. The distance between successive {111} planes parallel to P′V′S′ and P′V′Q′ has increased by 5.4%.

(c) Final position after complete twin shear.

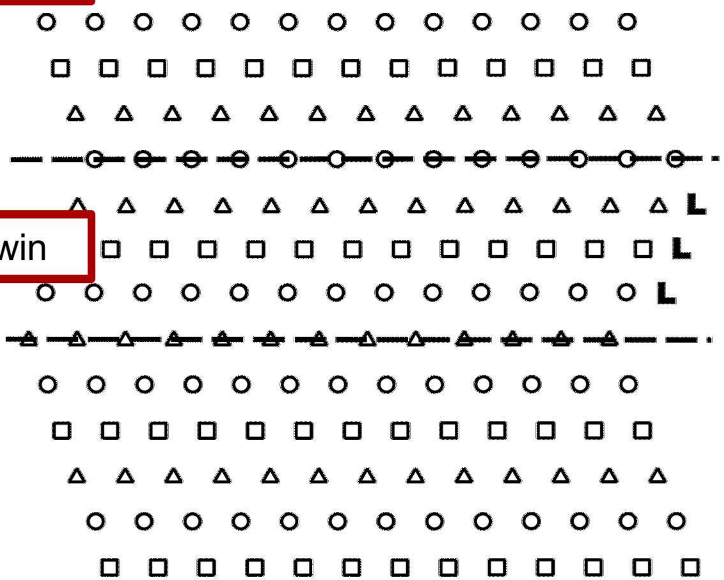


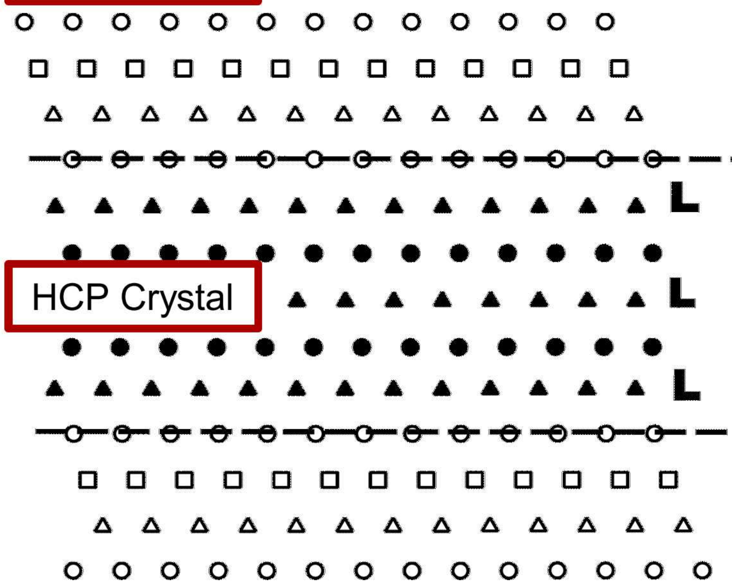
(d-e-f) Cross section through the {110} plane TQS perpendicular to PV.

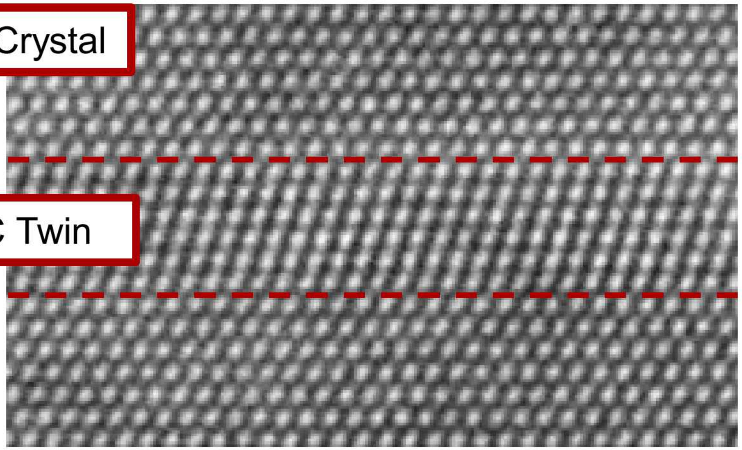
FIG. 2. Normal twin shear in a cubic close-packed arrangement of spheres. The horizontal {111} planes are sheared in the ⟨112⟩ direction perpendicular to PV.

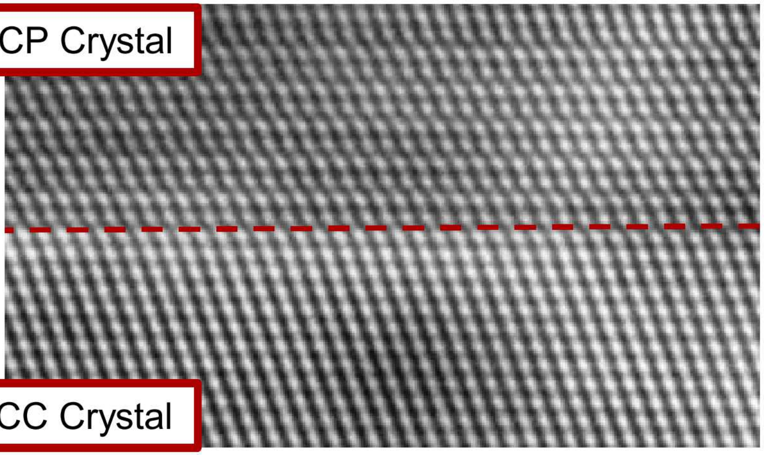
-Burgers and Bogers, 1964

Observed Nanostructures in Materials







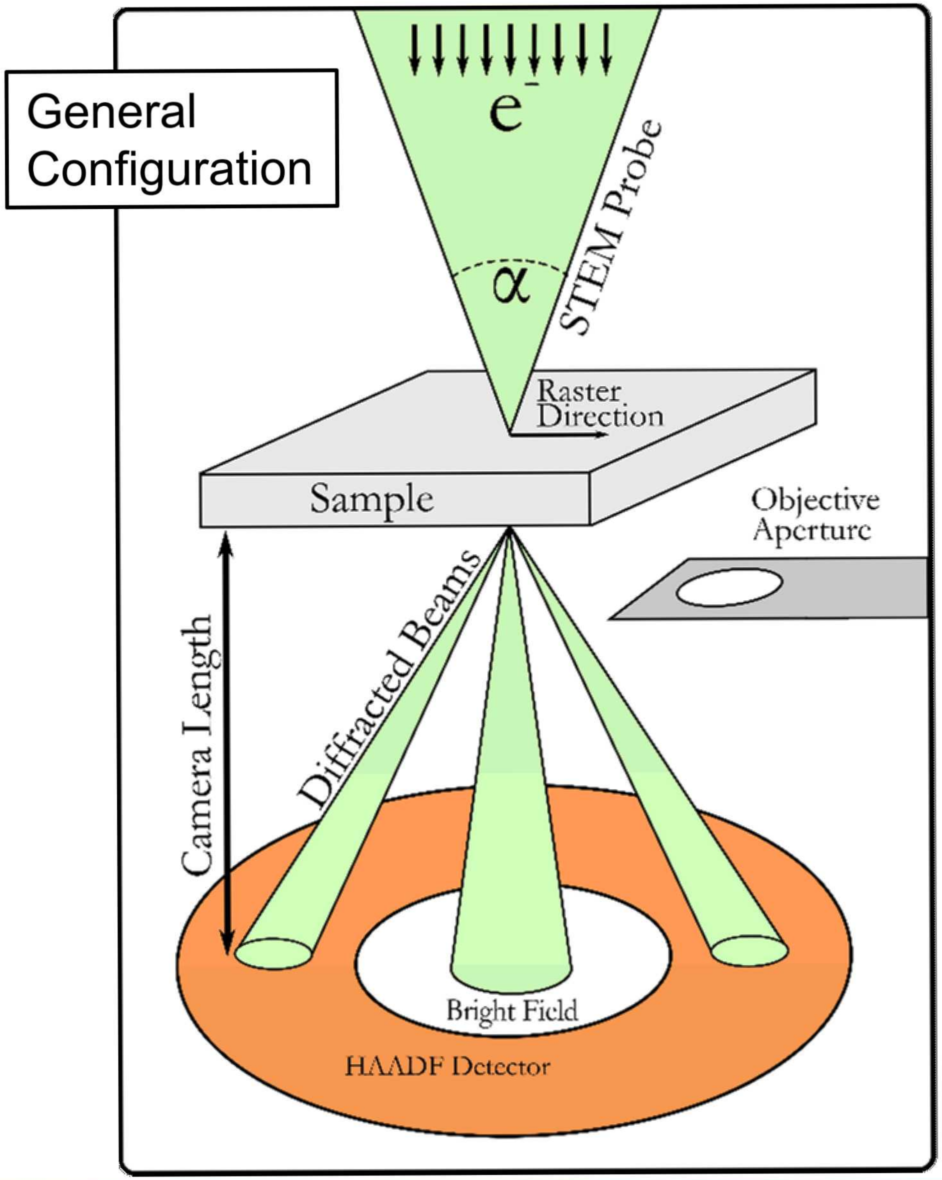


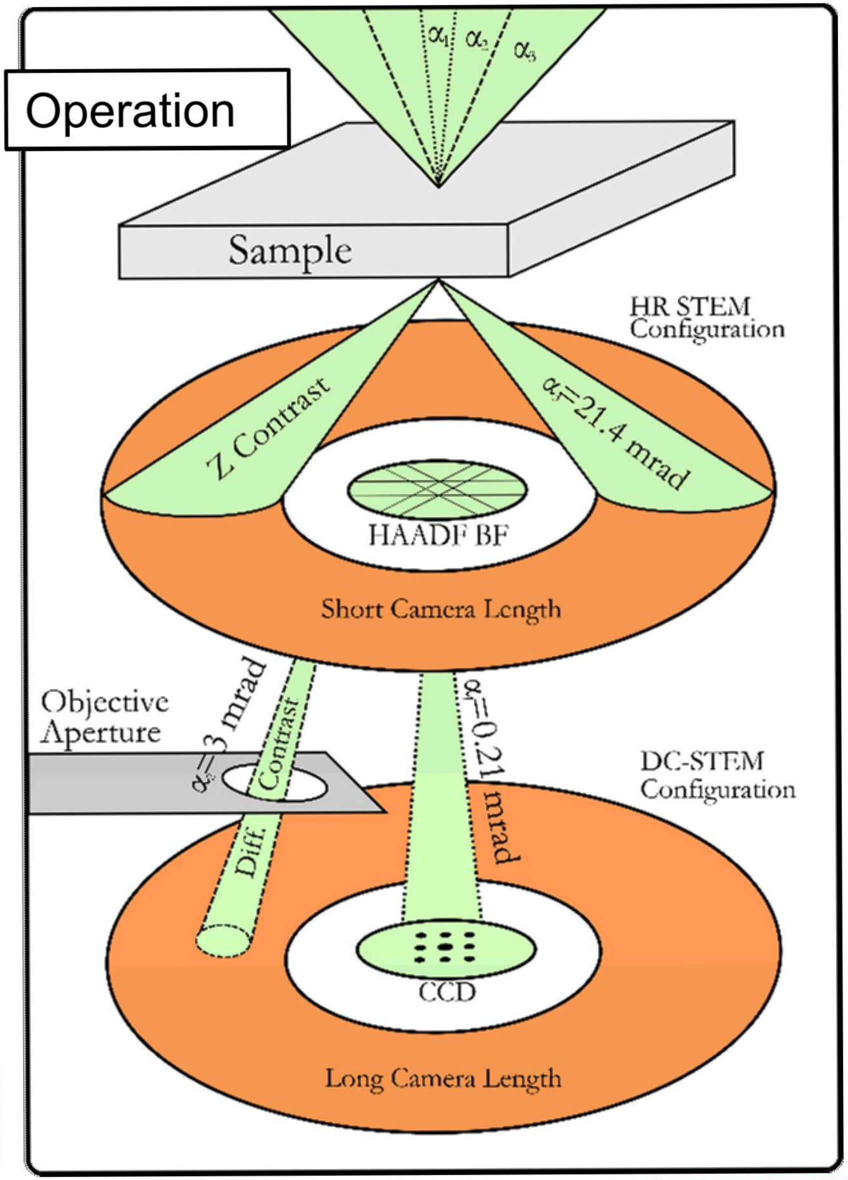
Microscope Overview

- Experiments (observations) were performed on Sandia CA's Thermo Fisher Themis Z probe corrected STEM/TEM.

- Will skip exact technical specifications here, however can perform:
  - High-Resolution(HR)-STEM
  - Nanoprobe-Diffraction
  - HRTEM
  - EDX
  - EELS
  - High Temperature Specimen Holders
  - Tomography Holders

Background on STEM

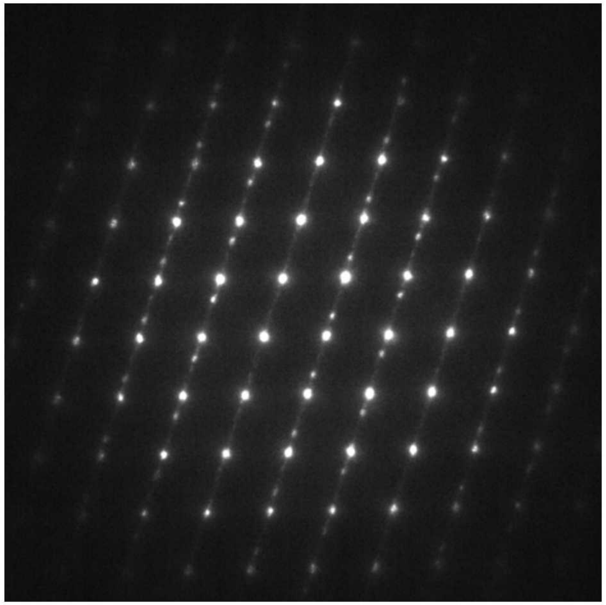


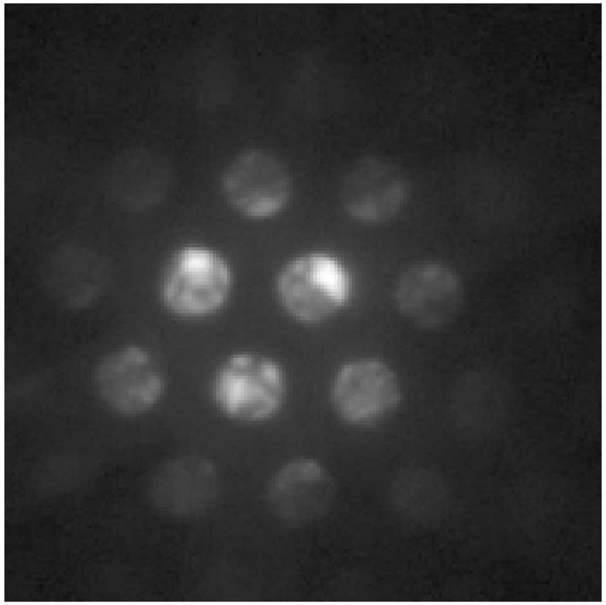


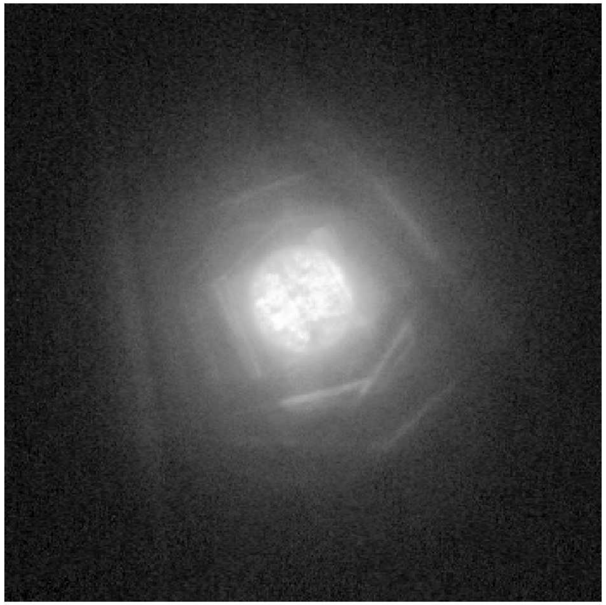
Examples of STEM Probe

All imaging types contain the same information, however the imaging condition will determine which is readily interpretable.

Nanobeam Diffraction	DC-STEM	HRSTEM
0.2 mRad Probe	3 mRad Probe	25.2 mRad Probe
230mm Camera Length	230mm Camera Length	115mm Camera Length







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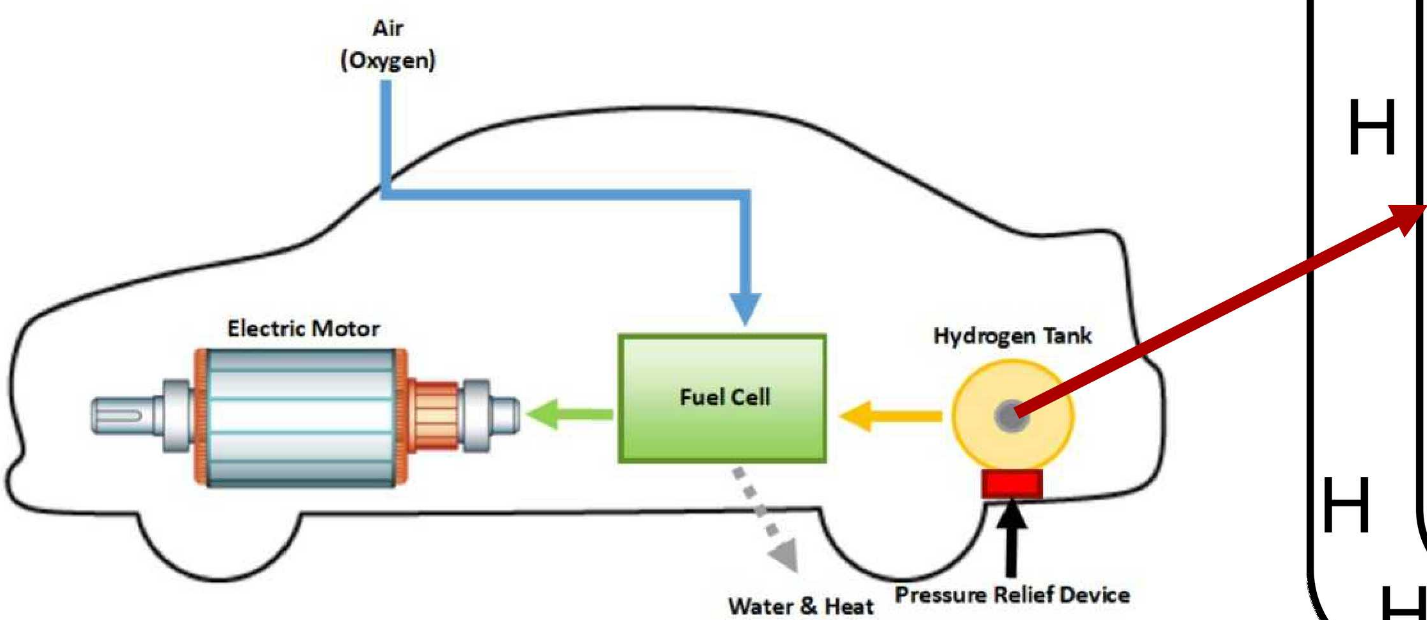
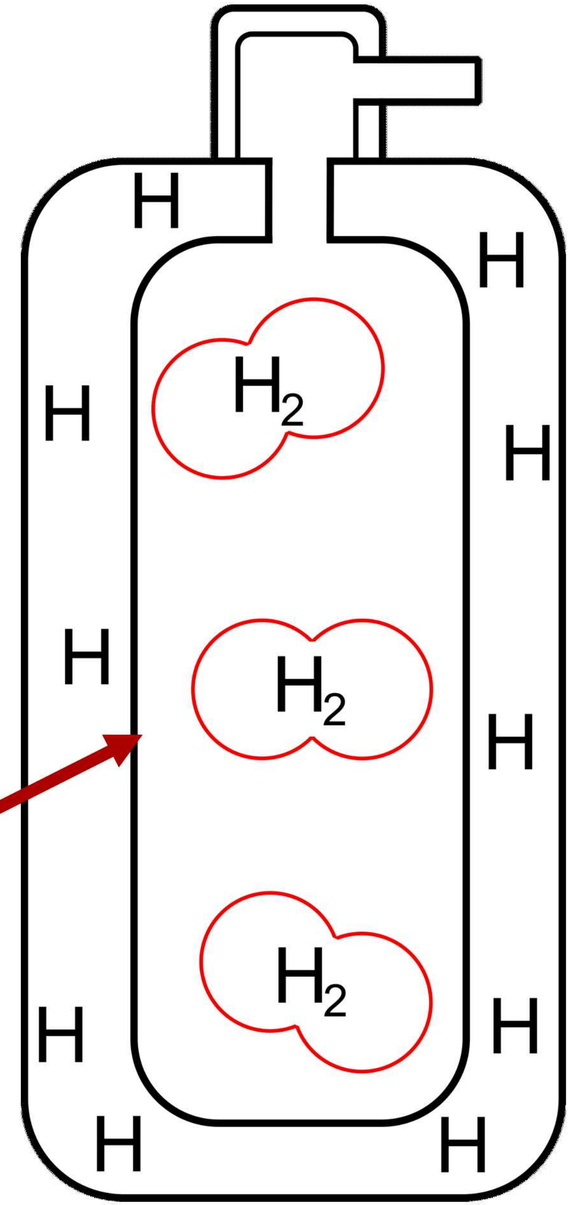
Interest in Hydrogen's Effect

- Metals have long been used to store hydrogen and its isotopes.
  - Fracture toughness and ductility is heavily decreased in hydrogen charged samples.
  - Understanding the effects of hydrogen on the microstructure and deformation behavior of metals has been a long term.





Historic Work on Hydrogen in Steel

Hydrogen Embrittlement, Internal Stress and Defects in Steel

By C. A. Zapffe,* Junior Member, and C. E. Sims,* Member A.I.M.E.

(New York Meeting, February 1941)

A New Model for Hydrogen-Assisted Cracking (Hydrogen "Embrittlement")

C. D. BEACHEM

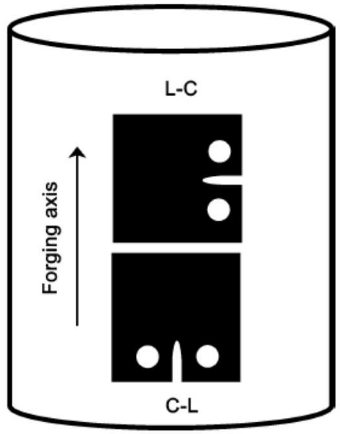
METALLURGICAL TRANSACTIONS VOLUME 3, FEBRUARY 1972–437

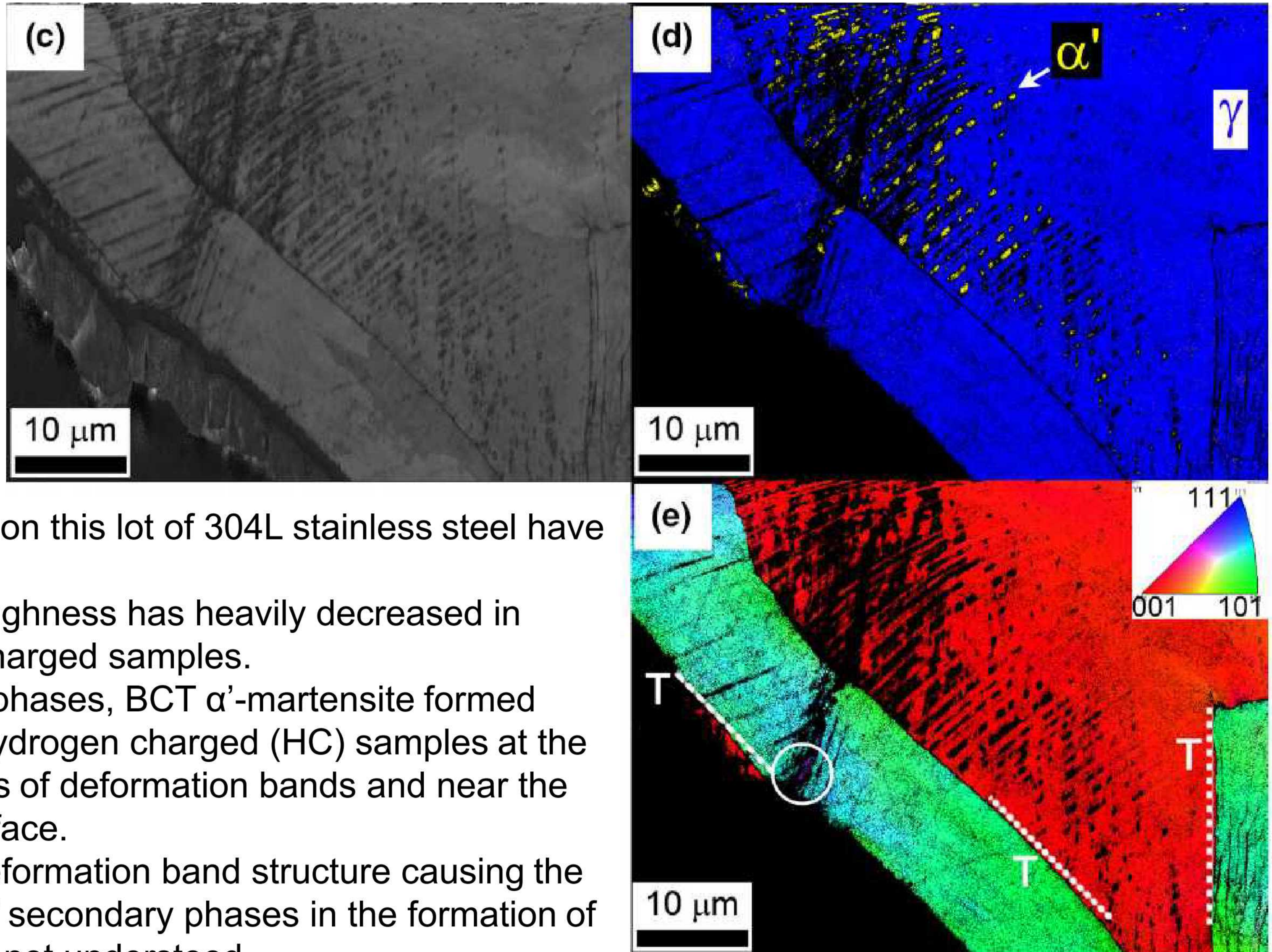
Effects of Low Temperature on Hydrogen-Assisted Crack Growth in Forged 304L Austenitic Stainless Steel

HEATHER JACKSON, CHRIS SAN MARCHI, DORIAN BALCH, BRIAN SOMERDAY, and JOSEPH MICHAEL

4334—VOLUME 47A, AUGUST 2016 METALLURGICAL AND MATERIALS TRANSACTIONS A

Previous Work on Planar Features





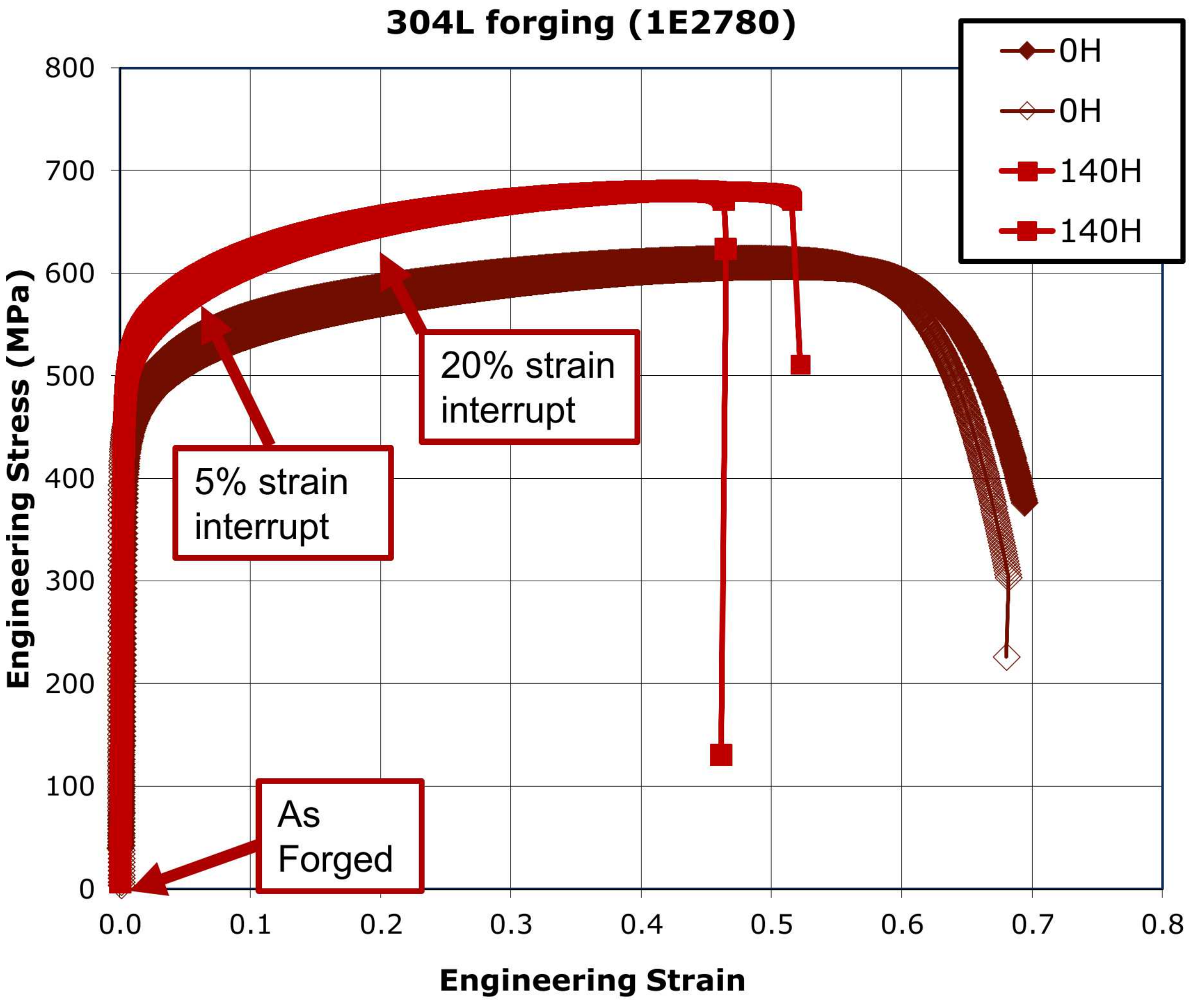
- Previous studies on this lot of 304L stainless steel have shown:
  - Fracture toughness has heavily decreased in hydrogen charged samples.
  - Secondary phases, BCT α'-martensite formed within the hydrogen charged (HC) samples at the intersections of deformation bands and near the fracture surface.
  - The intra-deformation band structure causing the formation of secondary phases in the formation of hydrogen is not understood.

-Jackson et al. 2016

Composition and Mechanical Data

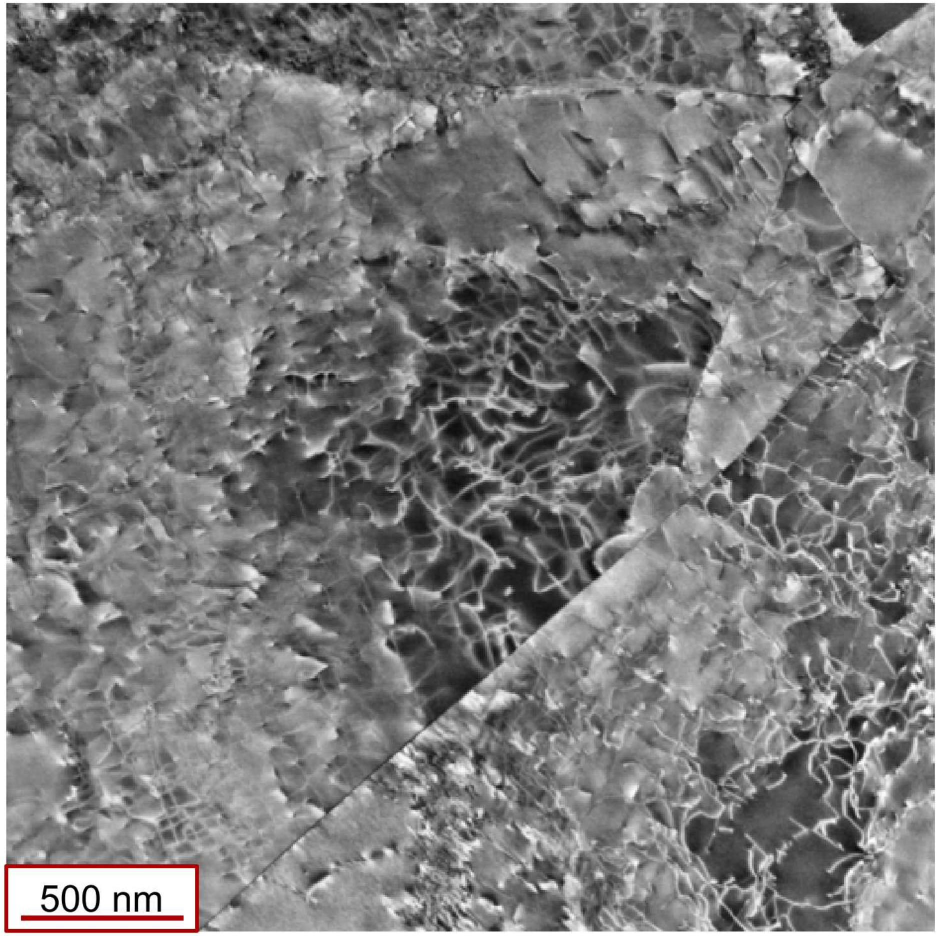
MCN	Fe	Cr	Ni	Mn	Si	C	N	P	S
200956	Bal	19.64	10.6	1.62	0.65	0.028	0.04	0.02	0.0042

- Several samples were deformed to fracture as well as intermittent strains.
- Initial as-forged microstructure taken from the grip region of tensile samples.
- Both HC and NC samples were deformed to 5% and 20% strain true strain.
- The samples were then sectioned using a diamond blade, mechanically thinned up to 4000 grit sandpaper, and electrochemically polished.

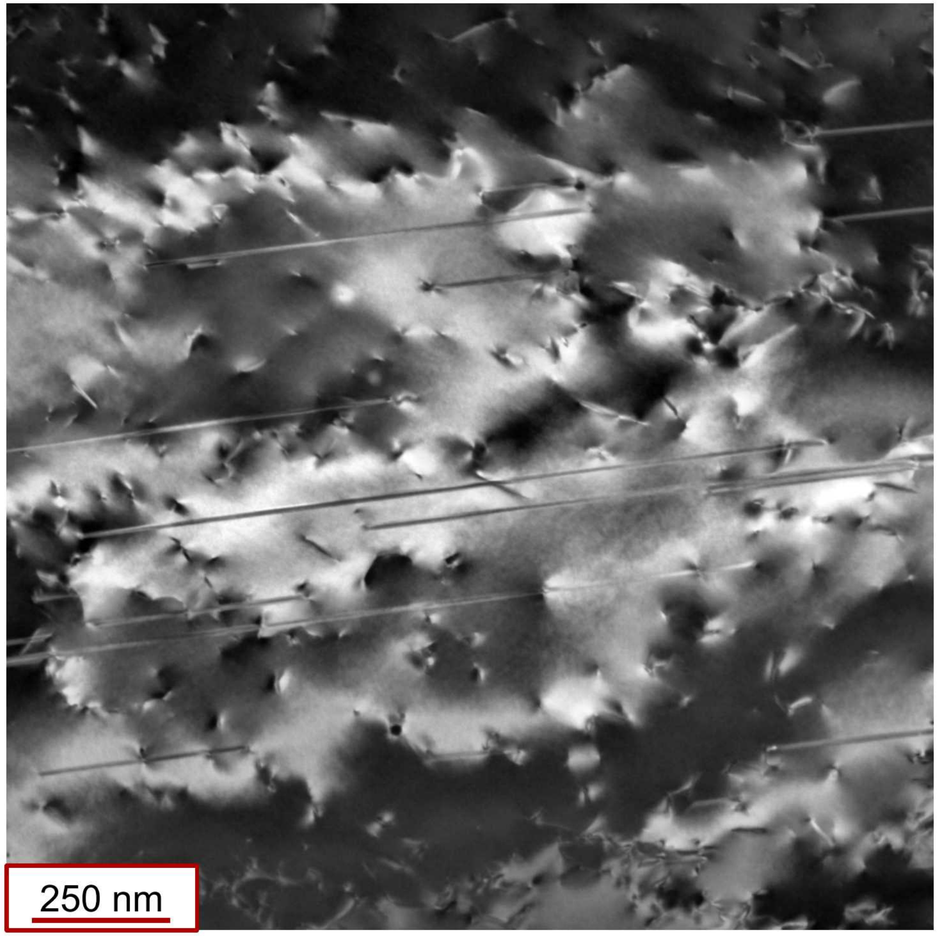


As Forged Microstructures

Forged H-Non-Charged



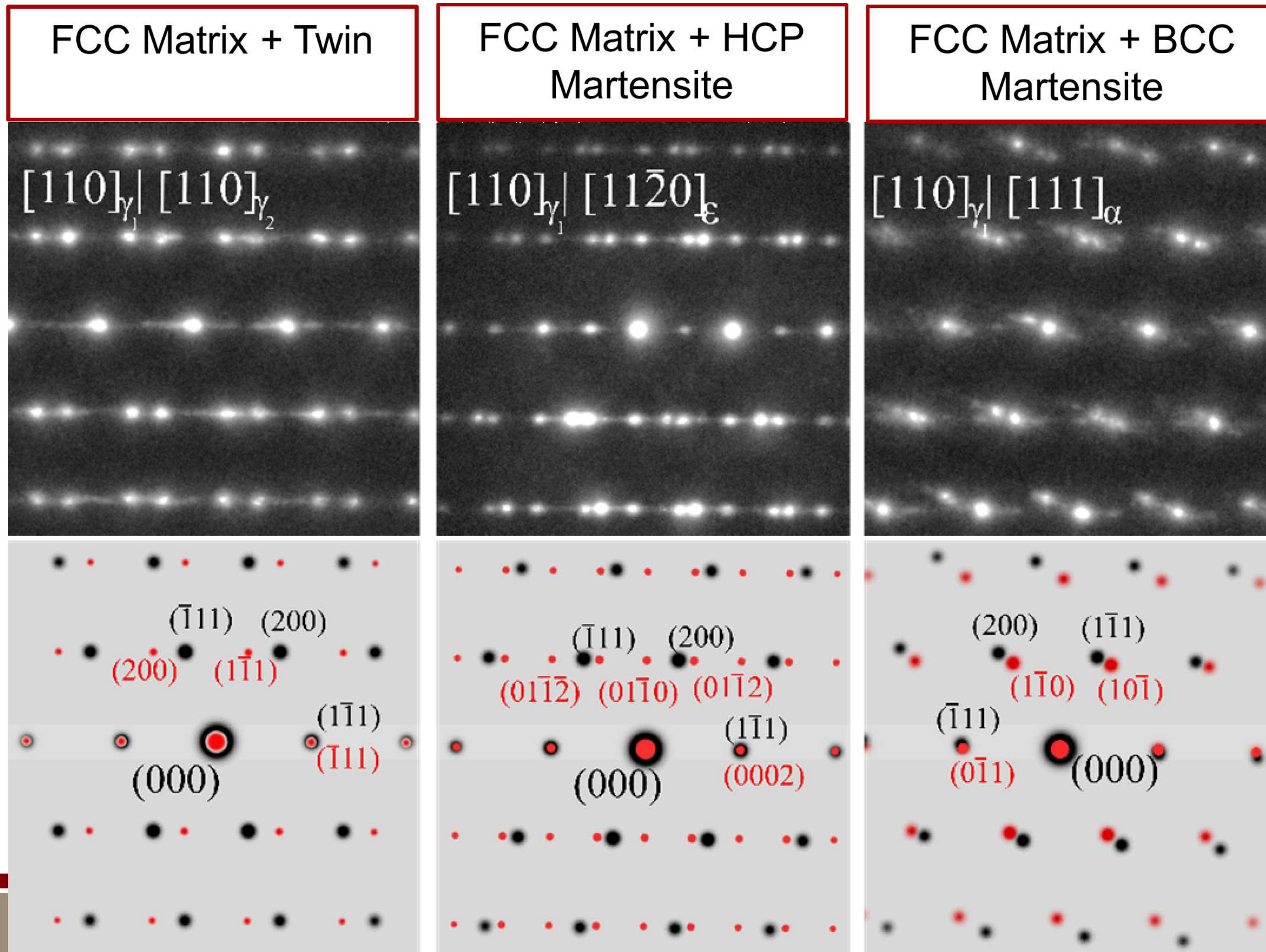
Forged H-Charged



-J.E.C.Sabisch et al. In Preparation

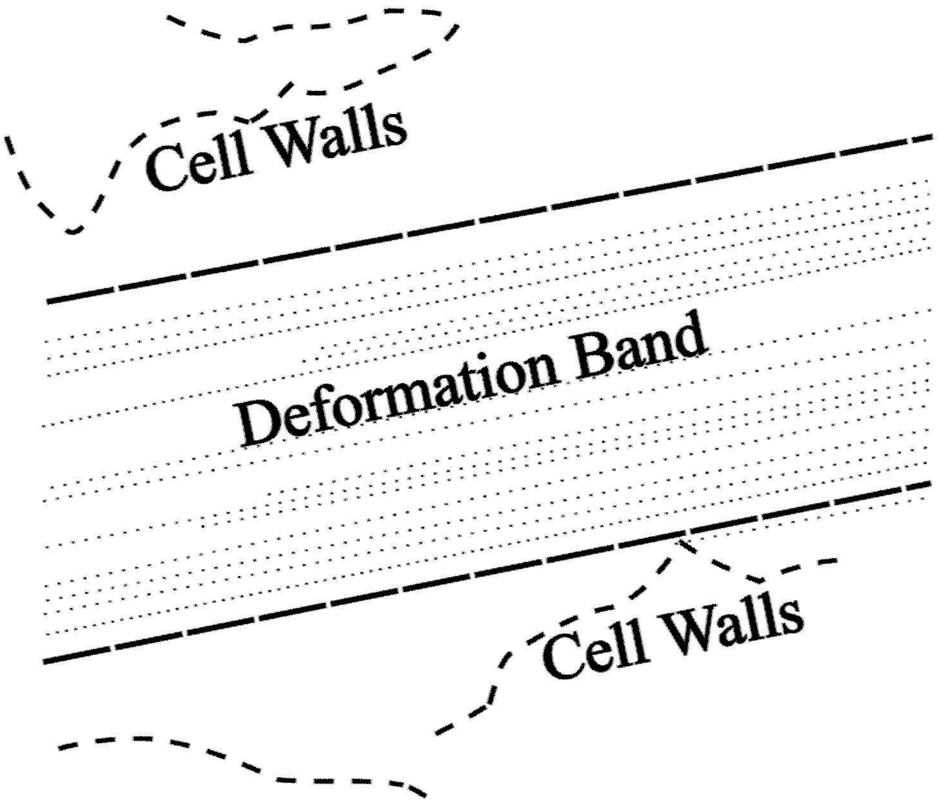
Phases in 304L Steel

- Simulations and experimental diffraction patterns for the common structures in 304L steel.
- These are superpositions of diffraction patterns from parent γ-austenite (FCC) and twinning (FCC), ε-martensite (HCP), or α'-martensite (BCC).

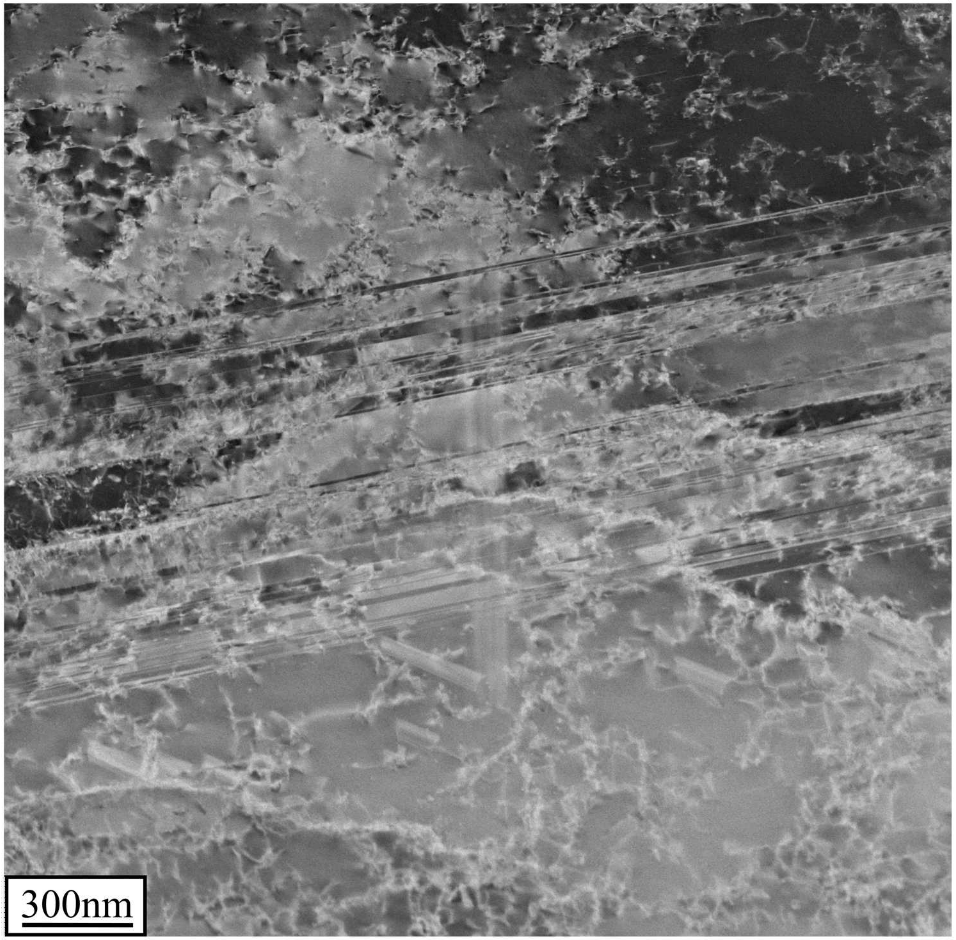


5% Strain Non-Charged Deformation Band

Schematic of Defect Structure



DC-STEM Micrograph



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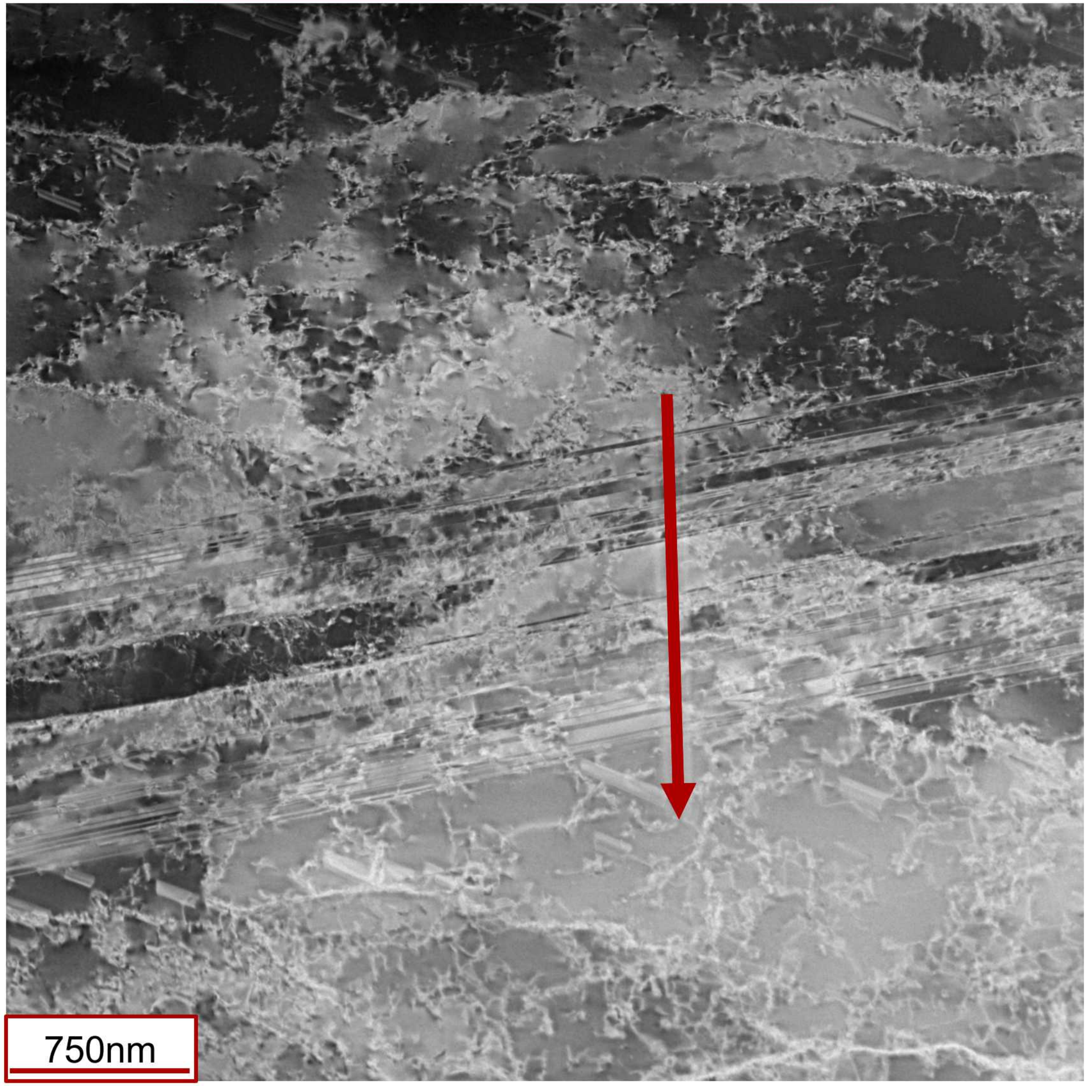
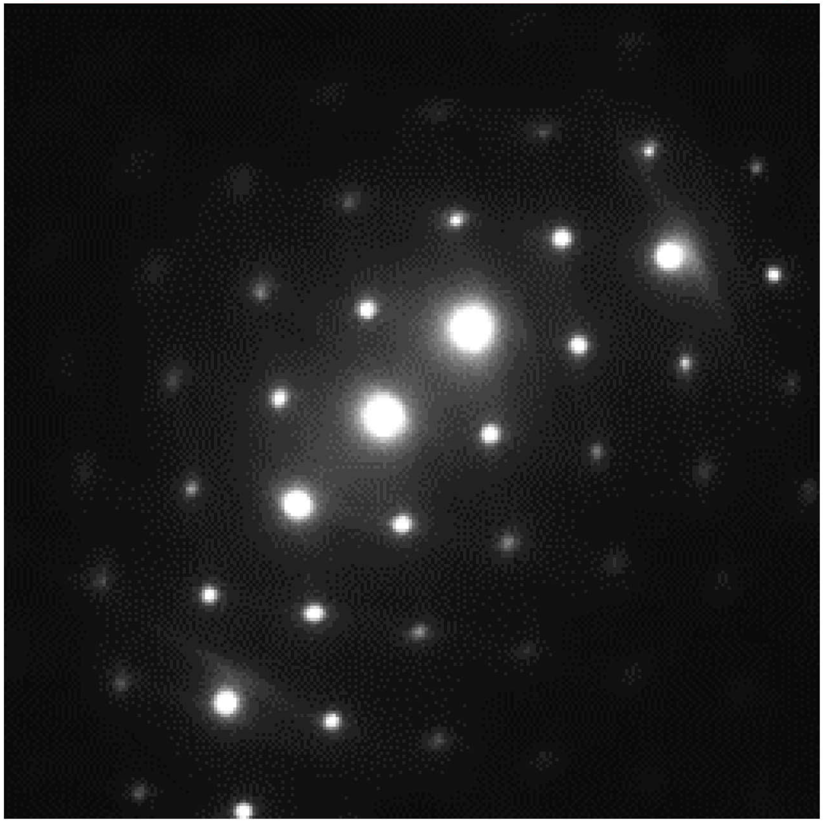
Deformation Band Diffraction Scans

DC-STEM Micrograph



Single Line Scan 350 Patterns

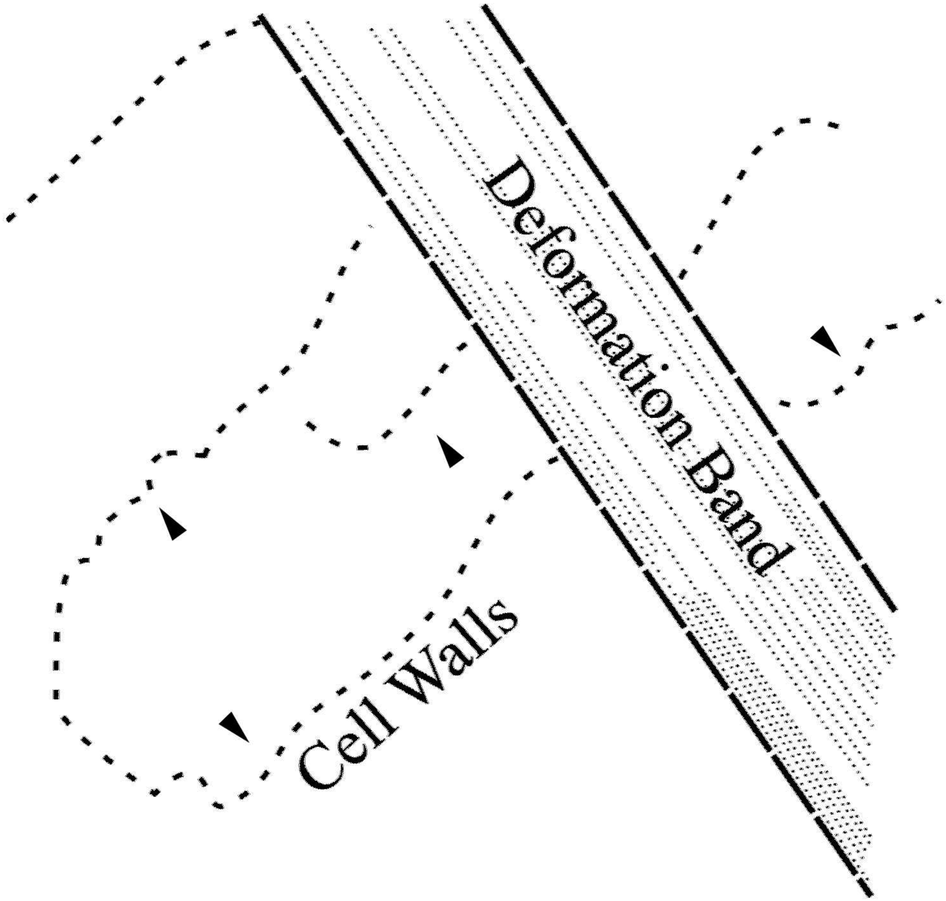


Typical deformation bands contain twins, with stacking faults (SFs) appearing as heavier streaking along $\{111\}$ reflections.

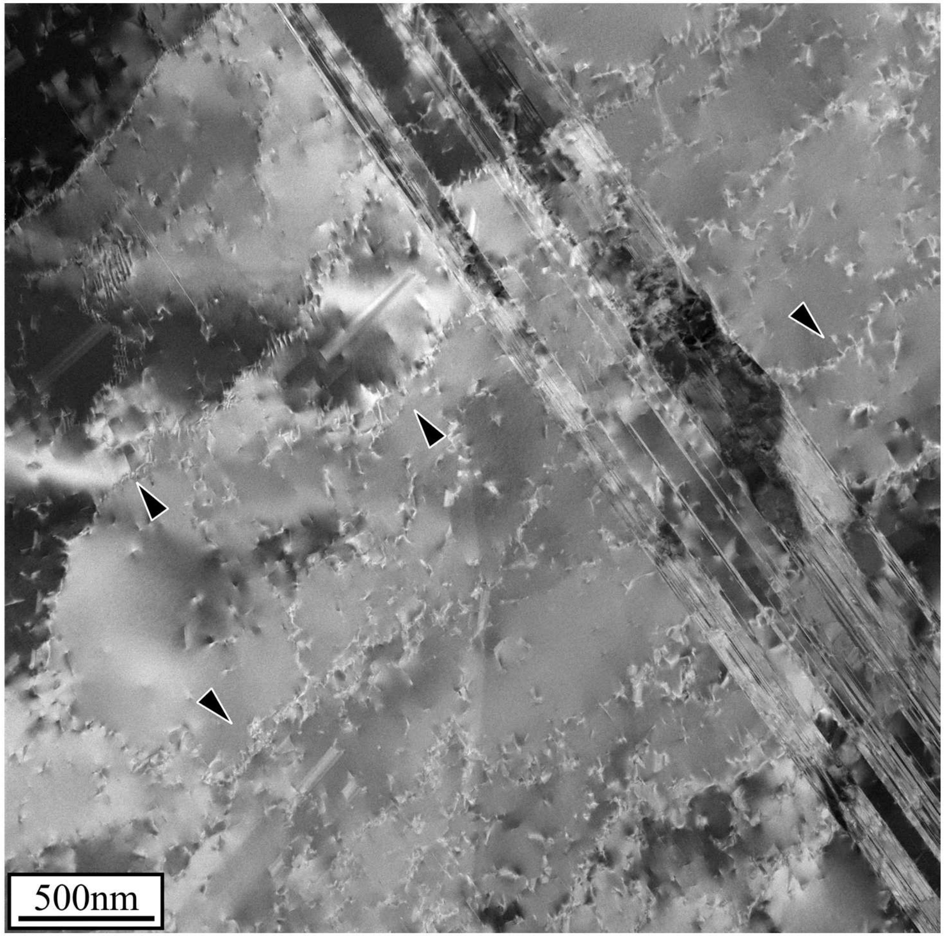
-J.E.C.Sabisch et al. In Preparation

5% Strain H-Charged Deformation Band

Schematic of Defect Structure



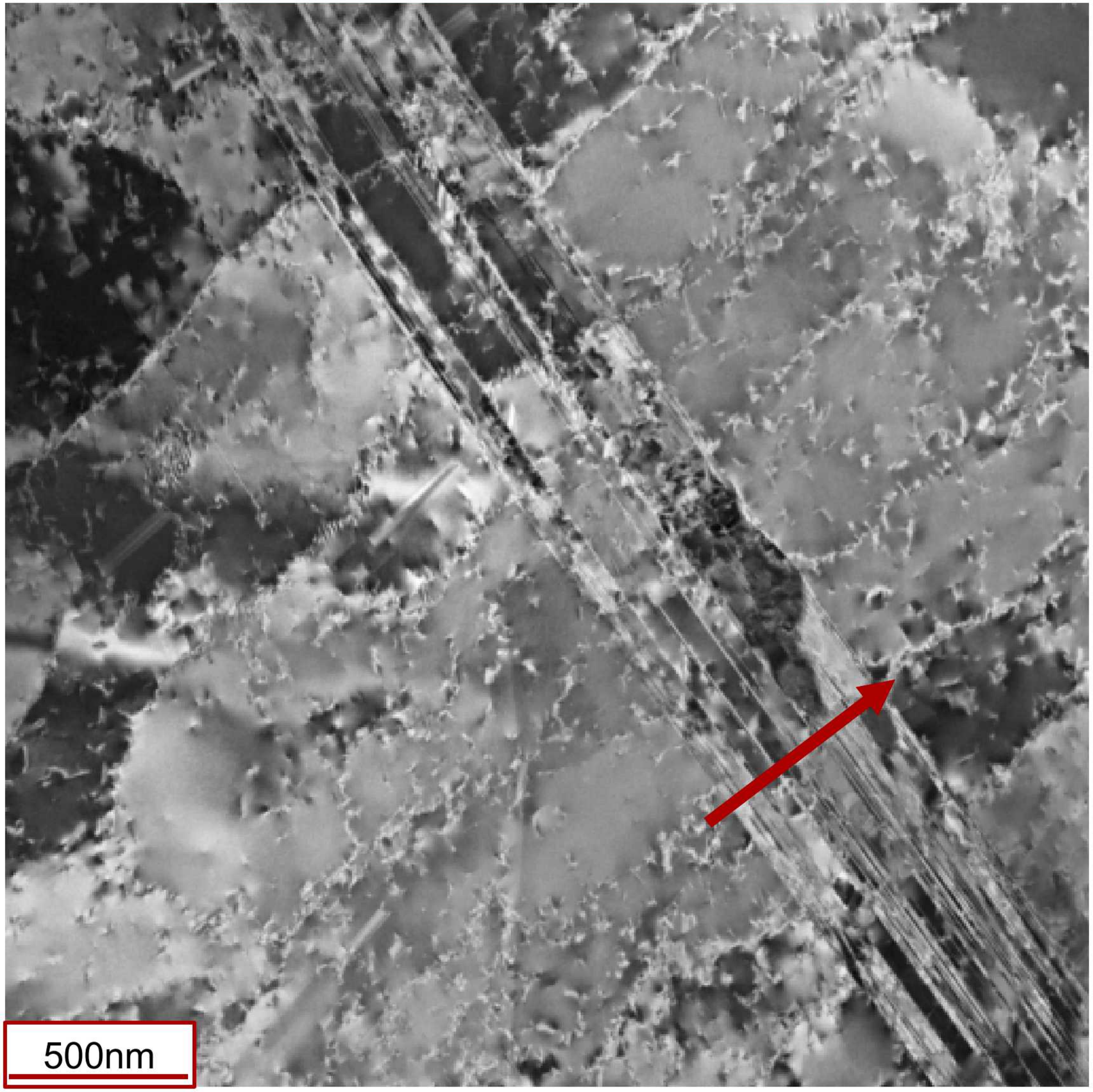
DC-STEM Micrograph



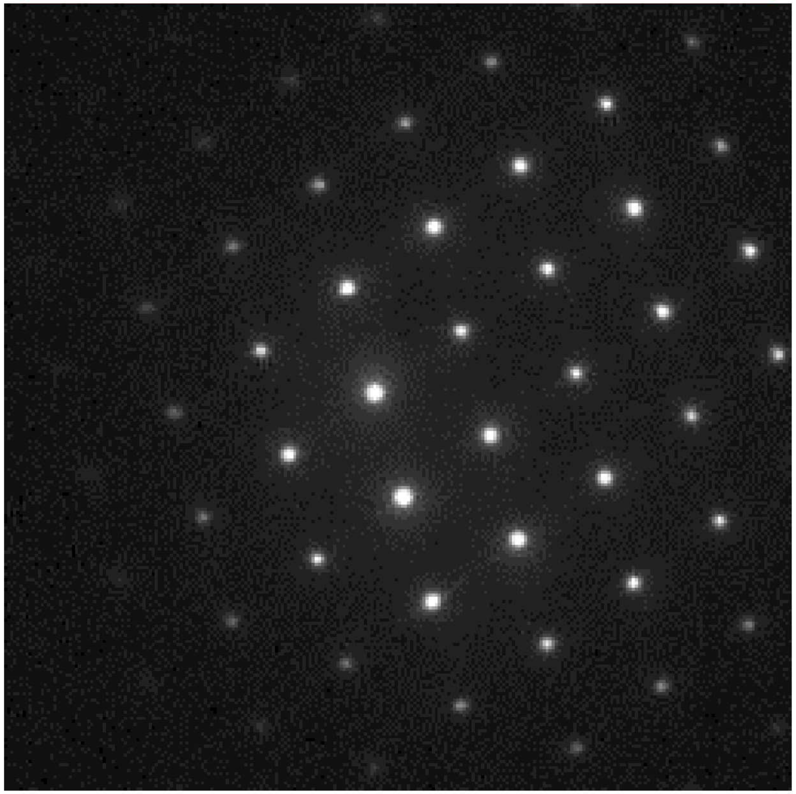
-J.E.C.Sabisch et al. In Preparation

Deformation Band Diffraction Scans

DC-STEM Micrograph

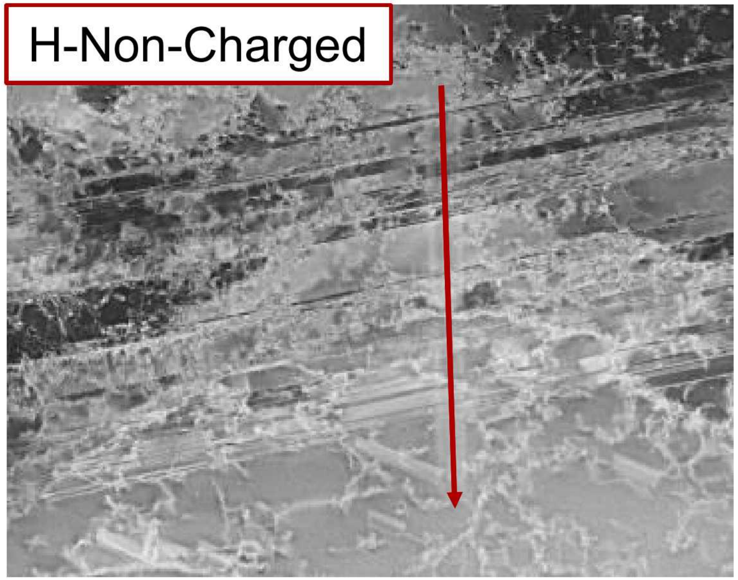


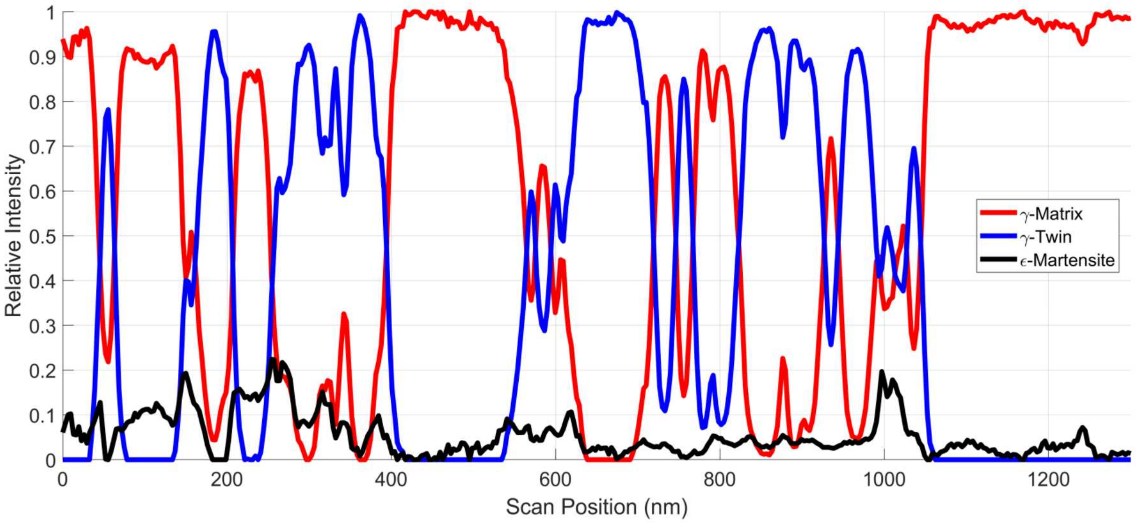
Single Line Scan ~200 Patterns

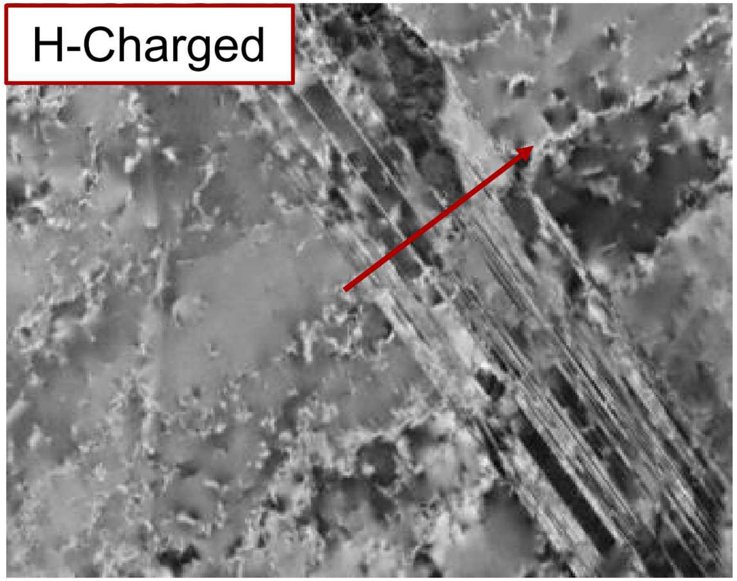


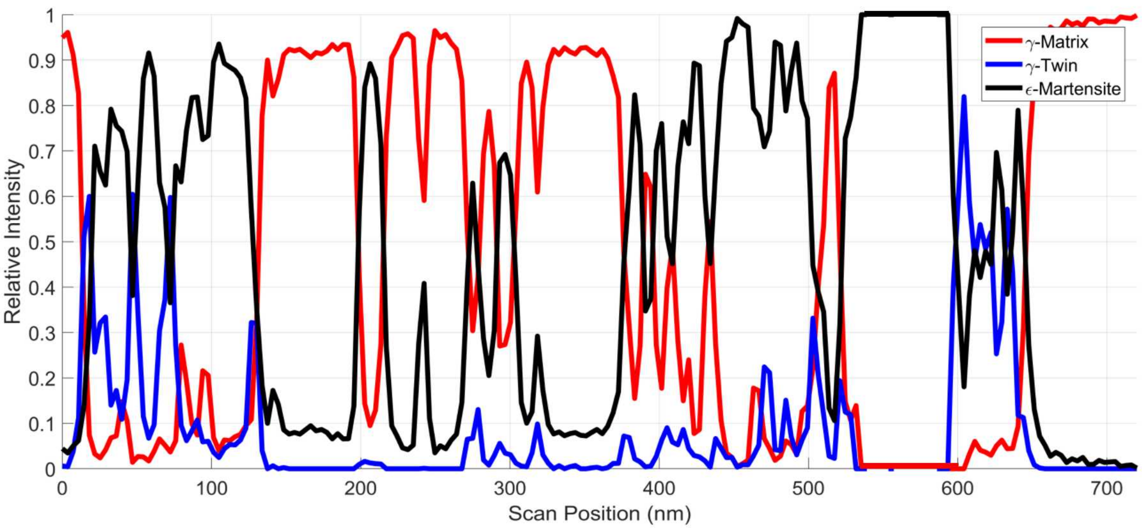
In HC samples ε-martensite dominates within the deformed region, with little dislocation content observed.

Quantitative Phase Measurements









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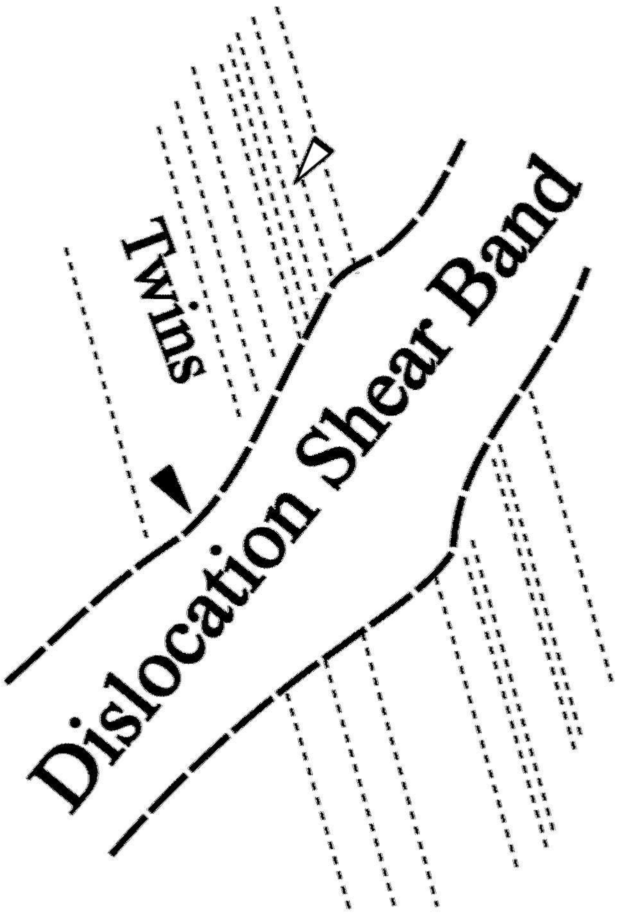
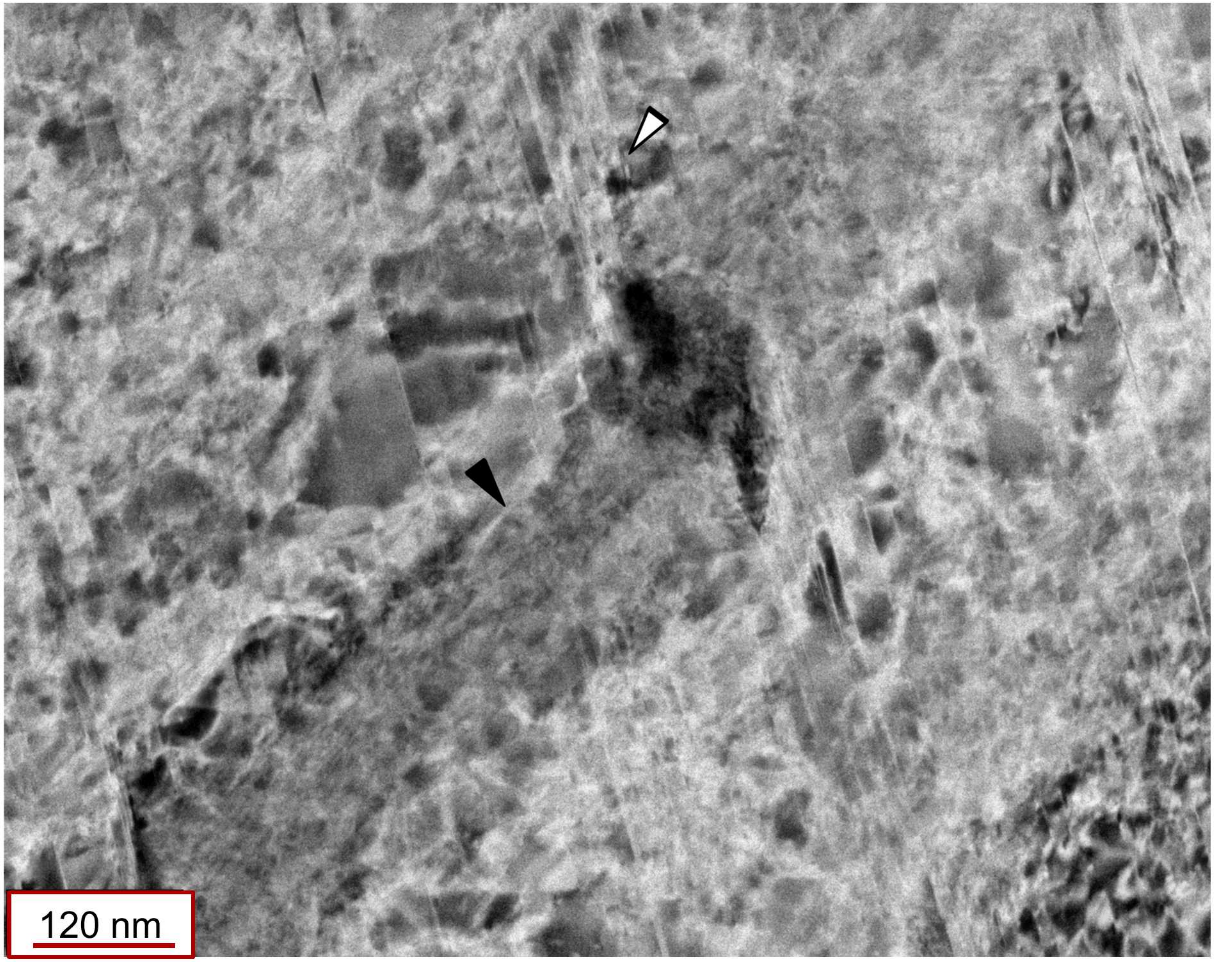
Deformation Bands in NC 20% Strain





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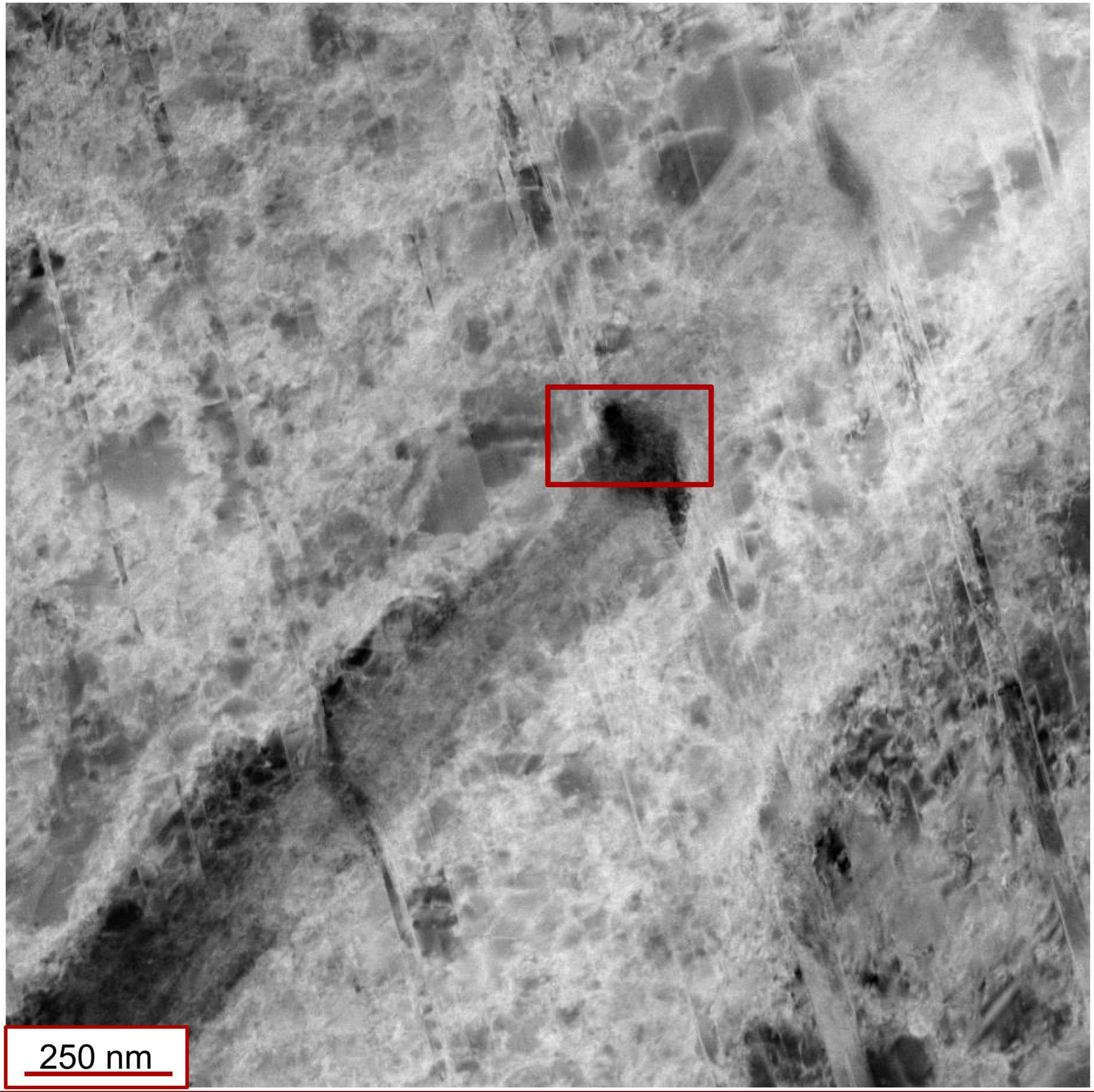
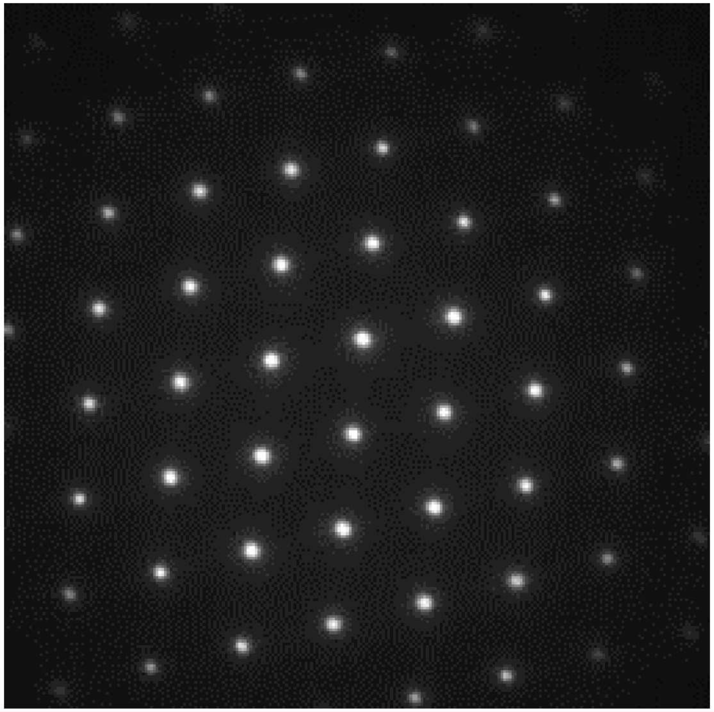
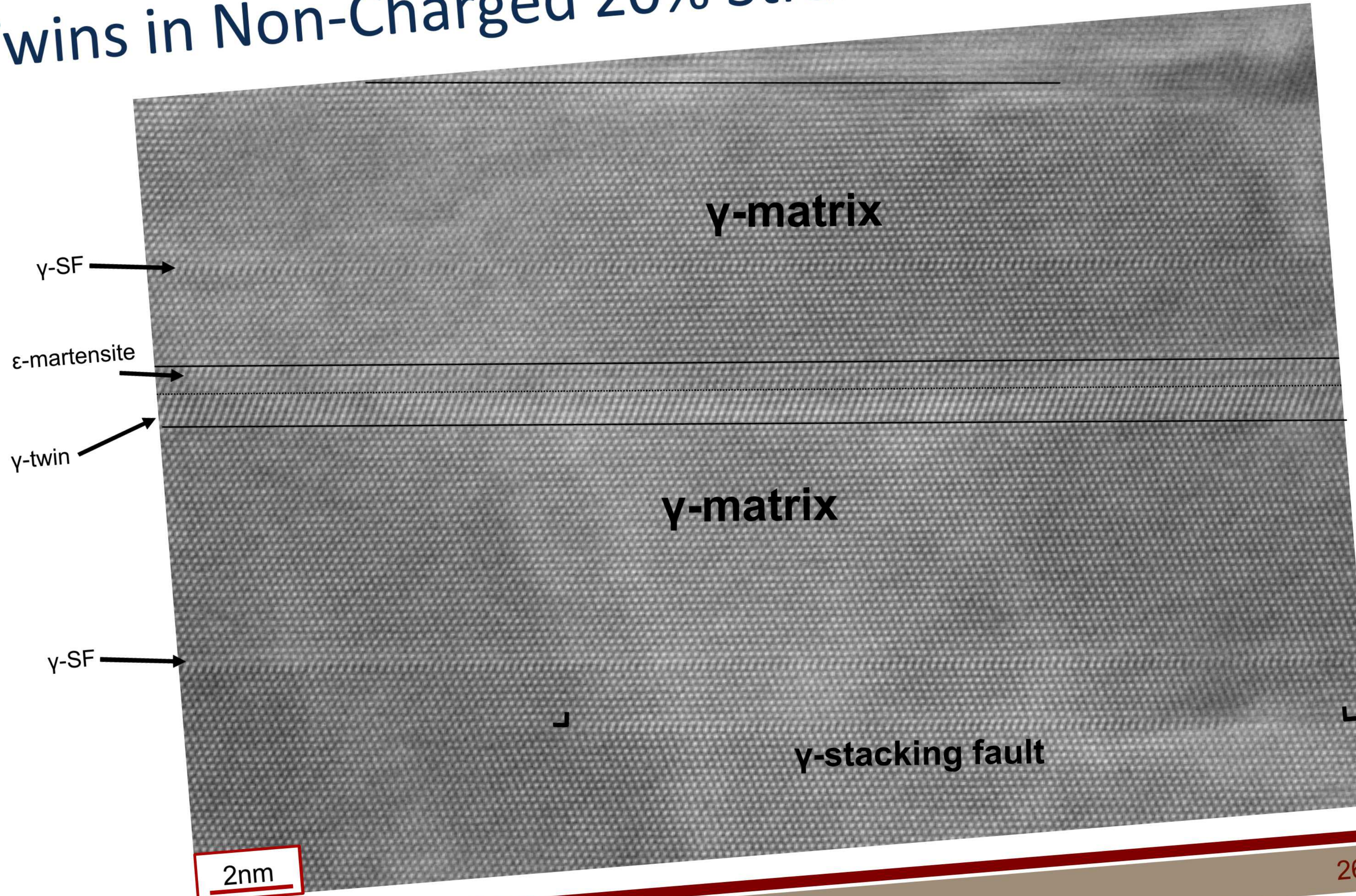


Throughout the double shear band intersection in non-charged samples, only some twin spots appear and no α'- or ε-martensite phase spots.

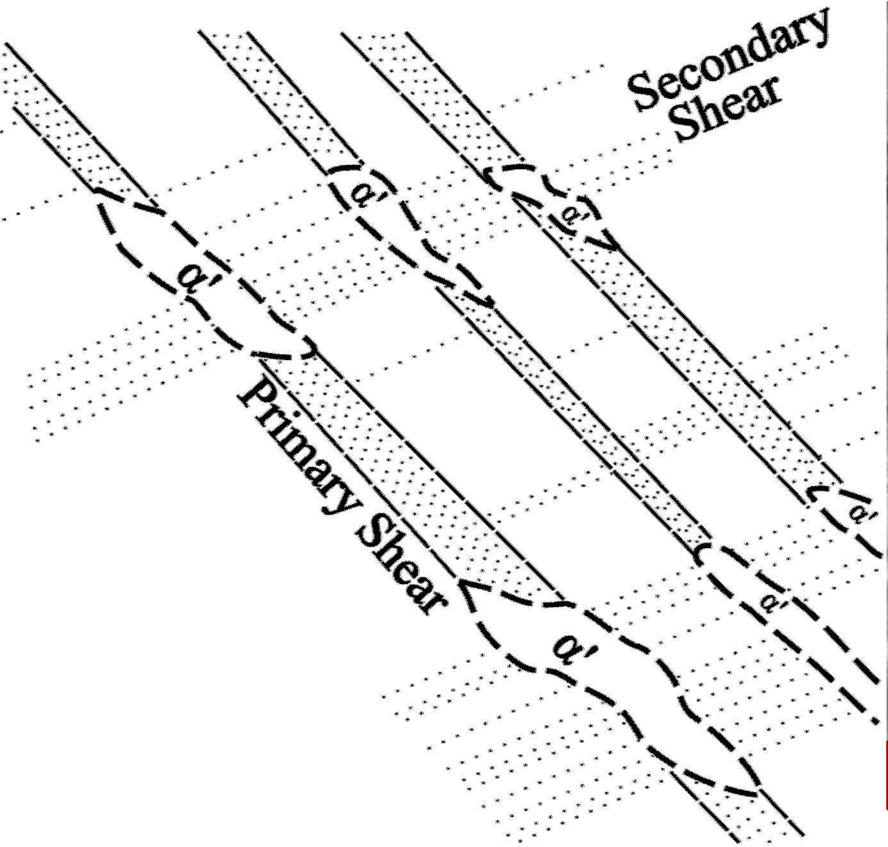


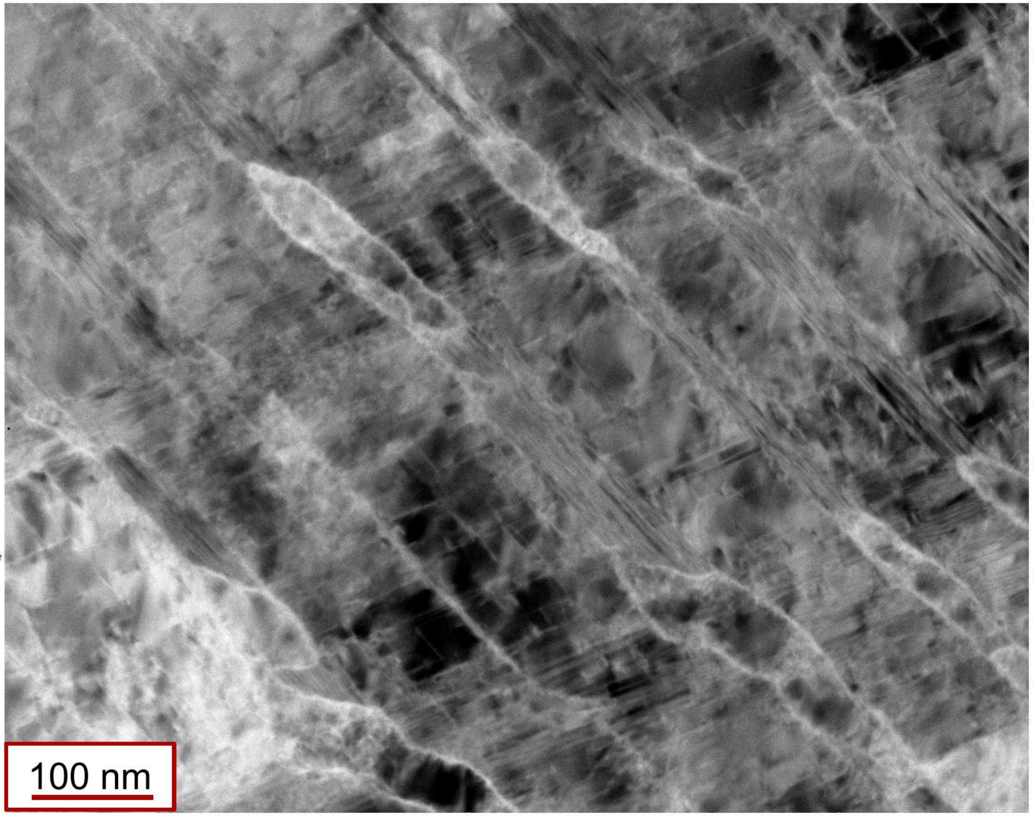
Twins in Non-Charged 20% Strain



Deformation Bands in H-Charged 20% Strain

Sandia National Laboratories





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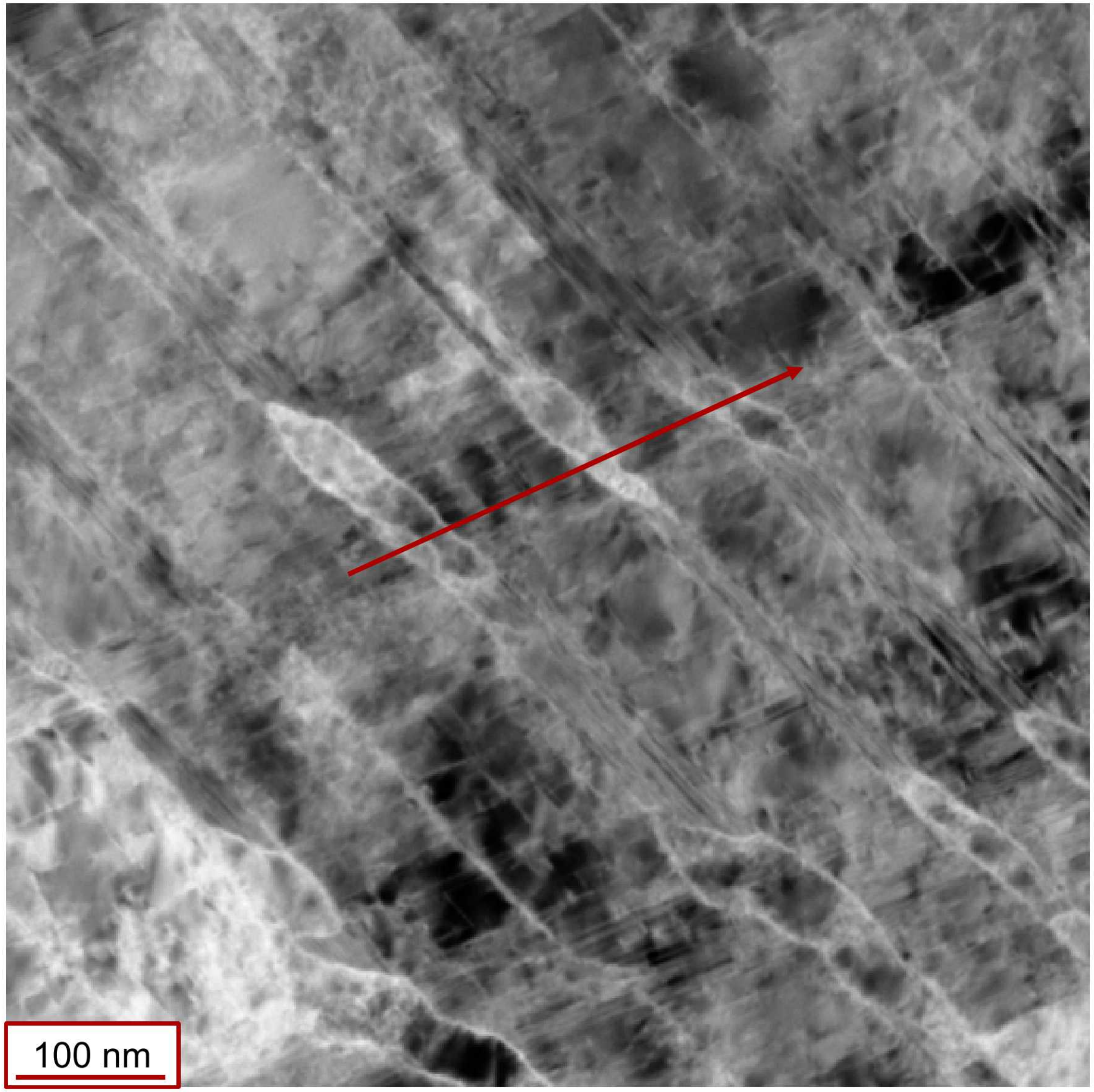
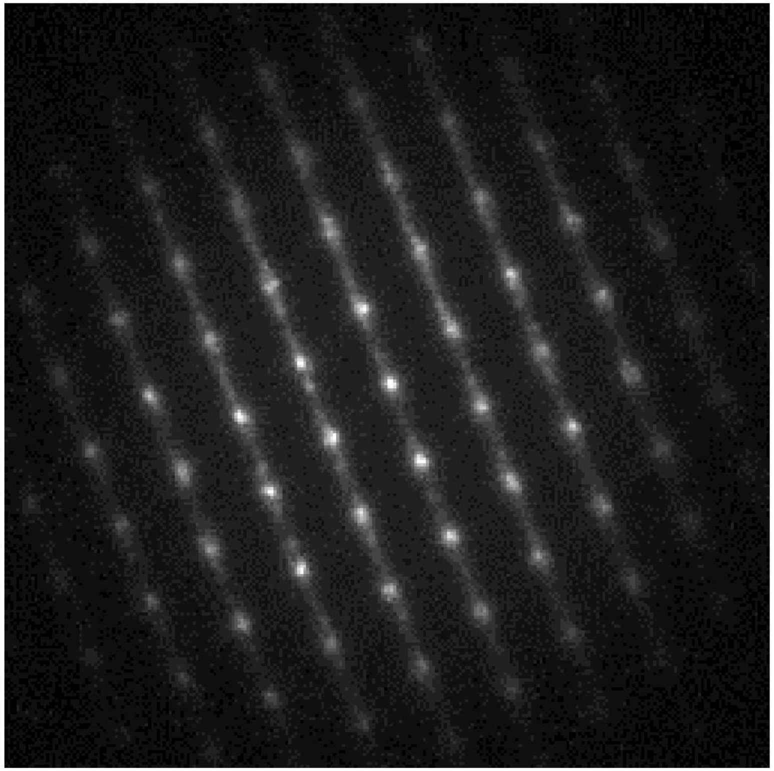
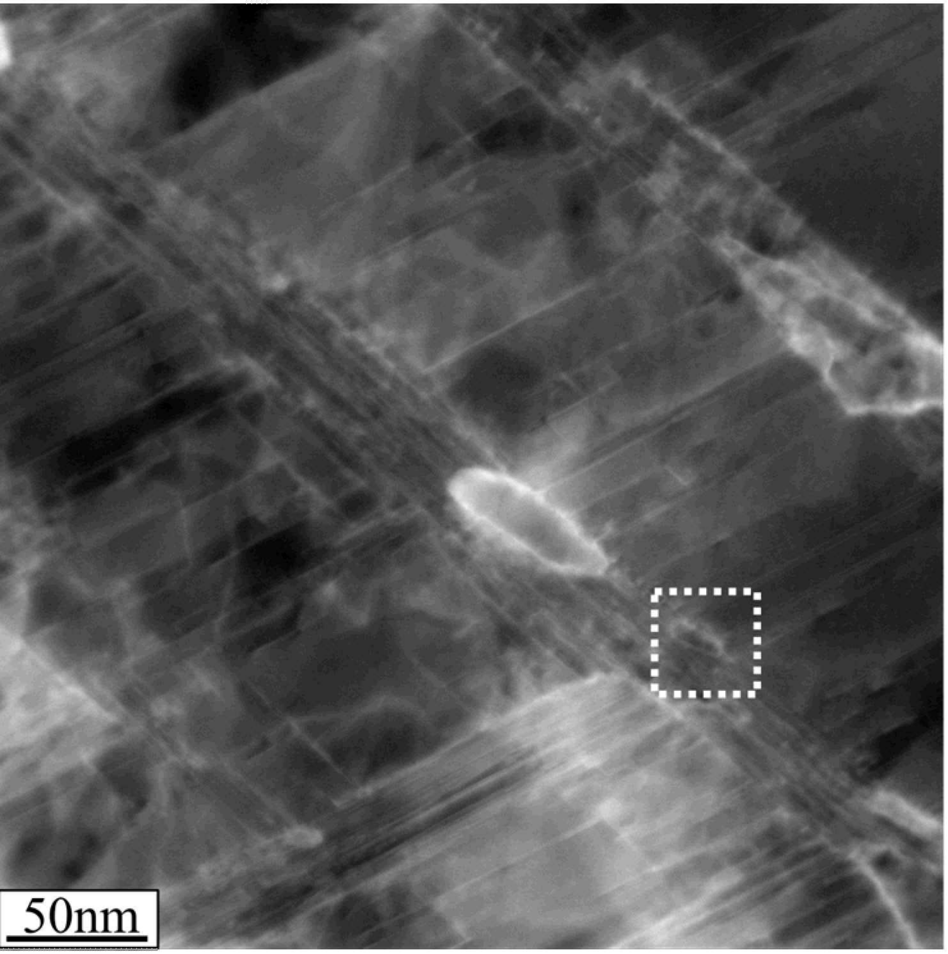
Deformation Bands in H-Charged 20% Strain

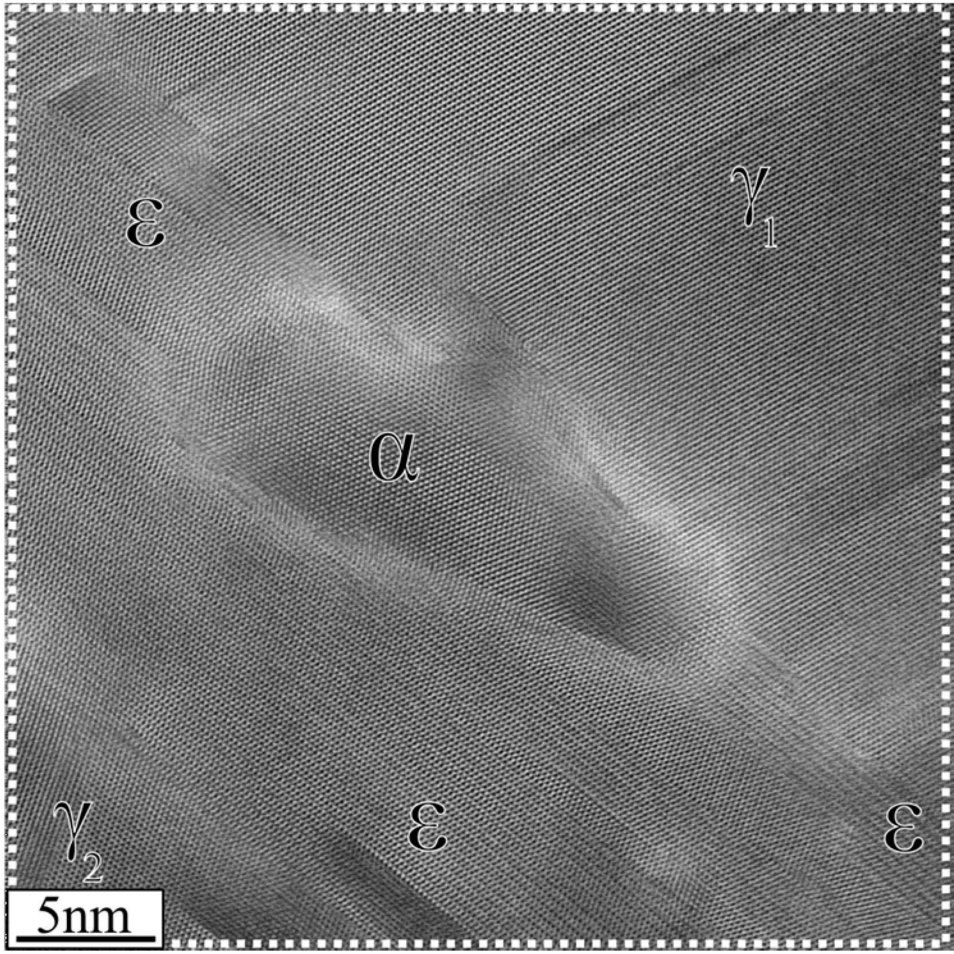


Here large regions of α'-martensite are formed, growing along the shear bands containing large amount of ε-martensite.

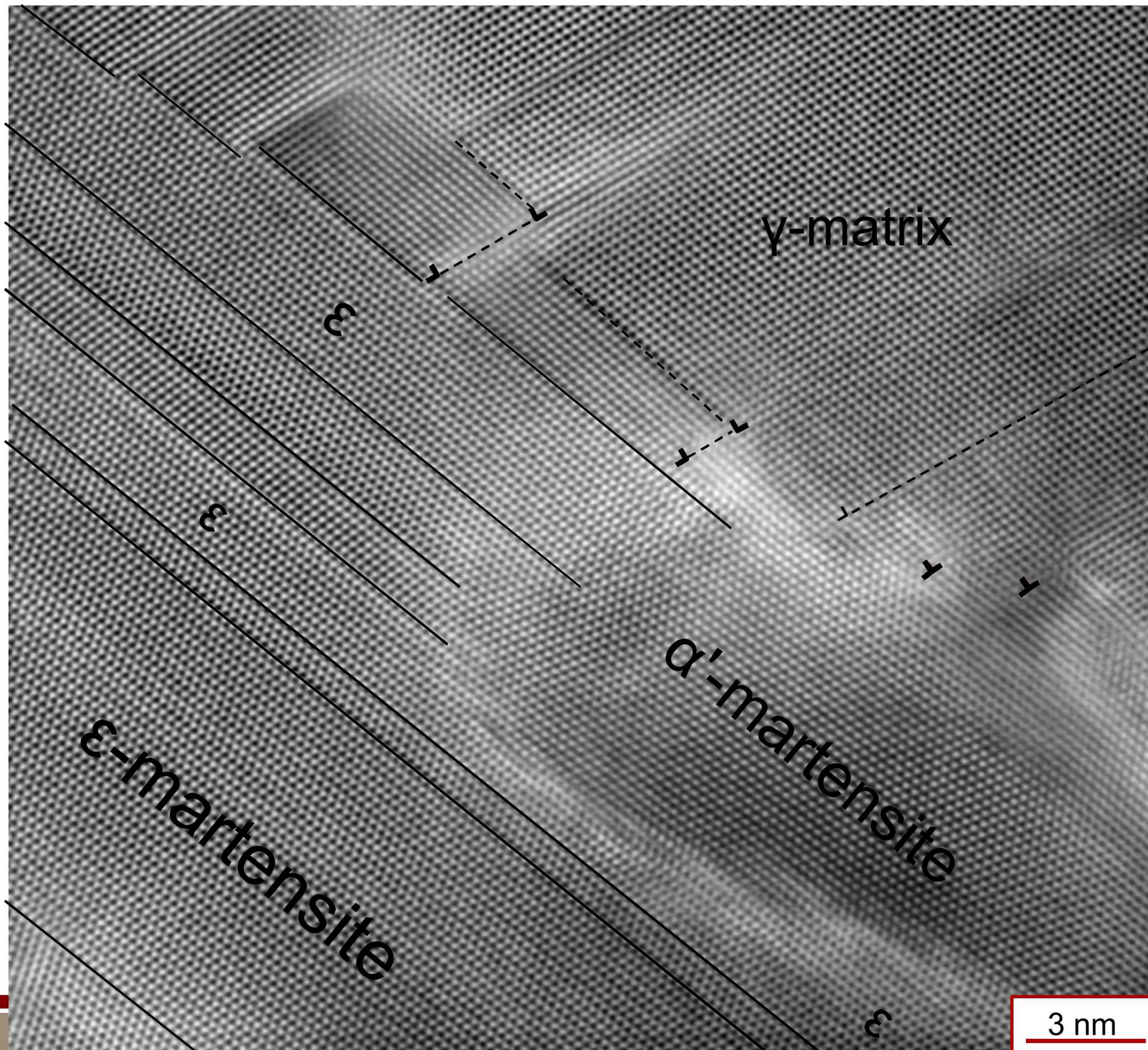


α'-Martensite in H-Charged 20% Strain





α’-Martensite Nucleus Structure



-J.E.C.Sabisch et al. In Preparation

H-Effect on Microstructure in Steel

- Hydrogen thermal precharging had a large effect on the defect substructure within deformation bands of 304L stainless steel.
- While NC samples are mediated by the formation of deformation twinning at strains below 20%, HC samples favor ε-martensite formation at all observed strain levels.
- With the sufficient development of ε-martensite laths, HC specimen also form α'-martensite at the intersections of two ε-martensite laden deformation bands, consuming ε-martensite to form α'-martensite.
- While α'-martensite is often attributed to be a main cause of the deleterious effects of hydrogen within steel, α'-martensite nucleation is only a secondary effect of the enhanced prevalence of ε-martensite within the microstructure.

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  - High strain samples (20% strain) were investigated with HRSTEM images showing the nucleus of secondary phases.
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  - Observations of void nucleation at inclusions within the copper matrix.
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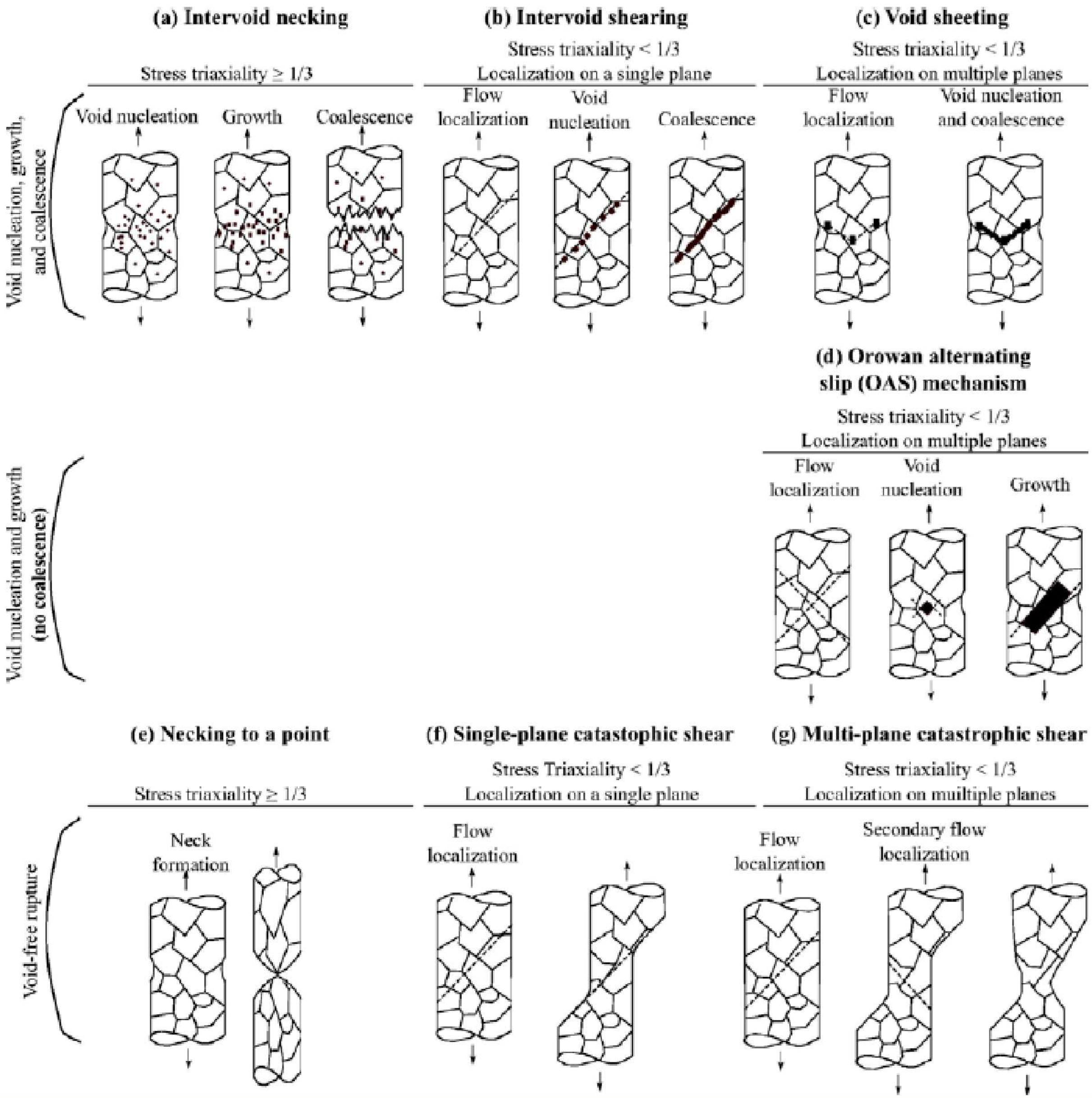
- Continuing work and conclusion.

The Void Question of Ductile Rupture

Voids have been shown repeatedly within the literature to be crucial to the ductile failure of metals. Multiple mechanisms have been postulated to show how void formation within any deformation microstructure can result in failure.

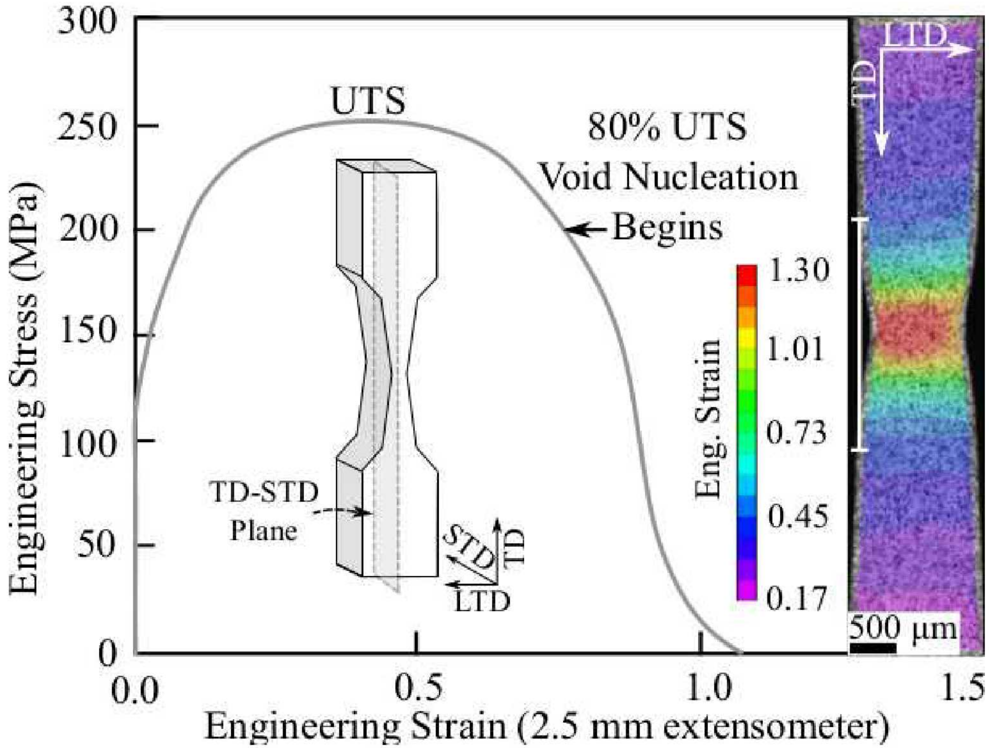
Key Questions

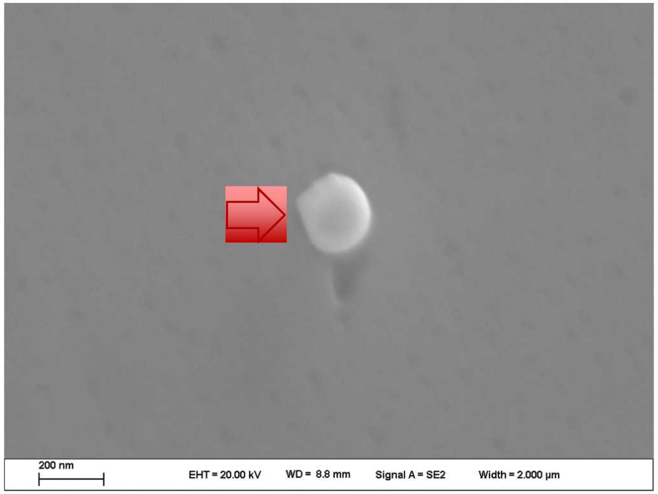
1. Is there a competition between "natural" void nucleation and "particle-stimulated" void nucleation?
2. What role does defect accumulation (*e.g.* the formation of cell block boundaries) play in void nucleation at particles and inclusions?



Experimental Approach

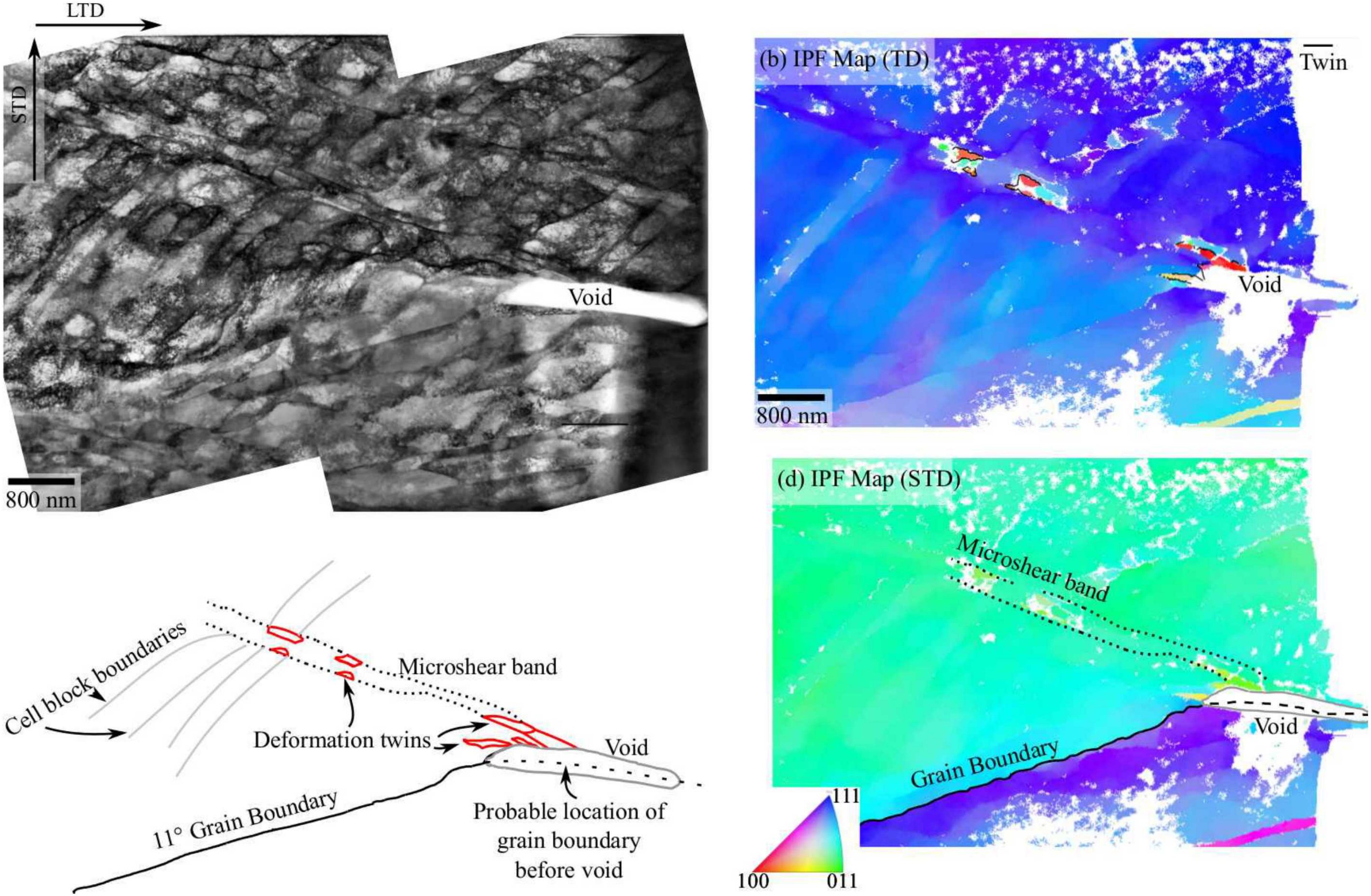
- Interrupted tension tests performed on a 99.9% Cu sheet material that contained ~200 nm CuO inclusions (area density of ~1 per 200 μm^2)
  - Void nucleation began at ~80% of the UTS. Most analysis performed on specimens interrupted at 60% of the UTS. Only voids that nucleated in the diffuse neck (before a shear band developed) were examined
  - More information on the fracture behavior of this material provided in Noell *et al.*, 2018, *Acta Materialia*





A ~200 nm CuO inclusion is shown

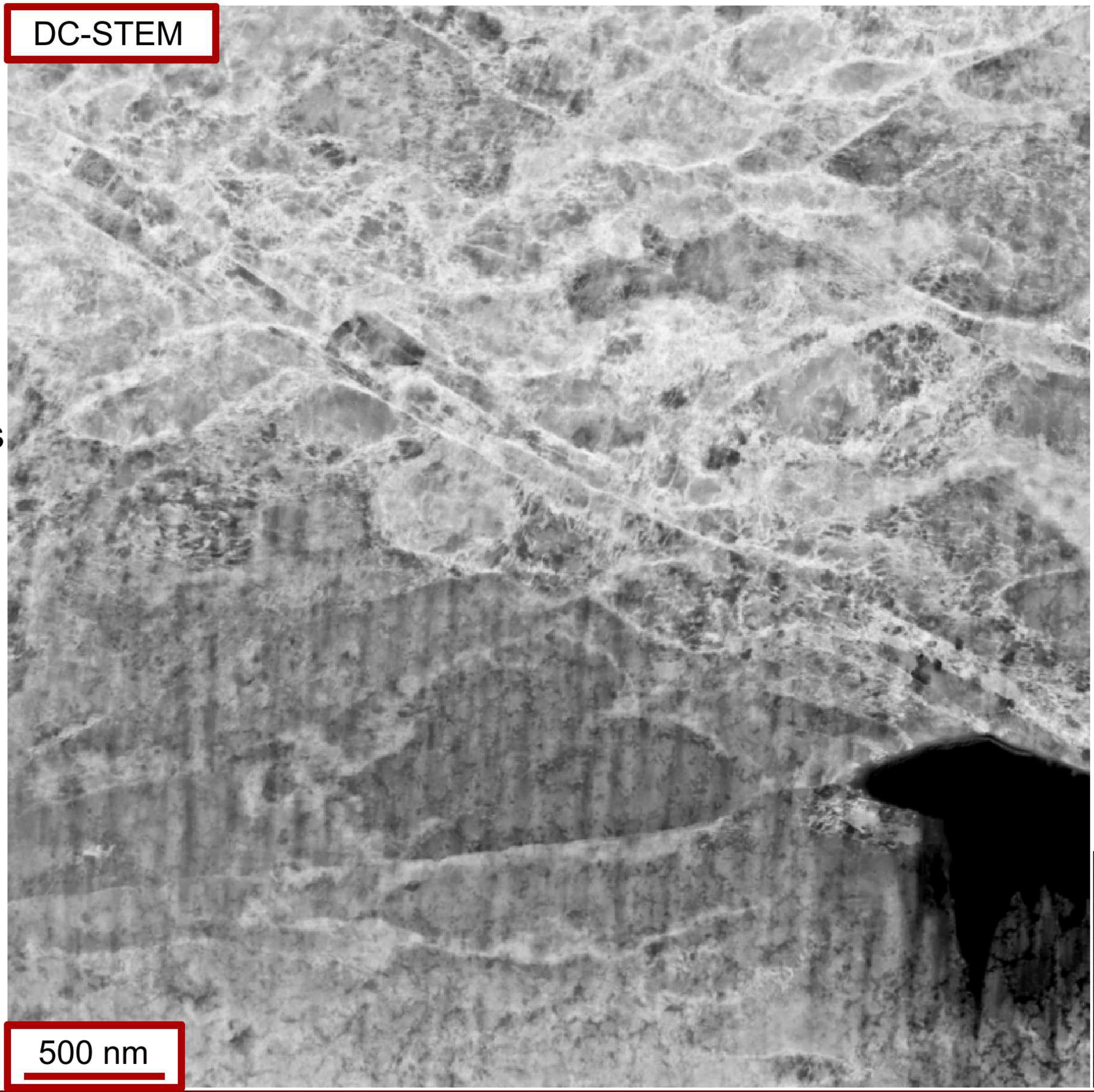
Deformation induced Voids



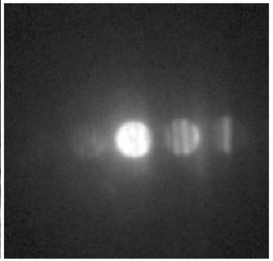
DC-STEM of Microshear Band

DC-STEM of microshear band

No particular zone was used in order to get the same nominal imaging condition as TKD. The TKD orientation maps maps are oriented normal to the foil generally.



Diffraction pattern was taken from the center of the microshear band

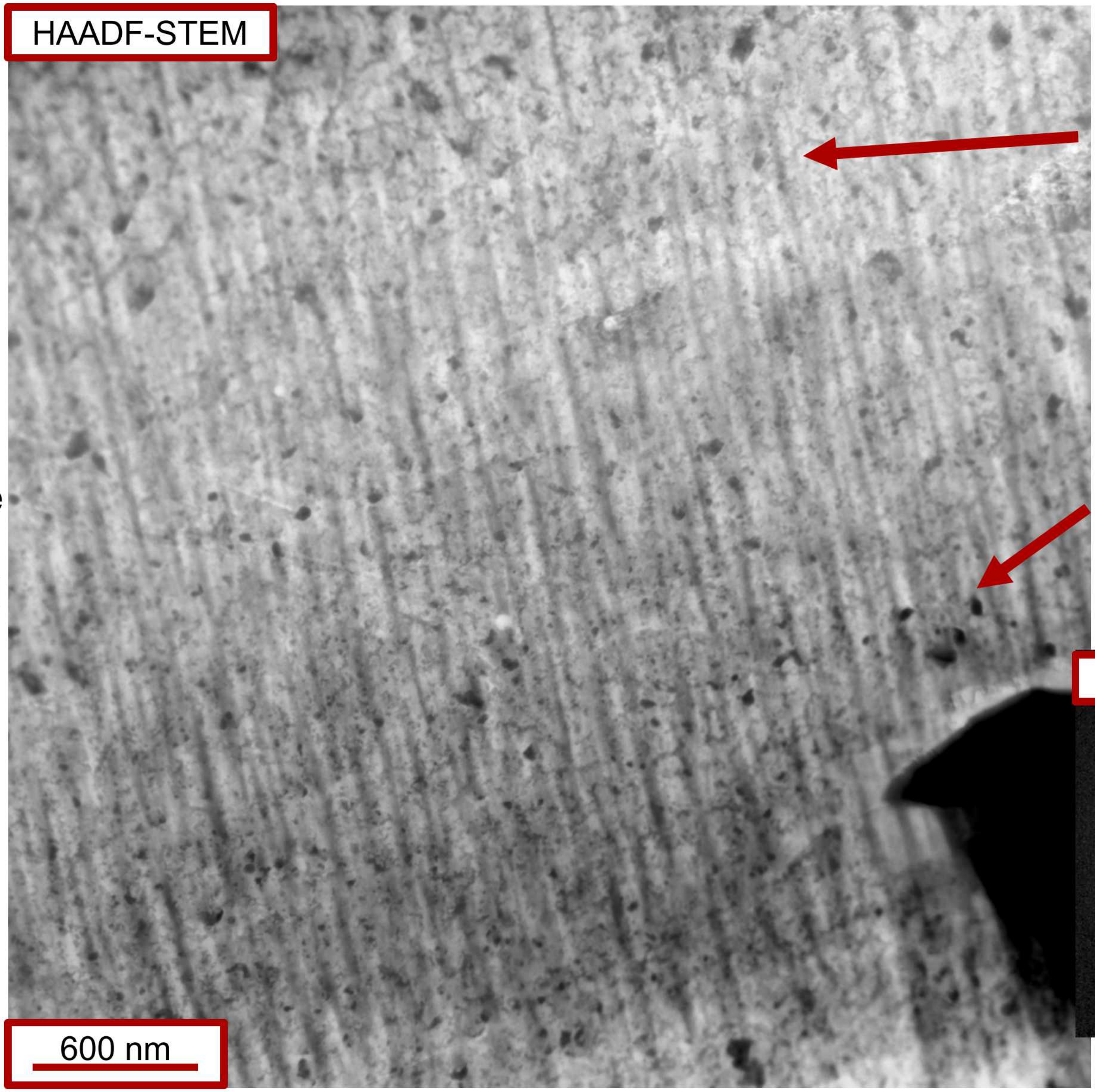


-Noell et al. Acta Materialia 2019

HAADF STEM of Microshear Band

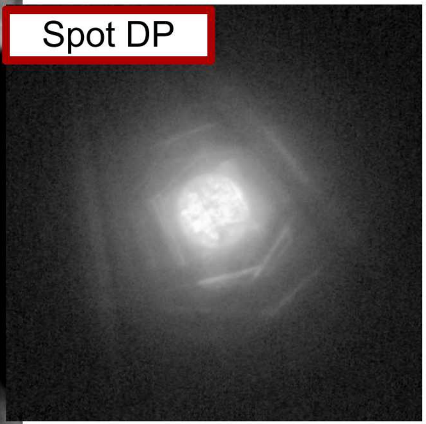
HAADF STEM
Shear band
STEM

No particular zone was used to get the same nominal imaging condition as was used for TKD. The maps are oriented normal to the foil generally.

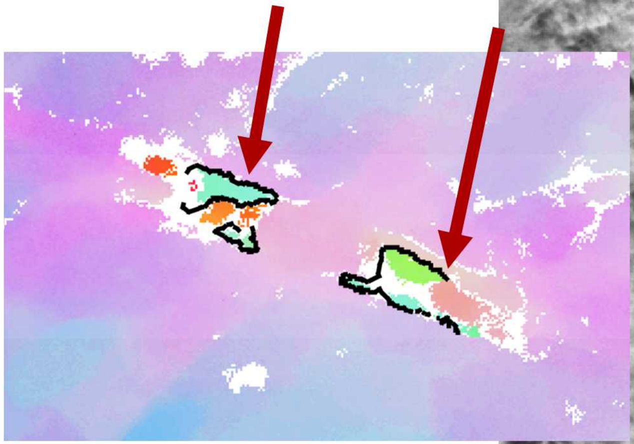


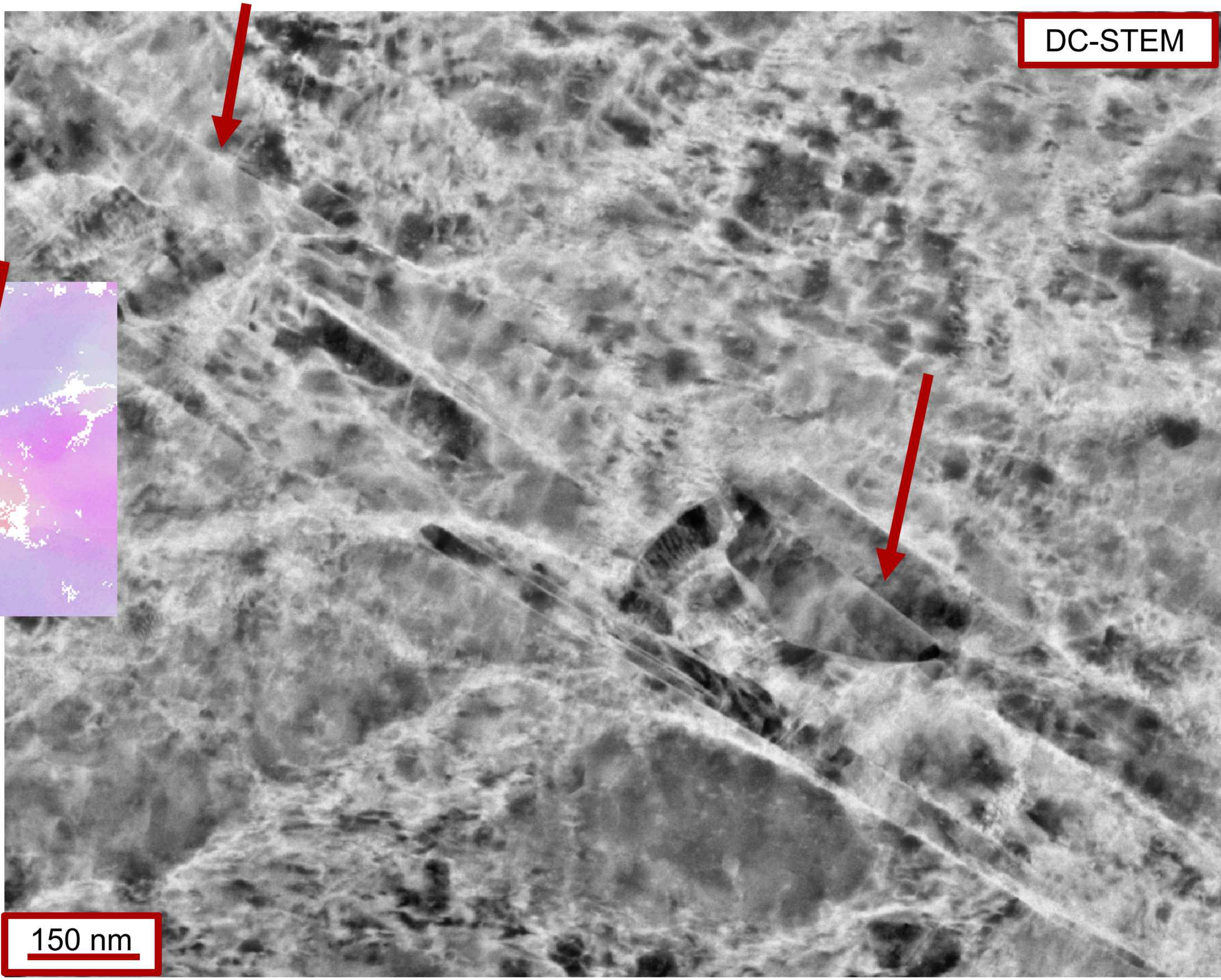
Stripes seen on the sample are due to thickness variations due to "curtaining" typical in FIB prepared samples

Dark spots are due to lack of material, ie voids.



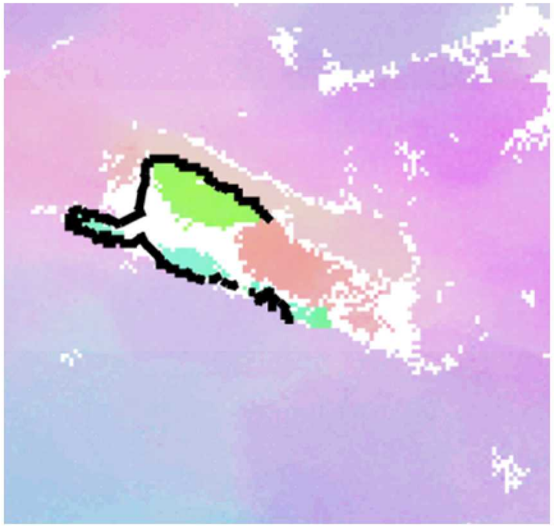
STEM Correlation to TKD



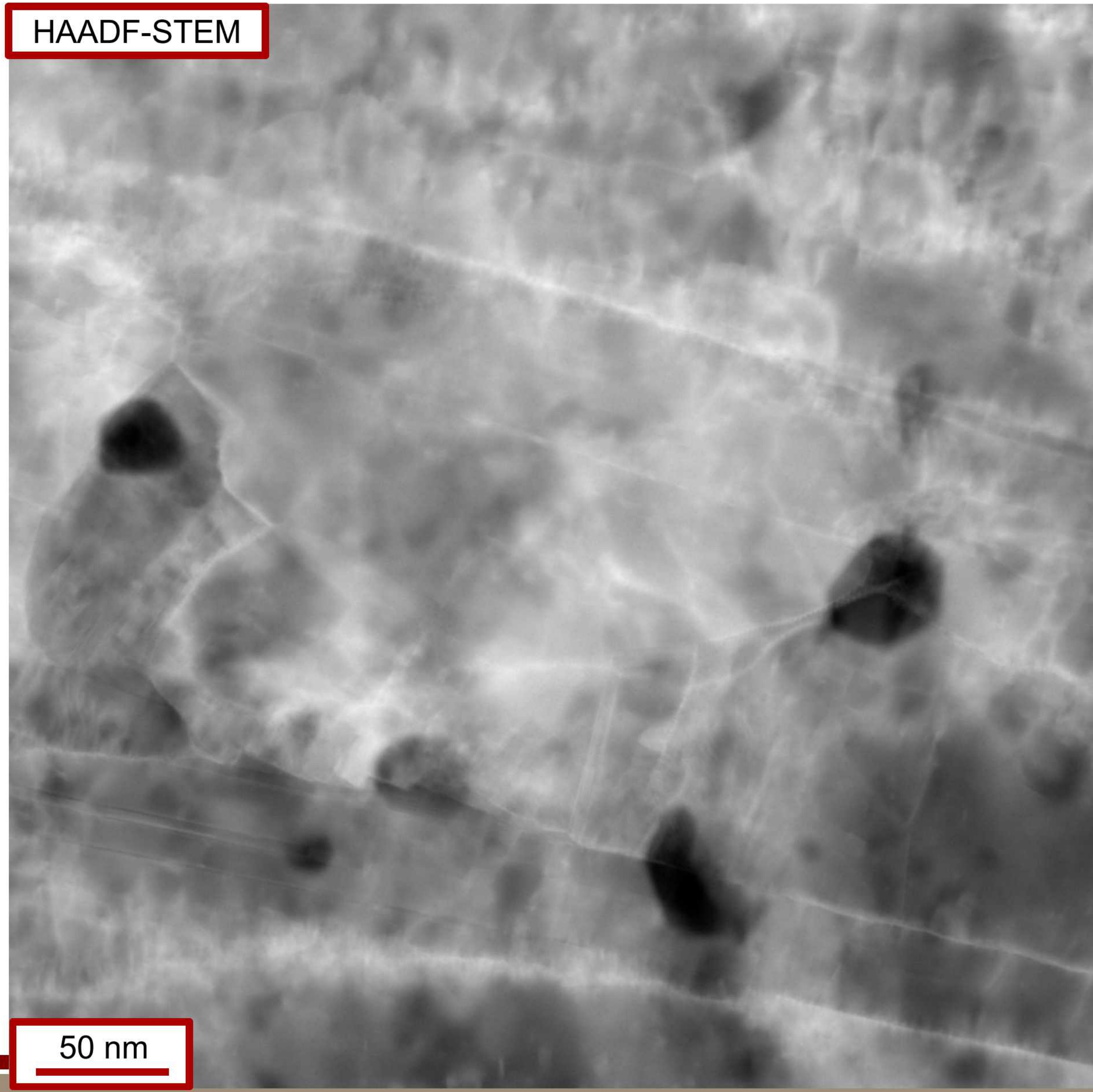


TKD was used to find twinned region within the microschear band to look at the interactions between deformation

HAADF STEM Mass-Thickness Contrast

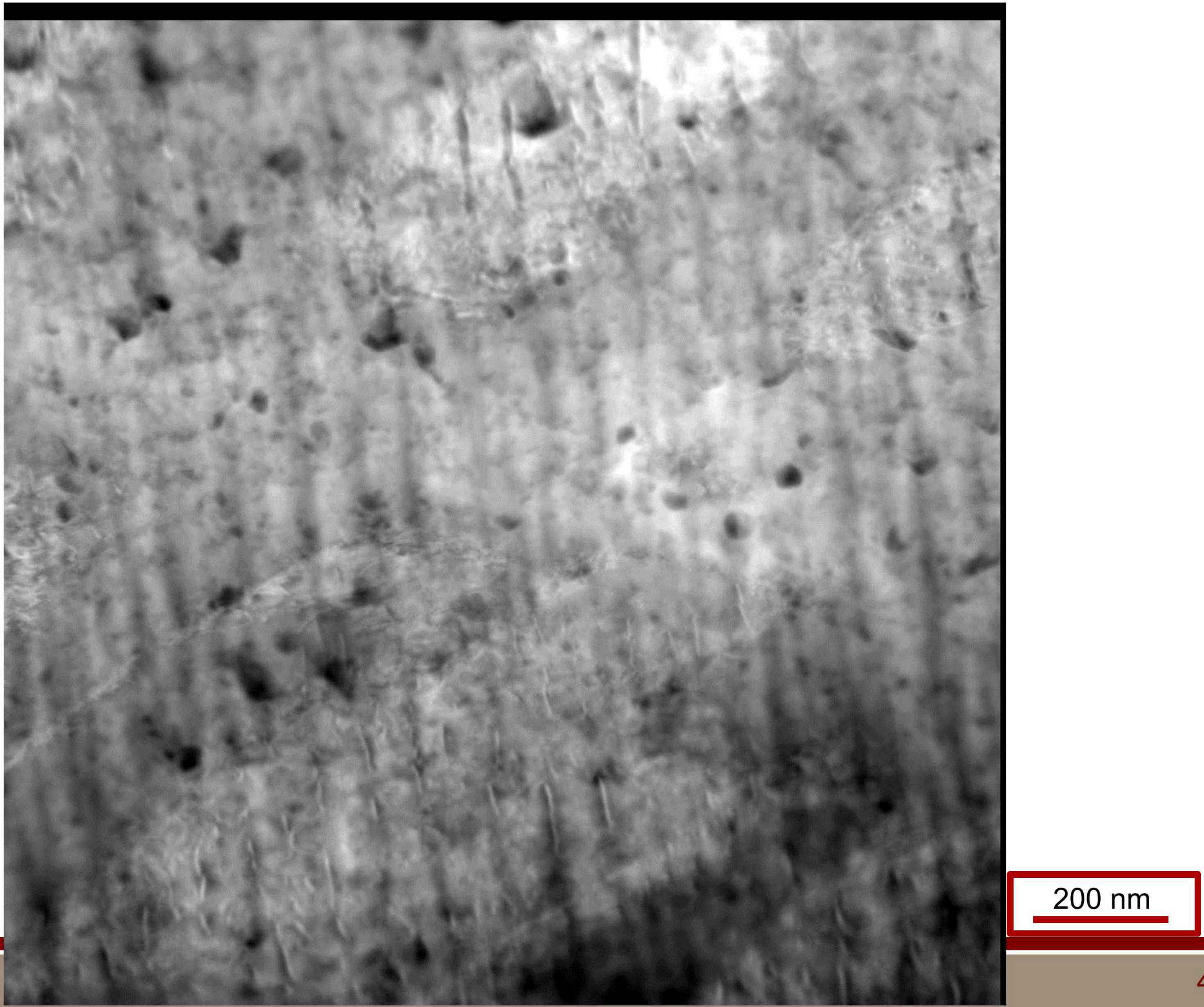


Using the HRSTEM probe (mass thickness contrast) multiple voids are visible surrounding the twin. The imaging condition is a [110] zone, with the twin boundaries parallel to the optic axis. The voids often appear at the intersections between twins, ie at the boundaries.



-Noell et al. Acta Materialia 2019

Mass-Thickness Void Tomography



-Noell et al. Acta Materialia 2019

Void Condensation in Pure Cu

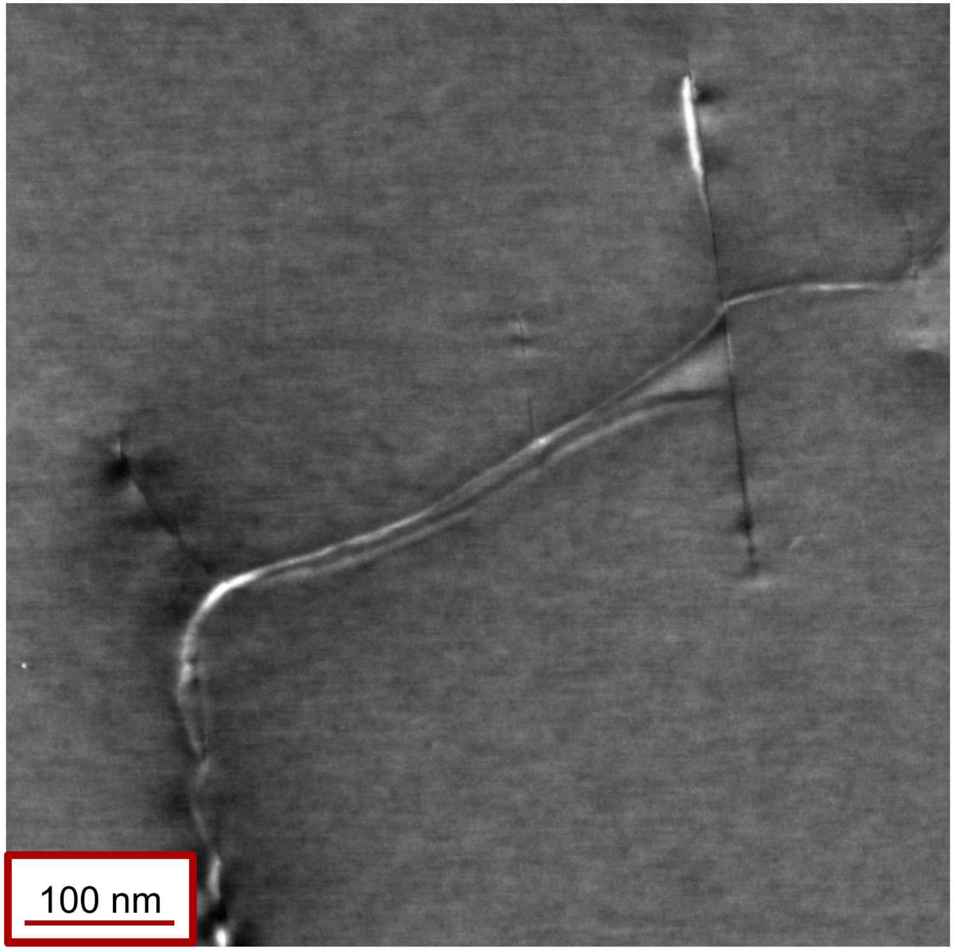
- We have made the first experimental observation that 10-100nm voids are found throughout the necked region of a pure Cu sample strained to 60% of UTS.
- This observation of nanoscaled voids throughout the specimen neck is direct evidence that vacancy condensation contributes to void nucleation during room temperature deformation.
- With the high density of nanoscale voids, it is apparent that ductile rupture is mediated by the small number of voids that grow to be on the order of microns from the nanoscaled voids.
- Additionally, the early stages of void nucleation appear to be dependent on void location, as dislocation structures, such as cell walls, are associated with void growth.

Outline

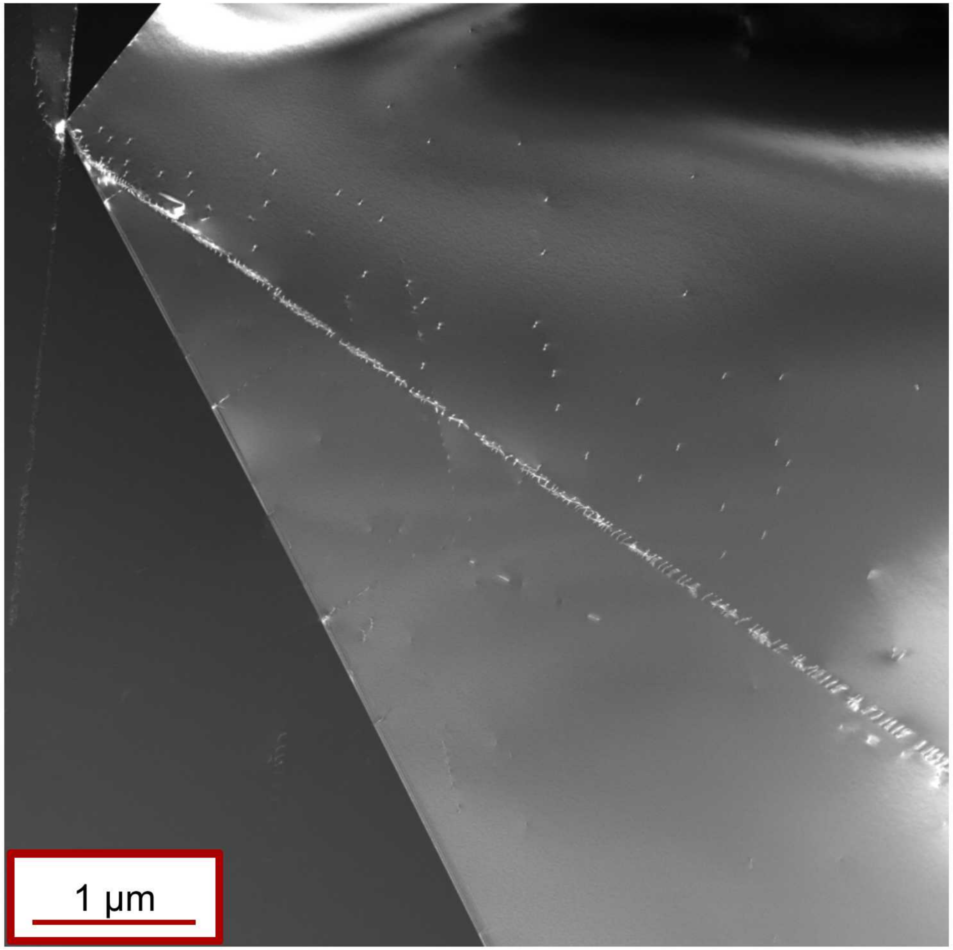
- General information on defects, microscopy, and materials.
- Microstructural effect of hydrogen on 304L stainless steel.
  - Observations of the microstructural evolution between hydrogen charged (HC) and non-charged (NC) samples below 5% strain.
  - High strain samples (20% strain) were investigated with HRSTEM images showing the nucleus of secondary phases.
- Investigation of ductile rupture in pure copper using high resolution STEM.
  - Observations of void nucleation at inclusions within the copper matrix.
  - High resolution and mass-thickness contrast STEM imaging of nanoscaled voids within the deformation shear bands within the necked region.
- **Continuing work and conclusion.**

Continuing *In-Situ* Experiments

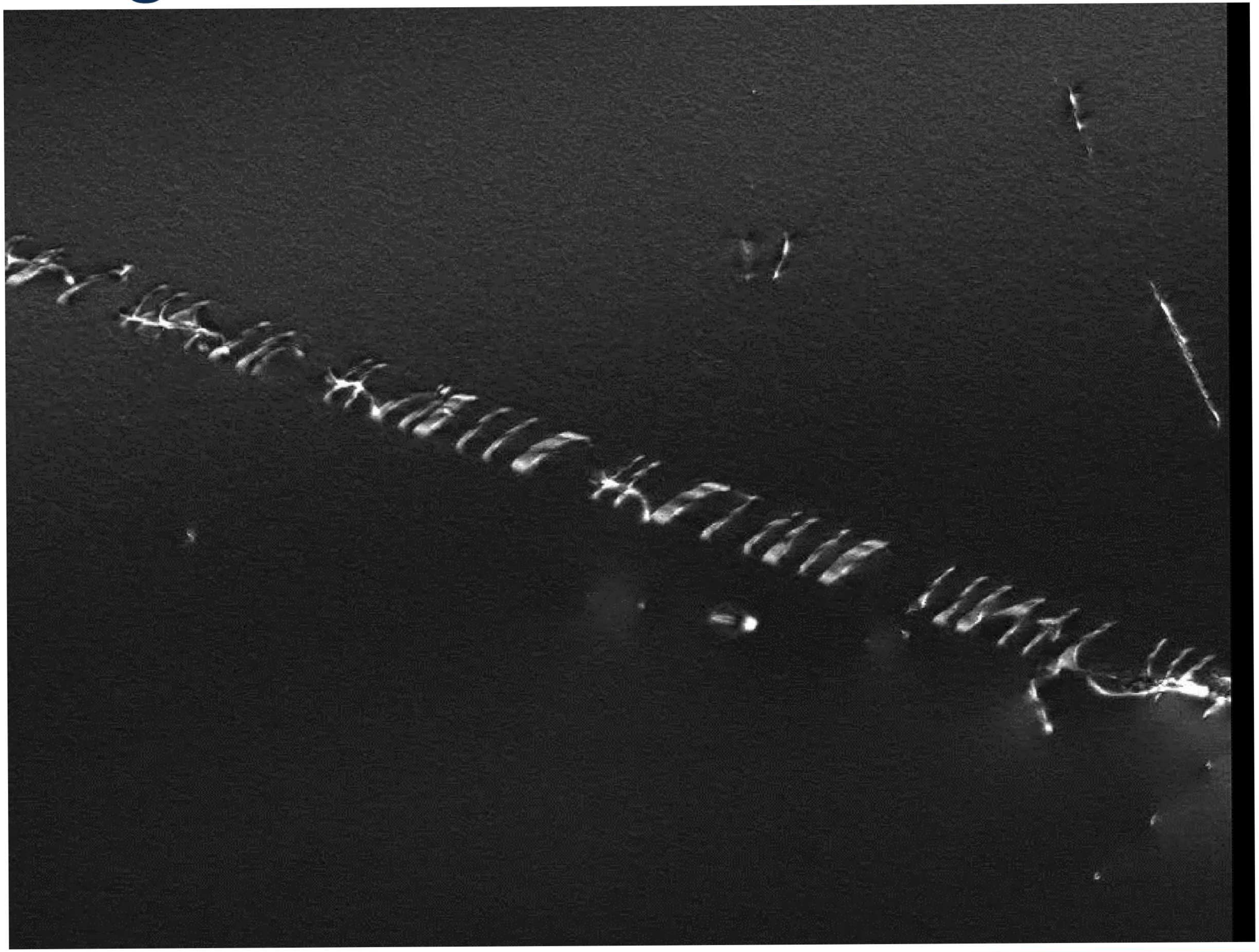
304L Dislocation situated along a twin boundary



316L Dislocation pileup intersecting a grain boundary

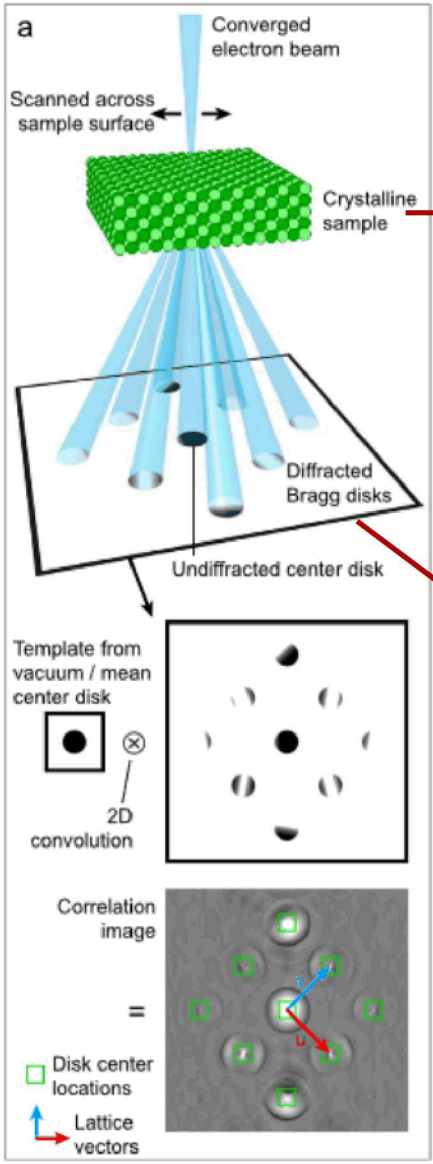


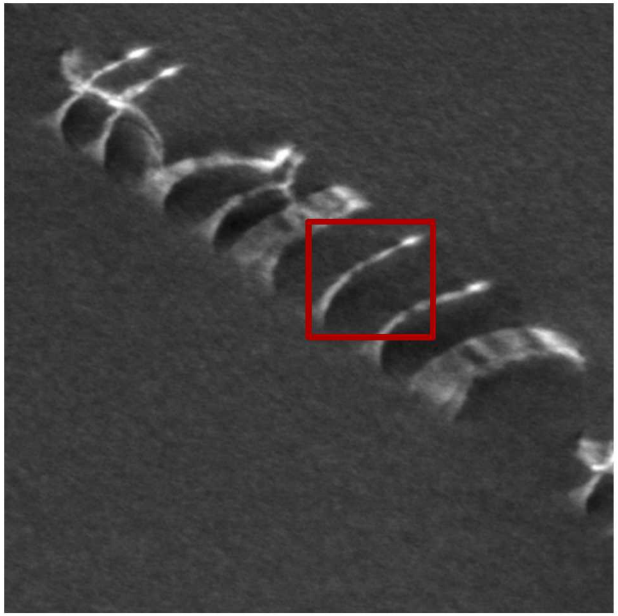
Continuing Dislocation Tomography



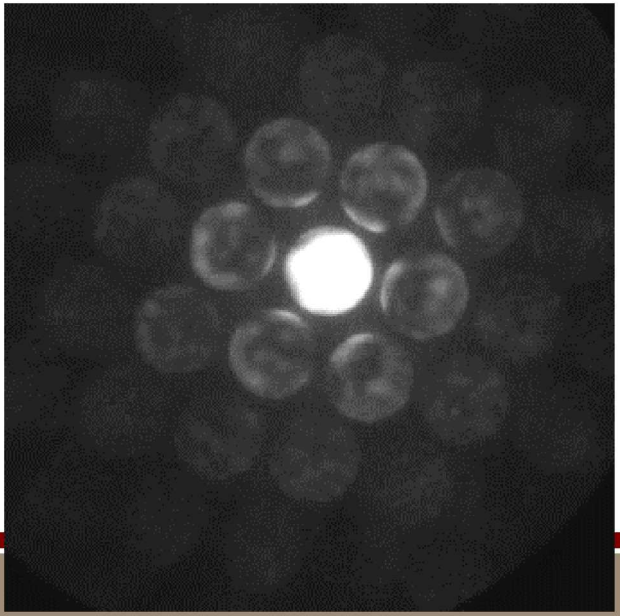
150 nm

In-Situ 4DSTEM Measurements





Samples of steel were exposed to hydrogen *in-situ* in a ThermoFisher FEI Titan ETEM at CINT.

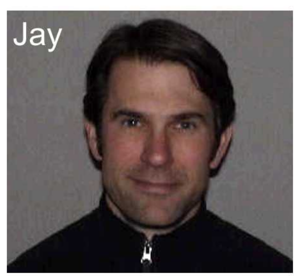


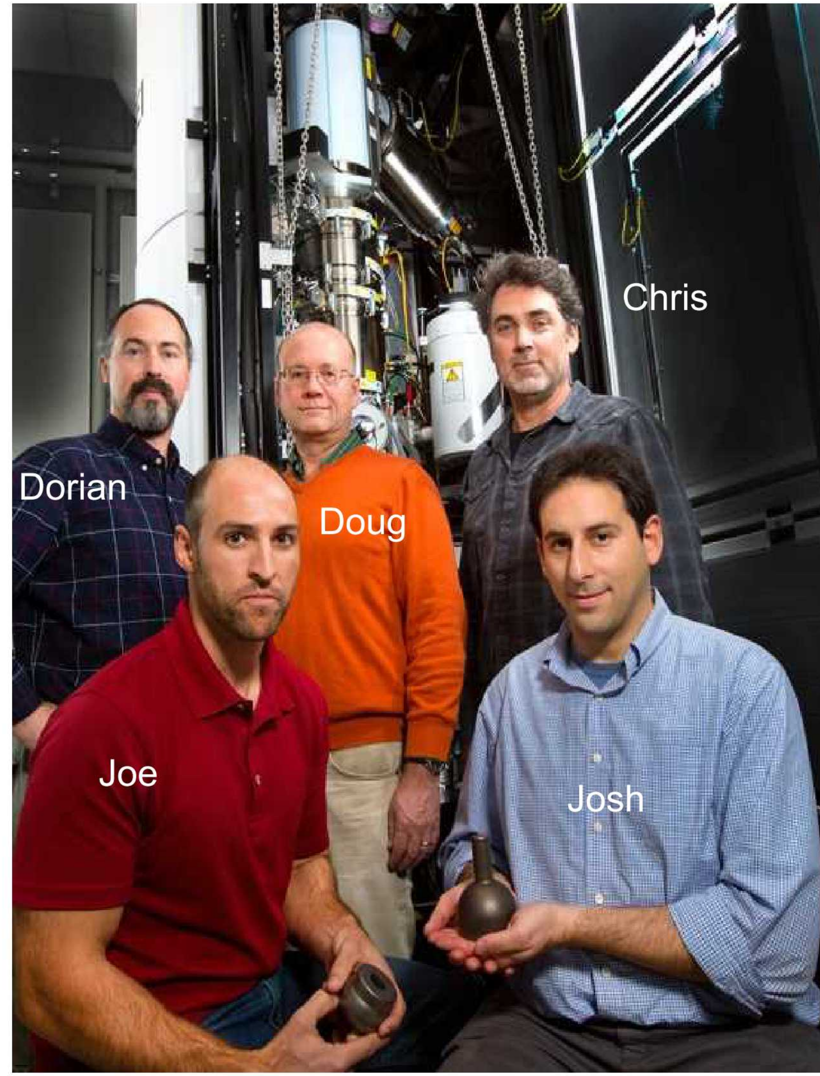
These resulting diffraction patters are to be used to determine the local strain around dislocation cores with and without hydrogen.

-Pekin et al. Ultramicroscopy 2017

Acknowledgements

- Thanks to: Doug Medlin, Chris San Marchi, Joe Ronevich, Philip Noell, Brad Boyce, Josh Sugar, Ryan Sills, Mark Homer, Warren York, Heidy Vega.





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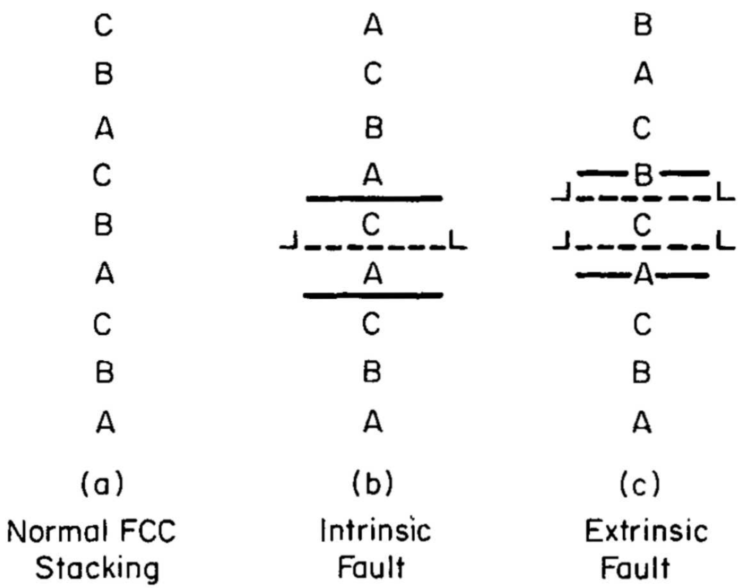
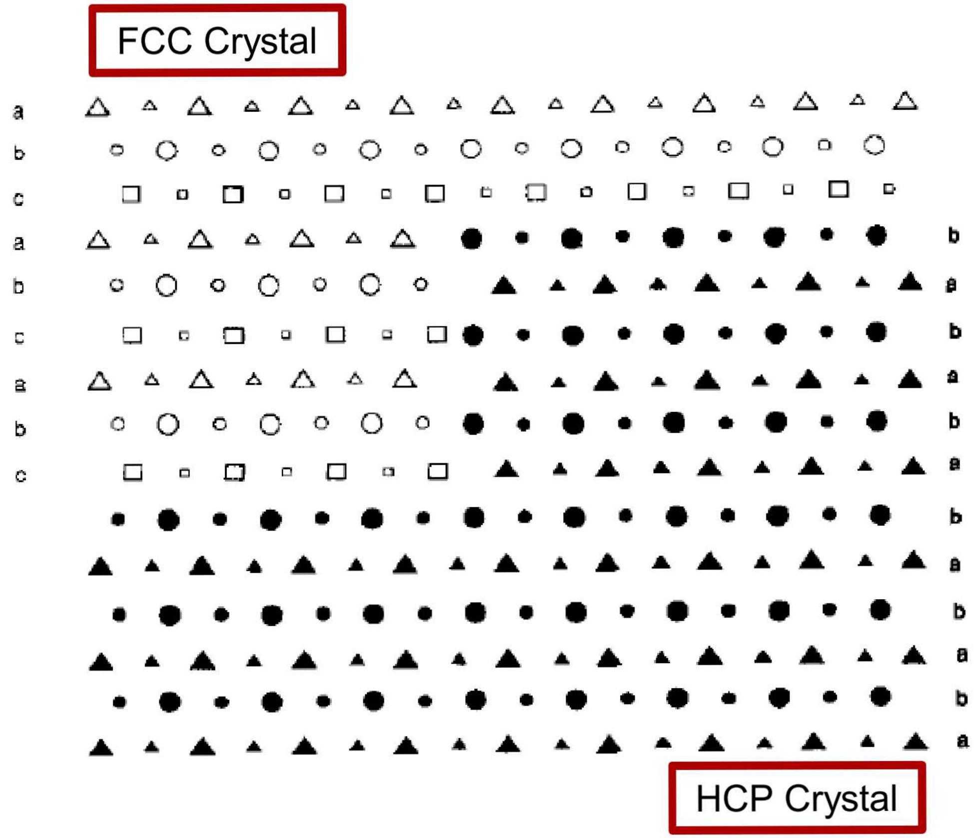
Extra Slides

Background on ε-Martensite Formation





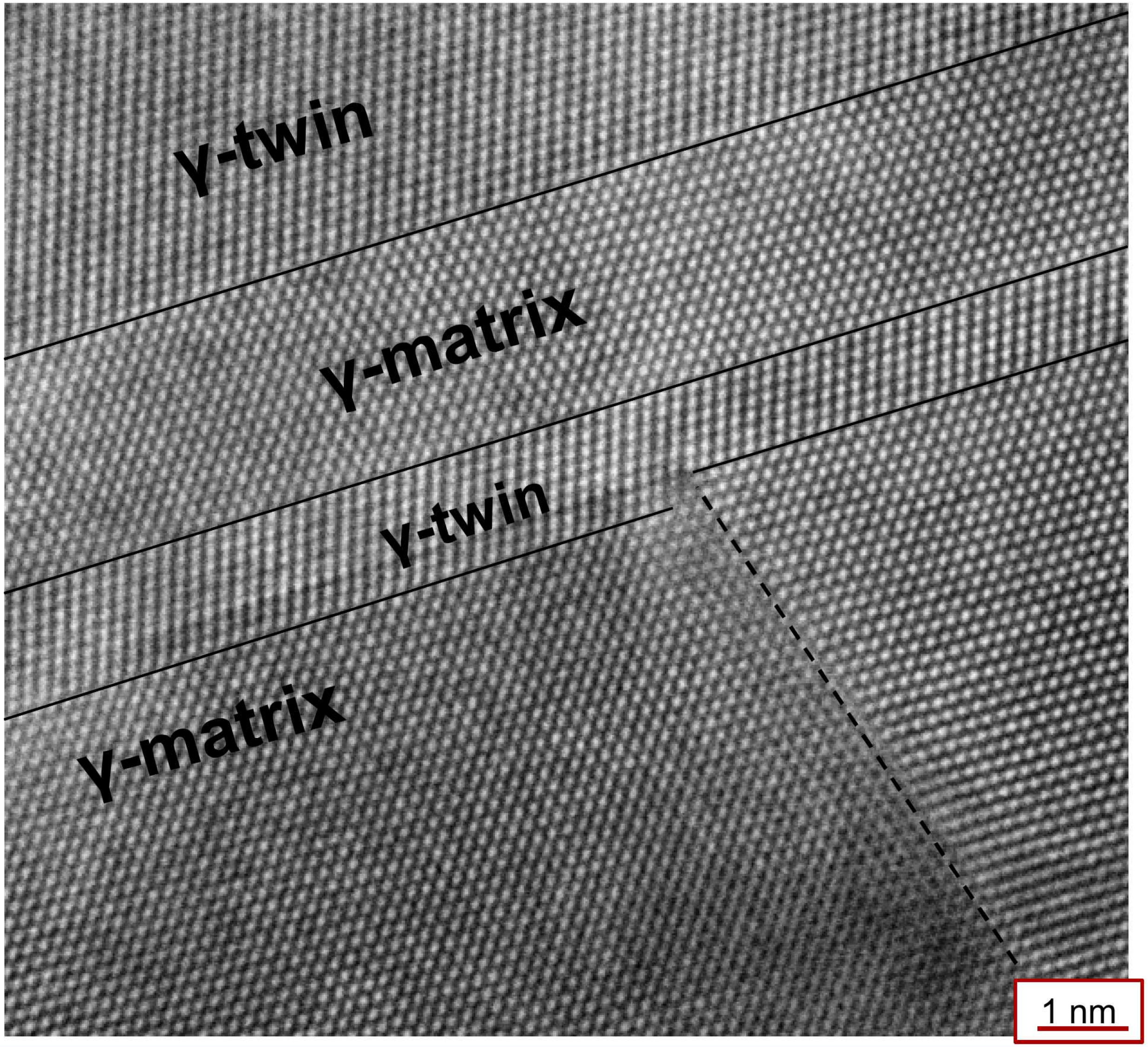
5% NC HRSTEM

Characteristic 5% NC HR-STEM image showing Twins and Dislocations

The two dislocations are $\frac{1}{6}\langle 112\rangle$ and $\frac{1}{3}\langle 111\rangle$.

HRSTEM shows streaking in DP's are due to stacking faults near the twin boundaries.

Twins and twin vary in thickness, from a few atomic planes to larger regions 1-100 nm thick.



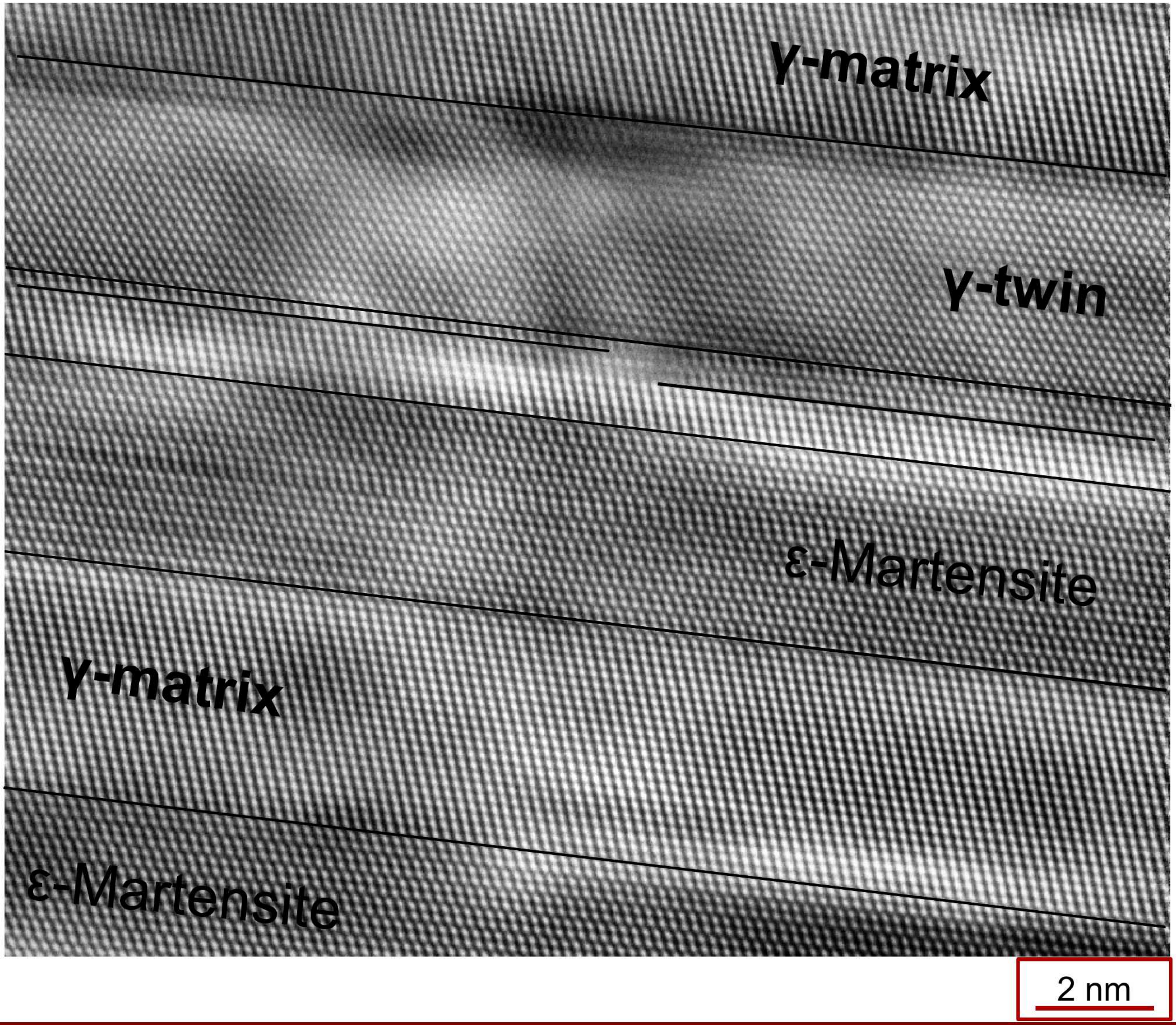
5% HC HRSTEM

Characteristic 5% HC HR-STEM image shows ε-Martensite and twinning intermixed.

ε-Martensite is more common here than twinning, as seen in nanobeam diffraction.

Twins and ε-martensite are generally very thin (less than ~20 $\{111\}$ planes) while spanning through most of the grain.

Twins also appearing within faulted ε-martensite.

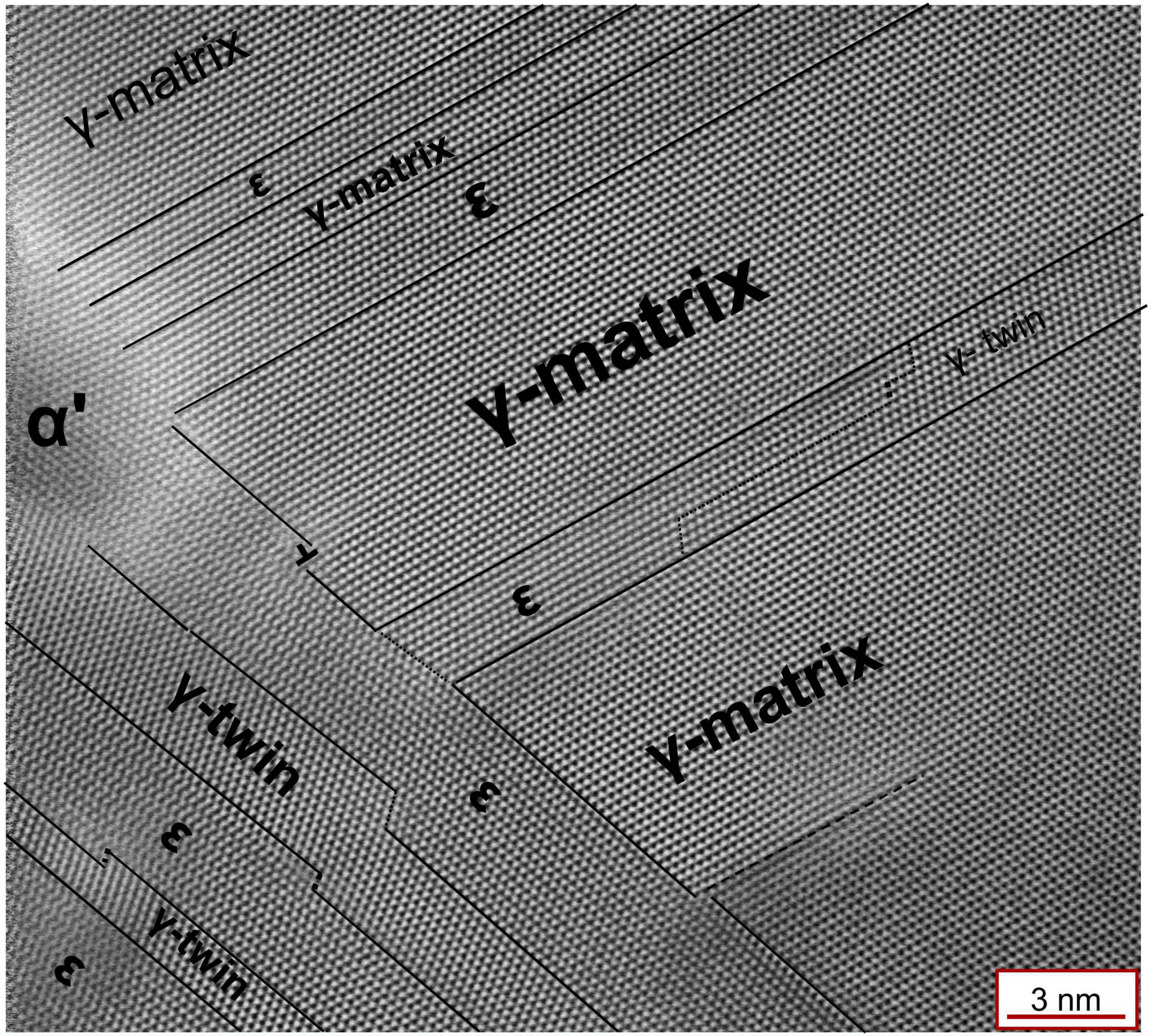


20% HC HRSTEM

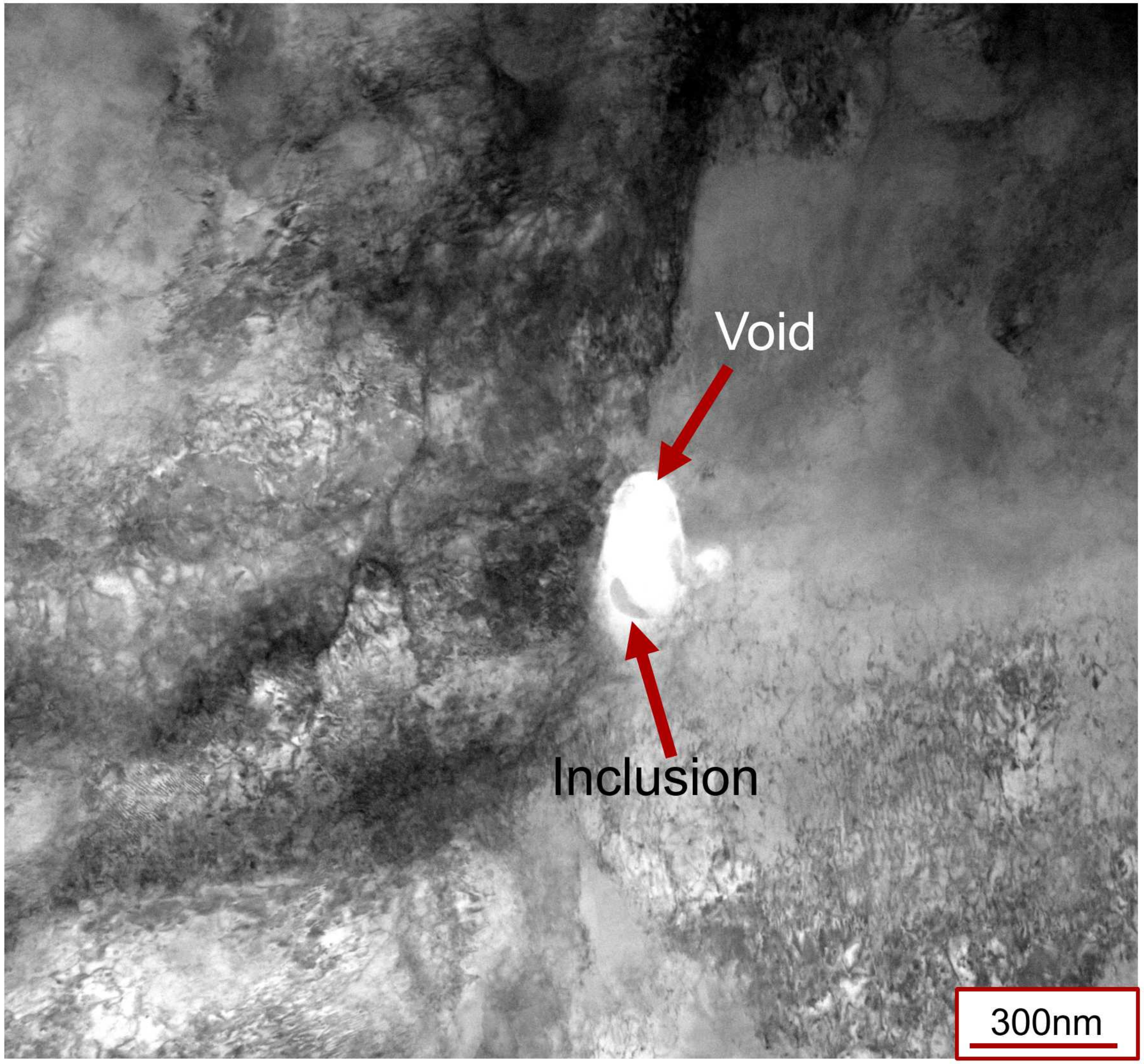
On this side of the α'-martensite nucleus, twins only a few $\{111\}$ planes in thickness are embedded within the ε-martensite.

Interfacial dislocations are seen at the boundaries between austenite and ε-martensite.

Interfacial dislocations appear to be the same as in the 5% strain sample.

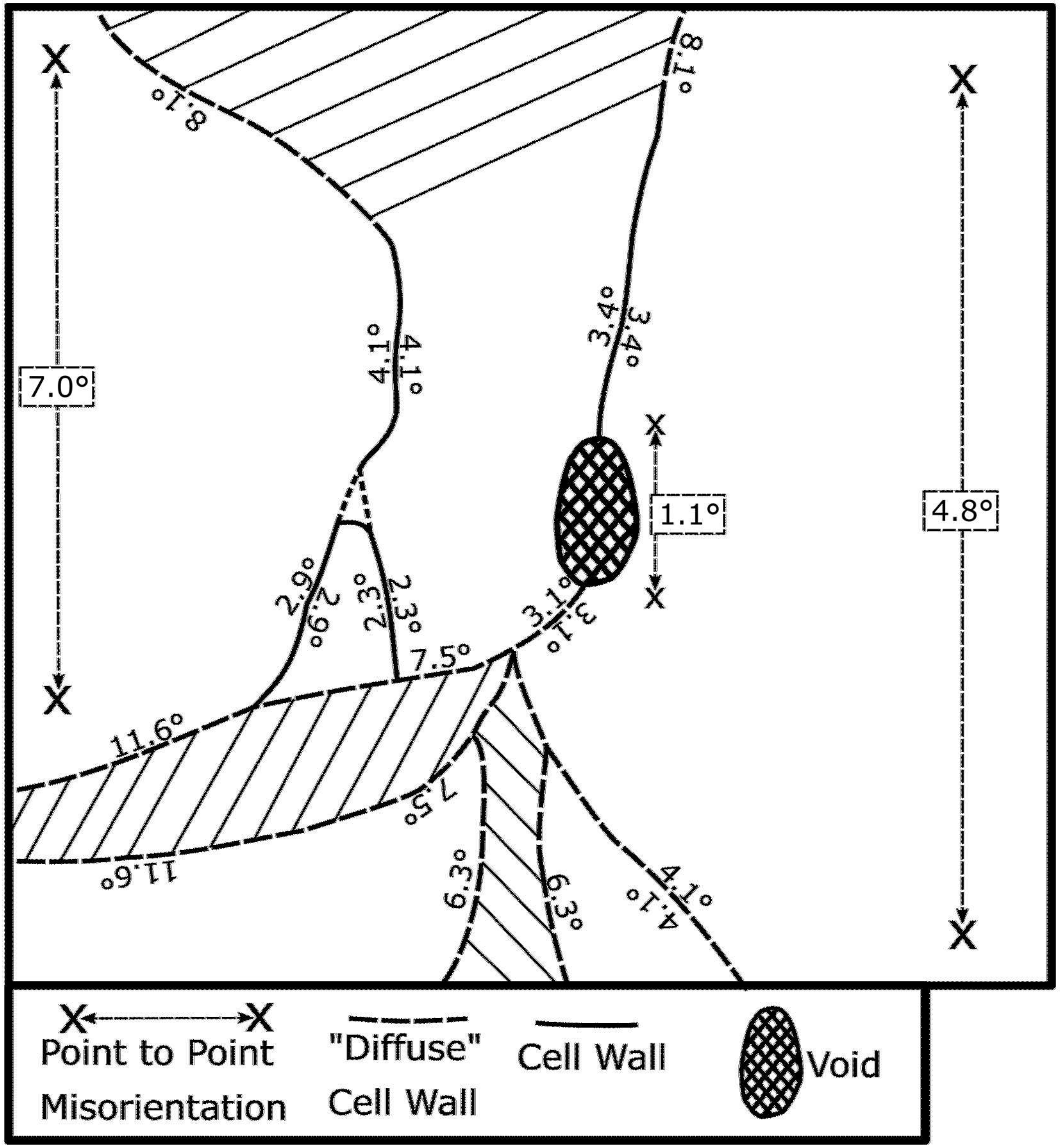


Void nucleation at 2^{nd}-phase particles



- Select diffraction patterns were chosen in order to manually identify the misorientation change surrounding the void.
- Cell block boundaries appear likely to become "diffuse" (not seen a few microns from the void).
- Diffuse boundaries show large misorientation changes (>6°) over the span of a few hundred nanometers.
- Misorientations appear larger further from the void.
- Void walls are orthogonal to the {224} and {111} reflections.
- Evidence of a copper oxide particle at the center of a void (discuss with Julian)

Void nucleation at 2nd-phase particles



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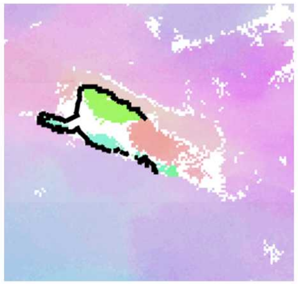
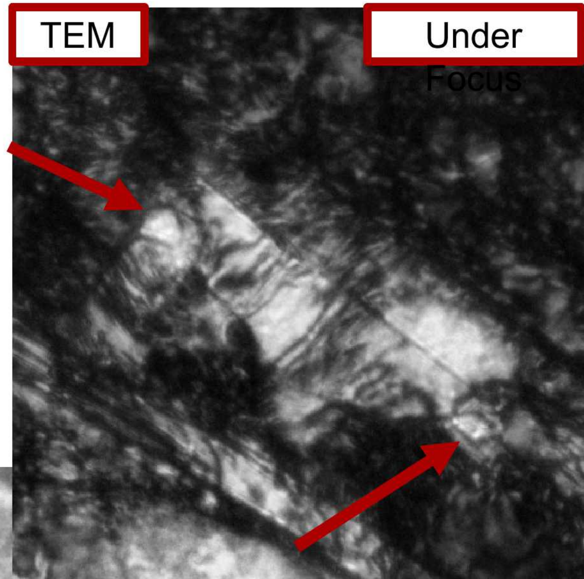
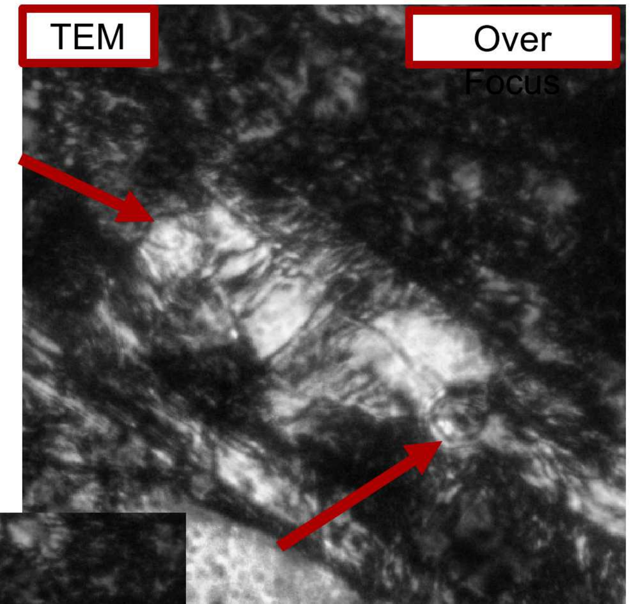
- Evidence of a copper oxide particle at the center of a void (discuss with Julian)

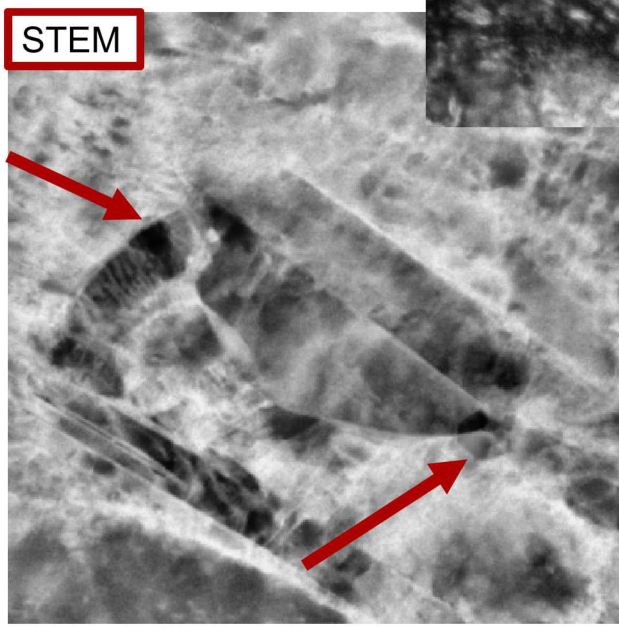
Phase contrast TEM to show Voids

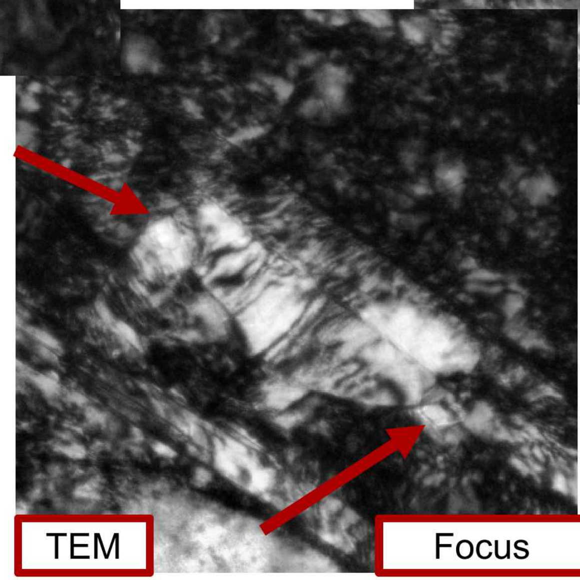




75 nm



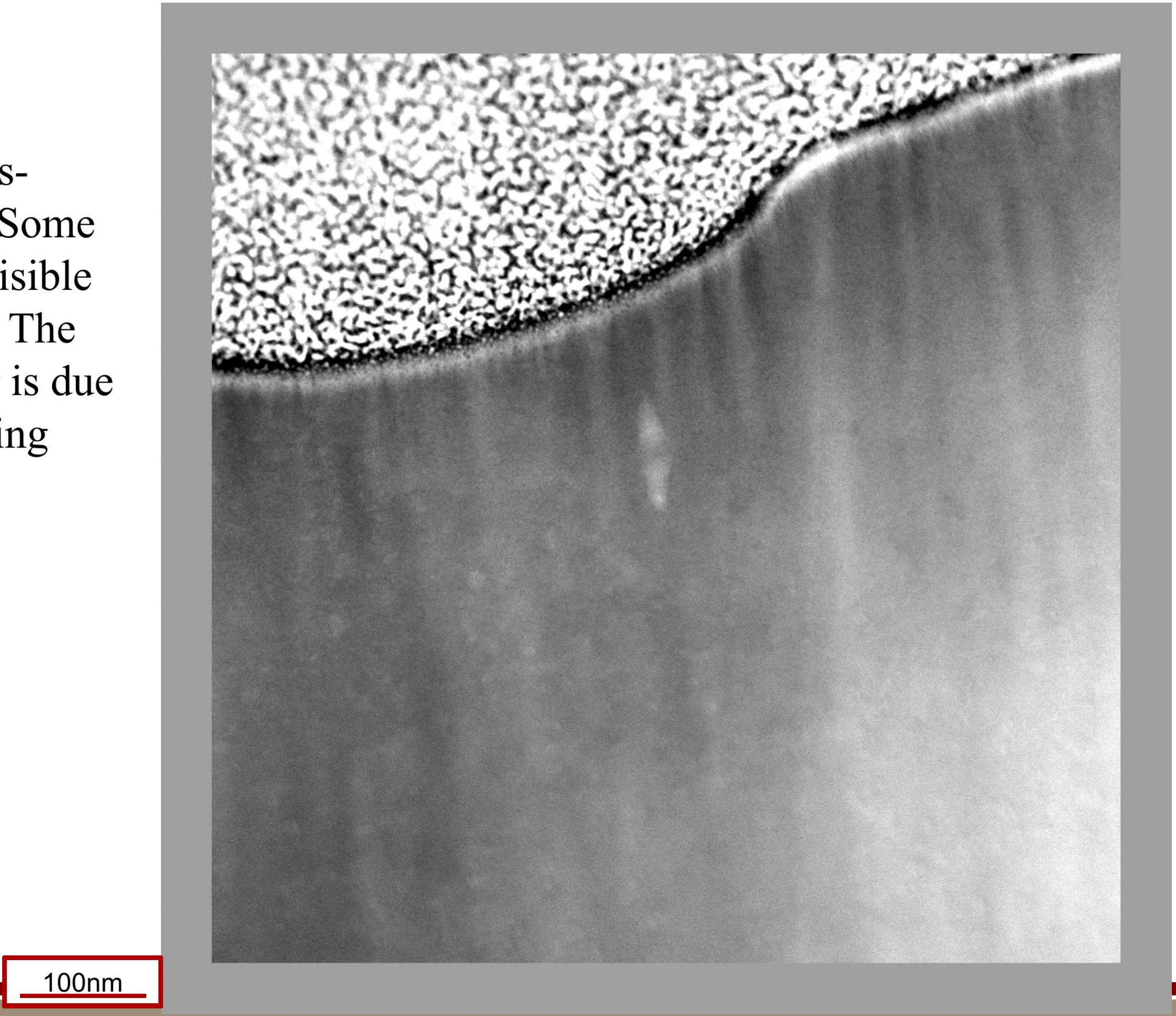




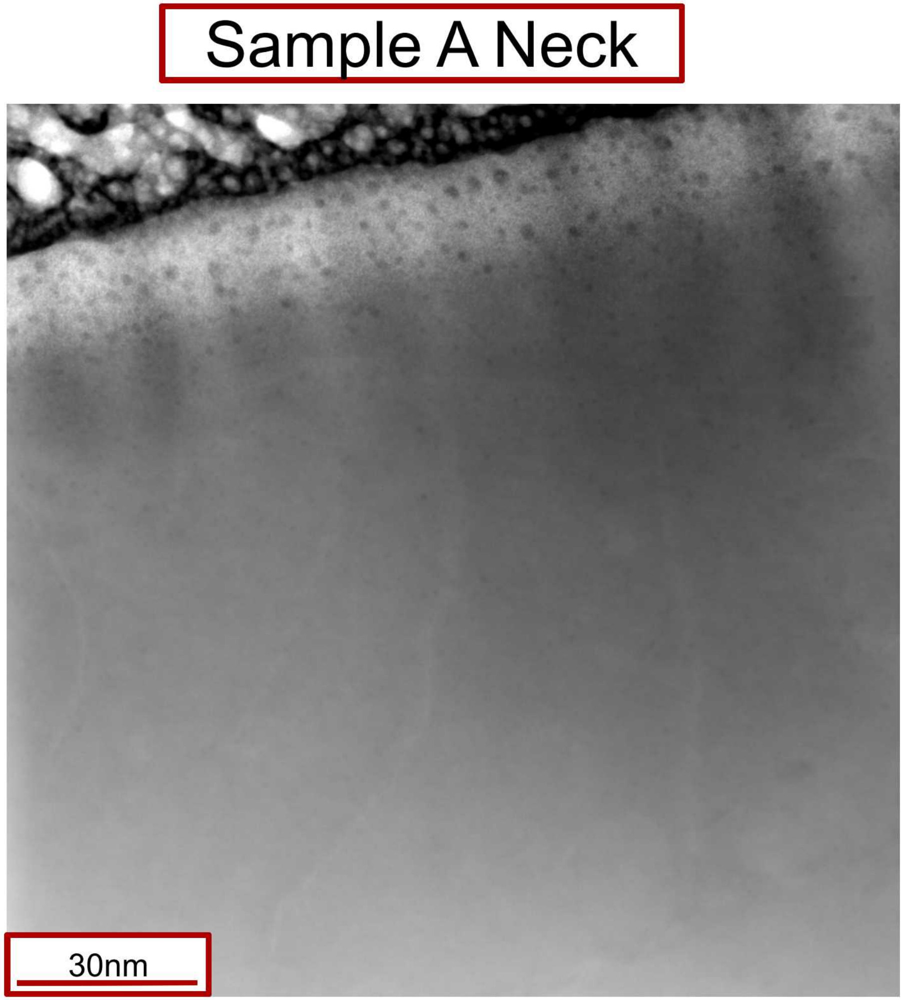
The arrows mark regions that are consistent with Phase contrast imaging of voids within the microstructure. Phase contrast with STEM mass thickness contrast is only possible with voids.

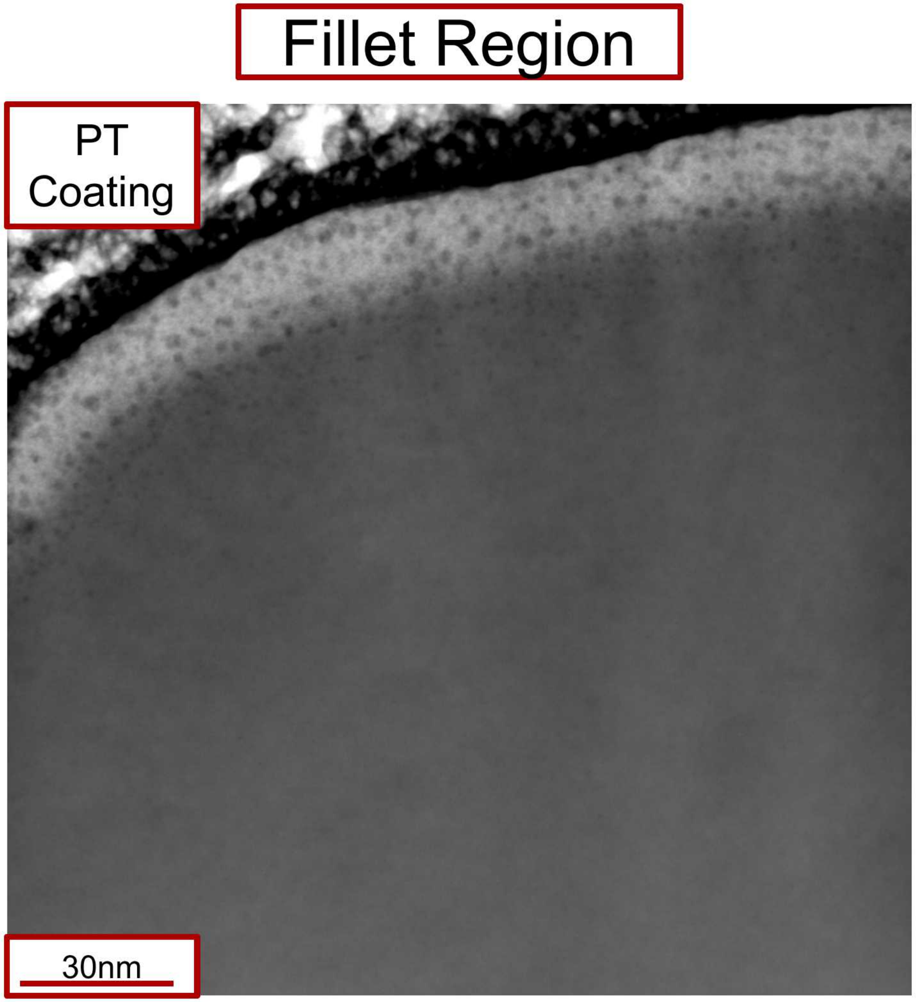
Fillet Sample Control Tomography

Fillet samples show extremely little mass-thickness contrast. Some surface damage is visible at the extreme tilts. The feature in the center is due to the beam depositing some material.



FIB Surface Damage





Small (~3nm) voids-like contrast appears in the Ga^{+} rich surface region for both Fillet control samples and samples from the Neck.

H-Effect on Dislocation Pileup

Fe Phase Diagrams