

LA-UR-20-27216

Approved for public release; distribution is unlimited.

Title: Aging & Lifetimes - Microscopy of Uranium Hydride in FY2020

Author(s): Schneider, Matthew M.
Tegtmeier, Eric Lee
Janish, Matthew Thomas
Richards, Andrew Walter

Intended for: Report

Issued: 2020-10-25 (rev.1)

Disclaimer:

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by Triad National Security, LLC for the National Nuclear Security Administration of U.S. Department of Energy under contract 89233218CNA000001. By approving this article, the publisher recognizes that the U.S. Government retains nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

Aging & Lifetimes

Microscopy of Uranium Hydride in FY2020

Matthew M Schneider

Eric Tegtmeier

Matthew T Janish

Andrew Richards

10/12/2020



Managed by Triad National Security, LLC for the U.S. Department of Energy's NNSA

Summary of Microscopy Conducted in FY2020

9/15/2019

Los Alamos, NM



- Overview
 - Pandemic Impacts
- SEM Work
 - Hydride & carbide counts
- PFIB
 - MAPS
 - Auto S&V
 - Ion beam sample interactions
- TEM
 - Mono-EELS development
 - Extending MLLS

Overview of Microscopy in FY2020

- FY2019 largely focused on a single sample, PC055 (5 Torr H₂)
 - Sample used for initial characterization & methodology development
- FY2020 expanded this work to PC019 & PC037 (1 & 2 Torr H₂)
 - Scanning electron microscopy (SEM) work used to non-destructively characterize as-reacted material
 - Carbide & hydride densities determined for 2 out of 3 samples
 - Focused Ion Beam (FIB) investigations enable sub-surface characterization and the preparation of transmission electron microscopy (TEM) samples
 - TEM results in high resolution, both spatially and spectroscopically
 - Bright/dark field imaging offers detailed examination of microstructure, phase relationships, and defect structures present in materials of interest
 - Electron diffraction used for preliminary phase identification and understanding crystallographic relationships across boundaries
 - Electron energy loss spectroscopy (EELS) used to determine electronic structure

Overview of Microscopy in FY2020

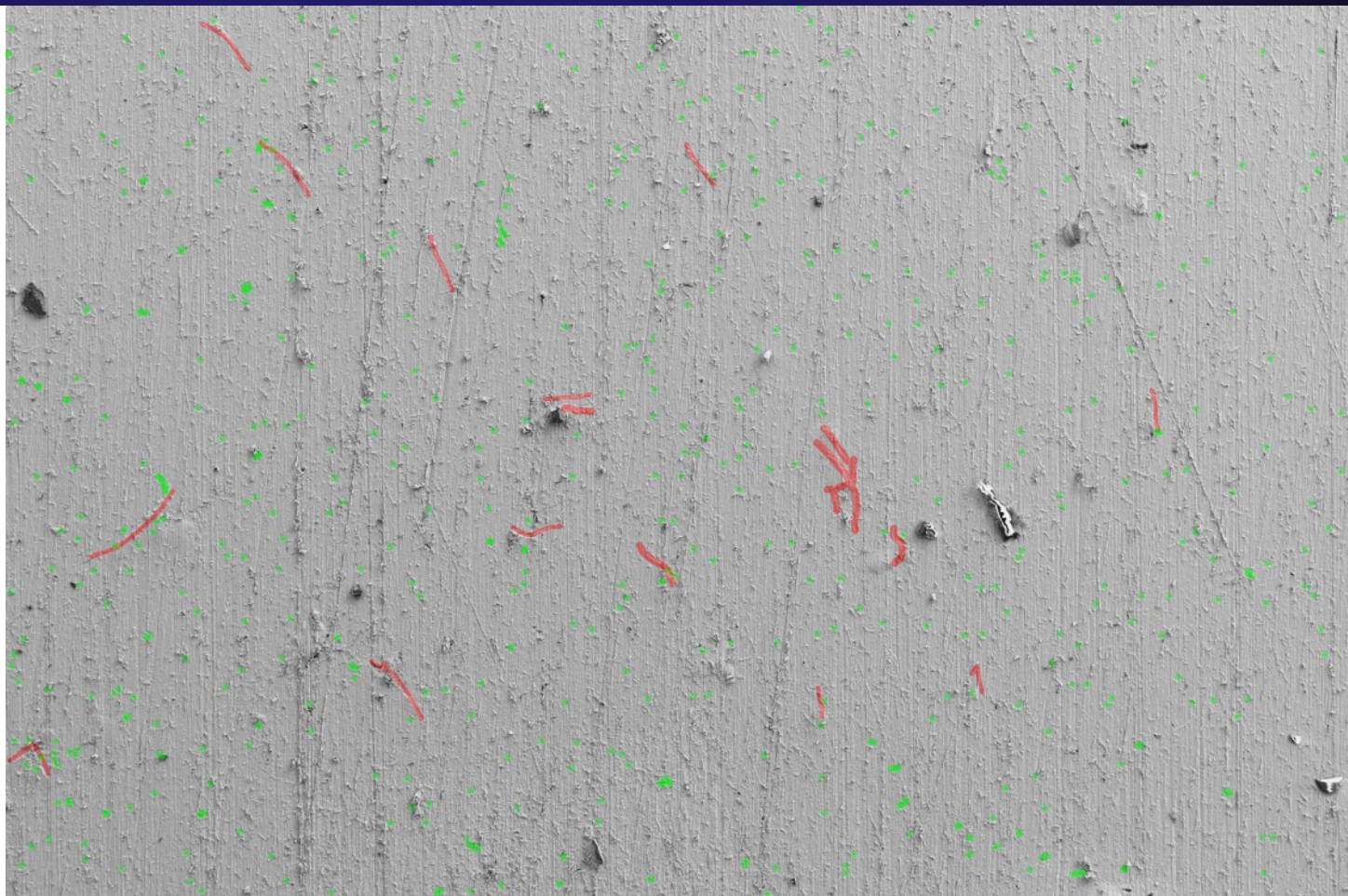
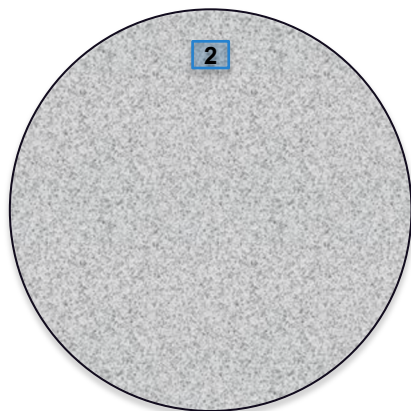
- Impact of SARS-CoV-2 Pandemic
 - FY20's work was largely anticipatory of the plasma FIB (PFIB) in Sigma coming online in a timely fashion
 - Sigma's new PFIB was accepted and signed-off on November 22nd, 2019
 - Authorization to begin FIB work on radioactive material occurred on 2/19/2020
 - The first parametric cell sample was examined the week of 2/25/2020
 - The initial session was focused on putting the new instrument through its paces and determining how well it was suited to our characterization needs
 - Serial cross-sections, initial preparation for *in situ* TEM experiments, a full-sample SEM montage, and an initial ~1 mm long line-out were all conducted in one week
 - On 3/15/2020, due to concerns related to the fledgling pandemic, several team members were instructed to begin working from home, this entirely halted the experimental work that had just begun weeks prior

SEM Work in FY2020

- SEM work on parametric cells PC019, PC037, and PC055 was continued in FY20, highlight include:
 - Based on the SEM micrographs, the number density of carbides for PC055 was characterized to be $271.0 (\pm 37.9)$ per mm^2
 - The number density of hydrides per unit area was for samples PC037 and PC055 was determined to be $9.0- (\pm 2.1)$ and $5.3 (\pm 0.8)$ per mm^2
 - An initial look at hydride/carbide interactions in sample PC055 revealed an unexpectedly large percentage of hydrides interacting with at least one, often more, carbides at the visible free-surface
 - These interactions included hydrides starting/ending at carbides, hydrides passing through cracked carbides (cause or effect?), hydrides growing directly along (*i.e.* wetting) carbide/metal interfaces, as well as hydride streamer's growth directions deflecting at the locations of carbides
 - These interactions, along with discussions including G. Louis Powell (Y-12, ORNL) and Wigbert Siekhaus (LLNL), have highlighted this as a key area to continue exploring in FY21

SEM Work – Carbide & Hydride Quantification – PC055

- A careful analysis of the number densities of **carbides** and **hydrides** was conducted on PC055
 - Hydrides were counted in five ROIs across the sample's diameter of the disc
 - Carbides were counted in three ROIs



10/22/2019 HV

use case det WD

mag tilt

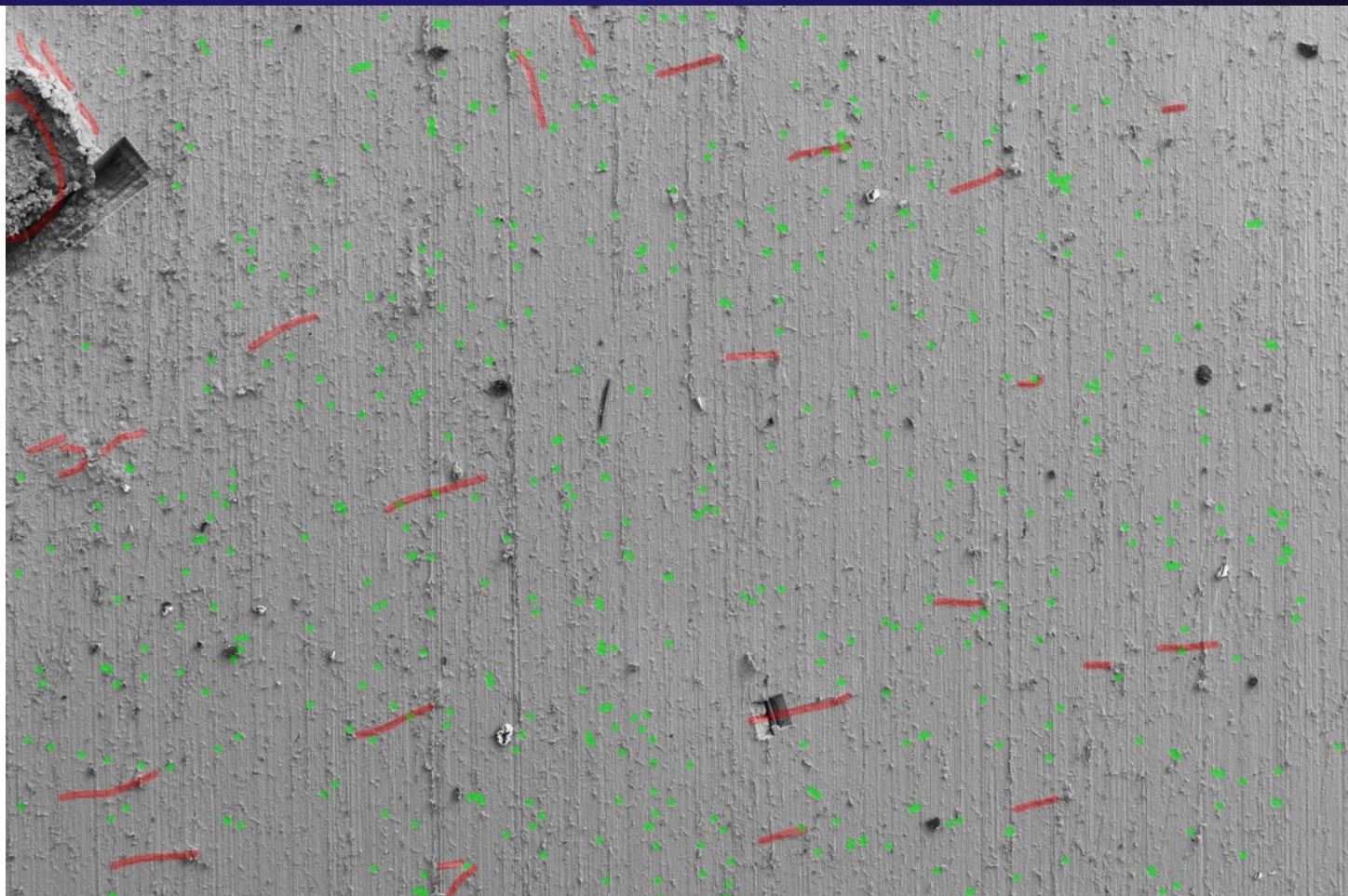
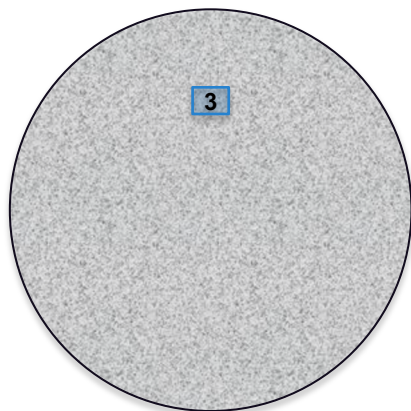
7:55:35 AM 10.00 kV OptiPlan ETD 10.5 mm 250 x 0.0 °

500 μm

PC055

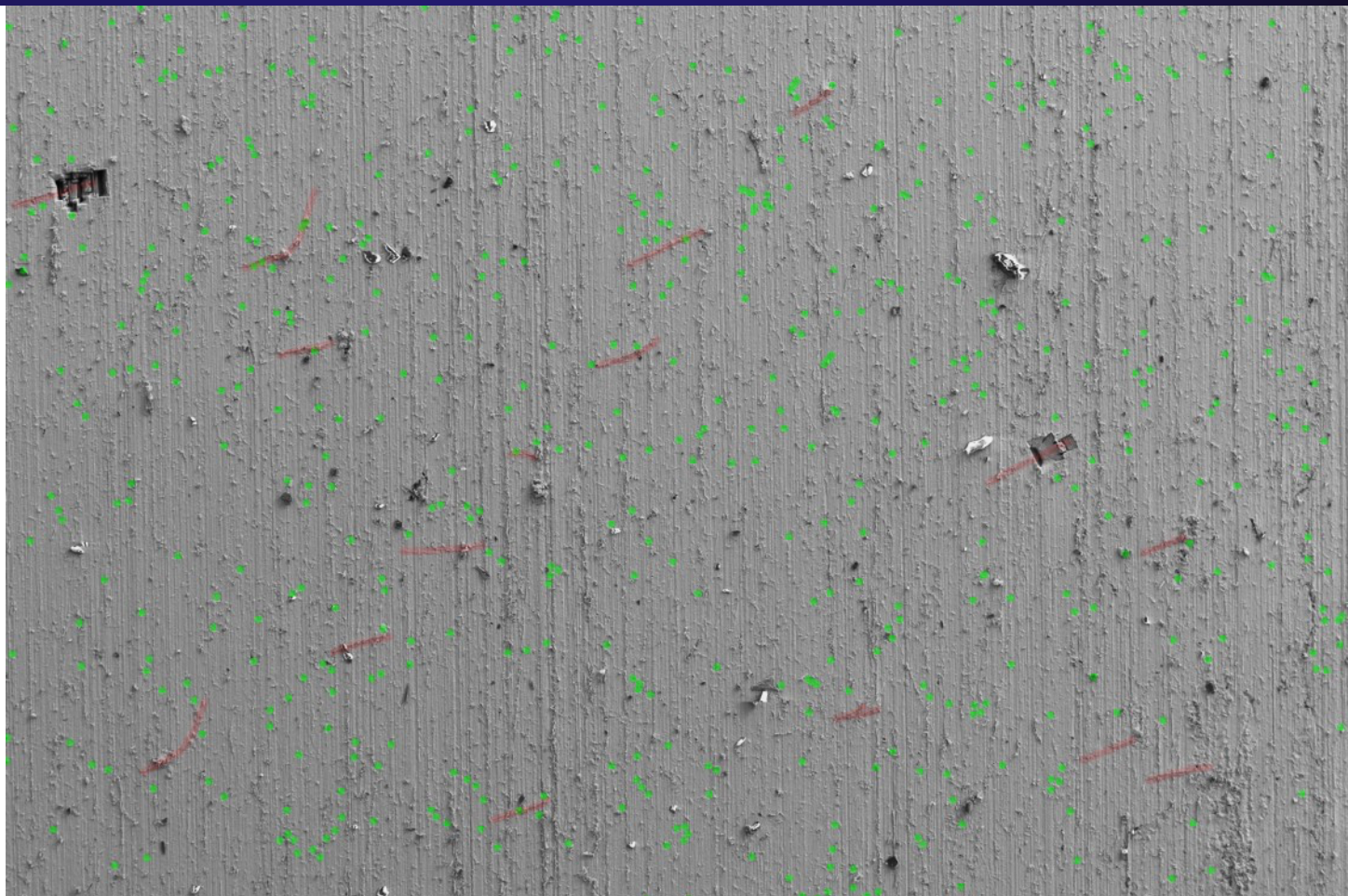
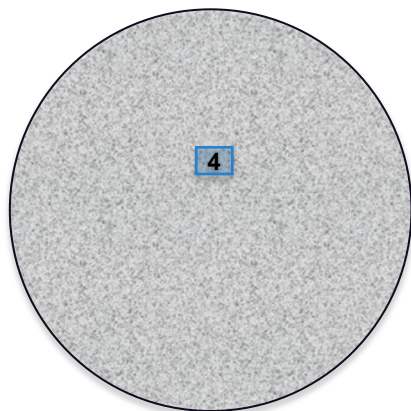
SEM Work – Carbide & Hydride Quantification – PC055

- A careful analysis of the number densities of **carbides** and **hydrides** was conducted on PC055
 - Hydrides were counted in five ROIs across the sample's diameter of the disc
 - Carbides were counted in three ROIs



SEM Work – Carbide & Hydride Quantification – PC055

- A careful analysis of the number densities of **carbides** and **hydrides** was conducted on PC055
 - Hydrides were counted in five ROIs across the sample's diameter of the disc
 - Carbides were counted in three ROIs

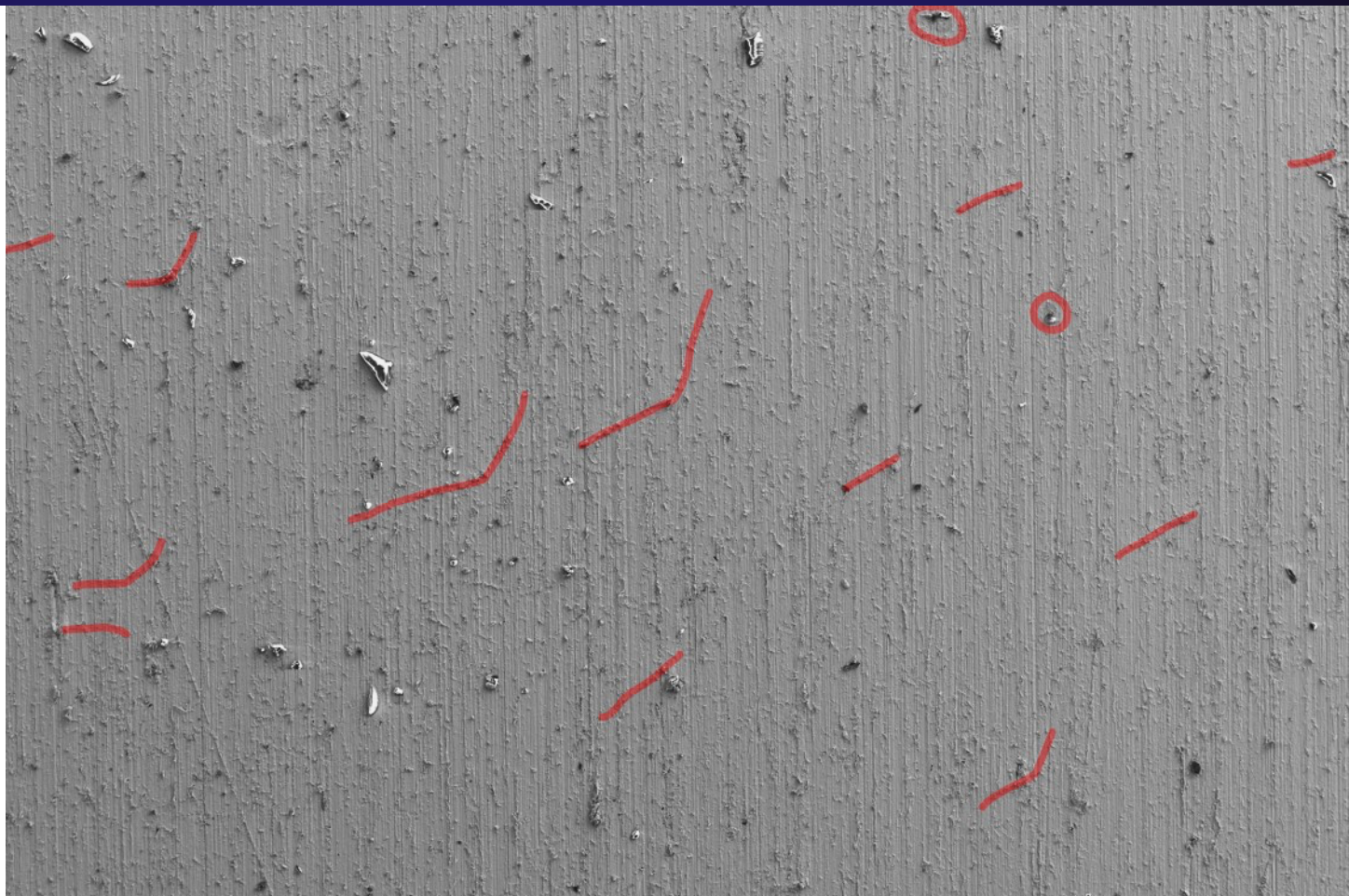
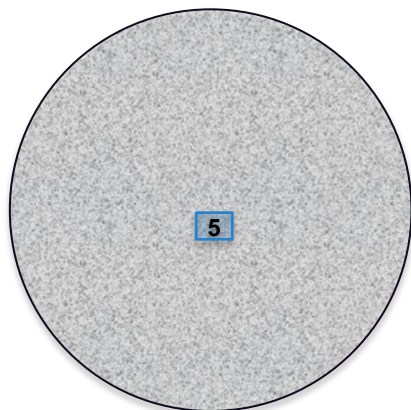


10/22/2019 HV use case det WD mag tilt
8:30:17 AM 10.00 kV OptiPlan ETD 10.5 mm 250 x 0.0 °

500 μ m
PC055

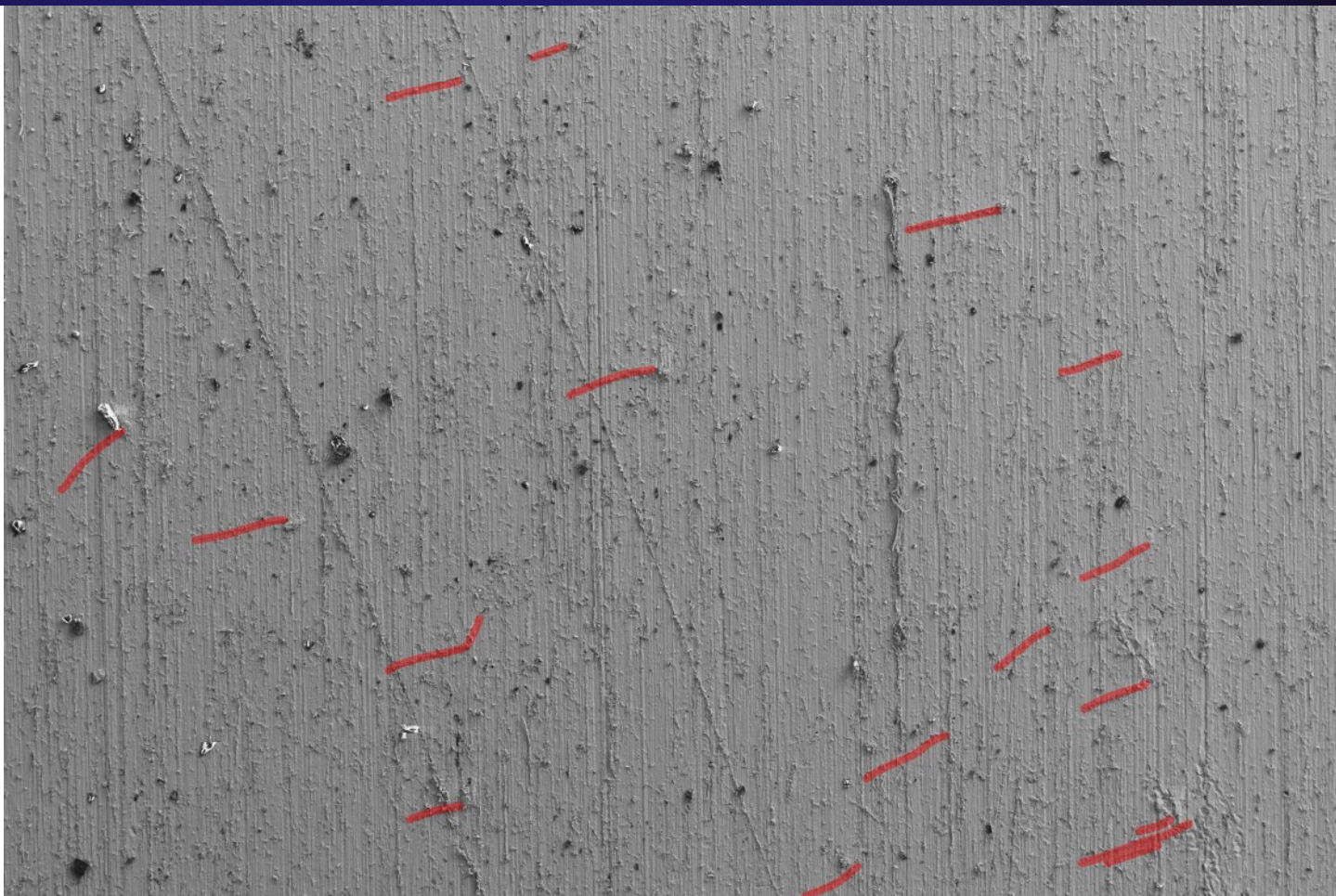
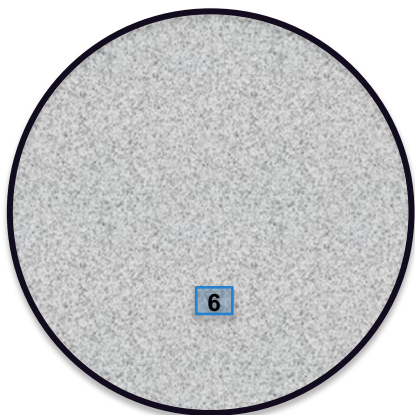
SEM Work – Carbide & Hydride Quantification – PC055

- A careful analysis of the number densities of **carbides** and **hydrides** was conducted on PC055
 - Hydrides were counted in five ROIs across the sample's diameter of the disc
 - Carbides were counted in three ROIs



SEM Work – Carbide & Hydride Quantification – PC055

- A careful analysis of the number densities of **carbides** and **hydrides** was conducted on PC055
 - Hydrides were counted in five ROIs across the sample's diameter of the disc
 - Carbides were counted in three ROIs



10/22/2019 HV

8:40:47 AM

use case det WD

mag tilt

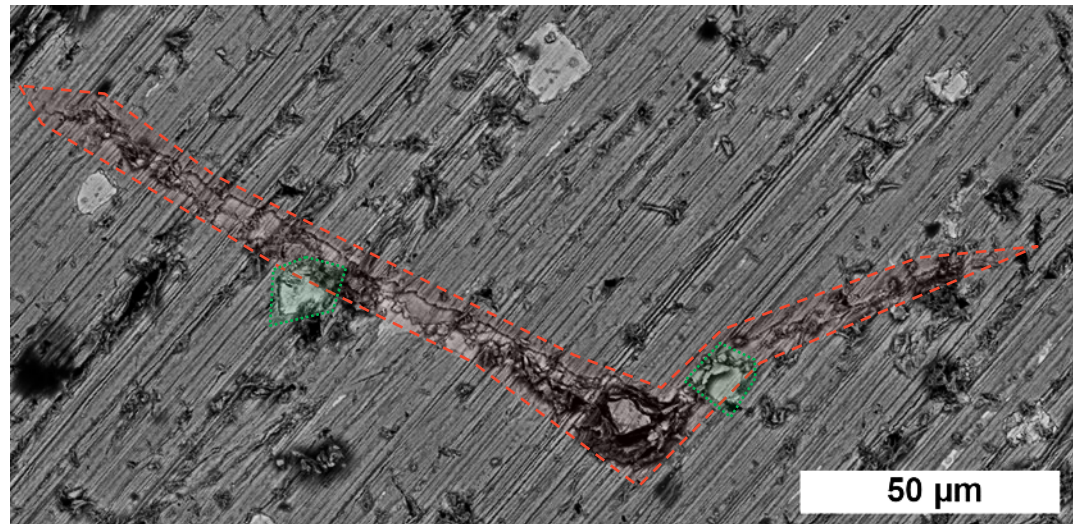
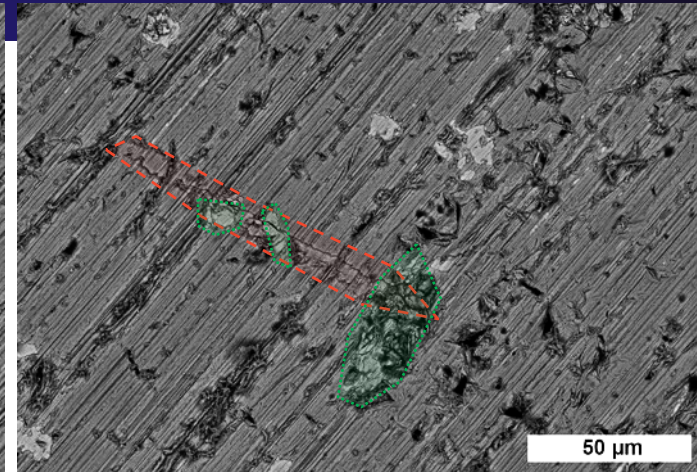
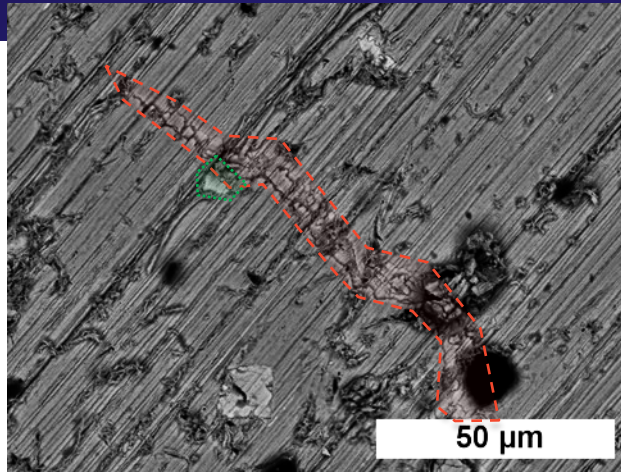
10.00 kV OptiPlan ETD 10.5 mm 250 x 0.0 °

500 μm

PC055

SEM Work – Hydride & Carbide Interactions

- Interactions of hydride **streamer** bodies intersecting/interacting with **carbides** on the sample's free-surface were examined
 - Hydride streamers are found to almost always (>90% of the time) interact with carbides, often with more than one
 - Hydrides are observed to pass adjacent to as well as directly through carbide bodies
 - Subsurface interactions are virtually guarantee an increase in the number of carbide intersections per hydride body
 - FIB work can help provide a better understanding of the interactions in three dimensions

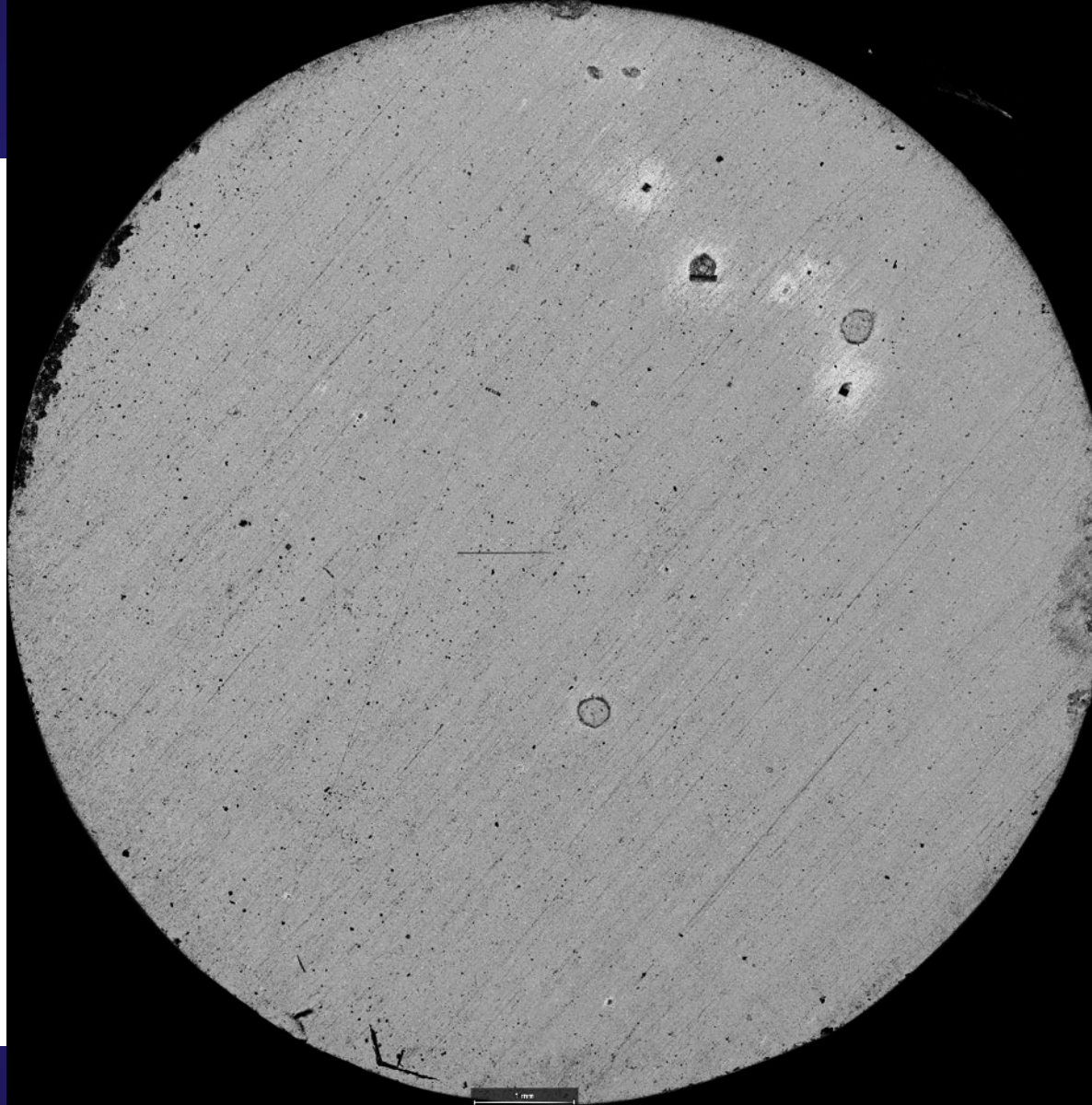


PFIB Work in FY2020

- A dual-beam Xe⁺ Plasma Focused Ion Beam/Scanning Electron Microscope (PFIB/SEM) was brought online in Sigma early in FY2020
 - Authorization to conduct ion-beam milling work on radioactive followed in mid FY2020; Aging & Lifetimes work commenced shortly thereafter
 - This new tool enabled several new key capabilities that will greatly benefit the Aging & Lifetimes programmatic work
 - Plasma FIB source enables removal of much larger volumes of material with the focused ion beam operating at up to 40x the beam-current of traditional LMIS-based FIB instruments
 - MAPS – Large-area SEM/FIB montages enables a detailed look at the entire sample while allowing the tracking of all sites of interest for correlative microscopy workflows
 - Slice & View – Destructive serial cross-sectioning enables three-dimensional reconstruction of volumes material
 - With some development work, integration of orientation imaging microscopy (OIM) and/or x-ray energy-dispersive spectroscopy (XEDS) are possible with currently owned hardware
 - AutoTEM – Automated preparation of TEM lamella greatly increasing experimental throughput
 - Many of these new capabilities were able to leveraged in the first (and only) session in FY2020, enabling a large amount of work to be conducted in just a few days

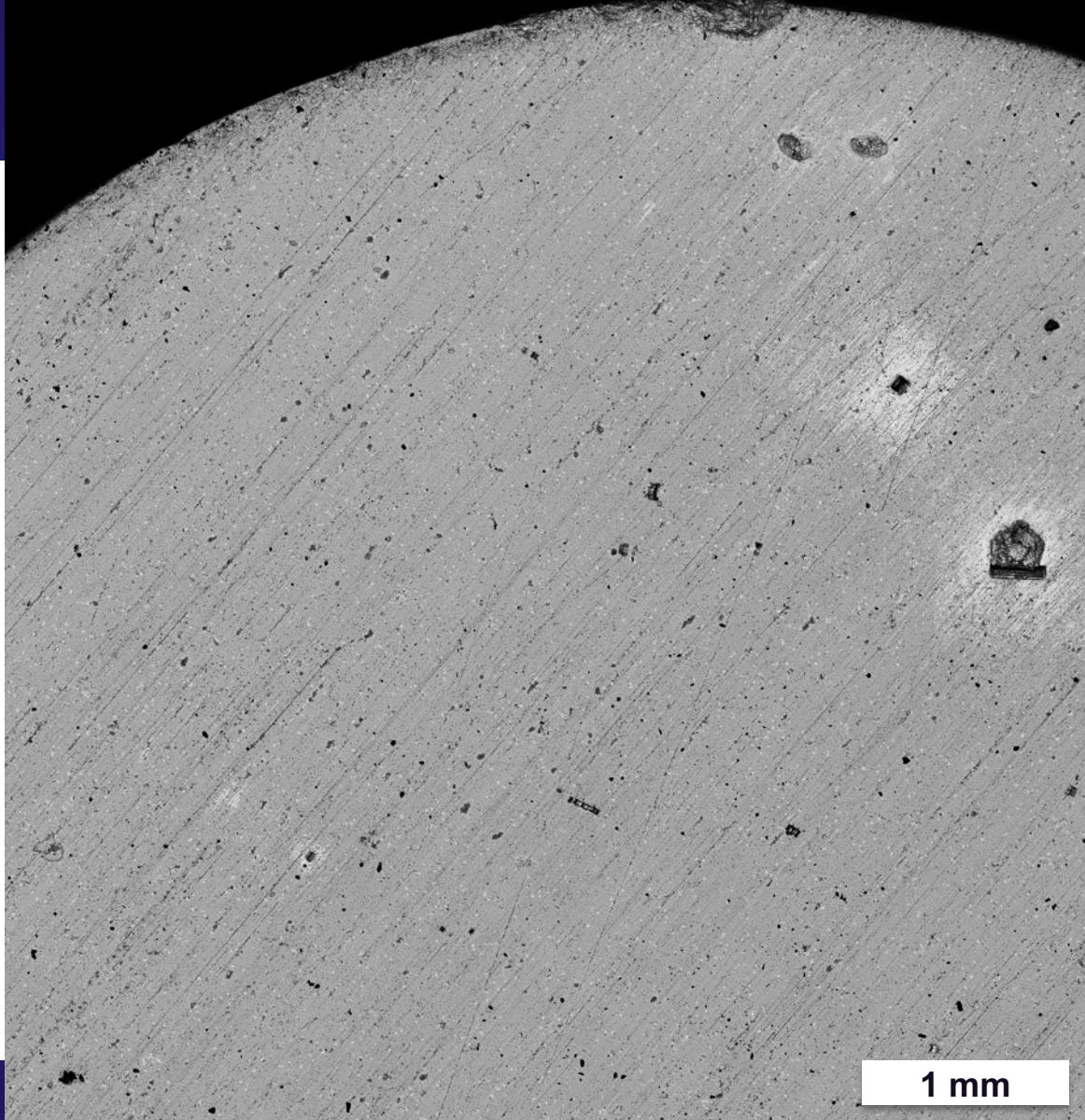
PFIB Work – Maps

- Whole-sample montages were collected with an automatically with the new MAPS software package
- The entire 0.5 inch disc was imaged at a resolution of 136 nm per pixel (81K x 81K, 6.56 giga-pixels!)
 - Secondary and backscattered electron micrographs were collected simultaneously
- With such large volumes of data now becoming routinely possible, image processing becomes the main bottleneck
 - A mobile workstation acquired at the end of July to be able to work on such datasets from home
 - Automated analysis is going to be required going forward
 - Automated carbide (and possibly hydride) counting should be doable with a trained neural network



PFIB Work – Maps

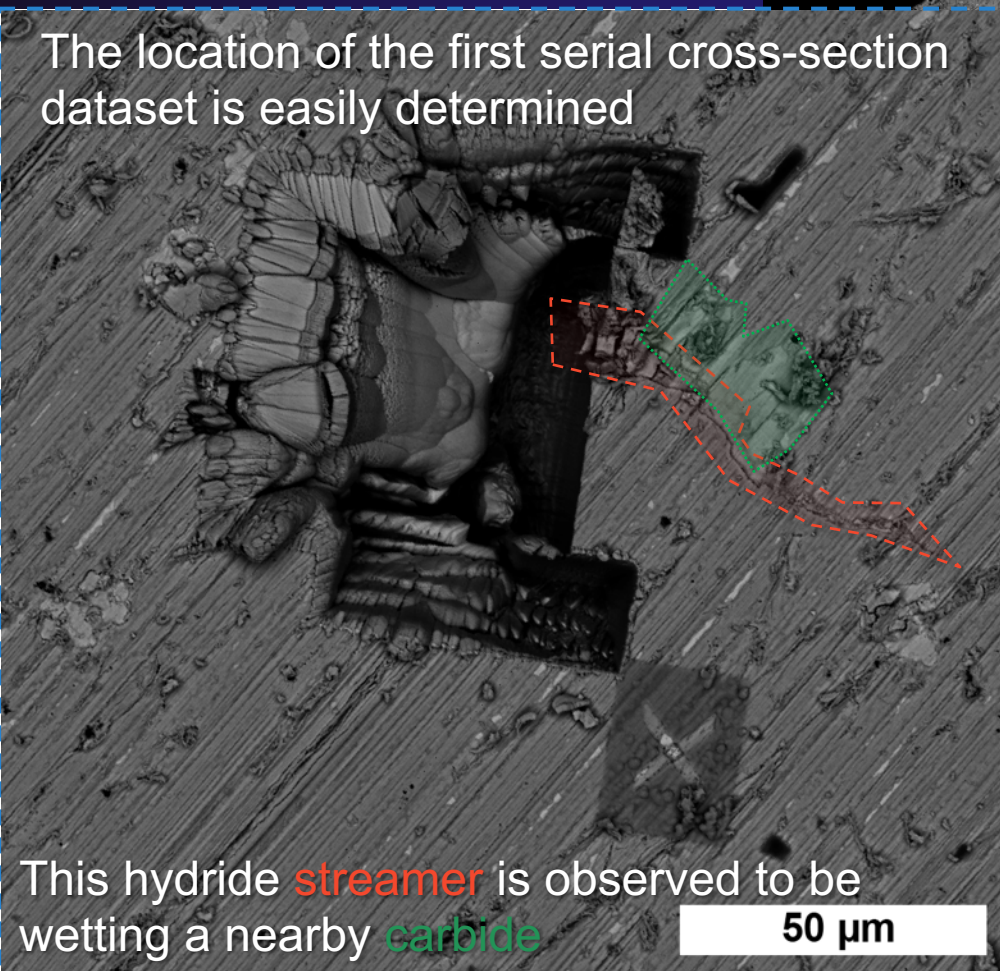
- Whole-sample montages were collected with an automatically with the new MAPS software package
- The entire 0.5 inch disc was imaged at a resolution of 136 nm per pixel (81K x 81K, 6.56 giga-pixels!)
 - Secondary and backscattered electron micrographs were collected simultaneously
- With such large volumes of data now becoming routinely possible, image processing becomes the main bottleneck
 - A mobile workstation acquired at the end of July to be able to work on such datasets from home
 - Automated analysis is going to be required going forward
 - Automated carbide (and possibly hydride) counting should be doable with a trained neural network



1 mm

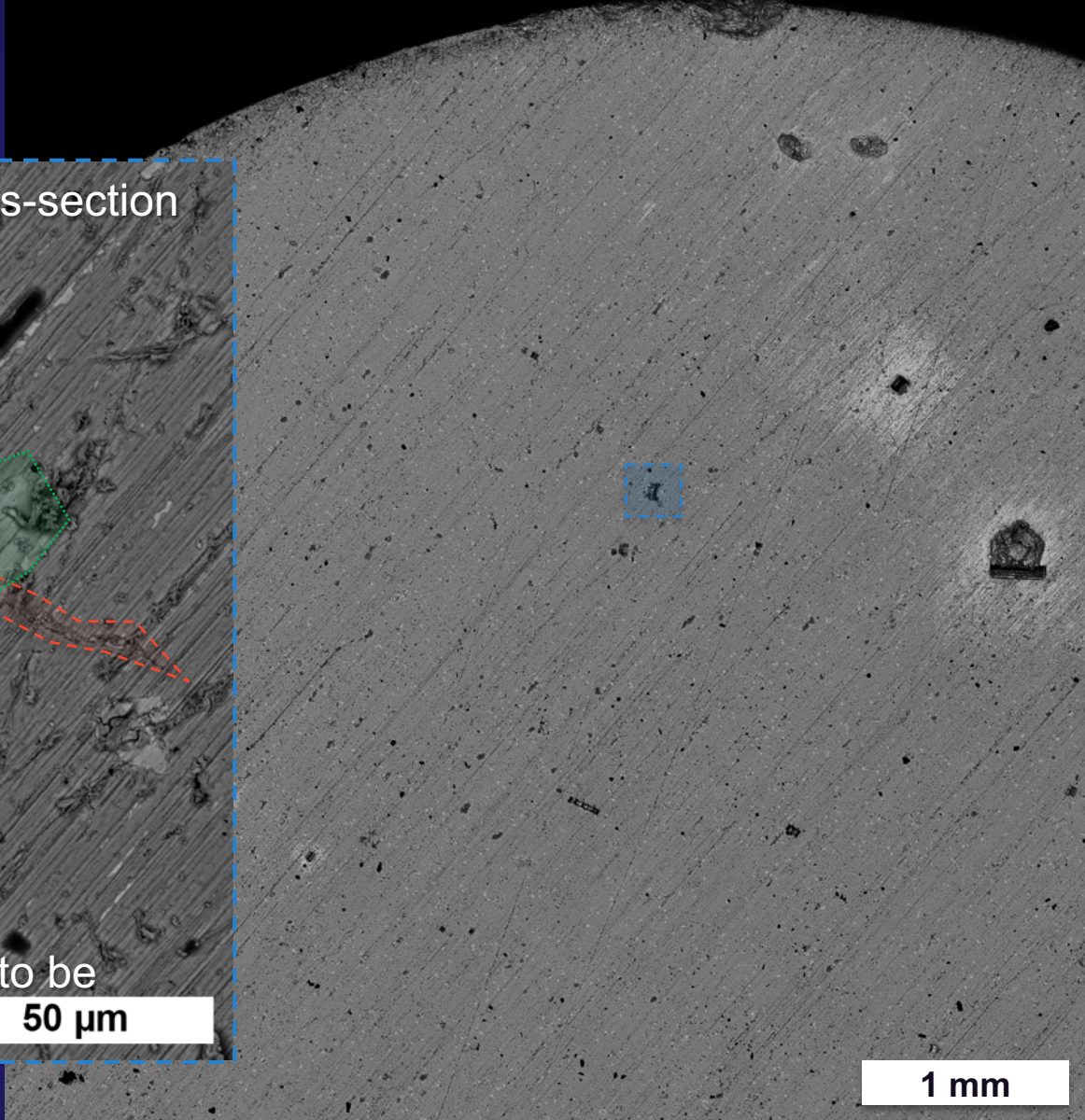
PFIB Work – Maps

The location of the first serial cross-section dataset is easily determined



This hydride **streamer** is observed to be wetting a nearby **carbide**

50 μm



1 mm

PFIB Work – Maps

Evidence of a previous TEM lift-out campaign during which four foils were extracted from a single hydride

This particular hydride **streamer** intersects a **carbide** at one end of its length

50 μm

1 mm

PFIB Work – Maps

A moderately early-phase blowout is observed shortly after rupture

Several roughly parallel **streamers** are observed around the blowout, often interacting with cracked **carbides**

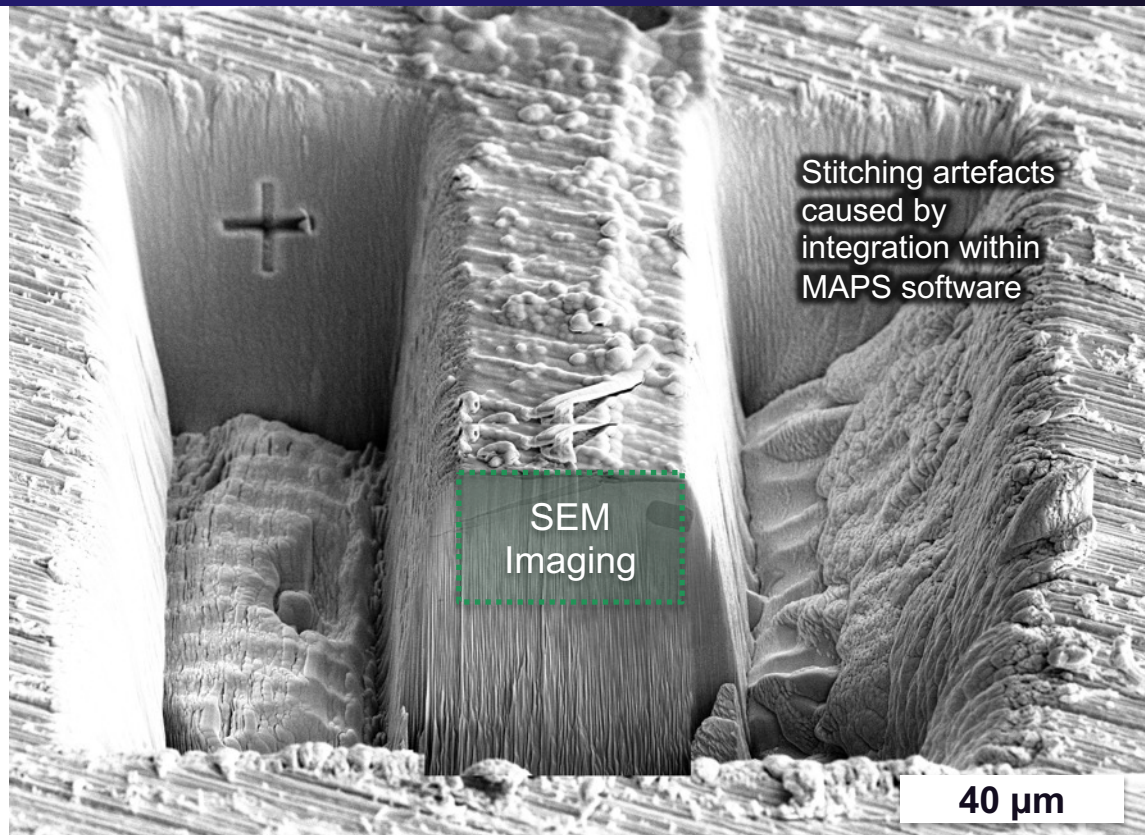
50 μm

1 mm

- These high-resolution montages are suitable for analysis via neural-networks to automate high-fidelity quantitative analytics
- Best possible statistics are generated by examining the entire sample surface area, automated analysis enables this
- Previously counted and annotated images are well suited for use as training datasets (*i.e.* supervised learning)
- Carbides show up readily in backscattered electron micrographs (as seen here), a high probability of success for automated analysis is expected
- Hydride visibility is sensitive to sample orientation relative to various secondary electron detectors. As such, it tends to be more finicky and possibly harder to automate counting thereof

PFIB Work – Auto Slice & View

- The PFIB's Auto Slice & View software package enables the automated collection of serial cross section datasets
 - The serial cross section runs take 4-48 hours depending on the volumes being interrogated, the imaging parameters, analytical data collected (e.g. EDS, EBSD, etc.), and the success of several automated image-adjustment algorithms
 - The ion beam is used to slice a set thickness, off of the exposed sample face, and then the freshly sliced face is imaged using the electron beam and various detectors; this process is repeated hundreds of times to generate SEM images at every slice
- A large volume containing a single hydride was selected and the site was prepped to allow an extended length of the hydride streamer to be examined

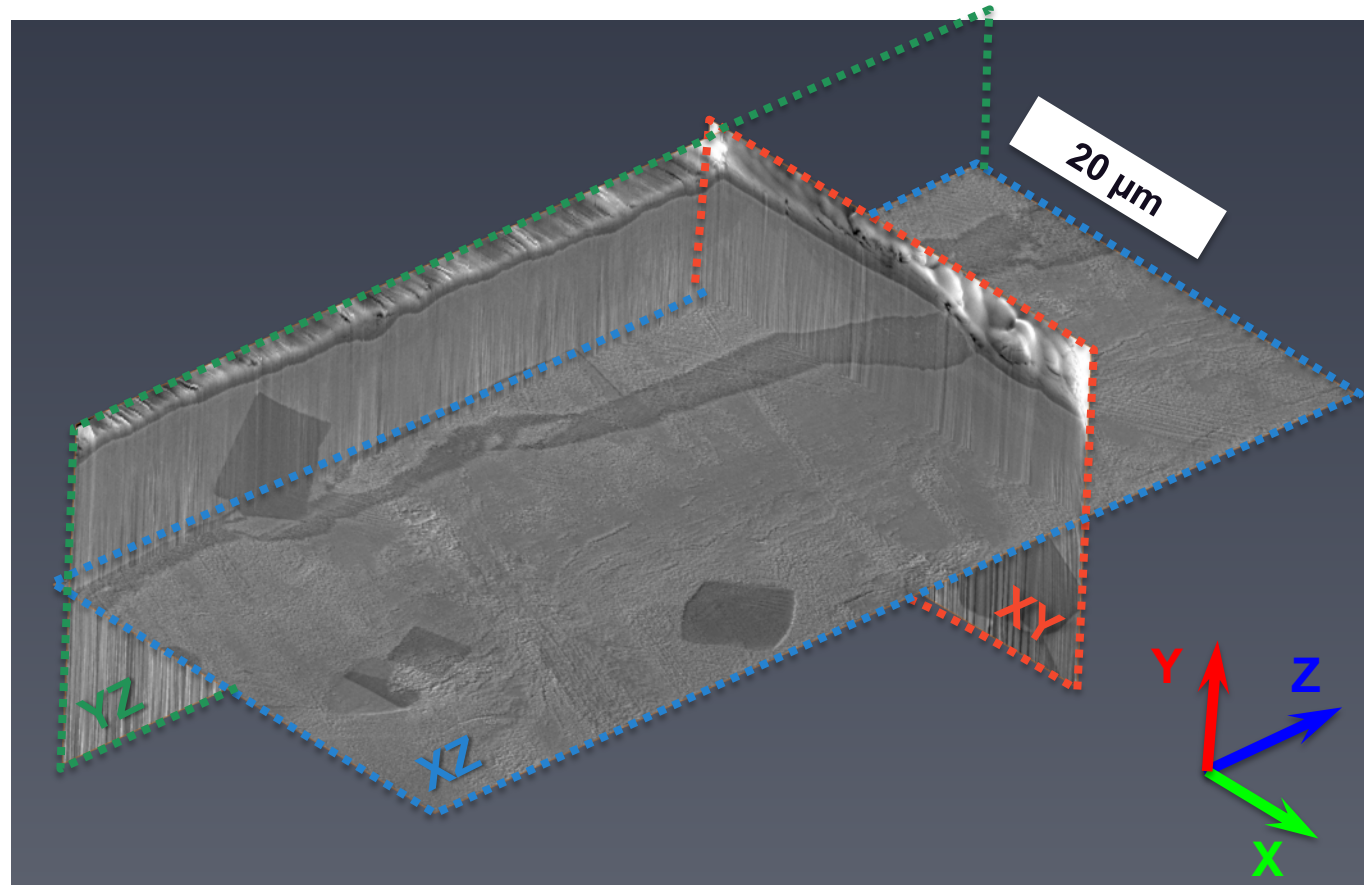


PFIB Work – Auto Slice & View

- The stack of SEM images recorded during the AS&V process are loaded into Avizo, an image processing and reconstruction application
- The dataset can be rapidly visualized as three orthogonal slices through the data-cube
- The stack of images are aligned, drift-corrected, and then each image is segmented into the various phases present
 - This segmentation process can be very labor intensive, depending on desired the level of fidelity
 - Once segmented, three-dimensional models are able to be constructed to enable the visualization of the various phases present and their spatial relationship to each other and other features of interest
 - Animations are rendered to best show the relationship between the images captured and the three dimensional spatial relationship of the segmented phases

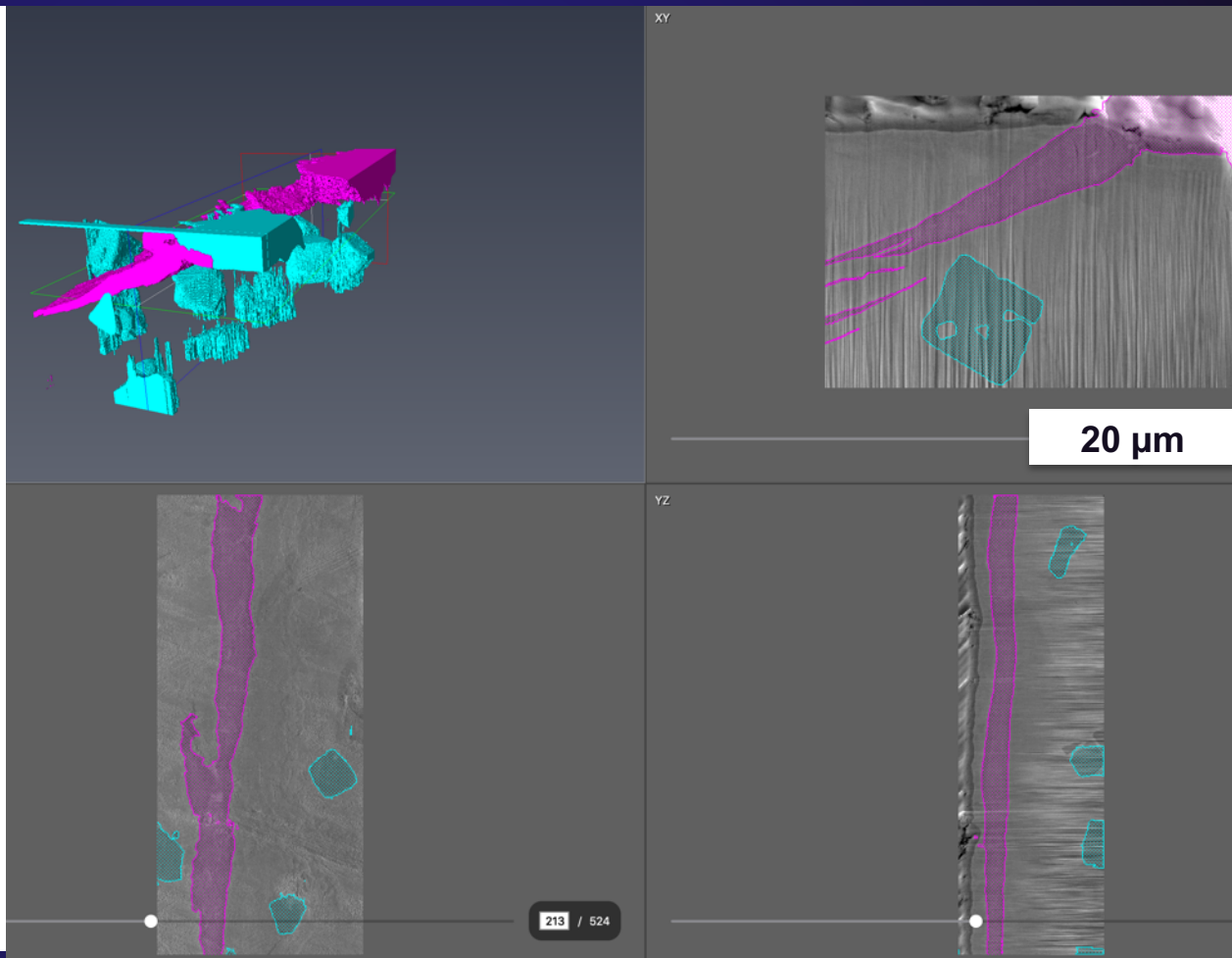
PFIB Work – Auto Slice & View

- Ortho-slices enable rapid exploration of the dataset
- The XY plane is the SEM image captured during the AS&V process
 - The XY and XZ planes are constructed based on the information contained in the stack of SEM images



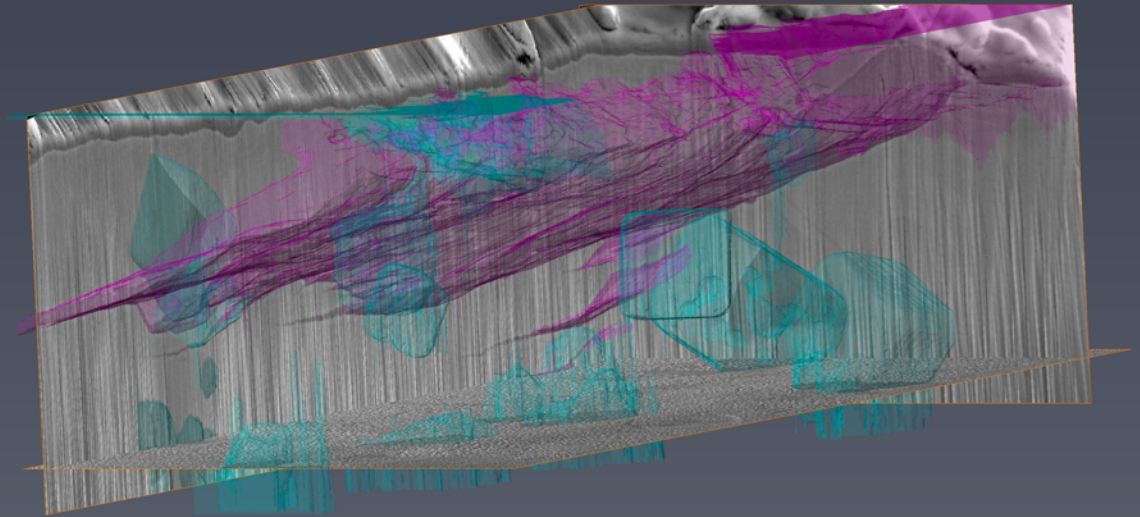
PFIB Work – Auto Slice & View

- Segmentation of the images is simultaneously conducted in all three orthogonal planes
- Various automated segmentation schemes are possible, though success has been limited and a significant portion of manual correction is required



PFIB Work – Auto Slice & View

- Once segmentation is complete, three dimensional surfaces are rendered
- Accurate and rapid quantification of various metrics of interest (e.g. phase fraction, volume fraction, intersectional areas between defined surfaces, etc.) is possible with high-fidelity segmentation

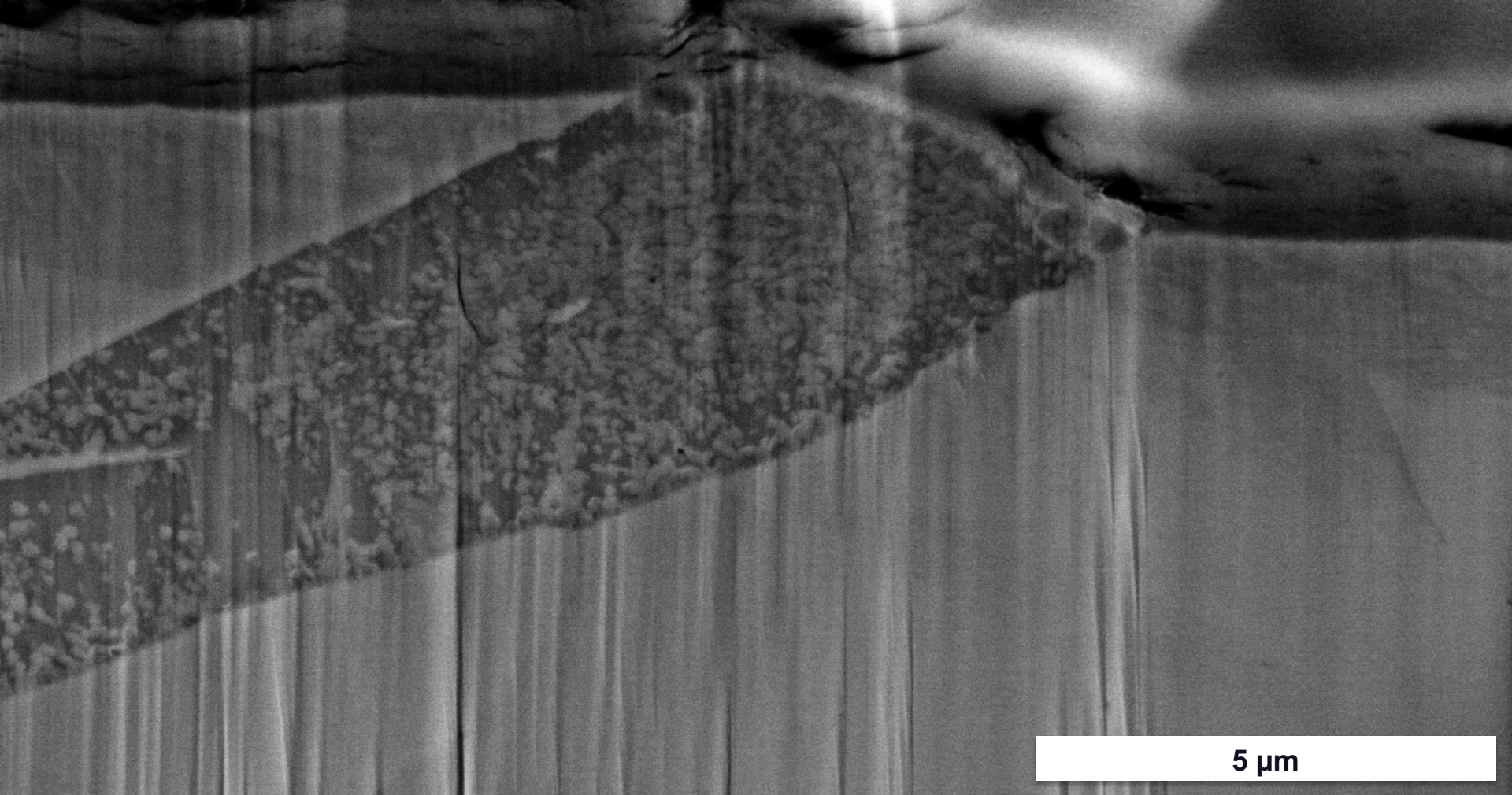


20 μm

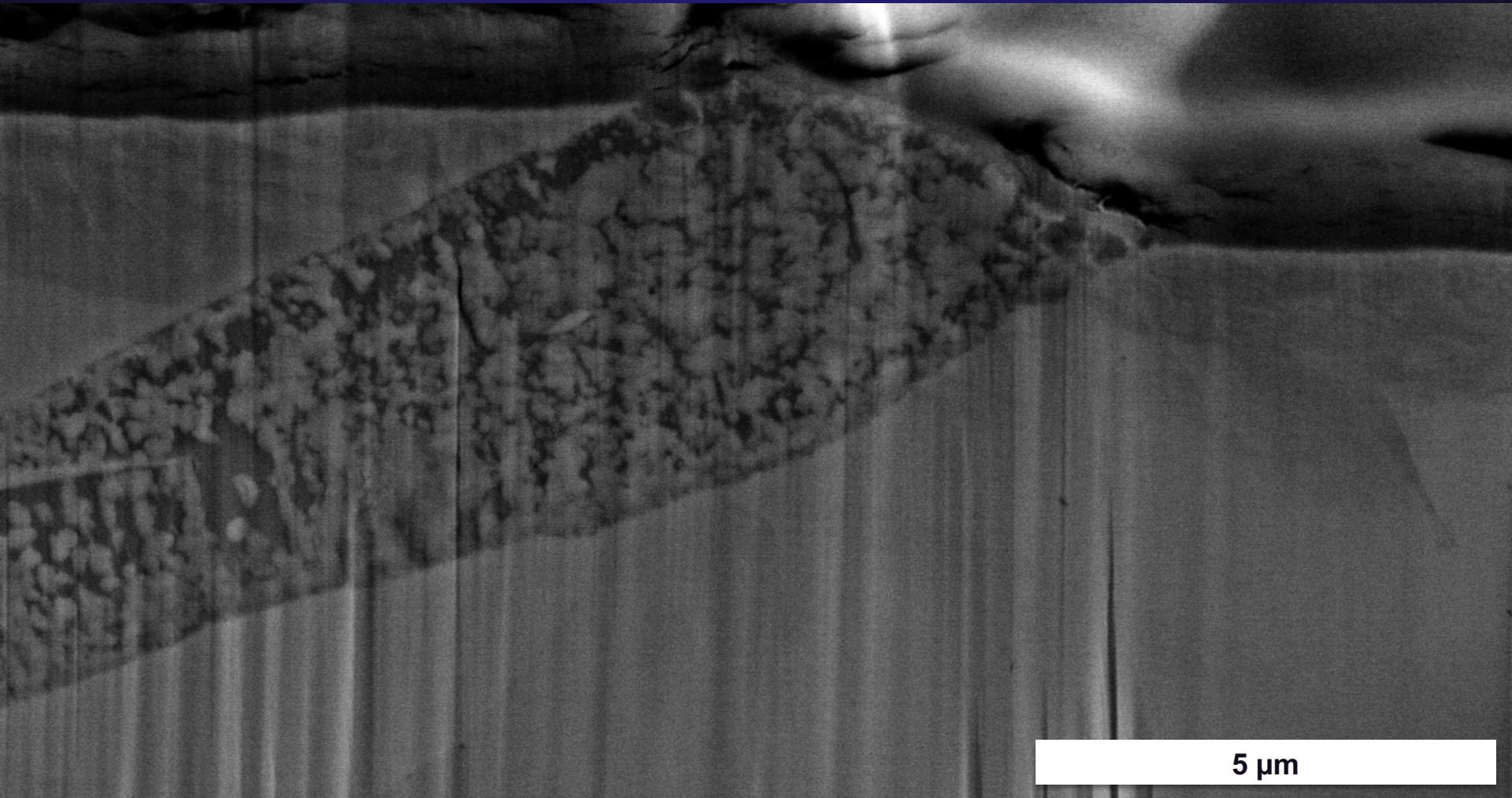
PFIB Work – Beam/Sample Interaction

- During the slice & view data collection process, careful examination of the hydride body yielded a counter-intuitive observation that will require follow up work to understand this beam/sample interaction
 - The ion beam current appeared to have an effect on the amount and possibly the form of metal present within the hydride
 - Higher beam currents induce more localized heating during the milling process
 - Heat's ability to decompose uranium hydride reaction is well known
 - The previous observation of metal within hydride streamer bodies had been discussed as a potential artifact from the milling process, however that possibility had been discounted as it appeared in samples prepared with very low beam currents (30 and 50 pA)
 - The confusing part of this observation is that higher currents yielded “cleaner” hydride, *i.e.* mostly devoid of metallic debris. Dropping to lower currents, yielded better surfaces for SEM imaging, but resulted in the repeated observation of metallic debris filling the hydride streamer body.
 - Full-frame images in the following slides are slices made 200 nm apart with a lower beam current immediately after cutting with a high beam current
 - Note the dendrite-like growth inwards from the metal/hydride interface

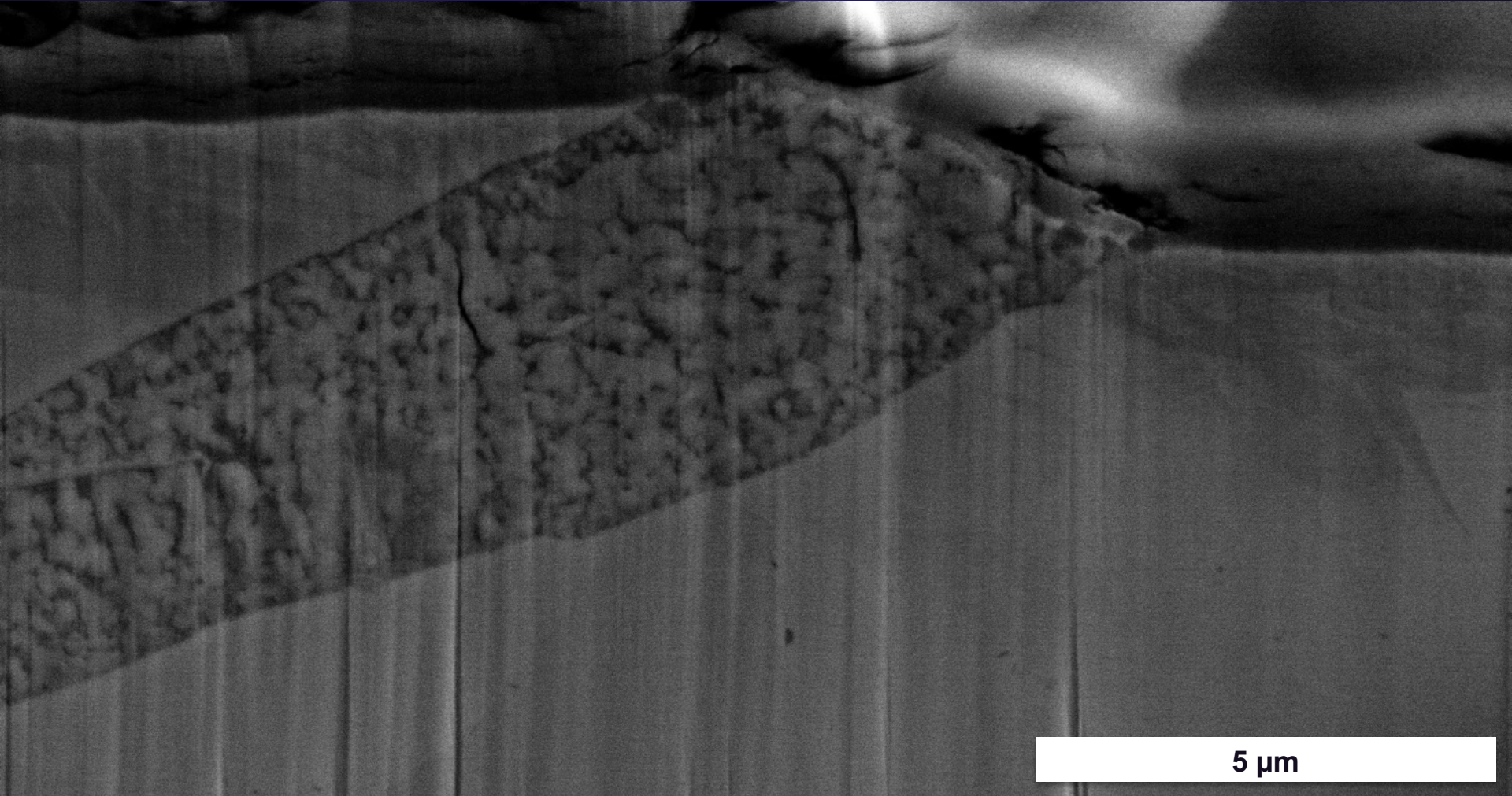
PFIB Work – Beam/Sample Interaction



PFIB Work – Beam/Sample Interaction



PFIB Work – Beam/Sample Interaction

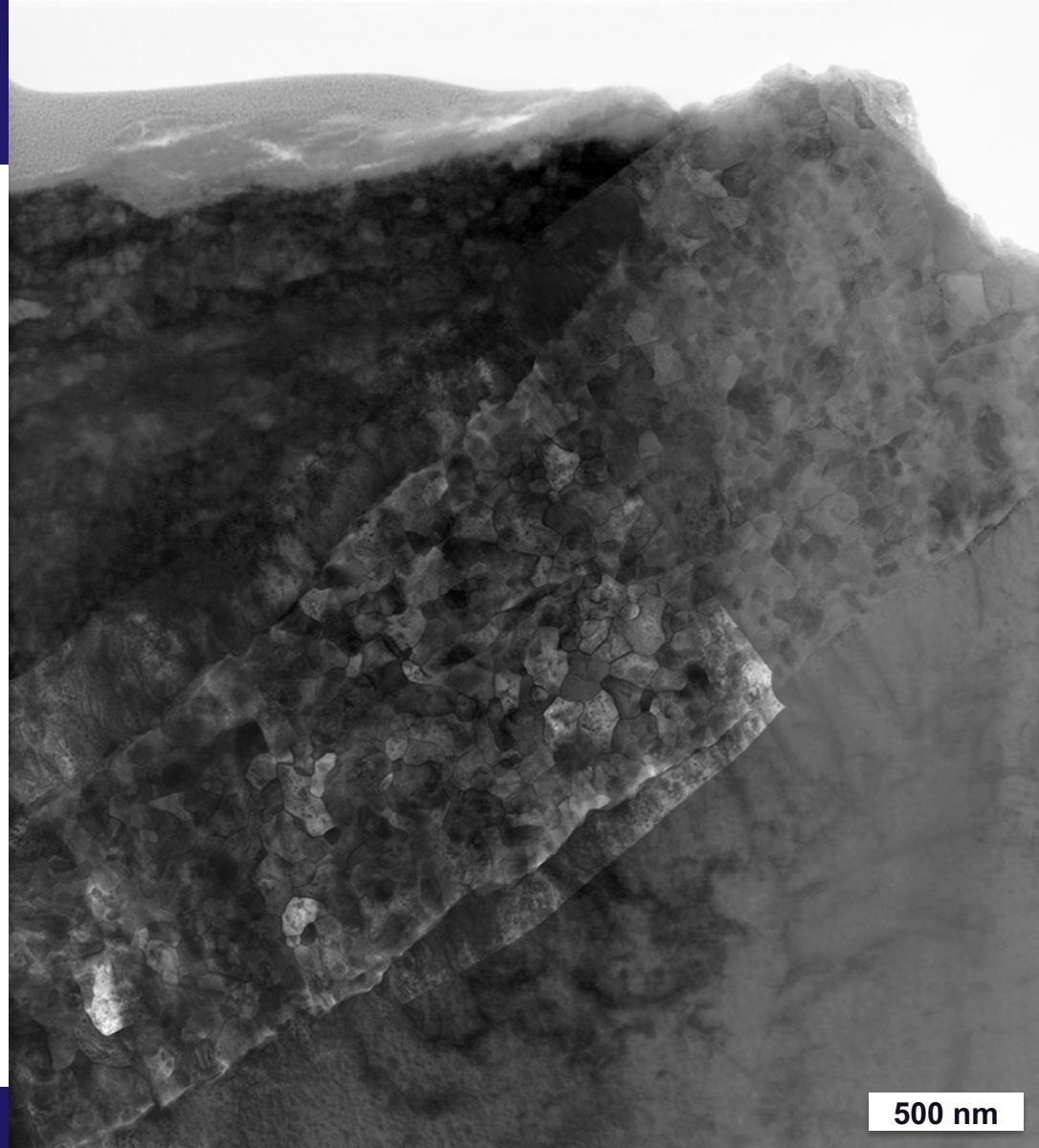


TEM Work in FY2020

- The first S/TEM samples from PC019 (1 Torr H₂) were prepared in the Ga⁺ FIB and examined with BF & DF S/TEM & EELS this FY
 - These lower H₂ dosed samples showed largely similar morphology
 - A new unidentified secondary phase was observed in one sample
- The work to develop the application of multiple linear least squares spectral processing to electron energy loss (EEL) data continued
- Initial monochromated STEM-EELS data were collected in order to obtain more accurate electronic structure measurements in both the metallic and the hydride phases of uranium to compare with the results from Ted Holby's ongoing DFT calculations
- Low-loss (0-50 eV) EELS data was collected to compare/contrast with valence band x-ray photoelectron spectroscopy (XPS) data previously recorded by Roland Schulze

TEM Work – BF-STEM

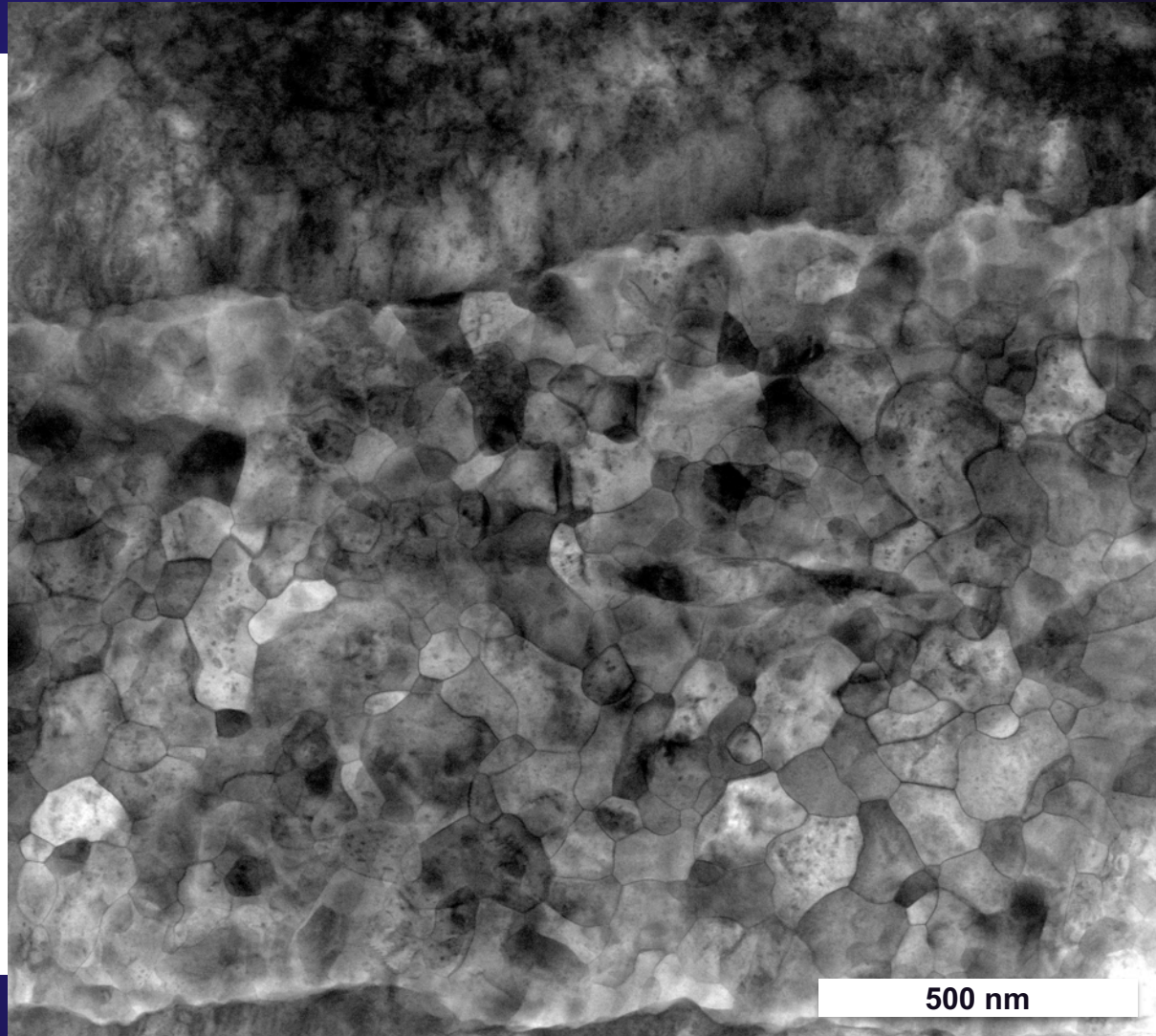
- Hydride streamers in PC019 appear initially similar to the morphologies observed in PC055
 - In this particular example, a significant portion of the hydride body is polycrystalline metal with large fractions of hydride concentrated along the bulk metal/hydride boundary
 - Dislocations are observed oriented perpendicular to the hydride/metal interface indicative of the metal deformation required to accommodate hydride growth



500 nm

TEM Work – BF-STEM

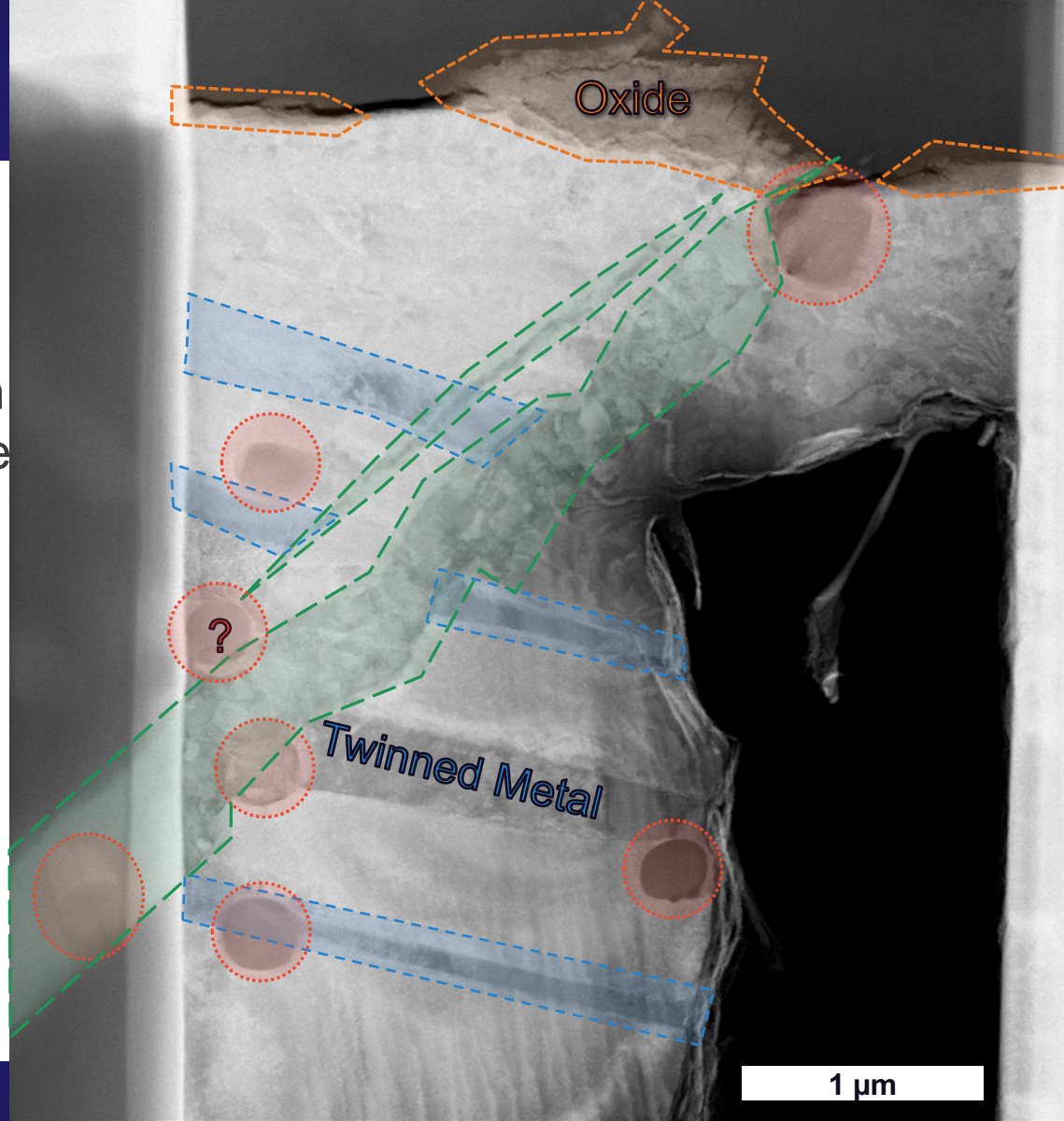
- The polycrystalline metal observed previously in PC055 appears to fill a larger portion of the hydride body in PC019, this is possibly an effect of the lower hydrogen dose
- The metal grains in the hydride body appear approximately equiaxed
- Dislocations are observed oriented perpendicular to the hydride/metal interface indicative of the metal deformation required to accommodate hydride growth



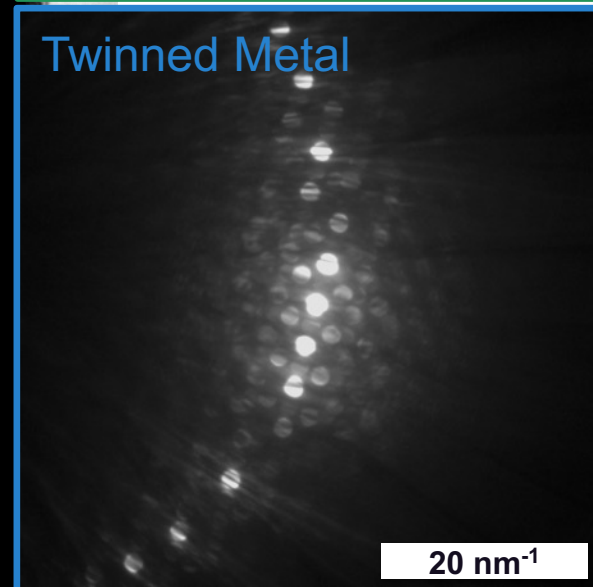
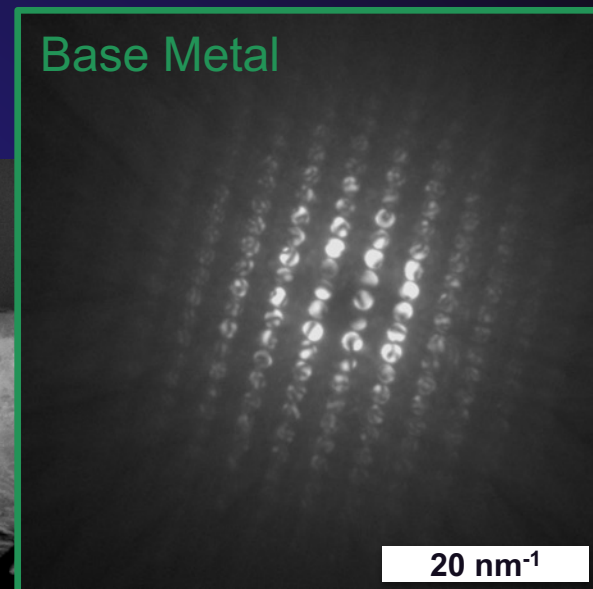
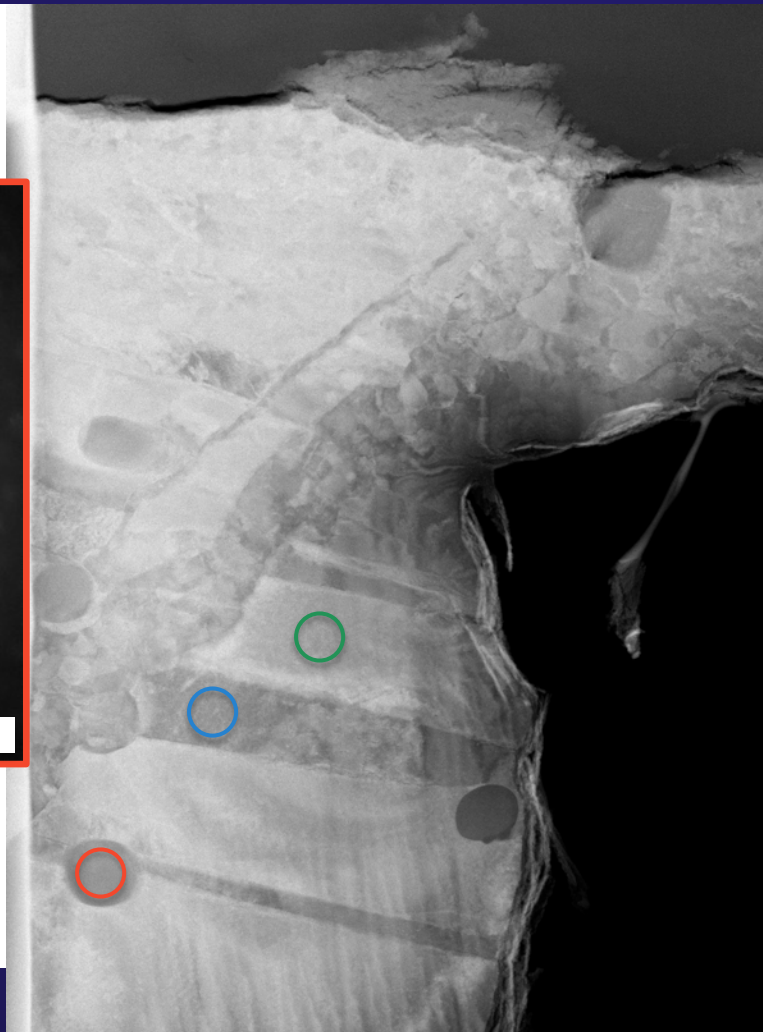
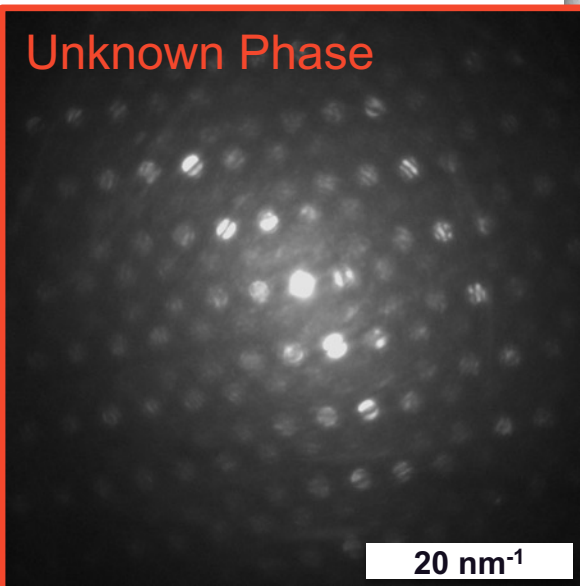
500 nm

TEM Work – DF-STEM

- Hydride body pulled from PC019 with a slightly different morphology
- Two streamers are observed in parallel, S&V data shows these often merge to become one
- In addition to the hydride, twinned metal along with a number of particles of an unknown spherical phase
 - Nano-beam electron diffraction (NBED) patterns were recorded and candidate phases can be compared to these patterns

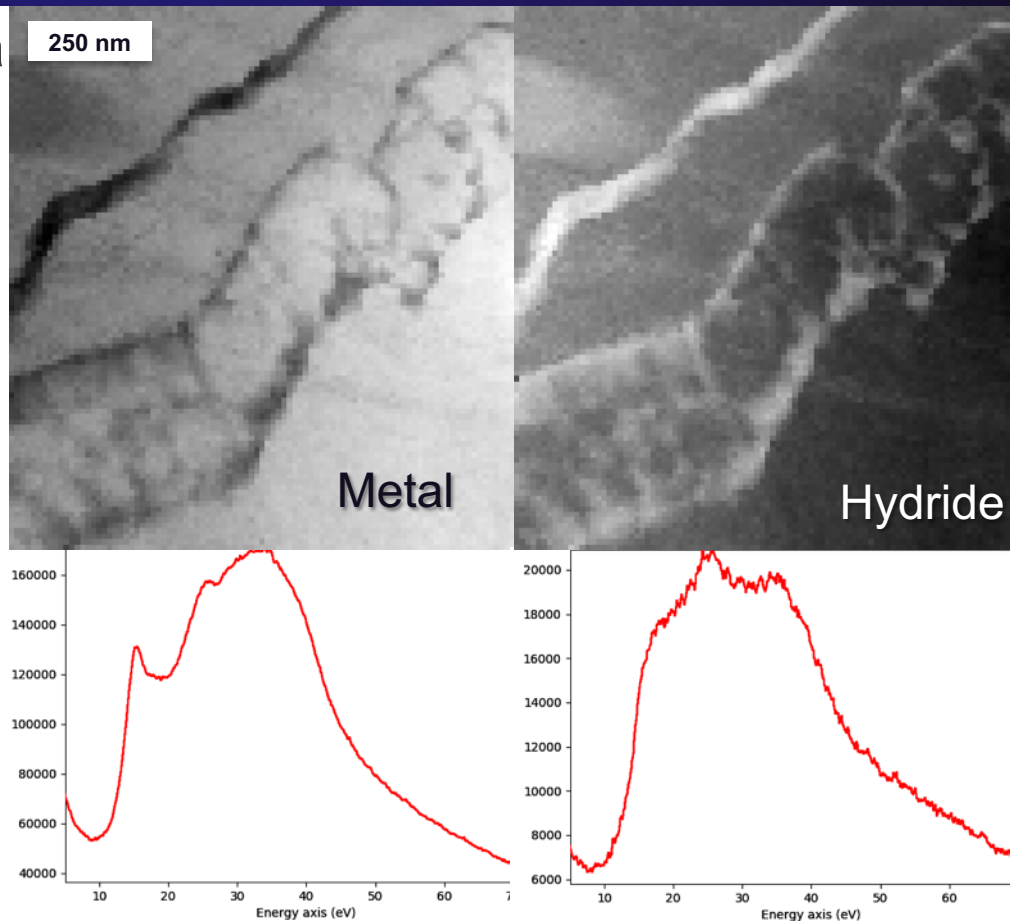


TEM Work – NBED



TEM Work – MLLS Hydride Mapping

- In STEM-EELS, energy loss spectra are collected at every pixel in the STEM image; the resultant data-cube has two spatial dimensions and one energy dimension
- MLLS signal processing separates a given signal into a linear combination of N input signals.
 - Reference signals are pulled directly from the dataset each of the collected spectra are decomposed into a linear combination of these signals
 - Fit coefficients are mapped back to spatial dimensions to allow phase-mapping



TEM Work – Mono EELS

- Note: energy axes are reversed in these data, each is presented as per convention for the given technique
- EELS data show the onset of metallic and oxide valence bands both begin at ~ 11 eV
- The maximum unoccupied density of states is delayed 2.1 eV from 15 eV in the metal to 17.1 eV in the oxide
- The background in the EELS data significantly reduces sensitivity due to the fact that the probe and the signal are both electrons, XPS avoids this problem
 - XPS spatial resolution is on the order of $1\ \mu\text{m}$, EELS spatial resolution can be sub-Å

EELS of Metallic Uranium and Surface Oxide

