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Vacancy-enhanced Hydrogen Degradation of Ni Alloys

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Samantha K. Lawrence

Collaborators: Brian P. Somerday, Yuri Yagodzinskyy, Esa Korhonen, Filip Tuomisto, Hannu Hänninen, Zachary D. Harris

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

Hydrogen Degradation: Outline

- Motivation & Definition
- Microscopic Mechanism Overview
  - Hydrogen-Enhanced Localized Plasticity
  - Hydrogen Enhanced Decohesion
- Current Investigation
  - Why Ni?
  - What do we expect?
  - Experimental framework
- Results
  - Positron Annihilation
  - Thermal Desorption Spectroscopy
  - Mechanical Behavior
- Summary

Hydrogen in Metals: Relevant & complicated

http://www.smdailyjournal.com/articles/lnews/2013-03-28/bolts-on-an-san-francisco-oakland-bay-bridges-new-span-found-to-be-faulty/1767495.html

http://sanfrancisco.cbslocal.com/2013/04/24/bechtel-engineer-says-caltrans-fell-on-its-face-over-new-bay-bridge-steel/

http://www.sfchronicle.com/bayarea/article/Experts-Caltrans-tapped-to-study-Bay-Bridge-tower-6419629.php

DEFINITION:

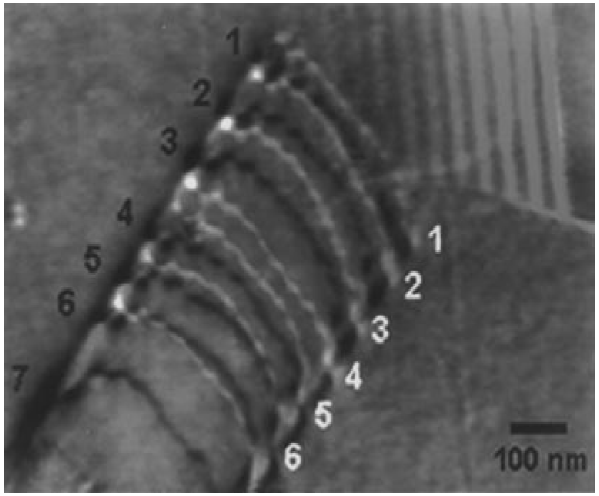
Degeneration in mechanical properties caused by presence of hydrogen in a material under stress

MOTIVATION:

Microscopic mechanisms leading to macroscopic failure are unclear, but grain boundary engineering has shown promise in mitigating degradation

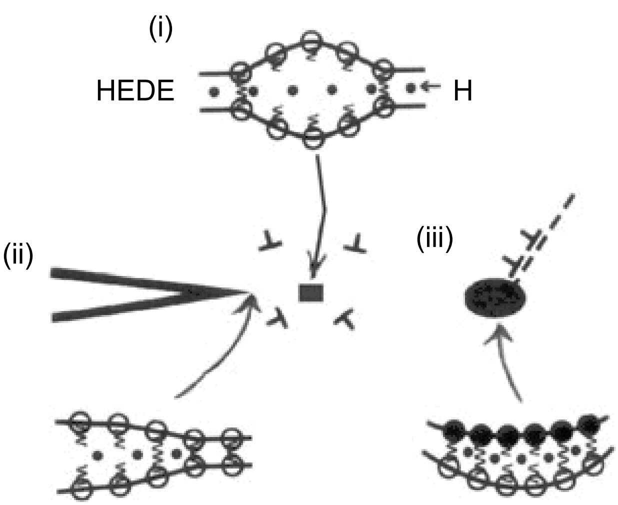
Hydrogen Degradation: Candidate Mechanisms

1. Hydrogen-enhanced localized plasticity (HELP)
   - Proposed to explain observed increase in strain localization prior to failure
   - H shields barriers to dislocation motion, "free volume" generation can lead to flow localization



Ferreira, P. J., Robertson, I. M. & Birnbaum, H. K. *Acta Materialia* **46**, 1749–1757 (1998).

2. Hydrogen-enhanced decohesion (HEDE)
   - H decreases the cohesive force, and corresponding surface formation energy, between atomic planes
   - Use local measurements of mechanical properties to estimate effects on cohesive energy

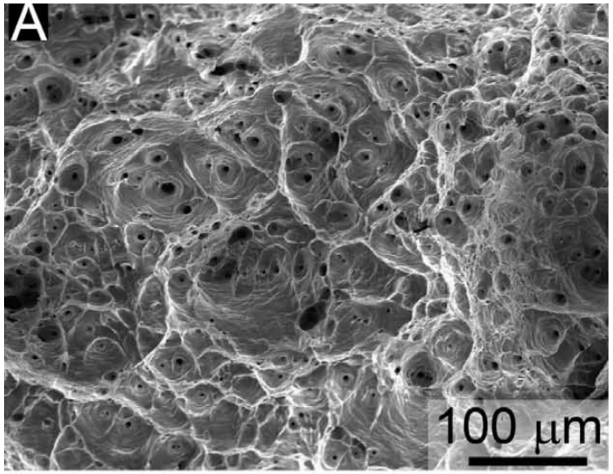


S.P. Lynch, Mechanisms of hydrogen assisted cracking – a review, pp. 449–466 in Hydrogen effects on materials behavior and corrosion deformation interactions, N.R. Moody, A.W. Thompson, R.E. Ricker, G.W. Was, and R.H. Jones (Eds), TMS, 2003.

Why nickel? Model material, IG fracture

Big Picture:

- Ni alloys are susceptible to IG fracture in hydrogen environments
- Ni-201 is nominally single phase with simple microstructure
- Mechanistic details, such as need for H segregation to grain boundaries, firmly established
- Ni is a model material for engineering alloys



S. Bechtle, M. Kumar, B.P. Somerday, M.E. Launey, R.O. Ritchie, *Acta Materialia* 57 (2009) 4148–4157.

Previous experiments reveal:

- Hydrogen-grain boundary interactions are dependent on misorientation
- Hydrogen inhibits cross-slip, but enhances slip localization
- Hydrogen induces measurable changes in mechanical properties
- GBE can lower propensity for hydrogen-induced intergranular failure

S.K. Lawrence, B.P. Somerday, N.R. Moody, D.F. Bahr: Grain Boundary Contributions to Hydrogen-affected Plasticity in Ni-201. JOM. vol. 66 pp. 1383-1390 (2014) DOI: 10.1007/s11837-014-1062-4

TDS & PAS Experiments Illuminate Mechanisms

1. Select multiple purities/microstructures of Ni to analyze grain boundary and texture effects
   - Single crystal, 5N pure reference Ni, Ni-201 with 50μm grains, Ni-201 with 1mm grains

2. Conduct PAS/TDS of SX, 5N-Ni in as-received condition
   - Baseline vacancy concentration and trap characteristics

3. Thermally charge under 62 MPa H at 300^{o}C for 144 hrs
   - 3000 appm hydrogen

4. Strain 50μm grain size tensile bar and 1mm grain size sample in tension at 293K or 77K
   - Nominally 10% strain

5. Conduct PAS/TDS of all samples after H-charging (and straining)

TDS Used to Assess Hydrogen Trapping

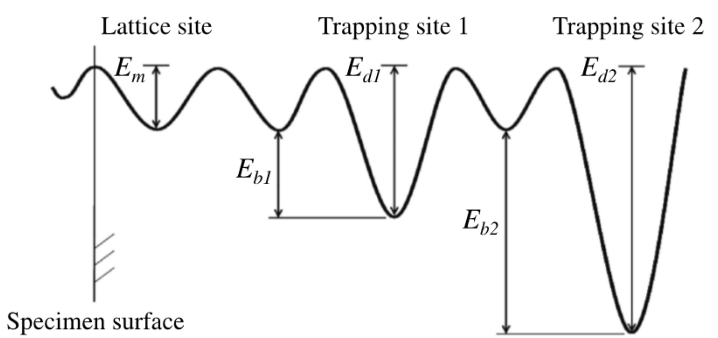
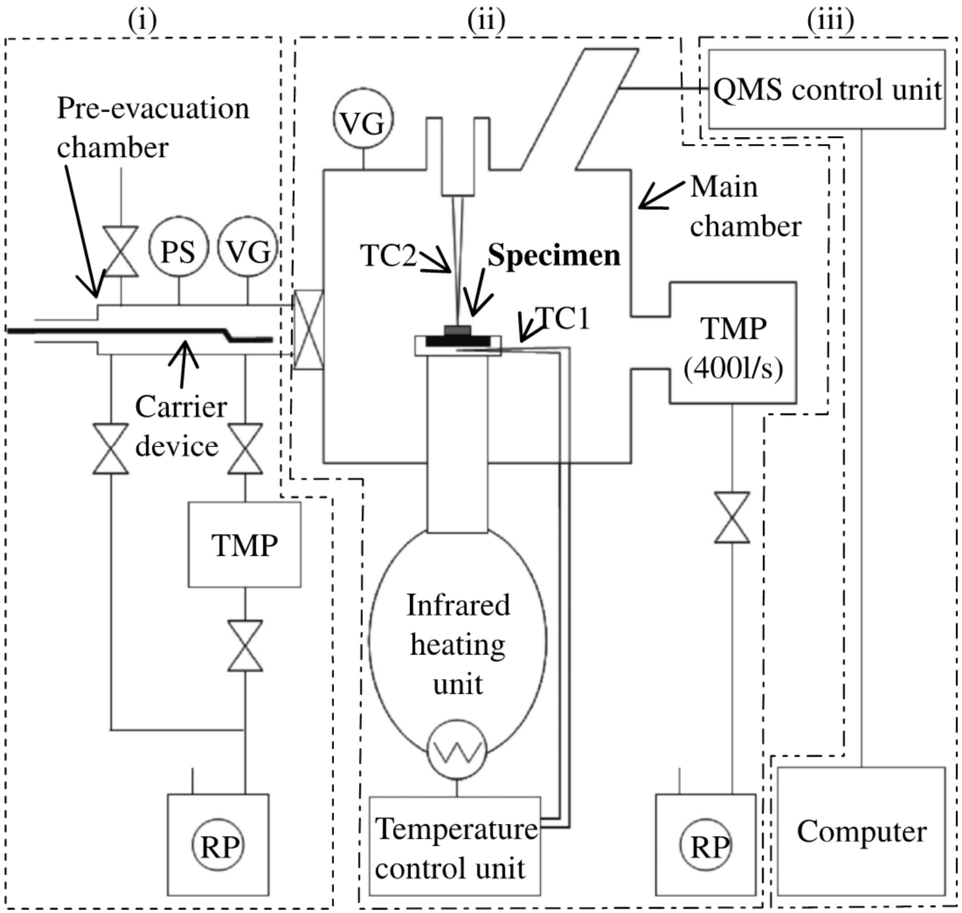
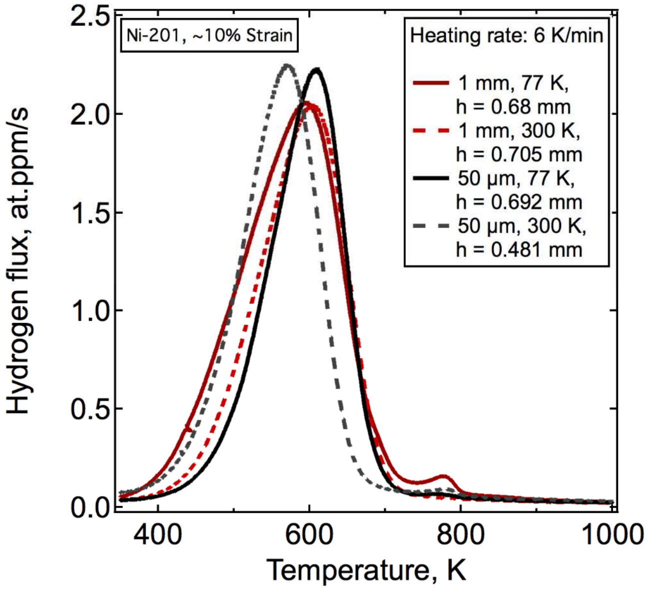


Fig. 1 Potential energy diagram of different states of hydrogen in a metal.

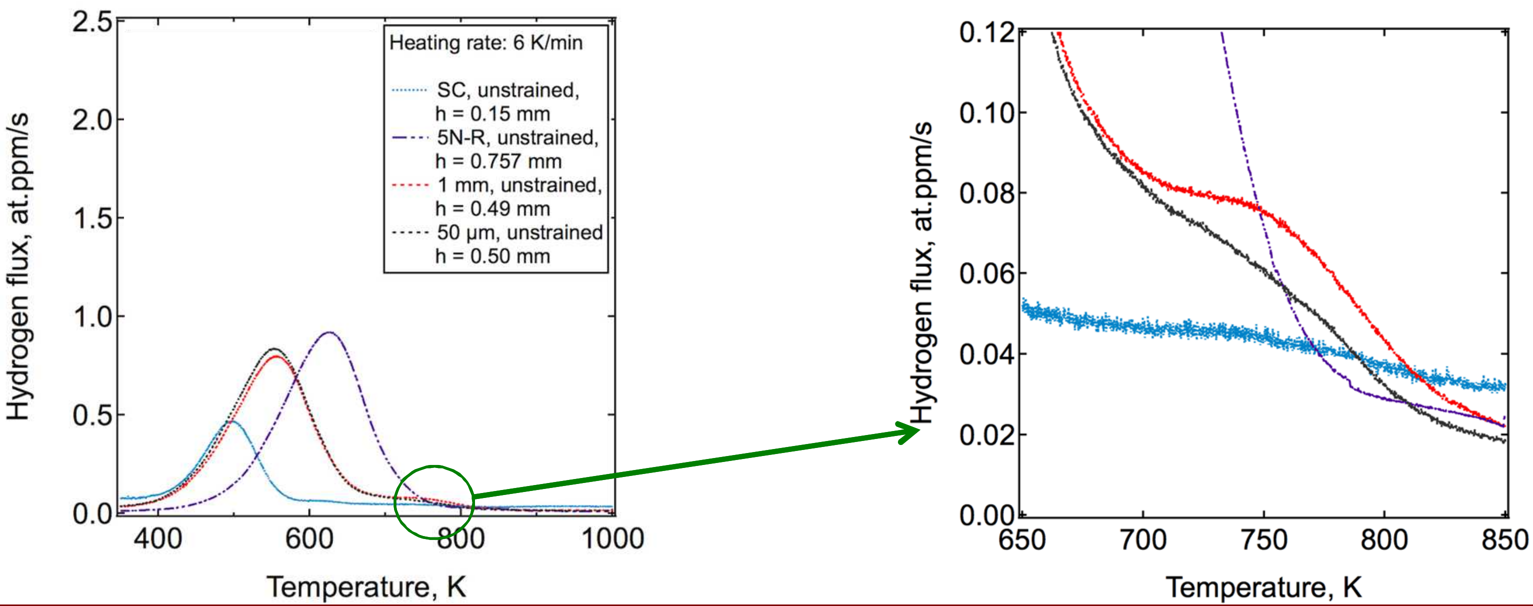


Izumi, T. and Itoh, G Mater. Trans. 2011; 52:130-134.

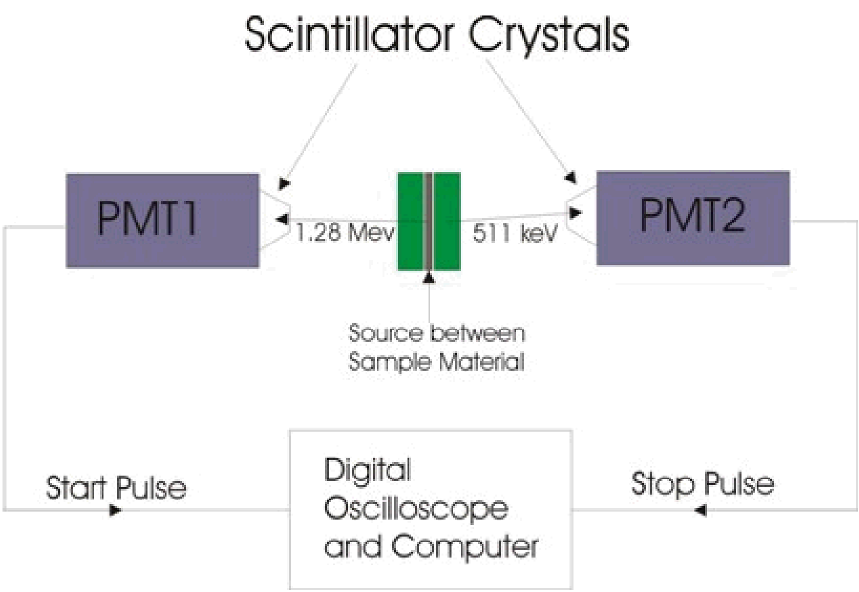
TDS Suggests Trap Sites Evolve with Processing

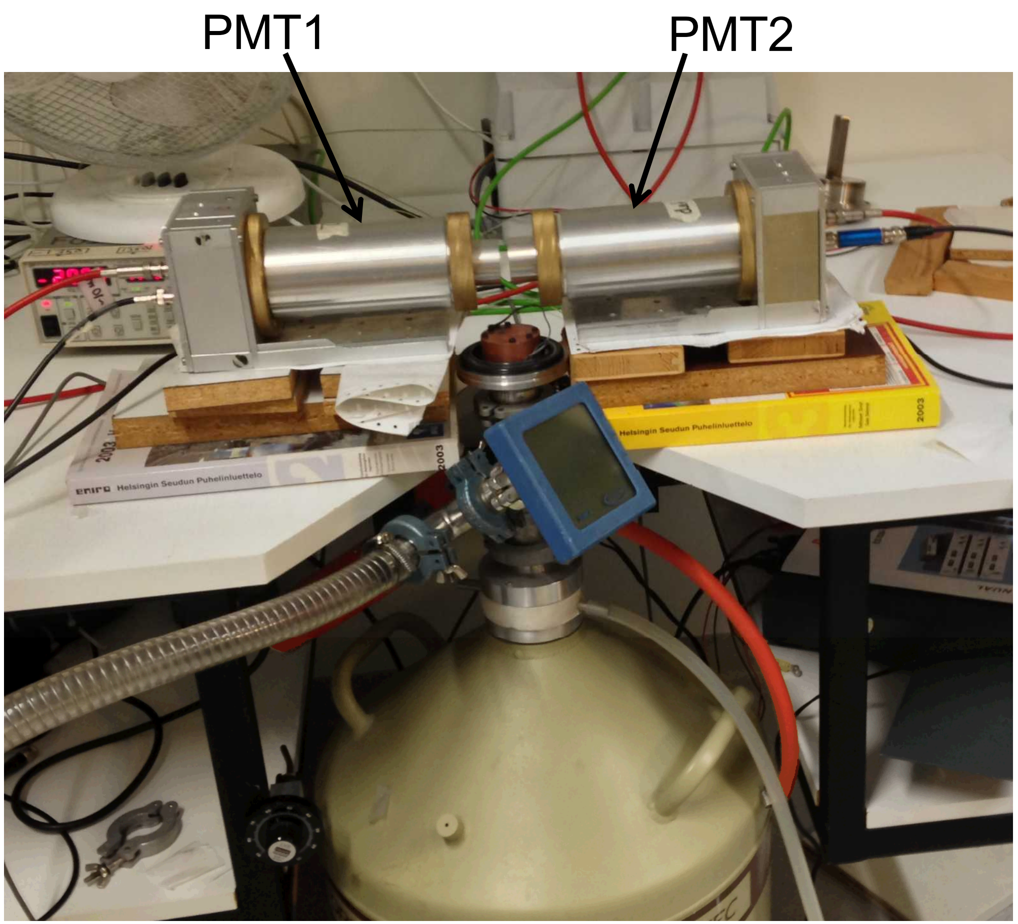


- Pre-charged and strained samples have c_H of ~3000 appm
- Main peak at ~600K
  - Pre-charged, unstrained samples have much lower c_H likely due to egress during ~16 hour cooling
- Secondary peak at ~750K for strained samples, shifts to ~770K for charged+strained samples corresponds release from stronger traps, like vacancy clusters

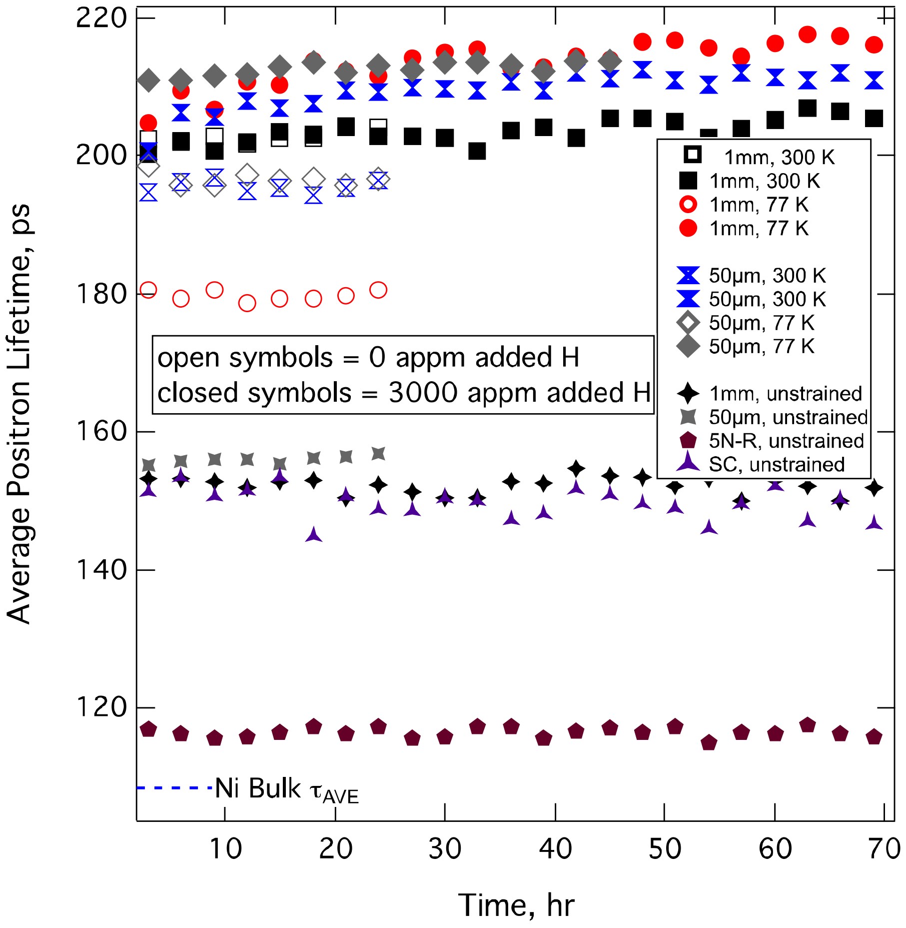


PAS Detects Free Volume Variation with H & ε





PAS Suggests Vacancies Created with H & ε



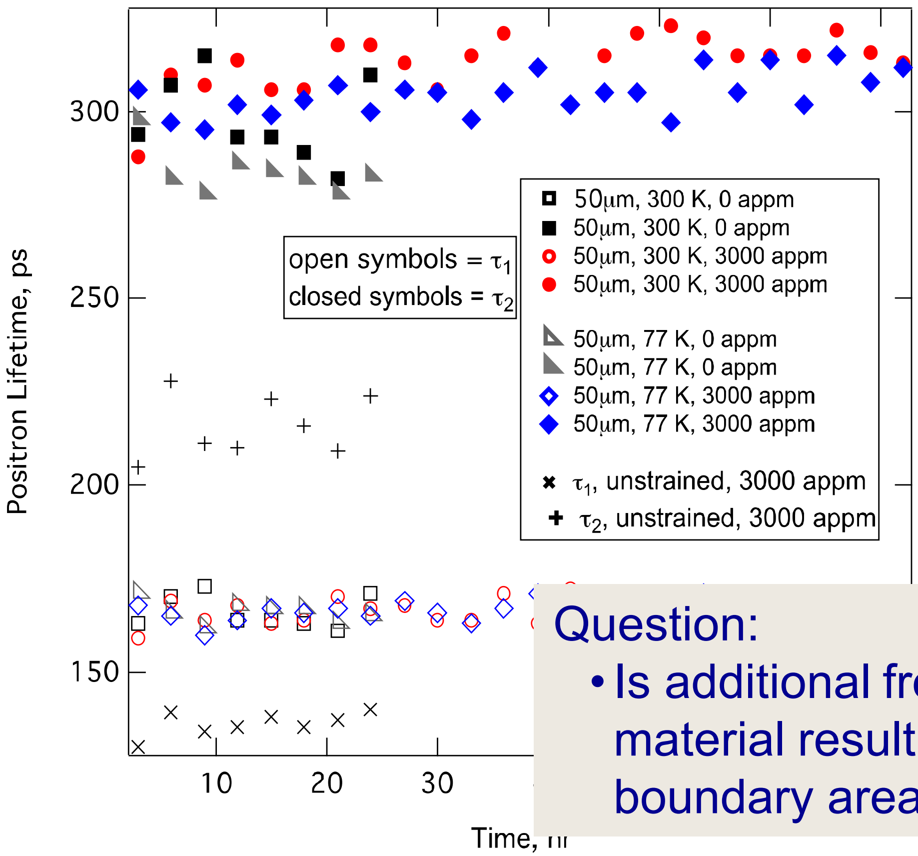
Statistical analysis suggests:

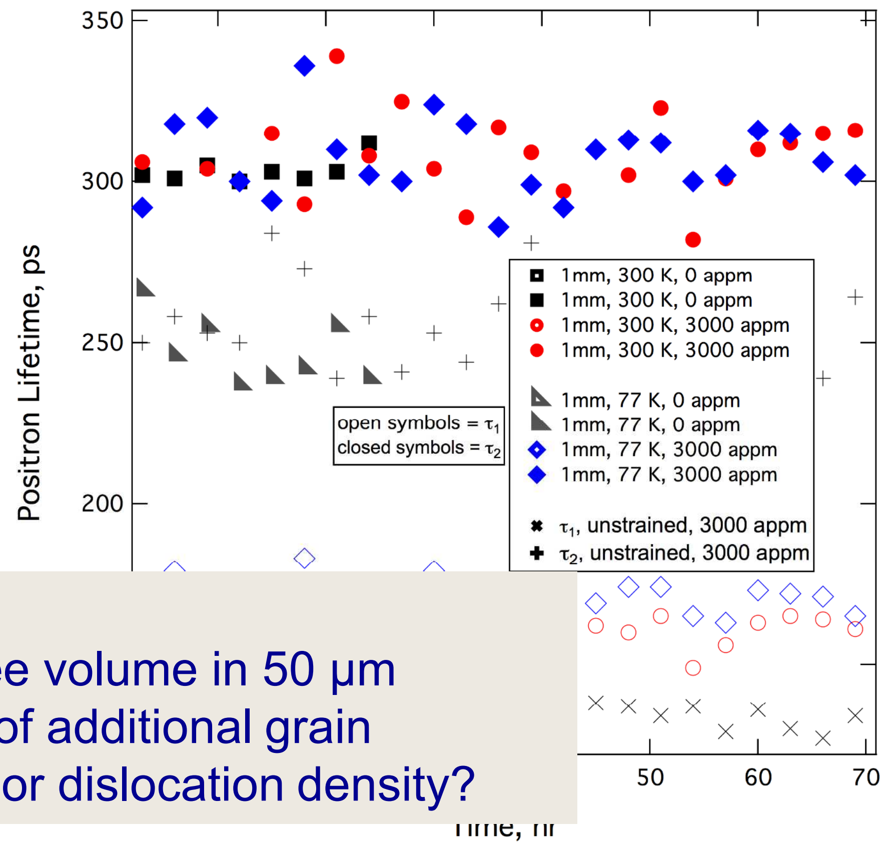
- Both strain and H-charging independently induce additional free volume in microstructure
- Grain size and deformation temperature affect τ values independently
- τ values and rate of increase tend to be higher for 50 μm material

Questions:

- What defects for straining vs. pre-charging & straining?
- Where is the free volume generated?
- What are temperature and grain size effects?

Temperature & Grain Size Impact Vacancies



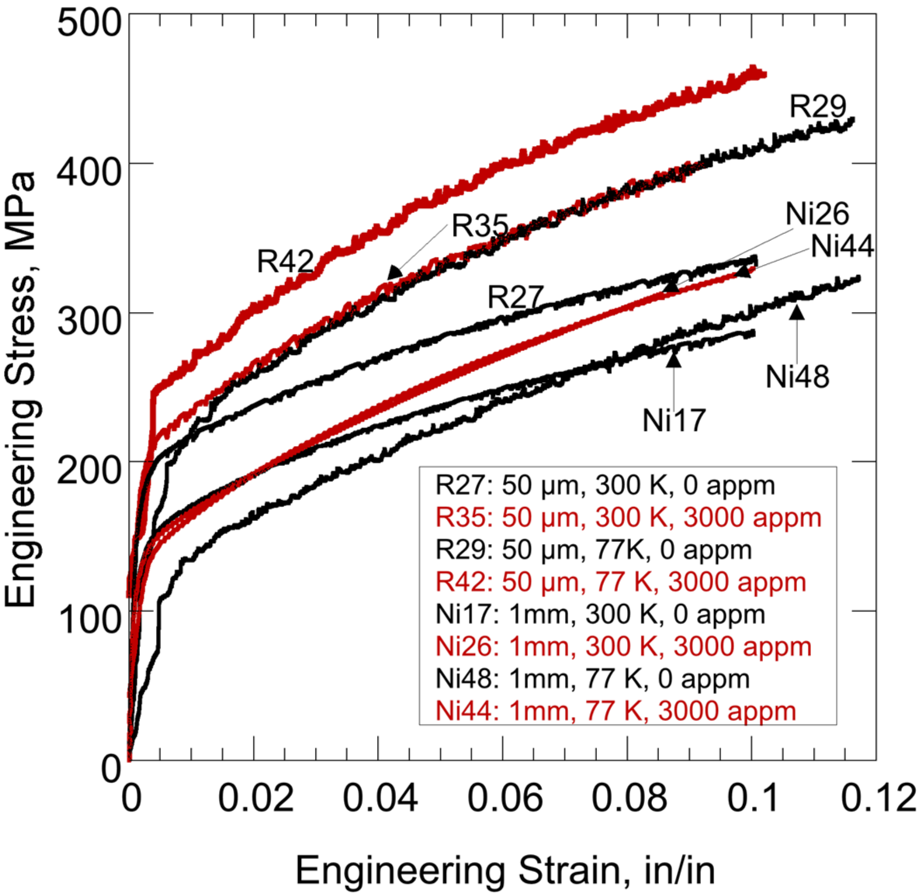


Question:

- Is additional free volume in 50 µm material result of additional grain boundary area or dislocation density?

- Non-unique τ_1: same defect type generated by independently straining or H-charging
- Unique τ_2 and increasing average values: H exacerbates generation of larger defects
- Increasing τ_2 most prominent for 50 µm grain size material
- τ_2 for material strained at 77 K slightly lower than at RT when not pre-charged
- τ_2 for material strained at 77 K considerably lower than at RT after H pre-charging

Yield Behavior Linked to H-enhanced Defects



Percent Change in Yield and Deformation Values

Sample	*YS*	*WH @ 6%*	*WH @ 8%*
50 µm, 300 K	8.1	57.7	68.8
50 µm, 77 K	52.0	15.8	12.2
1 mm, 300 K	0.03*	55.5	85.9
1 mm, 77 K	18.6	6.8	29.4

Summary & Conclusions

- Hydrogen enhances and stabilizes vacancies formed by thermal activation during elevated temperature hydrogen charging, as well as strain-induced vacancies, and encourages vacancy agglomeration.

- As grain size decreases, additional thermal vacancy sources become available and hydrogen enhances and stabilizes vacancy clusters formed from the increased monovacancy concentration.

- Ni-201 exhibits higher yield strength and work hardening when hydrogen-charged. Yield stress increases are most striking when hydrogen is immobile, suggesting vacancy clusters may induce dispersion-type strengthening. Conversely, solute drag effects and cross-slip restriction govern work hardening during room temperature deformation.

Results confirm hydrogen enhances free volume formation: does this free volume contribute to IG failure?

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Thank you! Questions?

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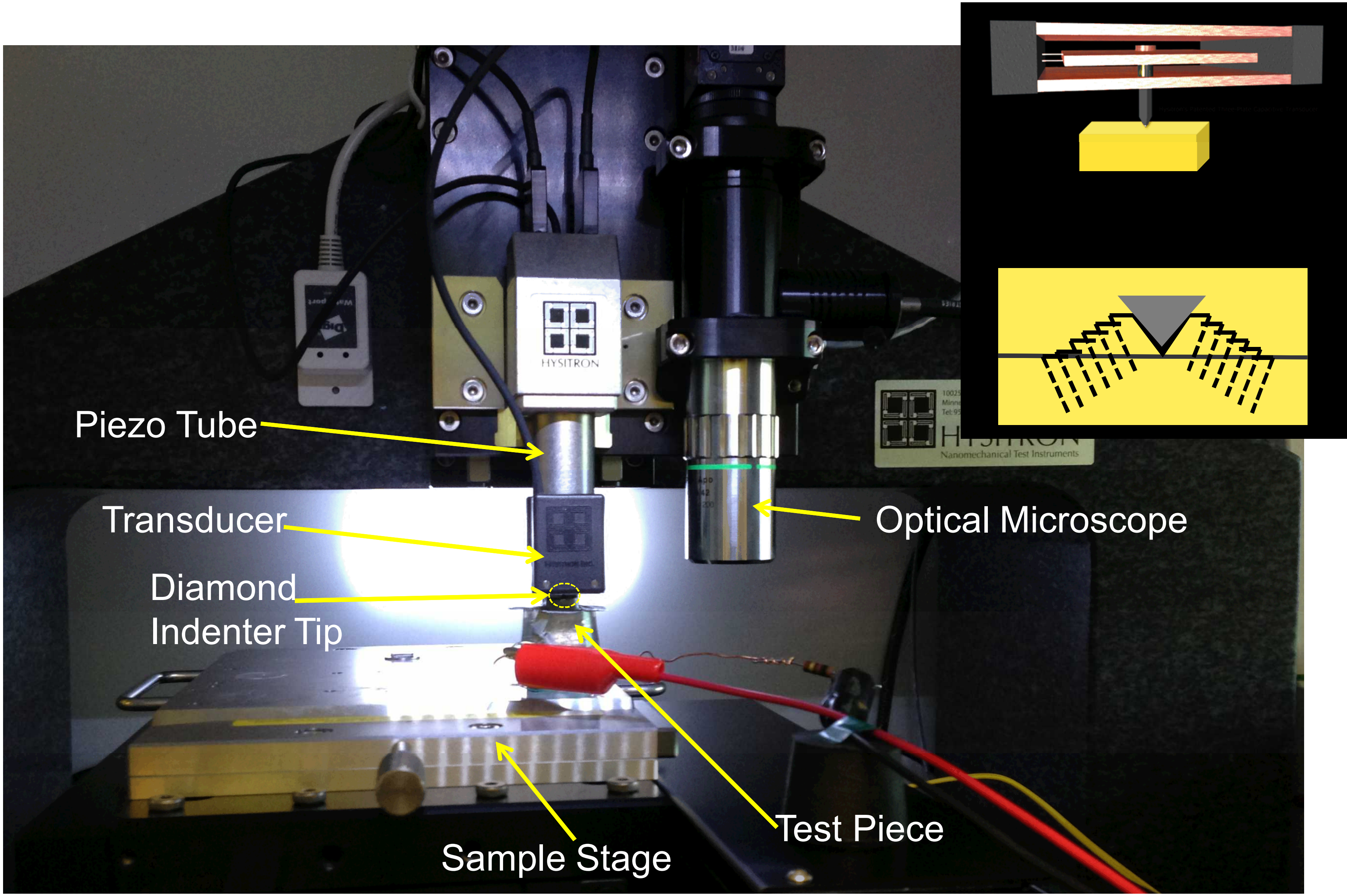
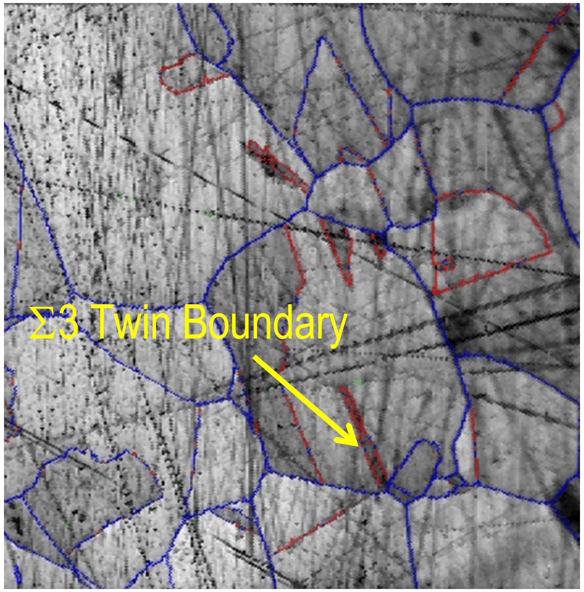
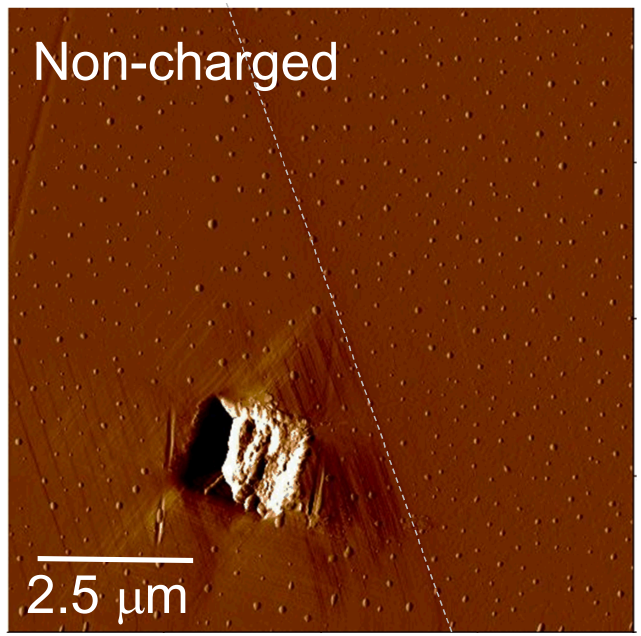
Backup Slides

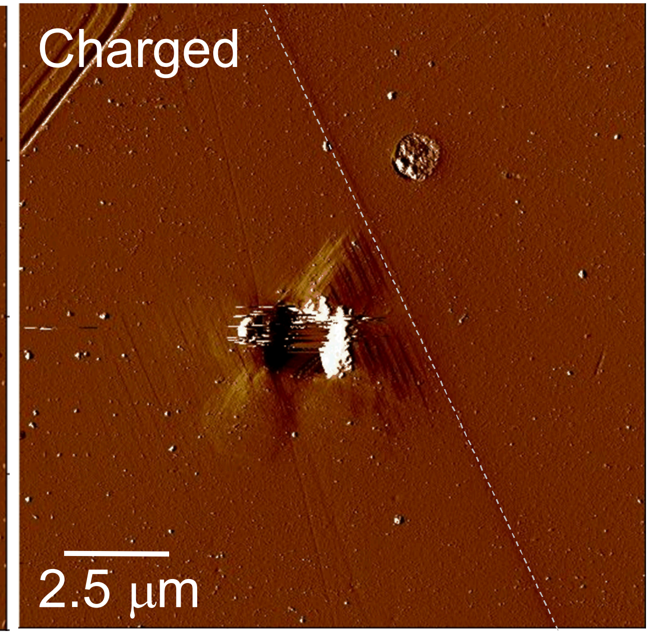
Nanoindentation: Background

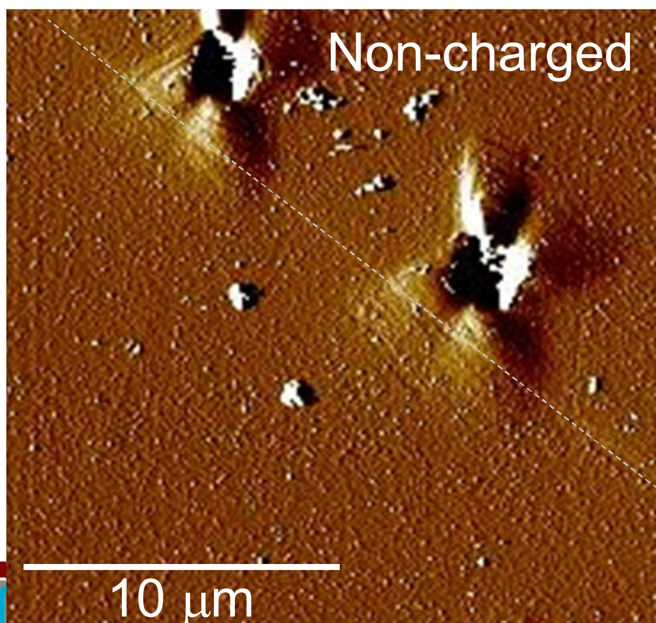


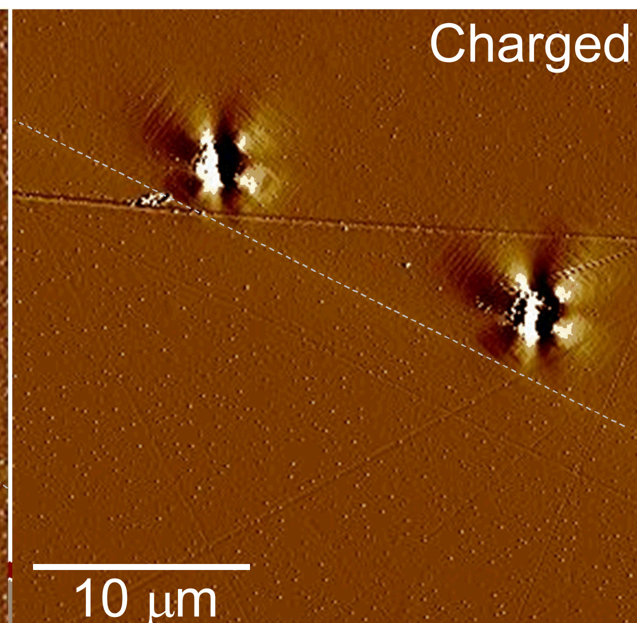
Boundary misorientation affects slip transmission

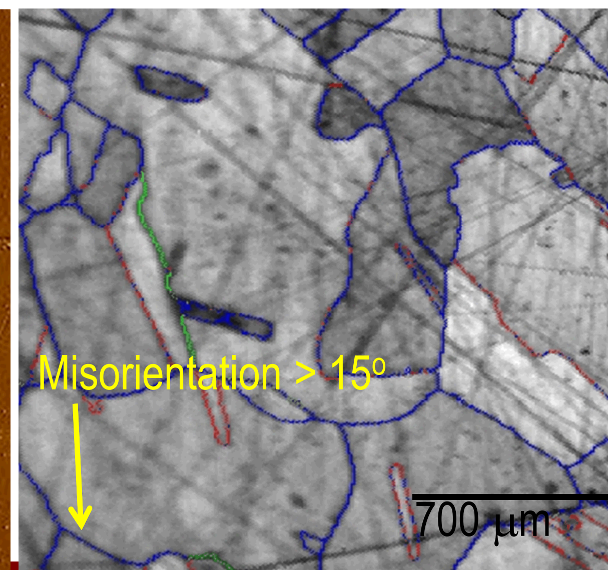




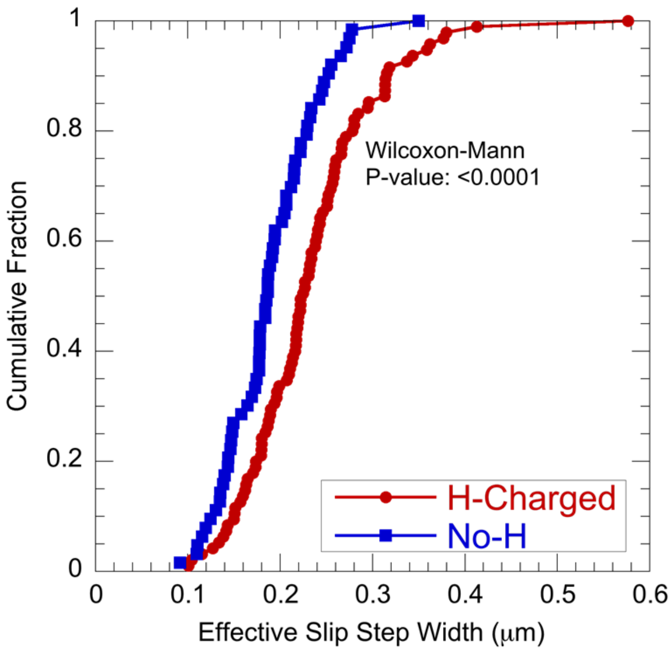


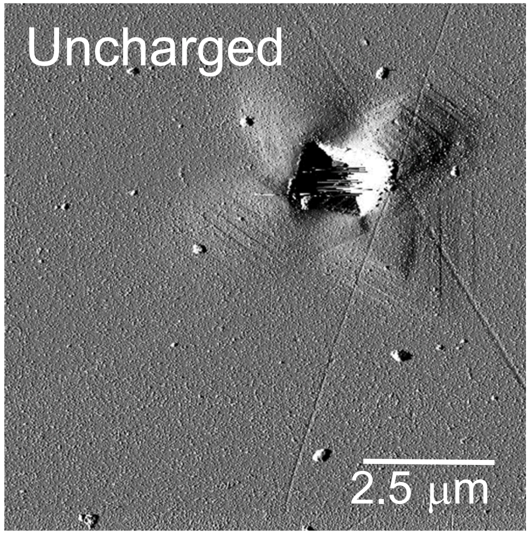


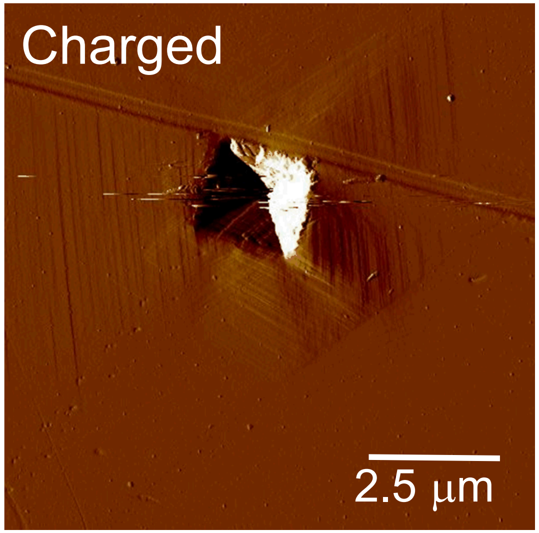




Hydrogen localizes slip induced by nanoindentation

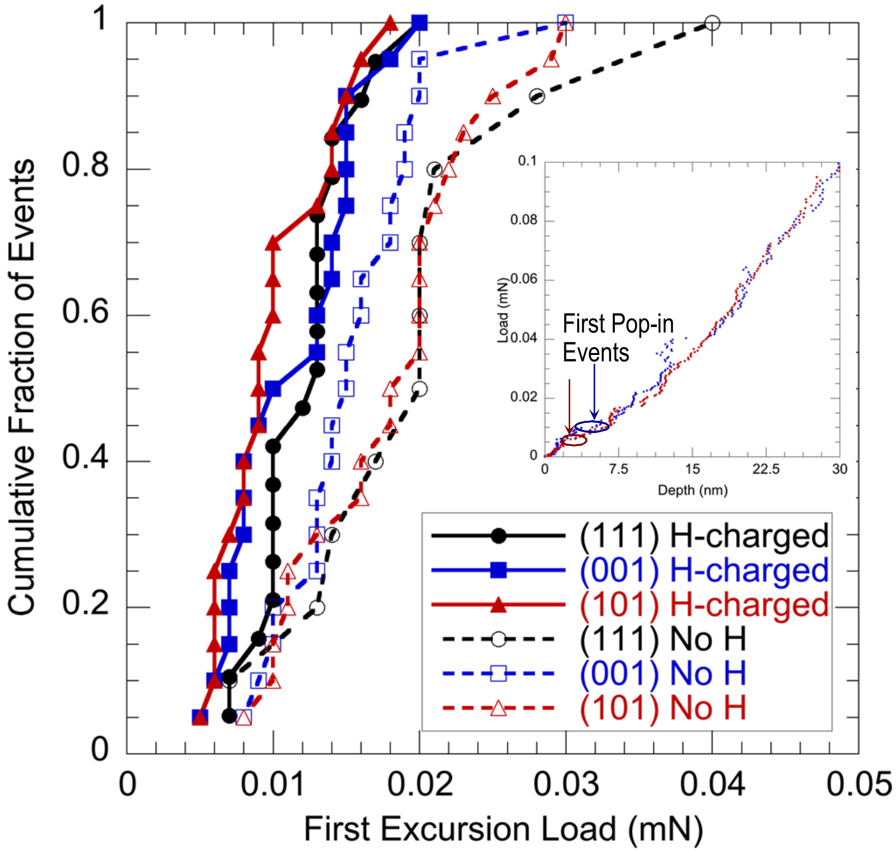


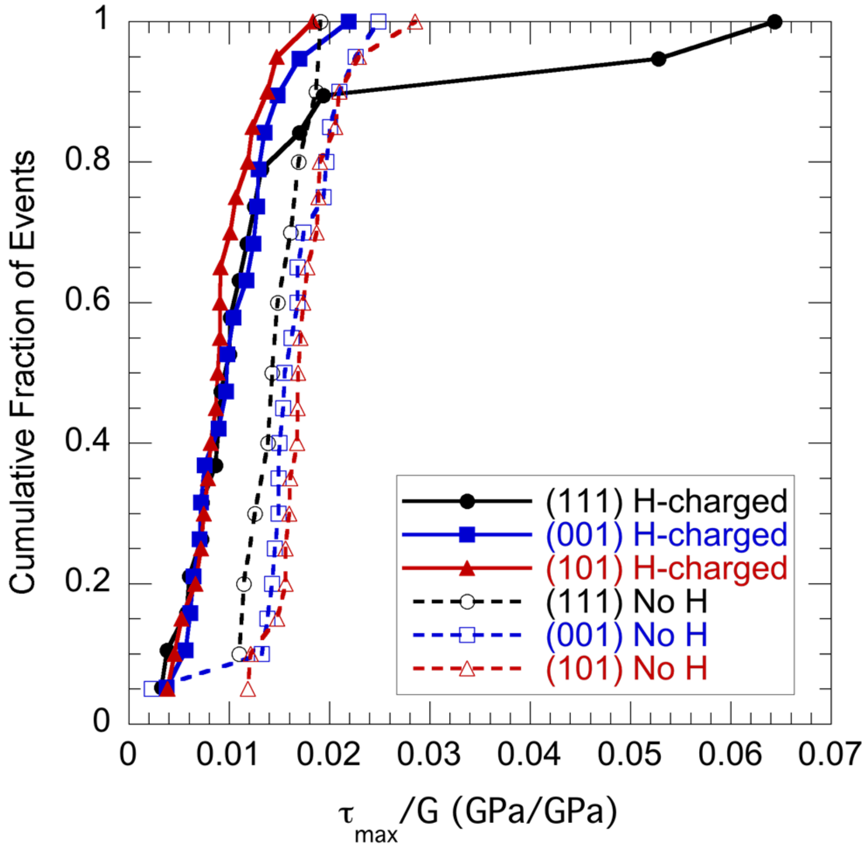




Indent Load (mN)	Normalized Pile-up Height, h/a (nm/nm)	
	Non-charged	*H-charged*
5	0.10	0.10
7	0.09	0.09
9	0.08	0.09

Shear stress to initiate plasticity decreases with H





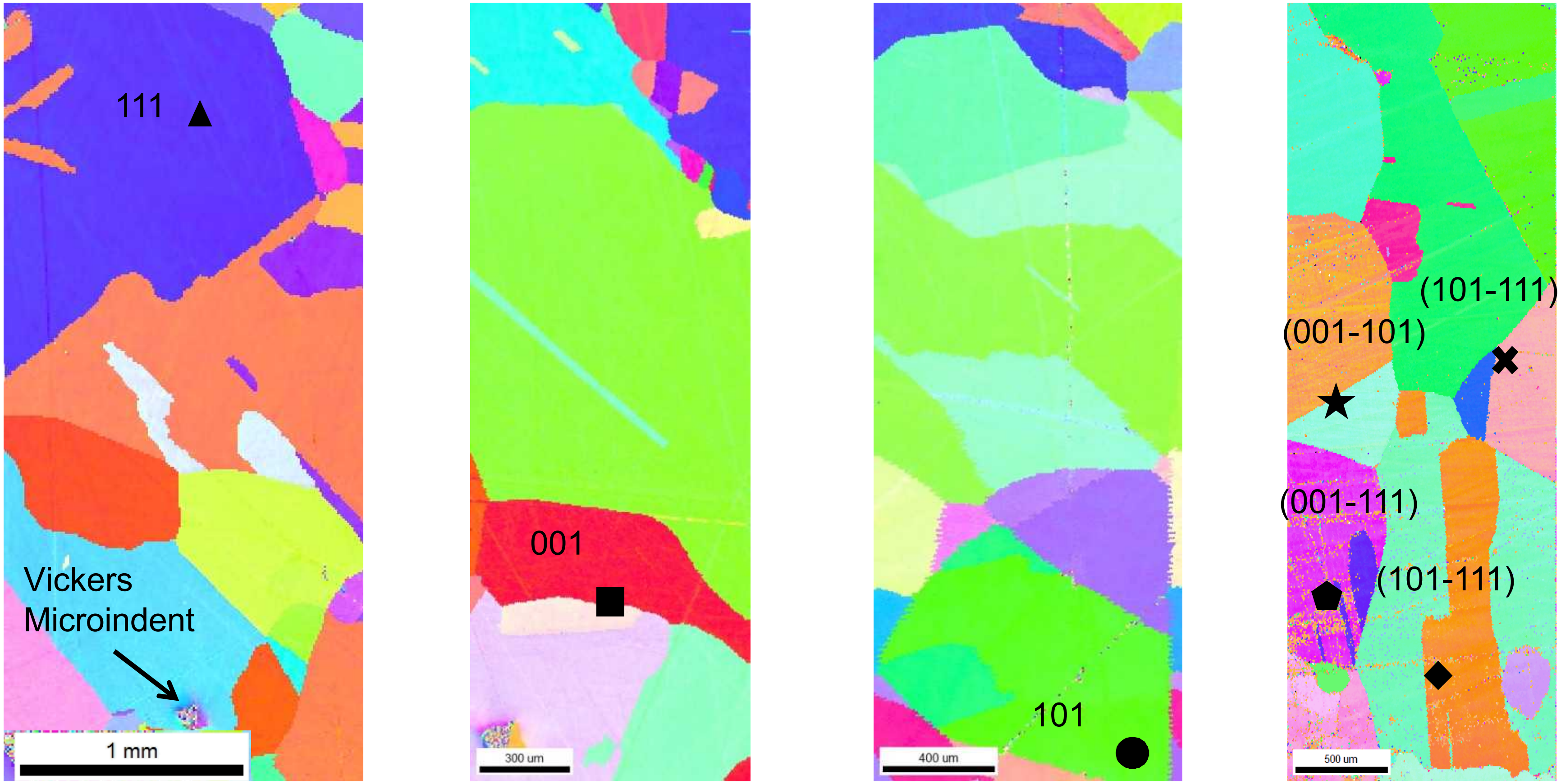
$$\tau_{max} = 0.31\left(\frac{6PE^*}{\pi^3 R^2}\right)^{1/3}$$

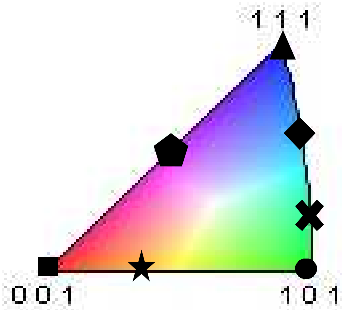
$$R = \frac{9P^2}{\delta^3 16E^{*2}}$$

$$\frac{1}{E^*} = \frac{(1-\nu^2)}{E} + \frac{(1-\nu_i^2}{E_i}$$

- *G* decreases ~26% with H
- Critical stress for dislocation nucleation decreases
- Orientation independent

Selected Grains: Cube directions & intermediate





Substantial *E* change, minimal *H* change with hydrogen

Orientation	Th. Modulus (GPa)	Indentation Modulus (GPa)		Hardness (GPa)	
	Calculated	*Non-charged*	*H-charged*	*Non-charged*	*H-charged*
001	194	202±7	155±12	2±0.2	2±0.2
101	215	209±6	171±15	2±0.1	2±0.2
111	222	224±7	180±33	2±0.2	2±0.9
001-111		221±17	179±19	3±0.5	2±0.3
001-101		228±16	177±21	3±0.2	2±0.3
101-111		224±12	190±24	3±0.3	2±0.3
101-111		218±21	189±18	3±0.4	2±0.2

- Verify measured property values are reasonable by comparing with theory, *via* Vlassak and Nix model:

$$M = 1.058\,\beta_{hkl}\left(\frac{E}{1-\nu^2}\right)_{isotropic}$$

Vlassak JJ, Nix WD. J Mech Phys Solids 1994;42:1223.