Hydrogen and Hydride Precipitation in SRF Nb Revealed by Ex-Situ Metallographic Technique

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The support for this work at FSU was from US DOE Award # DE-SC0009960 and the State of Florida. Additional support for the National High Magnetic Field Laboratory facilities is from the NSF: NSF-DMR-1157490.

Jefferson Lab

Contribution ID – TUXBA05

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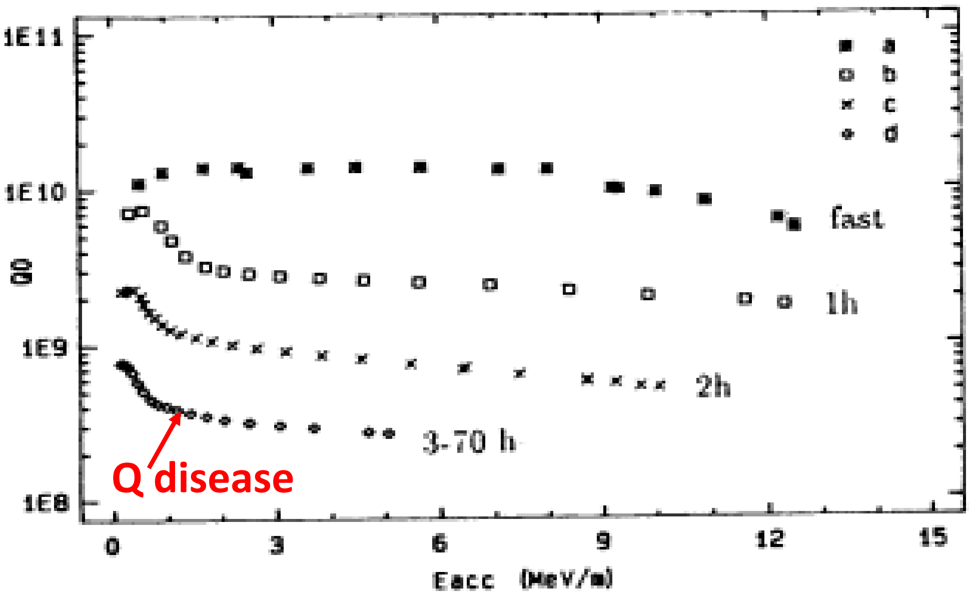
FLORIDA STATE UNIVERSITY

Outline of this talk

- Hydrides affect SRF performance
  - Non-superconducting precipitates
  - Microstructure hydride interactions can cause flux trapping
- Technique used to introduce hydrogen and image hydride pits
  - Intentional hydrogen loading
  - Cooling profile for hydride precipitation
  - Imaging for analytical microscopy
- Results and Discussion
  - General hydride pit characteristics in polycrystalline Nb.
  - Hydride pit comparisons in Nb with and without N doping
- Summary and Conclusions

Motivation- Hydrides, adversely affect cavity performance.

1.5 GHz, 1.8 K, Saclay, 1992, Bonin, and Roth



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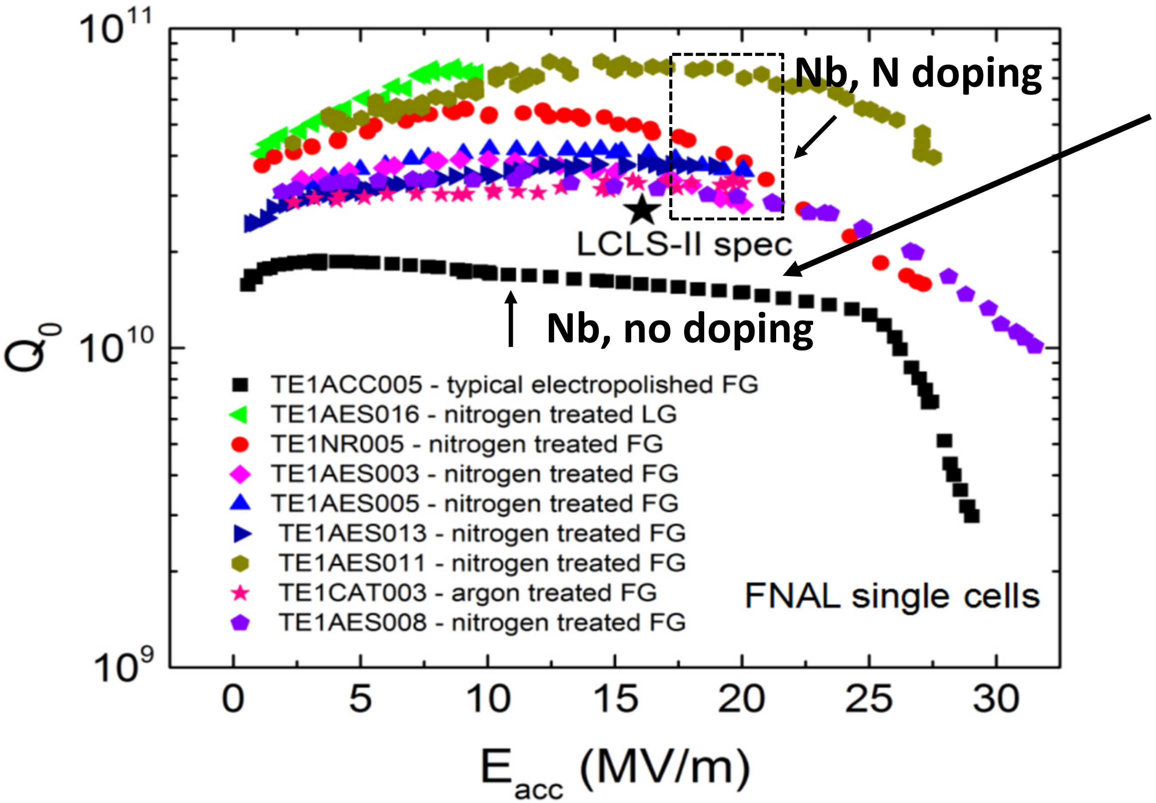
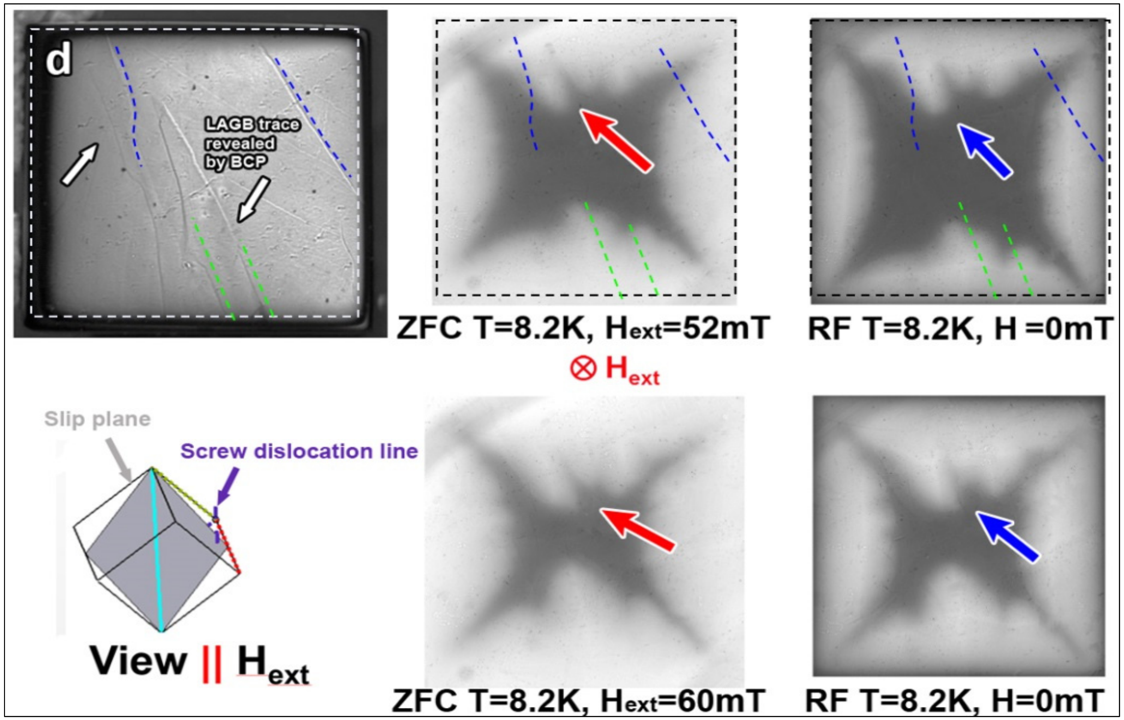


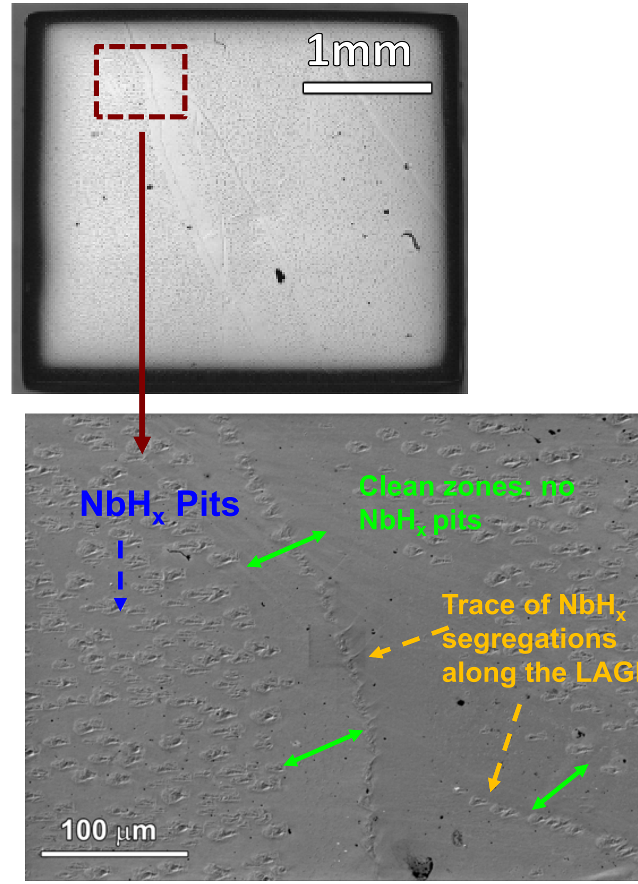
A Grassellino , A Romanenko, et.al, Supercond. Sci. Technol. 26 (2013)

- Is the medium field Q slope caused by nano-hydrides?
  - A Romanenko, F Barkov, L D Cooley and A Grassellino, Supercond. Sci. Technol. 26 (2013) 035003 (5pp) .
- Record accelerating gradients of 45MV/m have been attained in pure Nb. Repeatability?
- Dirty Nb (by doping or infusion) is pushing the limits of Nb….

Does N doping provide an added benefit by preventing hydrides?

Motivation- Microstructure hydride interactions can lead to DC flux trapping during cooling.



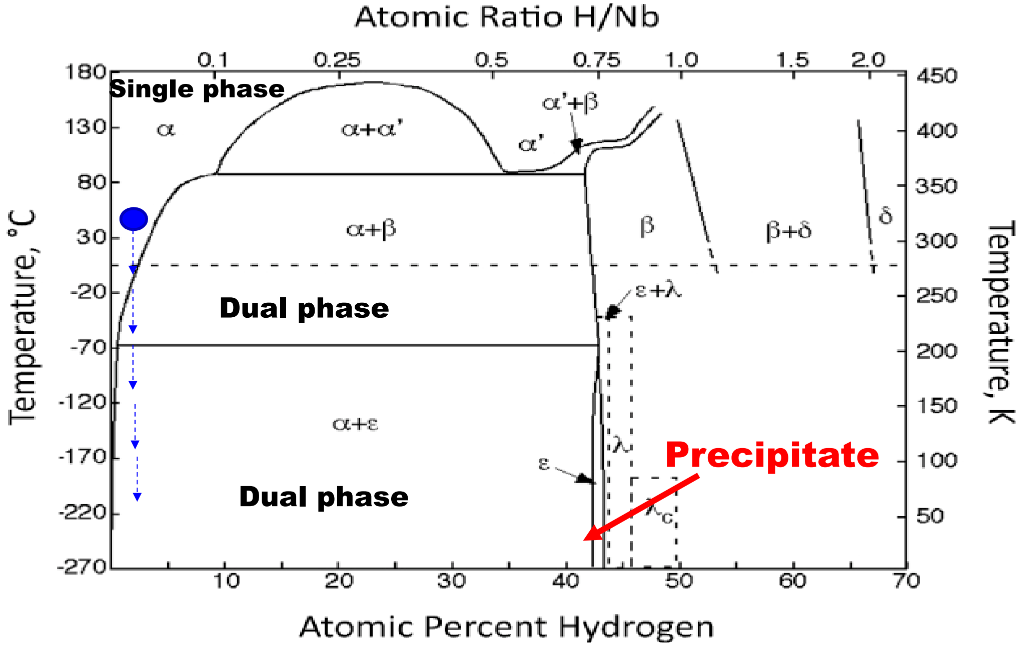


[Development of Low Angle Grain Boundaries in Lightly Deformed Superconducting Niobium and Their Influence on Hydride Distribution and Flux Perturbation]

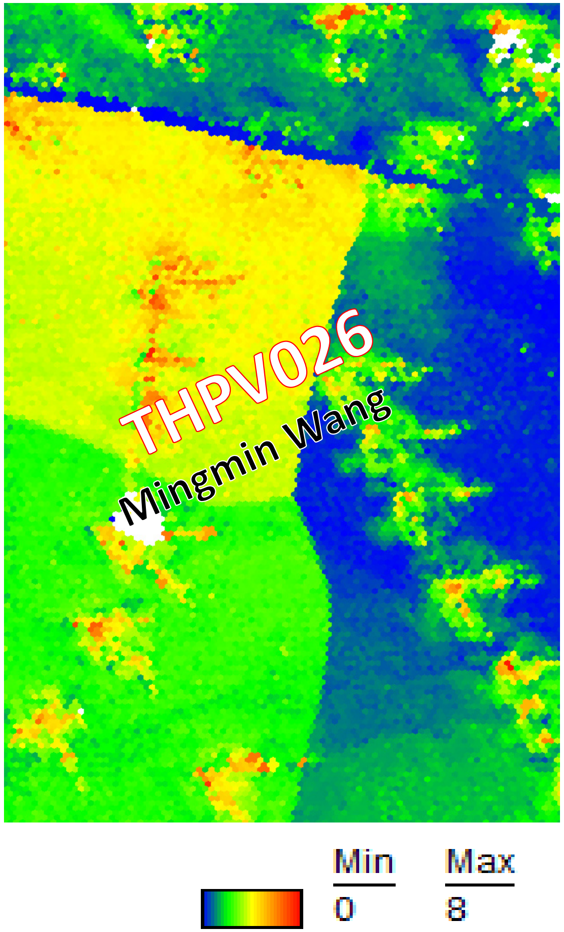
Sung, Z.-H, et.al, *J. Appl. Phys.*, 121, 19, 193903 (2017)

Are there microstructure correlations to hydride precipitation?

Preliminaries - Nb-H system: Hydrogen, and hydrides distort the Nb lattice



Lattice Parameter (Å)			
Composition	**a**	**b**	**c**
Nb	3.3139	3.3139	3.3139
α **- $NbH_{0.5}$**	3.4094	3.4181	3.4095
β **- NbH**	4.866	4.945	3.508

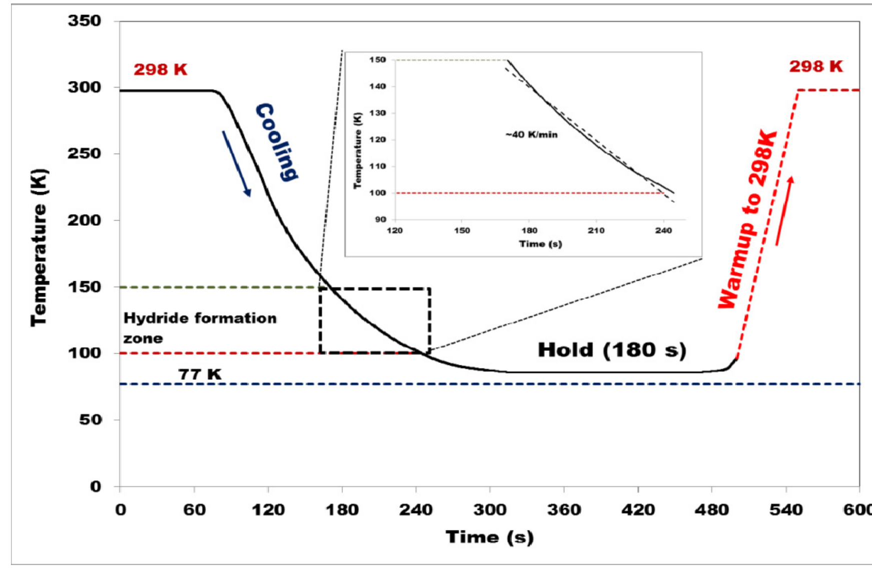


Methods: Surface hydrogen introduction and hydride precipitation

Polycrystalline RRR >250 Nb

1. As received Ningxia sheet meeting LCLS-II spec
2. Polycrystalline Nb wires with and without N doping

Surface hydrogen introduced higher than in SRF cavity Nb after treatments!



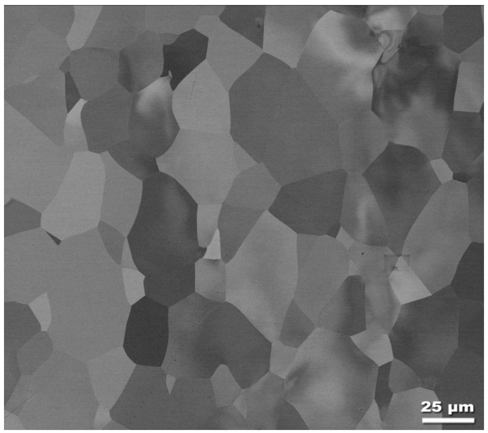
Mechanical polishing of cross section

Temperature cycle

F. Barkov, A. Romanenko, Y. Trenikhina, and A. Grassellino, ''**Precipitation of hydrides in high purity niobium after different treatments''**, J. Appl. Phys. **114**, 16490 (2013)

Final step -Vibromet 20 h, Colloidal silica (ph= 10.5)

Methods: Surface hydrogen introduction and hydride precipitation – Ningxia sheet

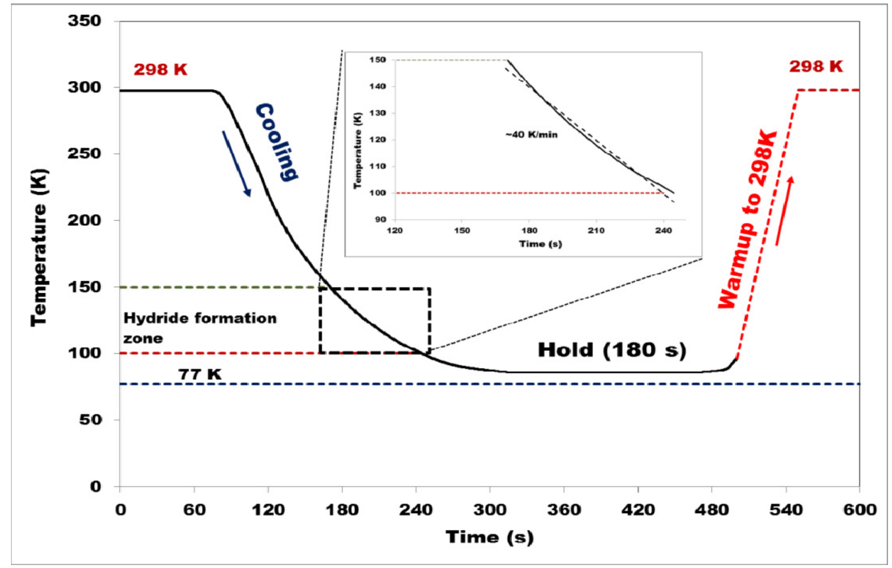


As received Ningxia sheet from JLAB

Mechanical polishing of cross section

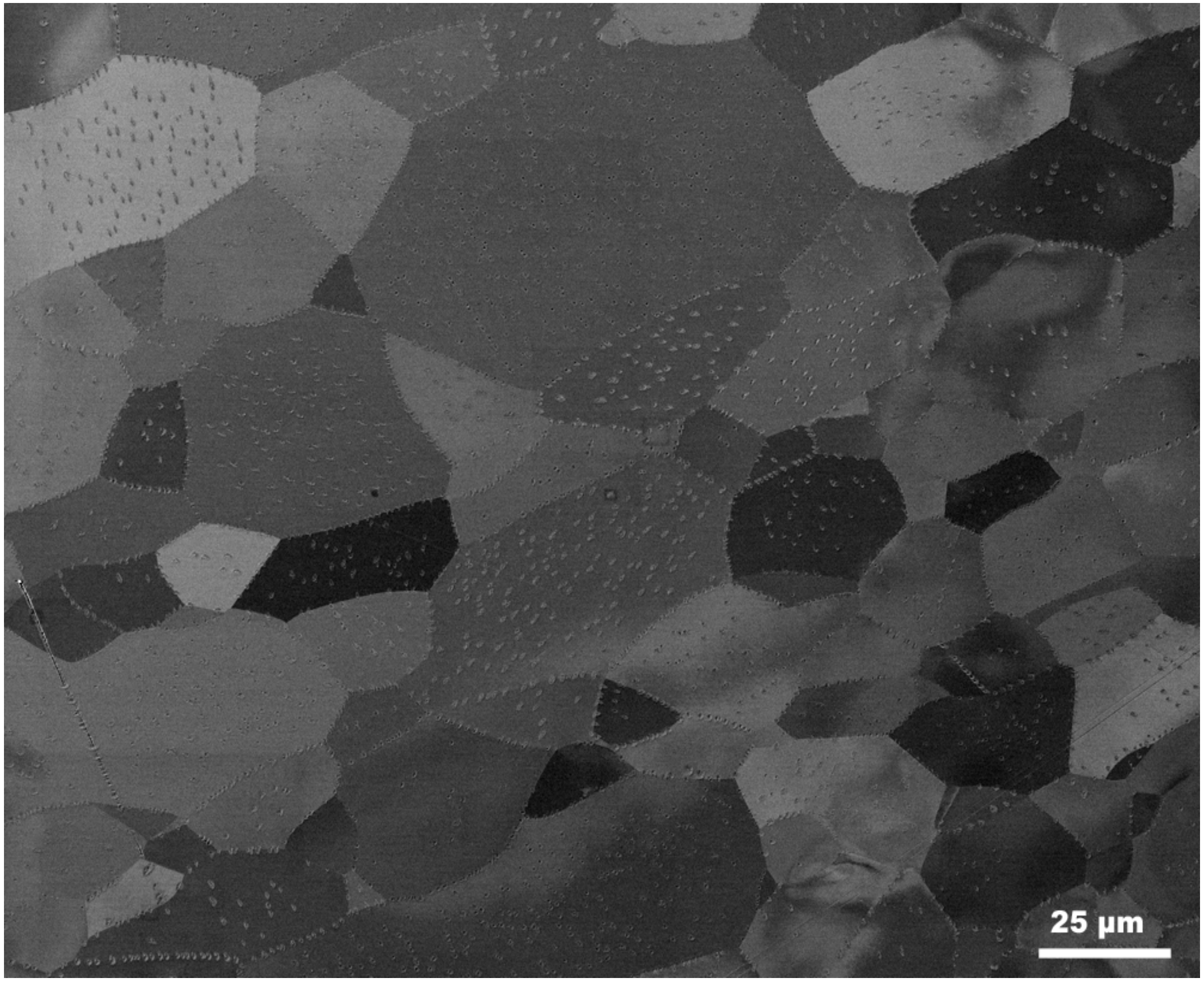
Final step -Vibromet 20 h, Colloidal silica (ph= 10.5)

Temperature cycle

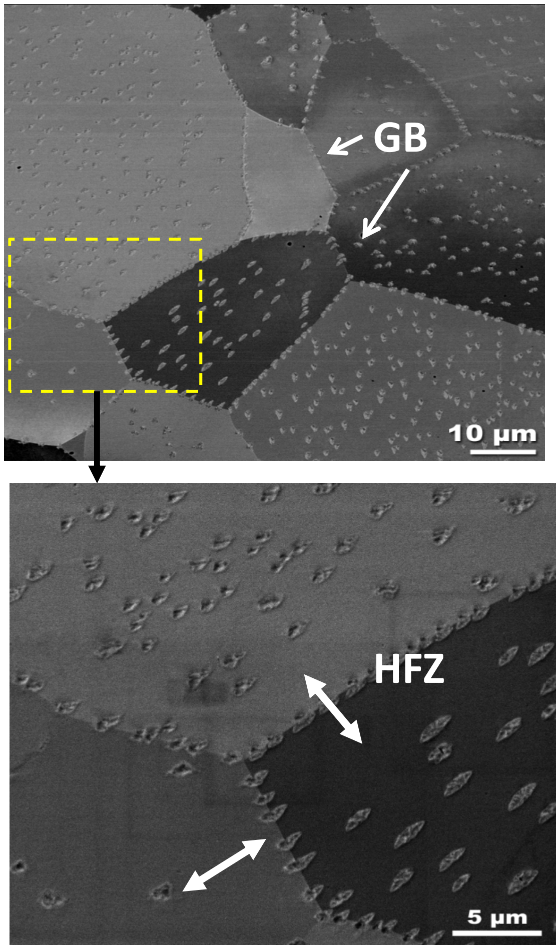


F. Barkov, A. Romanenko, Y. Trenikhina, and A. Grassellino, ''**Precipitation of hydrides in high purity niobium after different treatments",** J. Appl. Phys. **114**, 16490 (2013)

Backscatter image reveals pits left over by hydride precipitation. Contrast due to strain around pits.

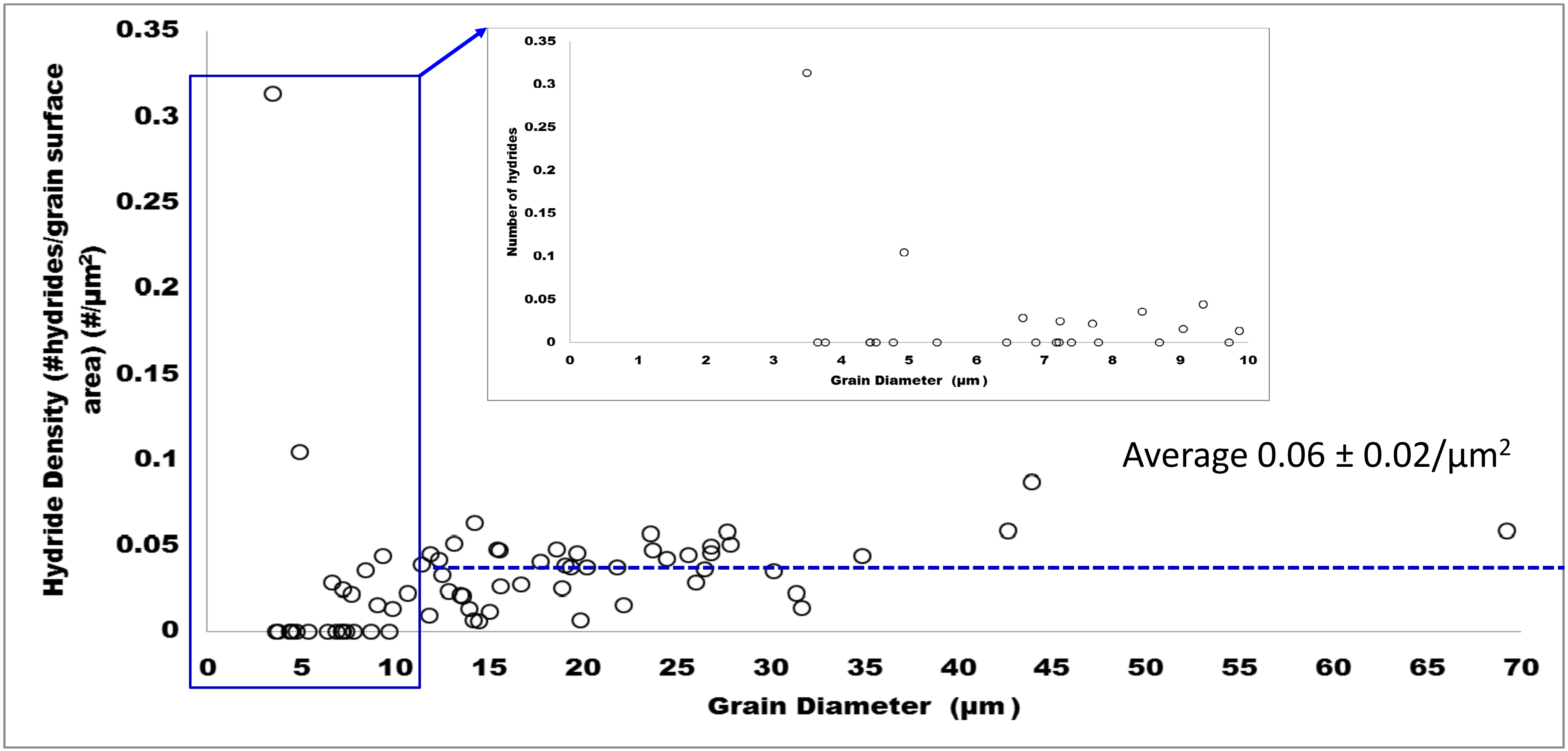


Result- Preferential segregation of hydride pits at GB's observed



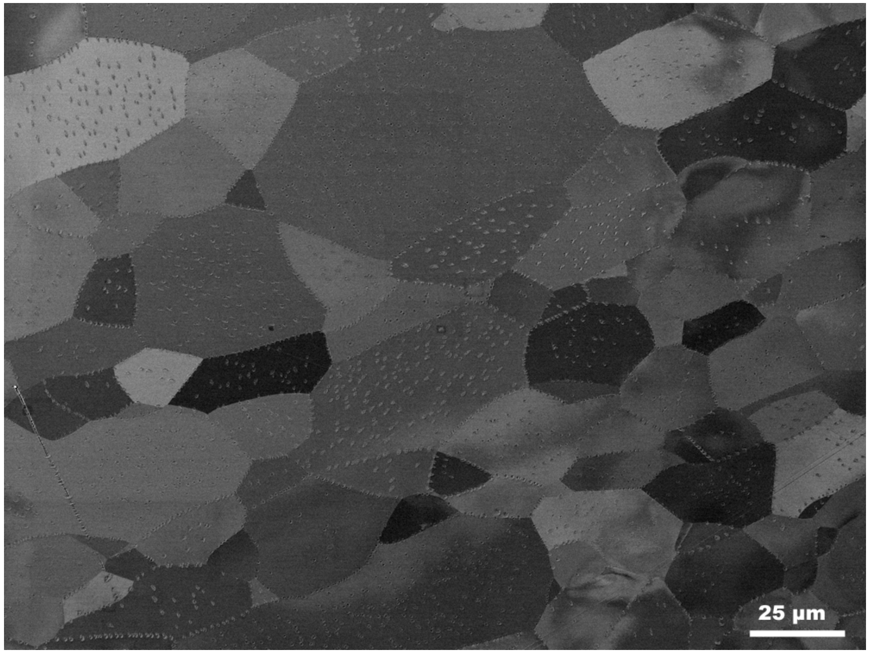
- Pits are present in-grain and along GB's.
- There is segregation along the GB, and a hydride free zone (HFZ).
- Hydride pit morphology depends on grain orientation.
- Some grains have no hydrides.

Result- Hydride pit density is constant for a grain size greater than ~10µm



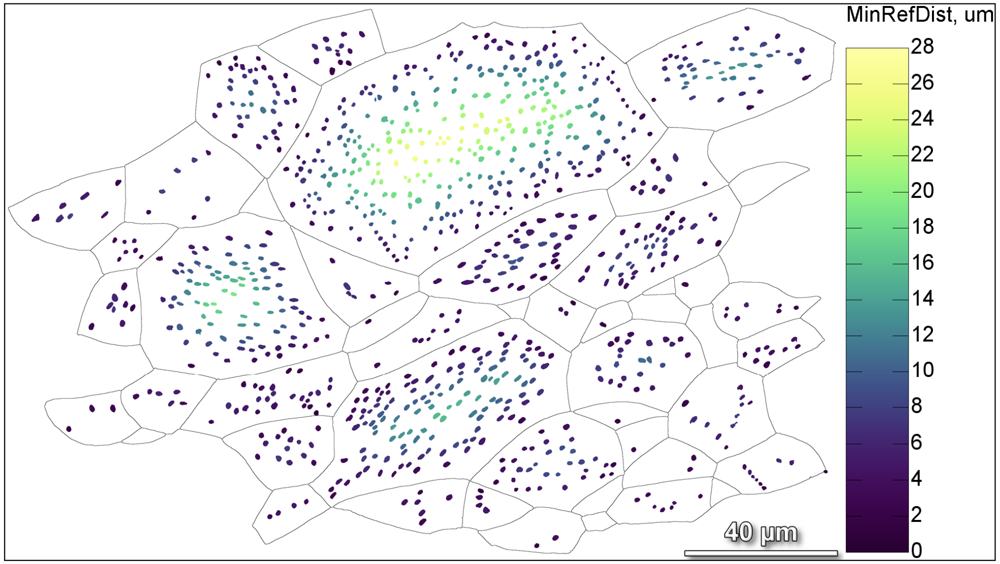
Result- Hydride pit free zone (HFZ) determined by analytical microscopy.

BSE image



Average hydride pit diameter: 1500 ± 300 nm

Digitized image for image analysis (Image J macros)



Color coded plot of minimum distance between hydride pits and grain boundary

Result- Hydride pit free zone (HFZ) determined by analytical microscopy.

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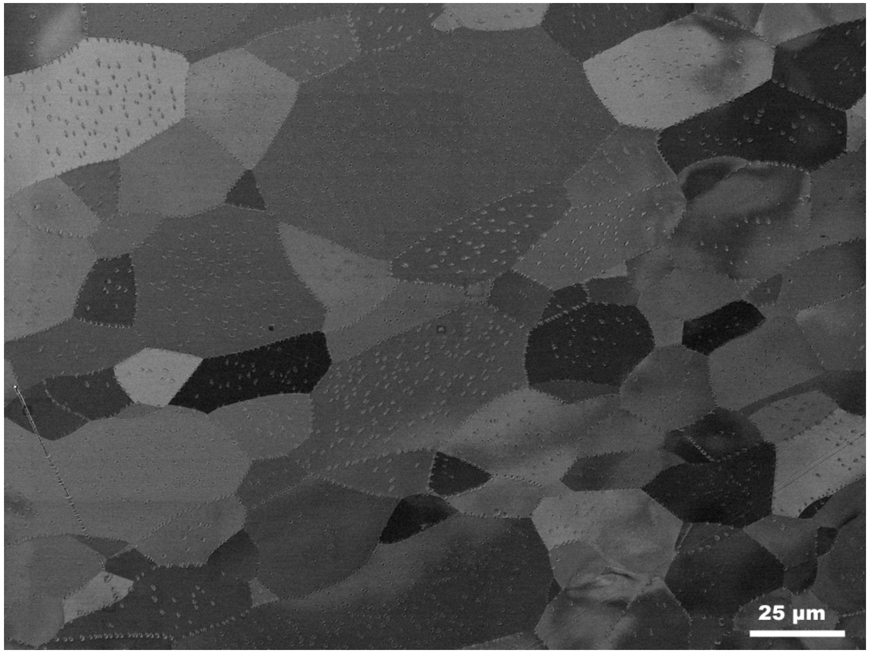

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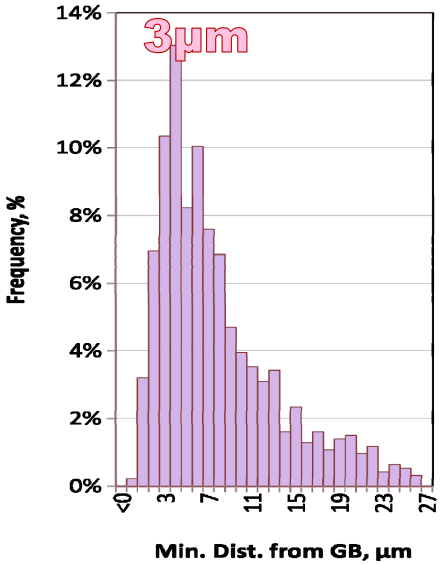


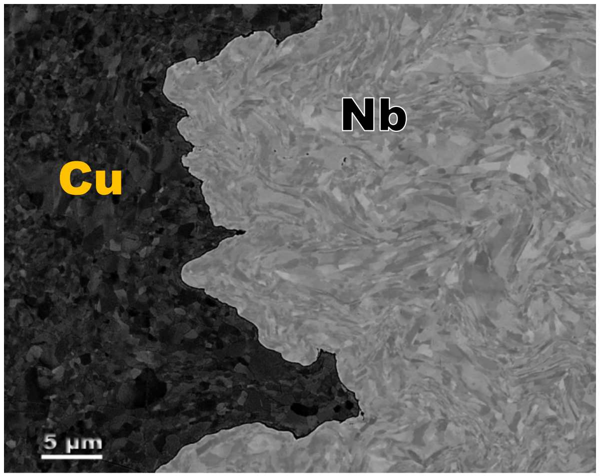
Color coded plot of minimum distance between hydride pits and grain boundary

Summary

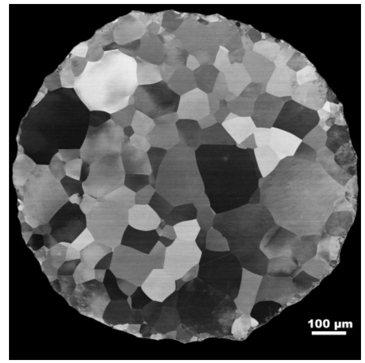
- Hydride pits generated show a microstructure dependence
  - Grain sizes less than 10 µm have very few hydrides.
  - Hydride pits appear to be segregated at the GB.
  - There is a hydride free zone around GB's with the average distance being 3µm.

- Characteristic features that could describe hydride pit behavior are:
  - Average hydride pit diameter size (nm), average hydride density (#/μm^2), HFZ (µm).

Experimental details: RRR> 250 SRF grade Nb drawn wires

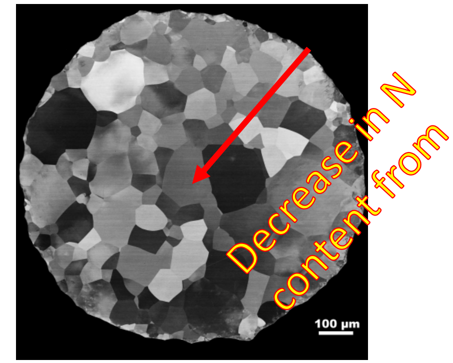


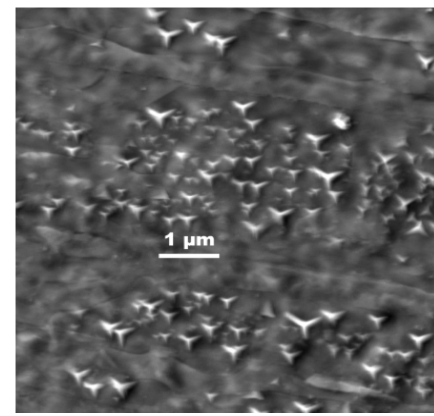
Cu removal (1:10, HNO_3 and EP)



800˚C/3h
52±42 µm

800˚C, 2N6





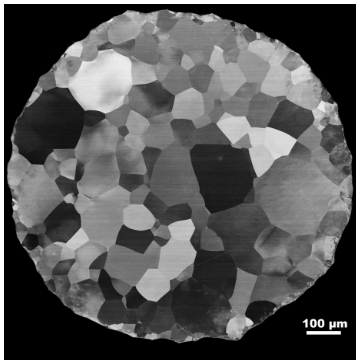
Nitrides on wire surface after 800˚C, 2N6

- SRF grade RRR > 250; Nb wire Ɛ=4.2
- Typical grain curling in bcc metals observed

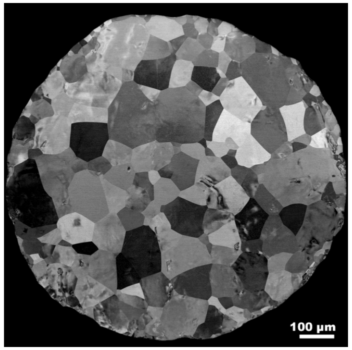
2N6-> 2 minute N_2 introduction at 25 mTorr, and 6 minute soak

Methods: Surface hydrogen loading and hydride precipitation

800˚C/3h



800˚C/3h + 8002N6

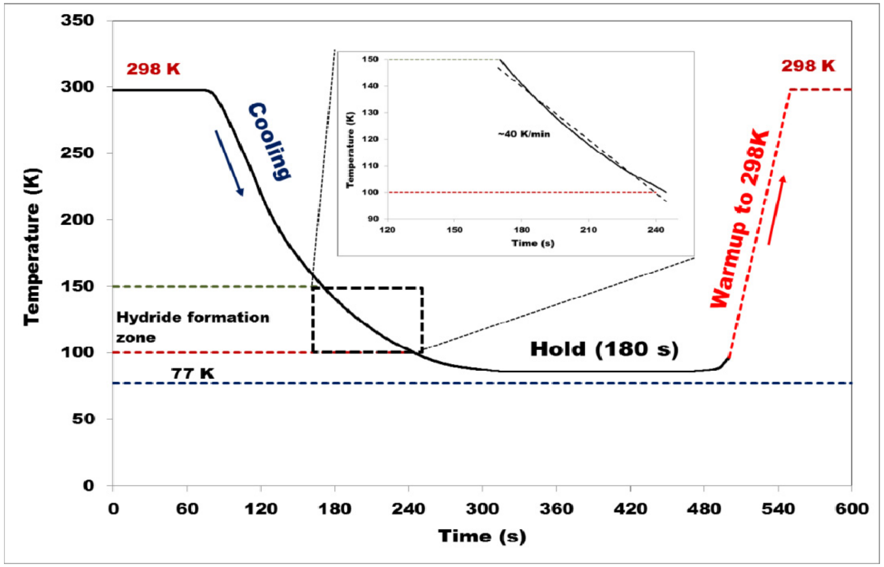


Surface hydrogen introduced higher than in SRF cavity Nb after treatments!

Mechanical polishing of cross section

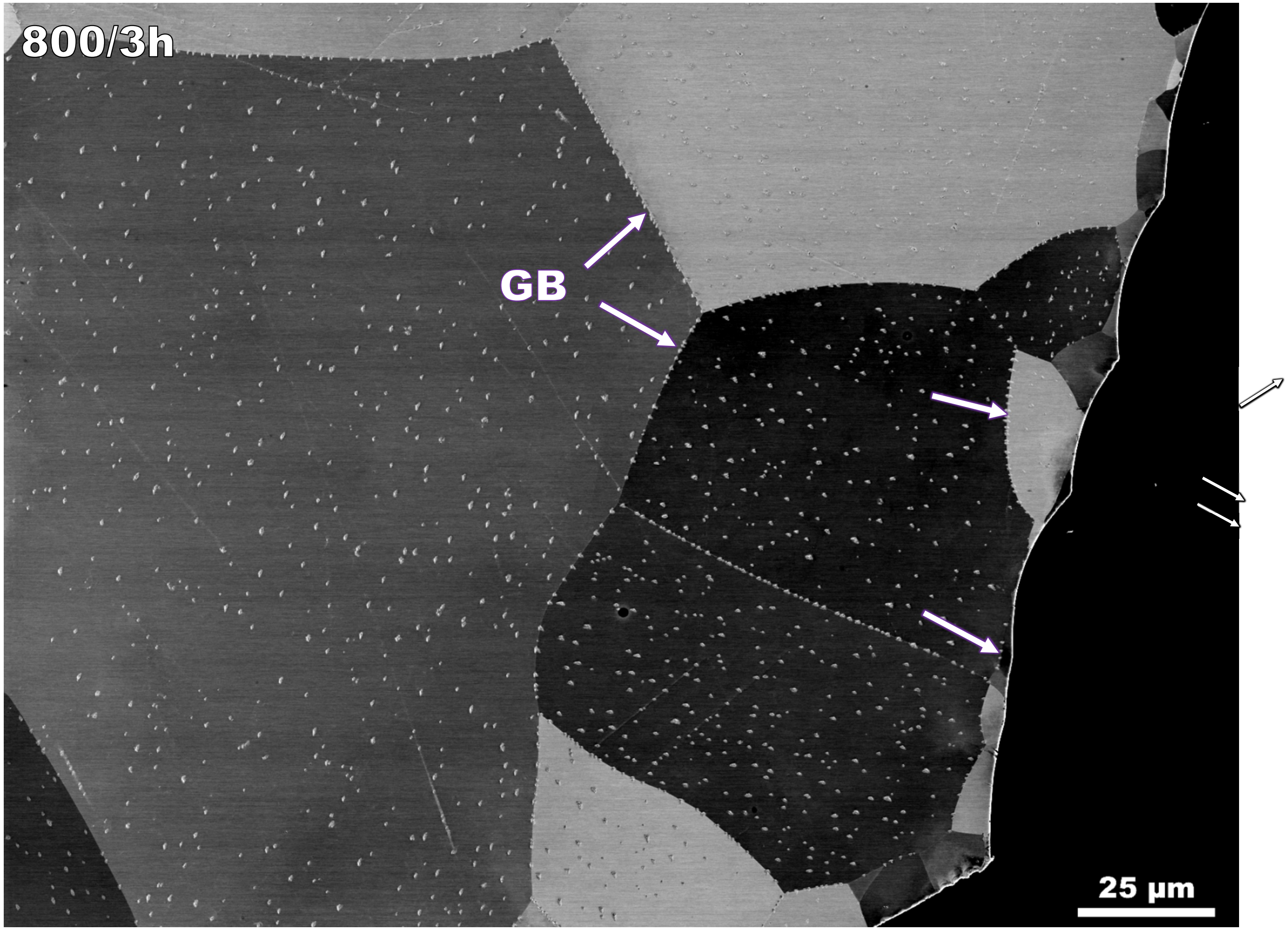
Final step -Vibromet 20 h, Colloidal silica (ph= 10.5)

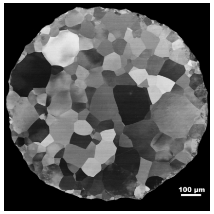
Temperature cycle



Hydrogen diffuses in Nb at 77K. Average distance covered in 180 s, is ~ 2µm.

Result- 800˚C/3h after cooling- Hydride pits observed throughout cross section





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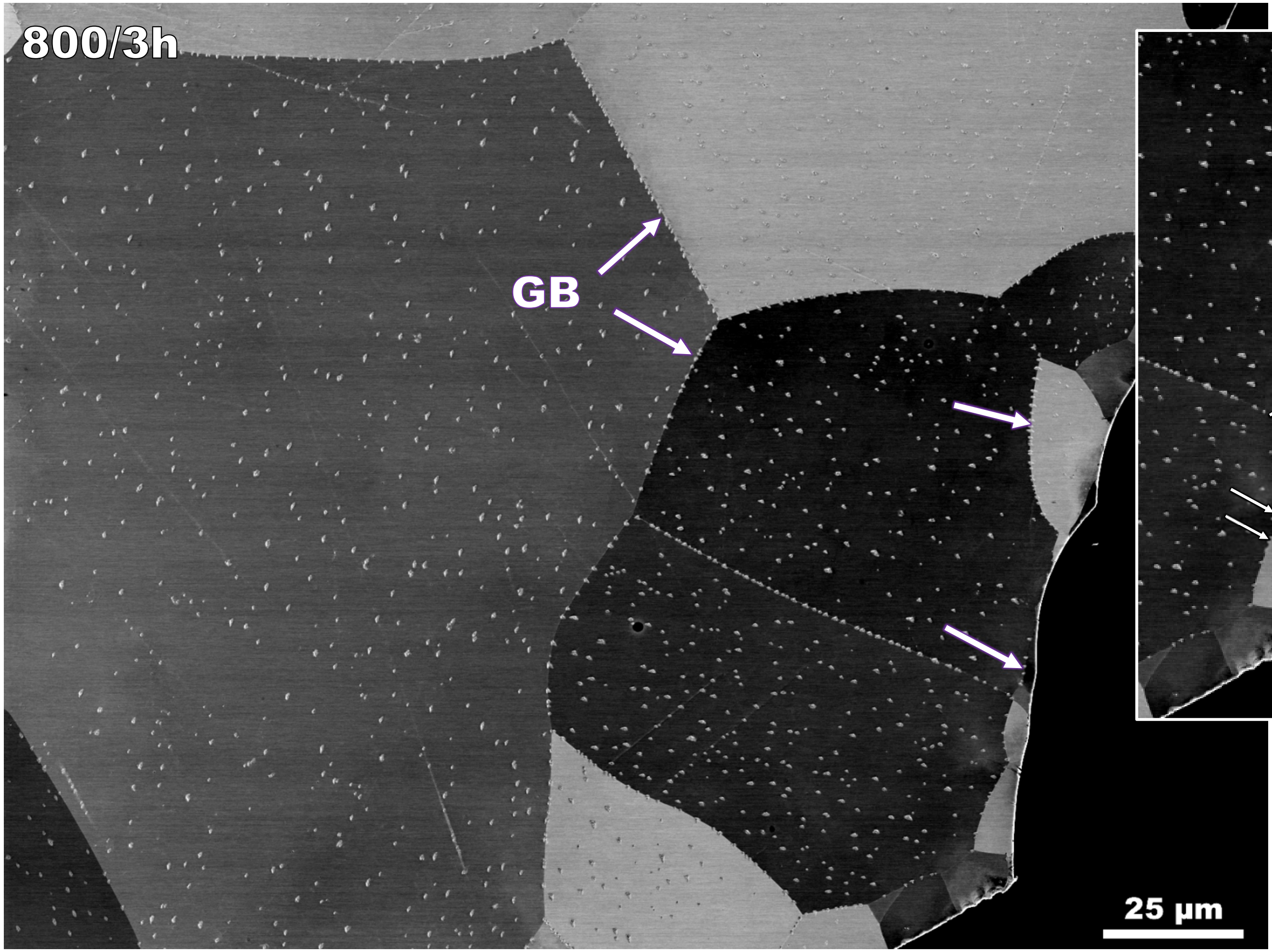

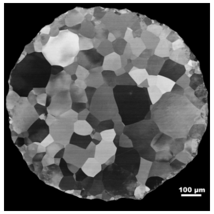

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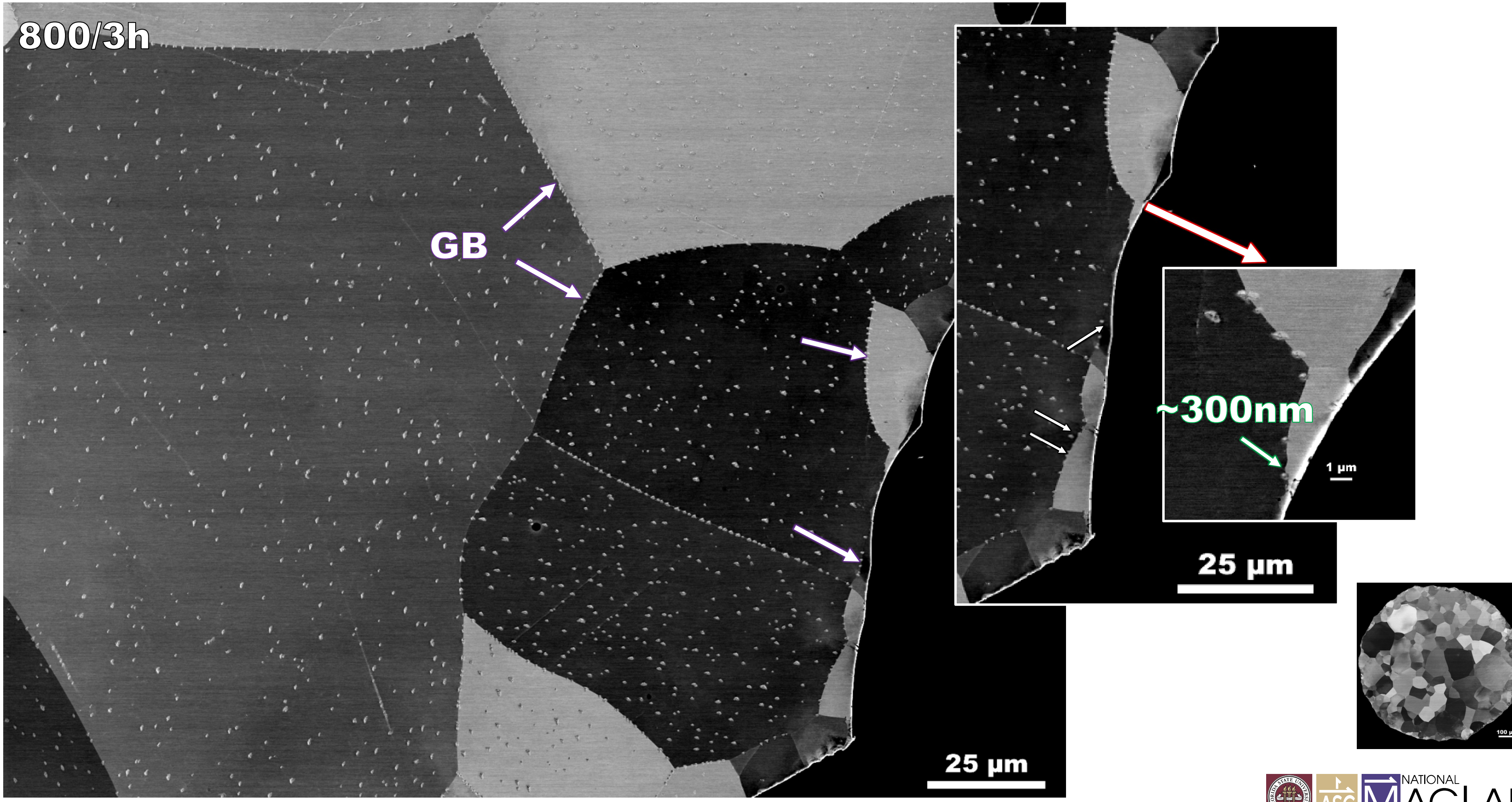
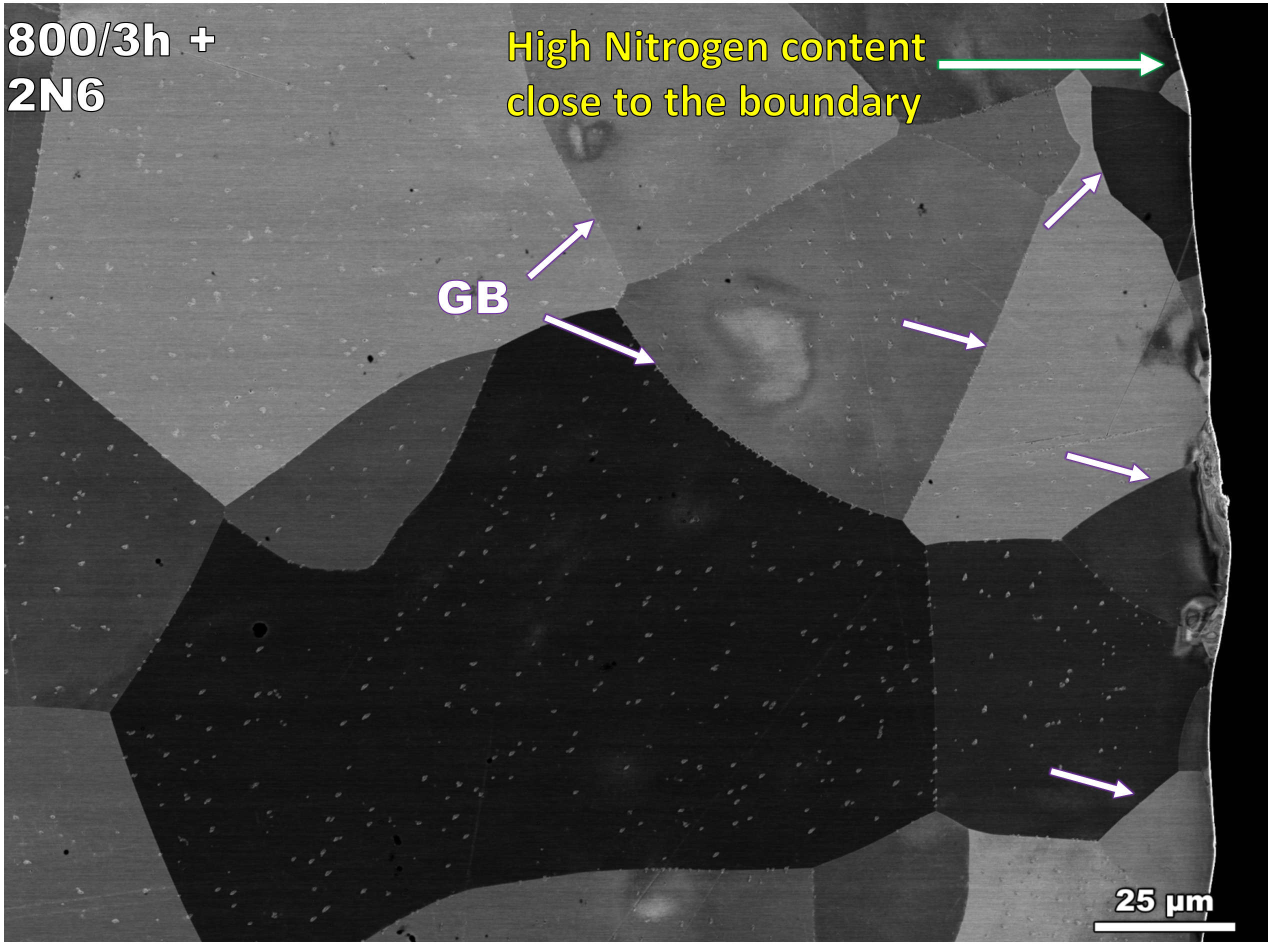
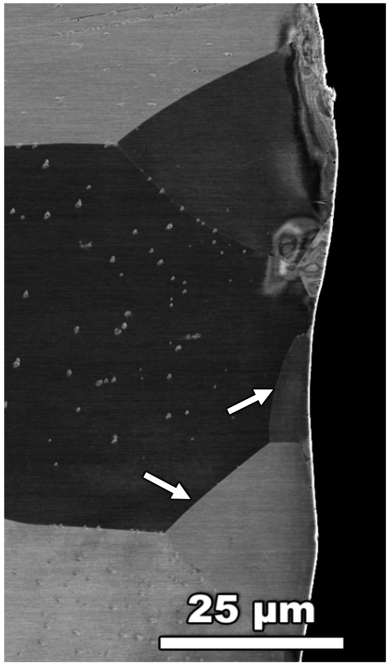
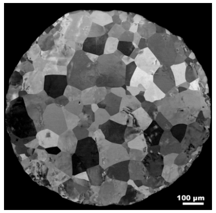


Result- 800˚C/3h + 2N6 after cooling- Lesser number of hydrides in cross section







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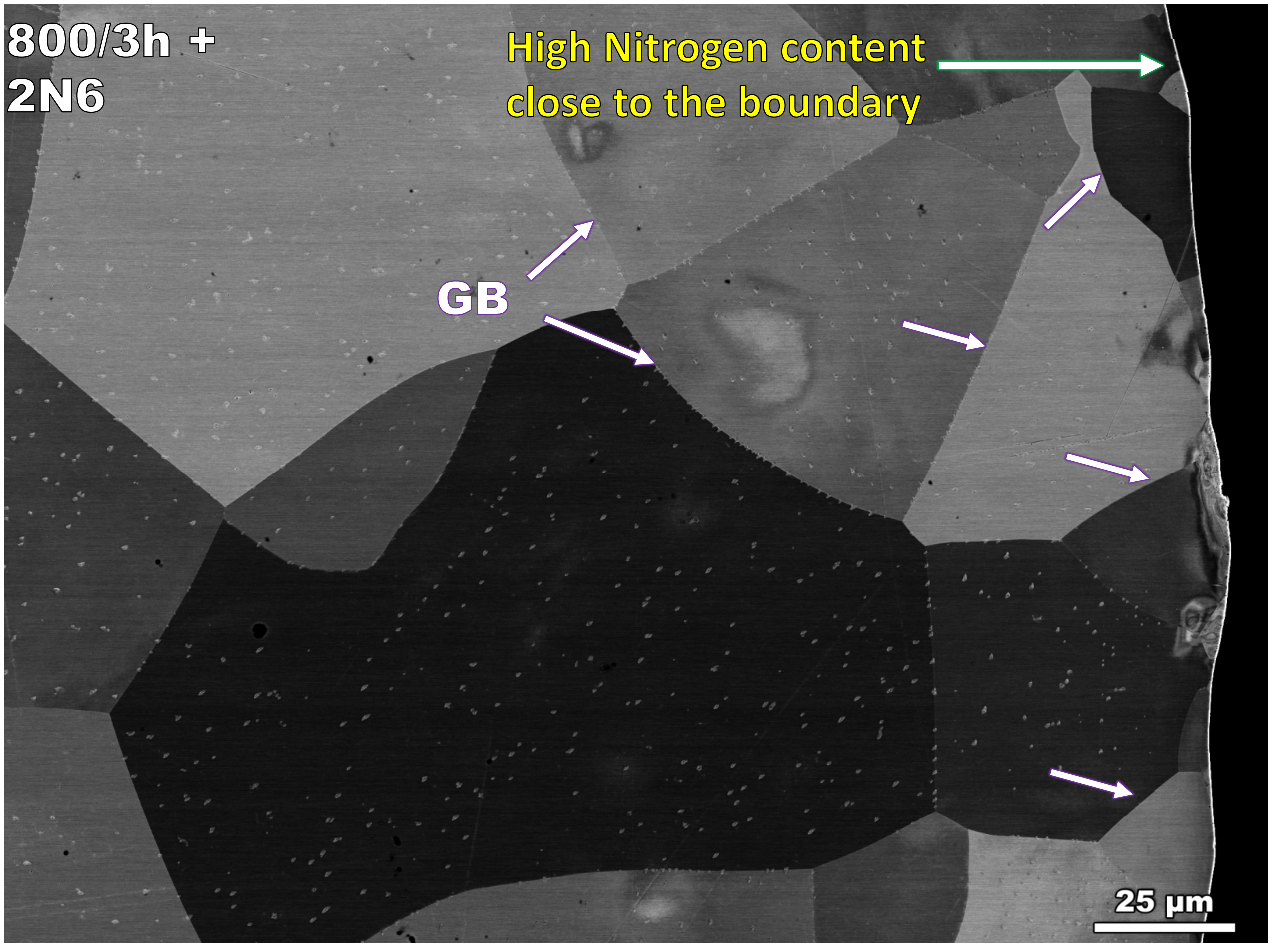
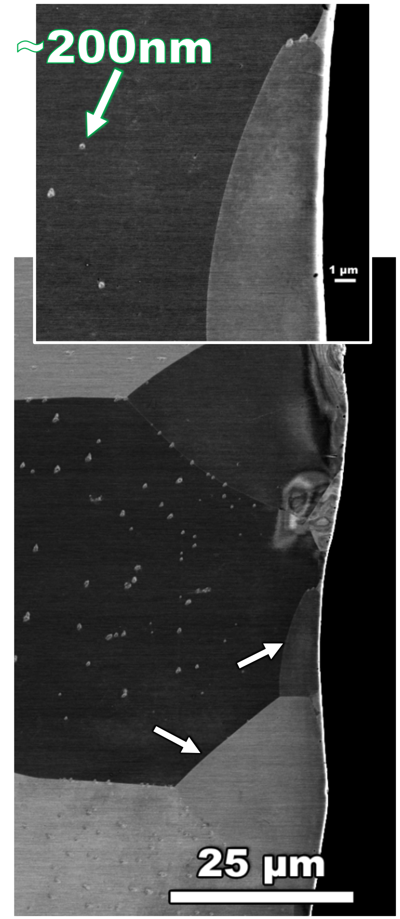
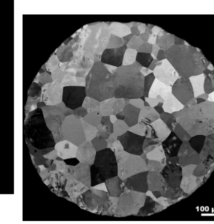
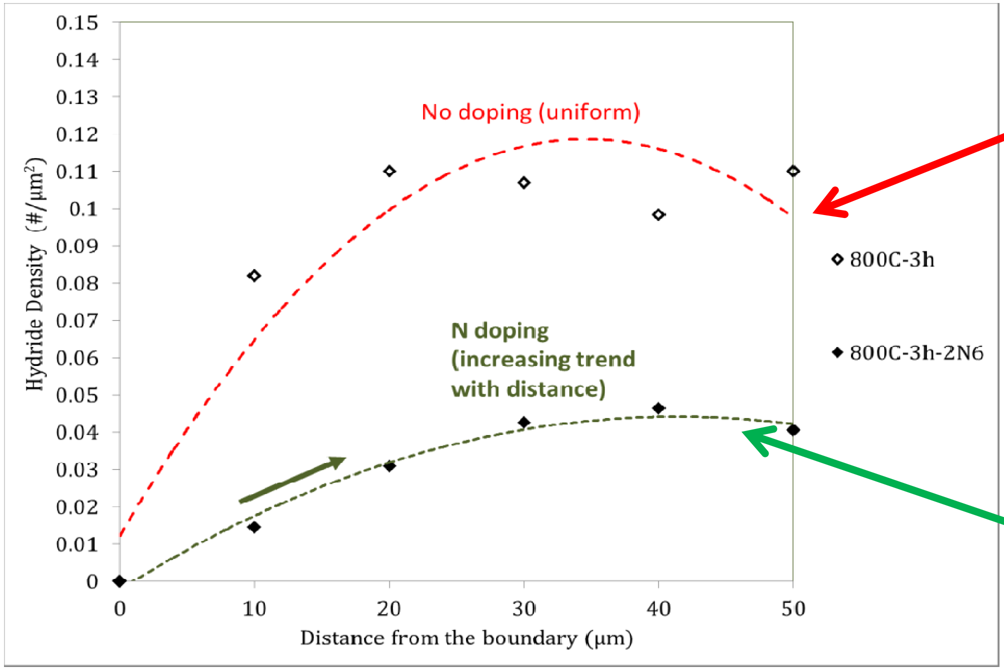


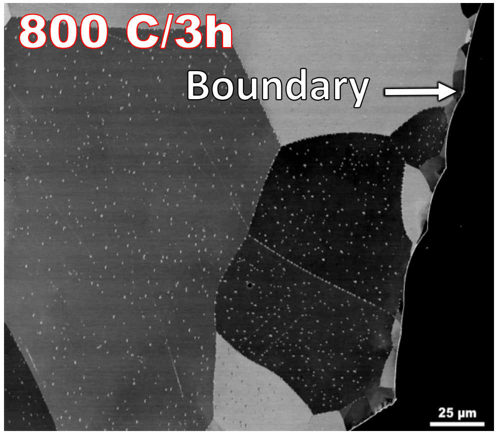


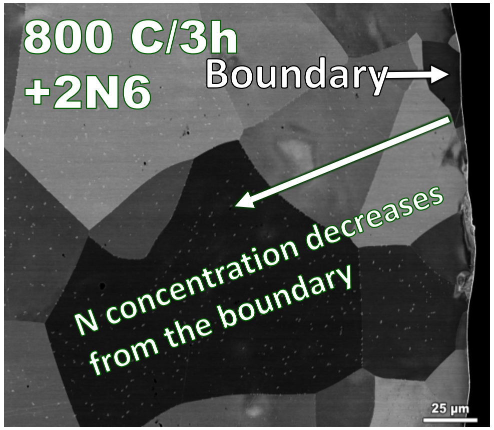


Result- Hydride pit density is reduced in N doped samples, close to the wire surface.

Density of hydride pits versus distance from the boundary.



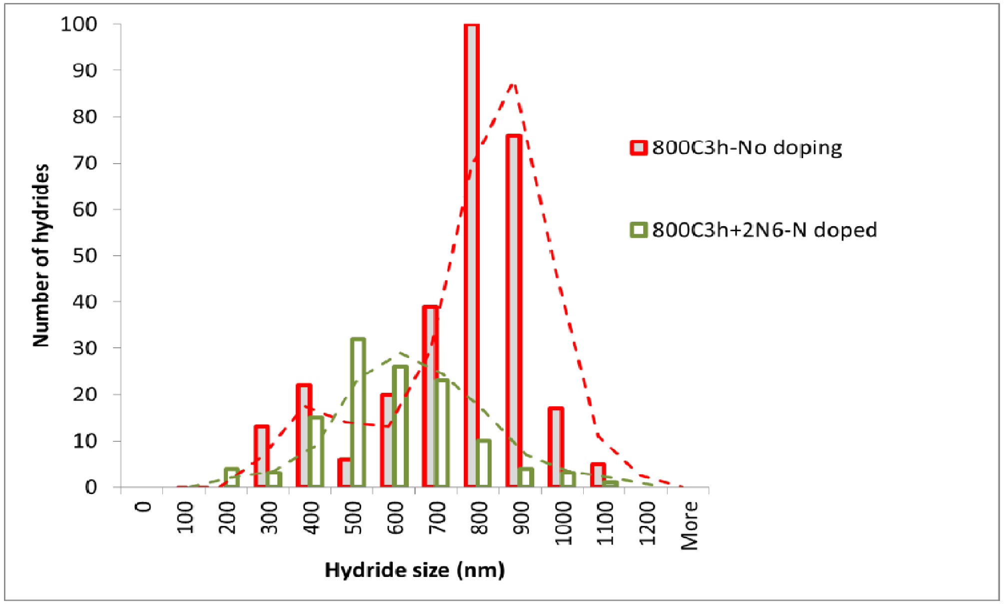


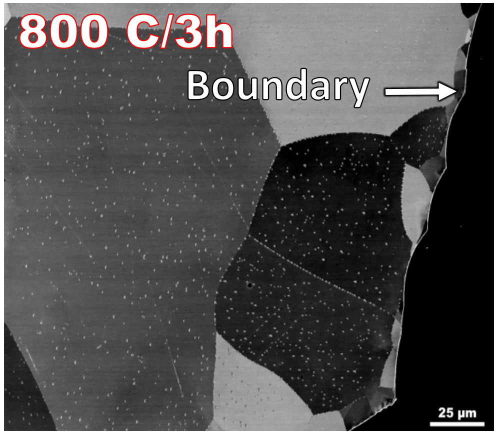


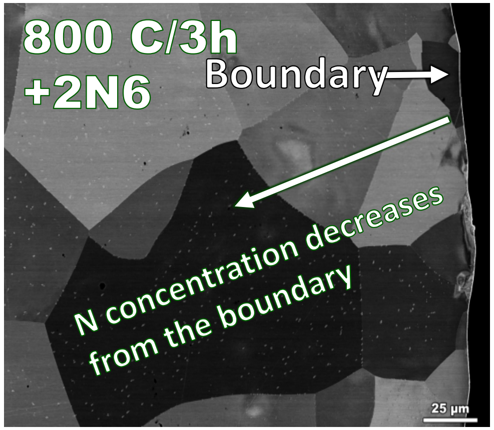
- Hydride pit density is uniform in the sample with no nitrogen doping.
- Hydride pit density is lesser within the first 50 μm of the N doped sample

Result- Hydride pit size is reduced in N doped samples, close to the wire surface

Hydride pit diameter within 100 µm x 100 µm from the boundary.







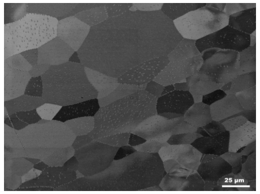
Average hydride pit size in:

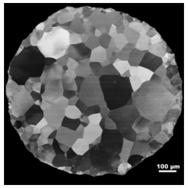
a) N doped Nb sample is 580 ± 350 nm,

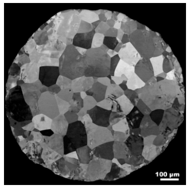
b) Nb sample with no doping is 750 ± 430 nm.

Summary- Hydride pit characteristics vary depending on Nb microstructure and doping

Sample	Average grain size (µm)	Average hydride size (nm)	Average hydride density (#/µm^2)	HFZ (µm)
Polycrystalline Ningxia sheet- As received.	37±21	1500 ± 300	0.06 ± 0.02	3
Polycrystalline Nb wire (800C/3h)	52±42	750 ± 430	0.07 ± 0.04	1
Polycrystalline Nb wire (800C/3h) + 8002N6	50 ± 34	580 ± 350	Varies	-



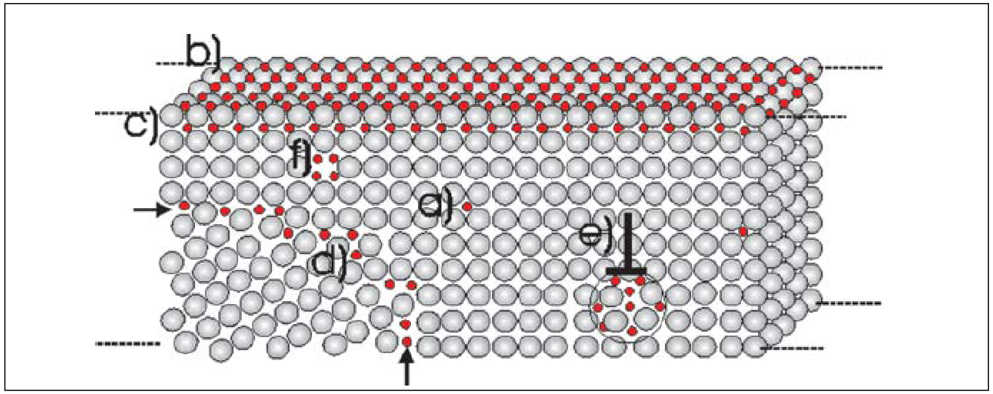




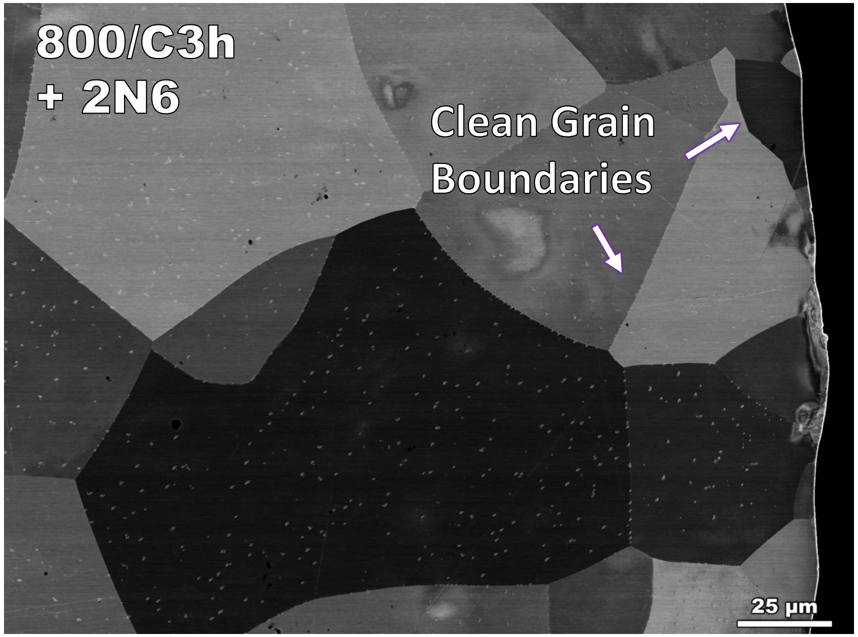
Limited counting statistics – 100 µm x 100 µm area

Distribution of hydride pits is non-uniform in N doped samples

Discussion- Hydride pits as a tracker of interstitials and defects?



A. Pundt and R. Kirchheim, "Hydrogen in Metals: Microstructural Aspects", Annu. Rev. Mater. Res. 2006. 36:555–608,



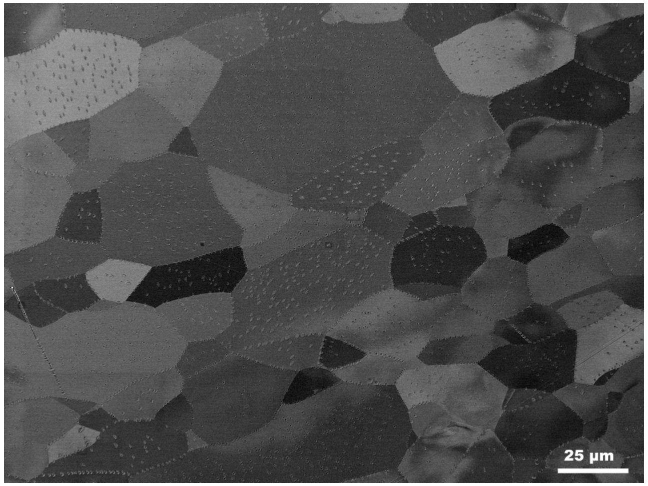
- Trap sites for H in the low concentration range: interstitials, vacancies, dislocations, GB's, , and free surface…
- Can statistical analysis of hydride pits be a technique to relate microstructure with hydride precipitation?

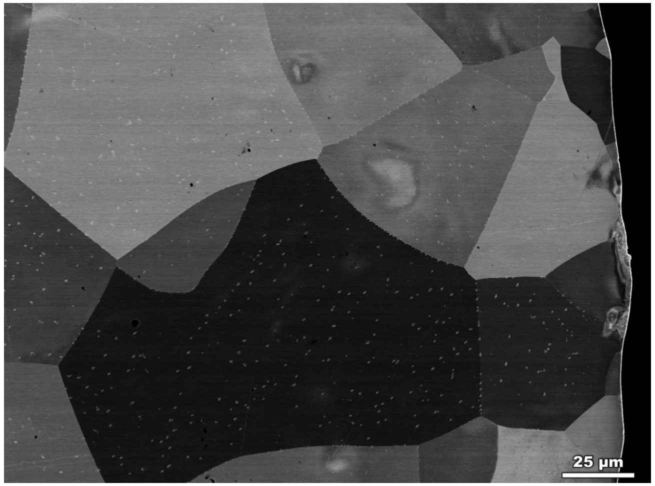
Do a lack of hydride pits imply presence of interstitials?

Summary and Conclusions

- Hydride pit distribution is dependent on the Nb material and processing treatments.
- Clear evidence that hydride pit density, and numbers are reduced by N doping of SRF grade Nb.
- N doping could be effective in preventing hydride precipitation in SRF cavity Nb where hydrogen levels are much lower
- Observation of hydride pits in the range of 150-200nm, indicates initial hydrides formed could have similar dimensions.
- The technique developed could be a low cost tool to investigate different Nb starting material including variations in: N doping, and surface treatments (EP, BCP, and heat treatments).

THANK YOU





THBP002- Role of Nitrogen on Hydride Nucleation and Stability in Pure Nb by First Principle Calculations.

THBP016- Impact of Heat Treatment and Doping on Flux trapping in SRF Grade Niobium Coupons.

THBP026- Investigation of the Effect of Strategically Selected Grain Boundaries on Superconducting properties of High Purity Niobium.