

Hydrogen-Enhanced Generation of 'Free-Volume' in the Course of Plastic Deformation of Ni-201

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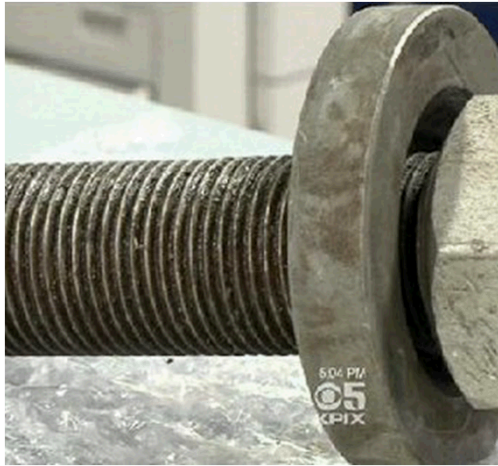
Hydrogen Degradation: Outline

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

Hydrogen in Metals: Relevant & complicated



<http://www.smdailyjournal.com/articles/news/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

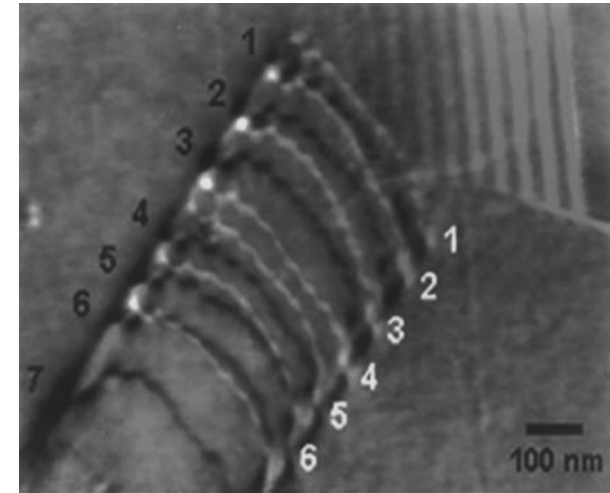
MOTIVATION:

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)

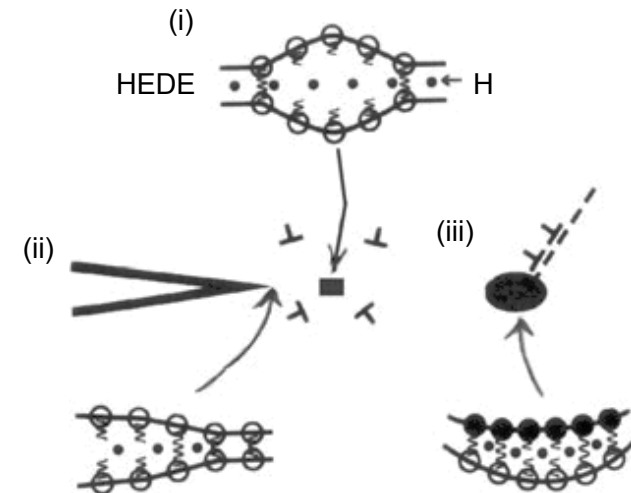
- Proposed to explain observed increase in strain localization prior to failure
- H shields barriers to dislocation motion, “free volume” generation can lead to flow localization



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

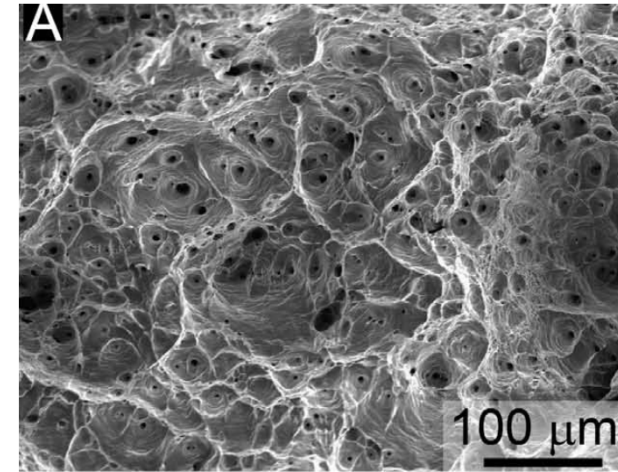


S.P. Lynch, Mechanisms of hydrogen assisted cracking – a review, pp. 449–466 in *Hydrogen effects on materials behavior and corrosion deformation interactions*, N.R. Moody, A.W. Thompson, R.E. Ricker, G.W. Was, and R.H. Jones (Eds), TMS, 2003.

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:

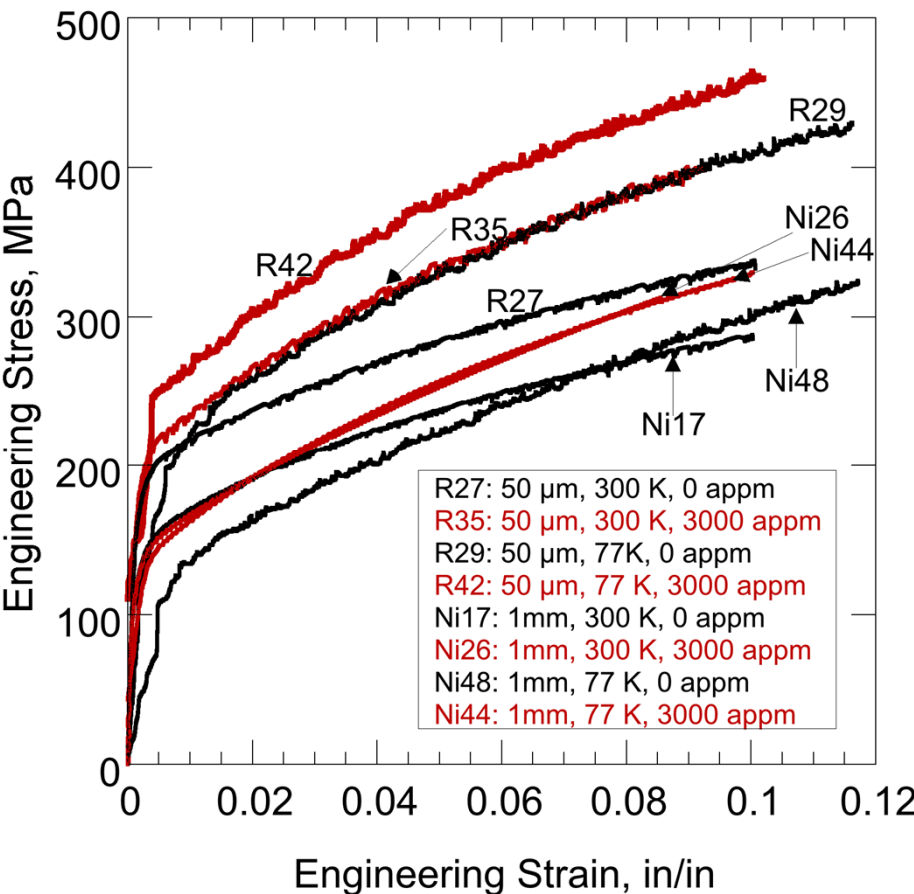
- Hydrogen-grain boundary interactions are dependent on misorientation
- Hydrogen inhibits cross-slip, but enhances slip localization
- Hydrogen induces measurable changes in mechanical properties
- GBE can lower propensity for hydrogen-induced intergranular failure

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 50 μ m 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°C for 144 hrs
 - 3000 appm hydrogen
4. Strain 50 μ m 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)

Measurable Change in Yield Behavior with H



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



Questions:

- Grain size contribution?
- Dislocation densities?
- Contribution of hydrogen and strain-induced free volume?

TDS Suggests Trap Sites Change with Processing

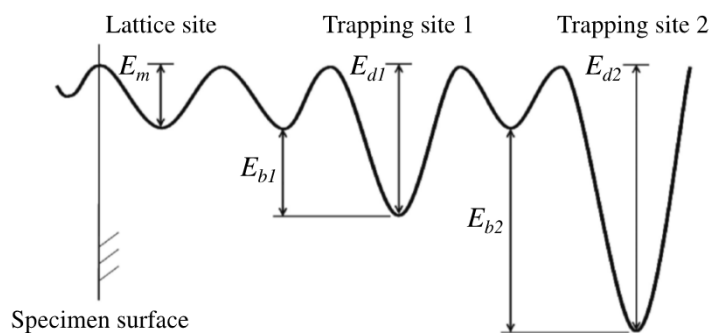
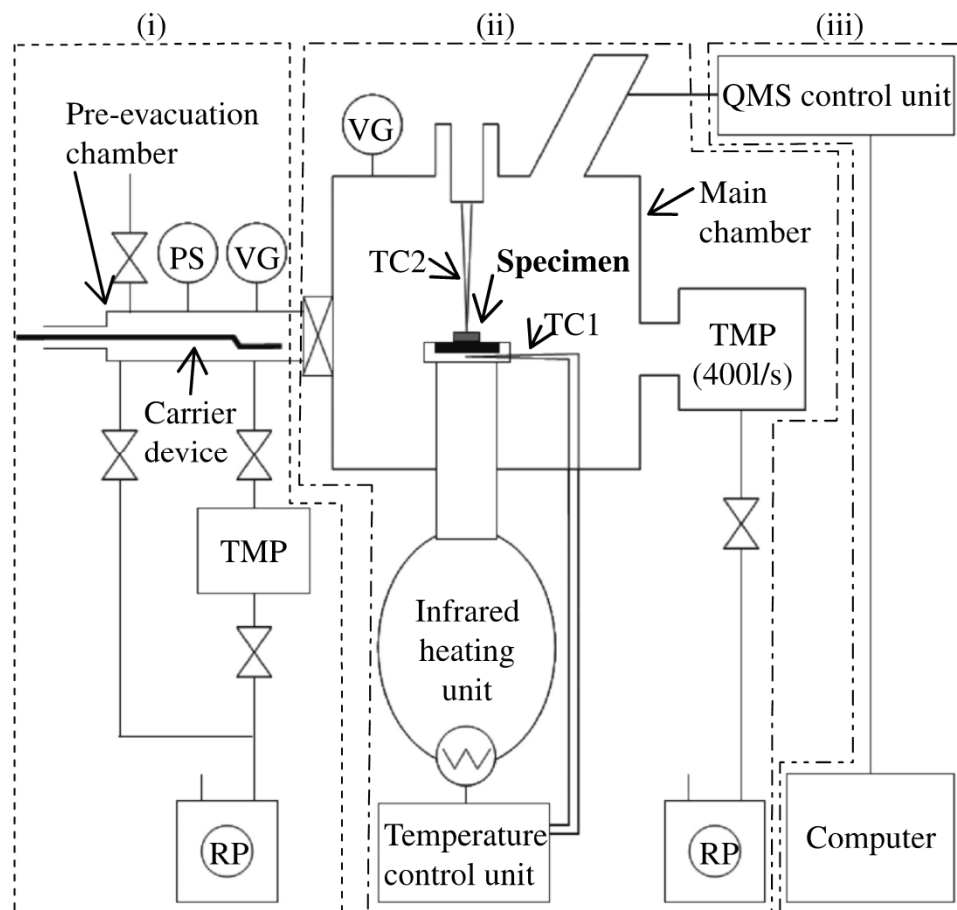
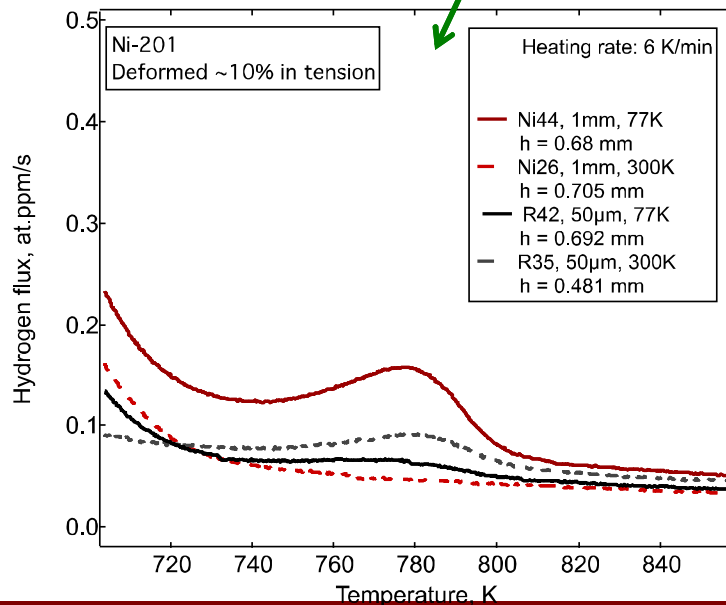
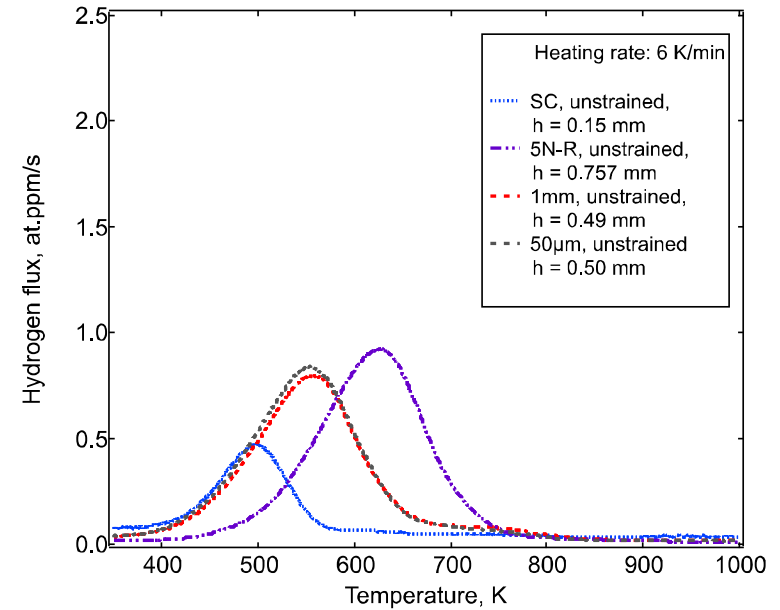
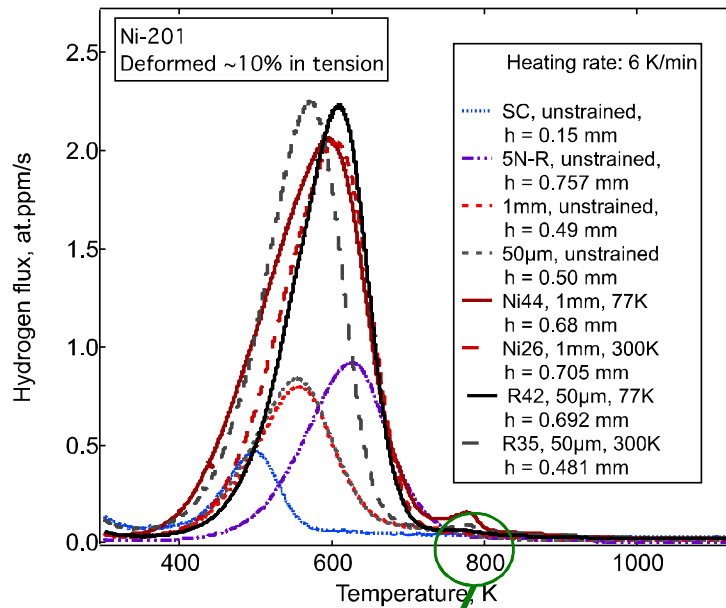


Fig. 1 Potential energy diagram of different states of hydrogen in a metal.

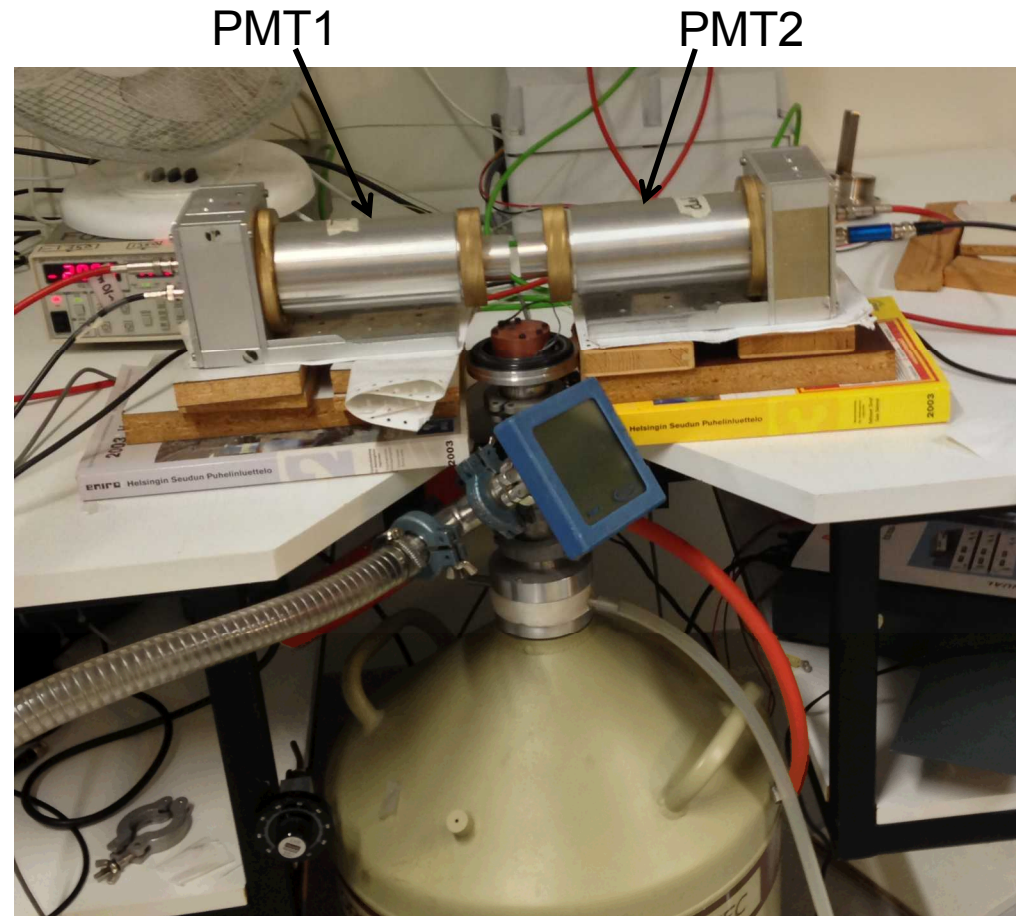
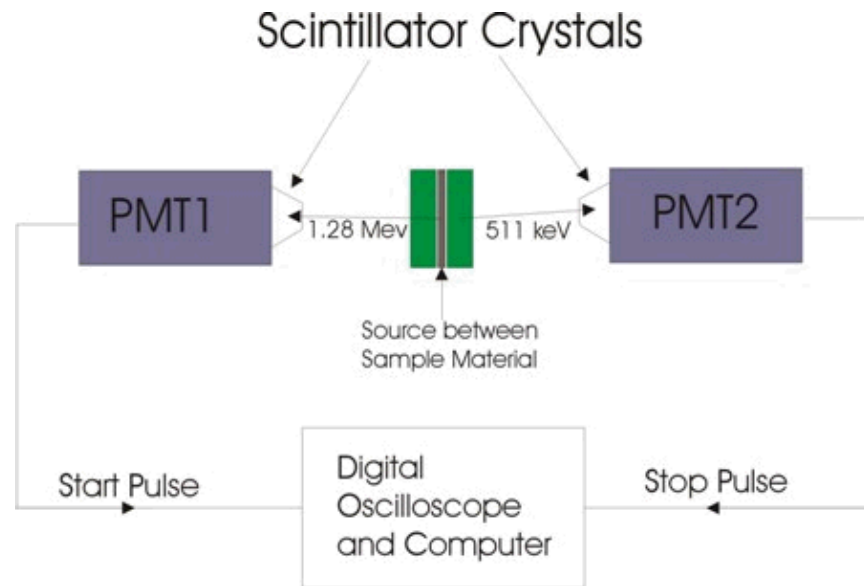


TDS Suggests Trap Sites Change with Processing

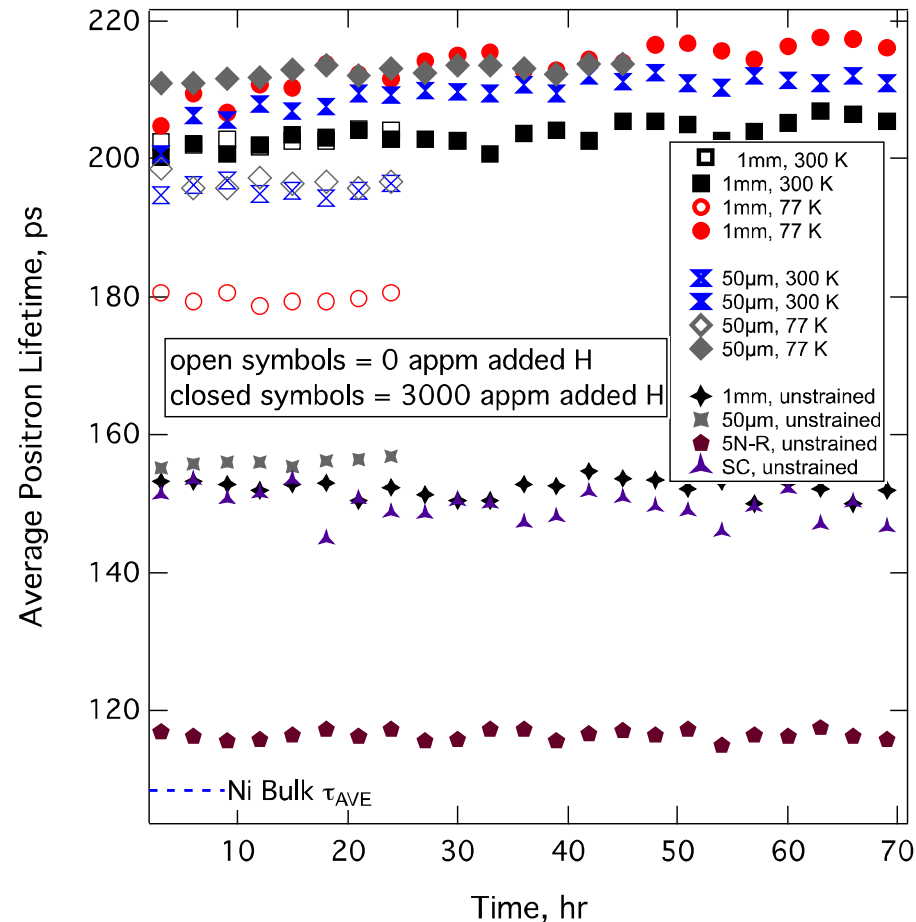


- Pre-charged and strained samples have c_H of ~3000 appm
- Main peak at ~600K
 - Pre-charged, unstrained samples have much lower c_H likely due to egress during ~16 hour cooling
- Secondary peak at ~770K for strained samples, corresponding to desorption from deformation induced vacancy clusters

PAS Suggests Free Volume Created with H & ϵ



PAS Suggests Free Volume Created with H & ϵ



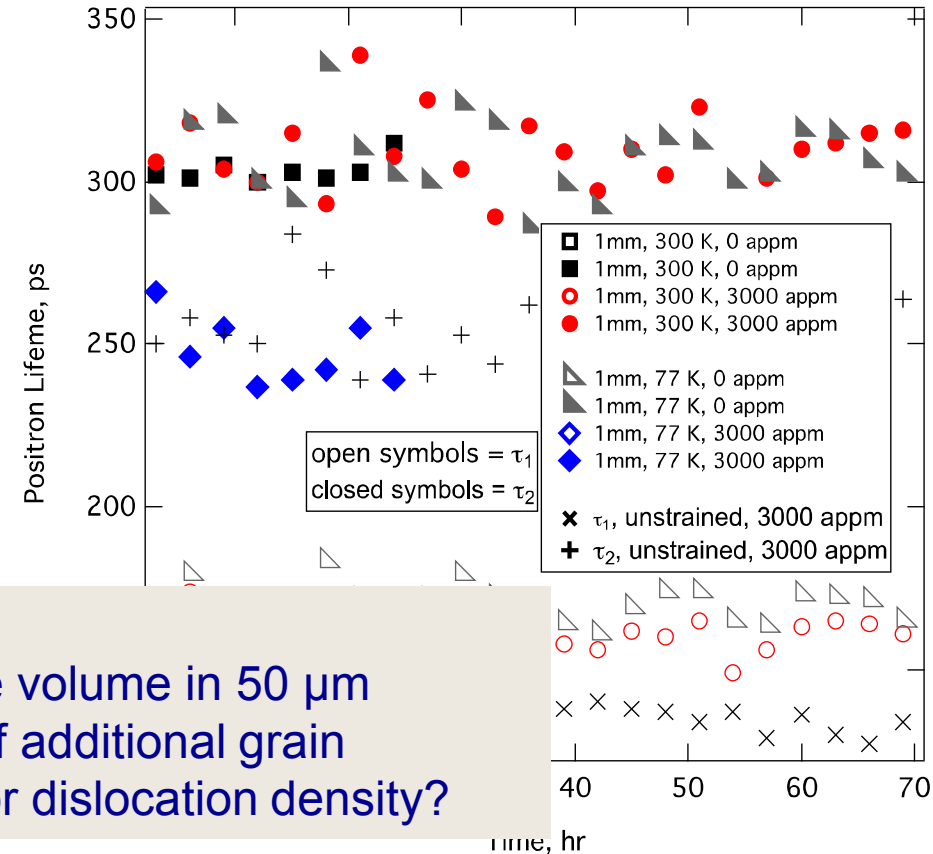
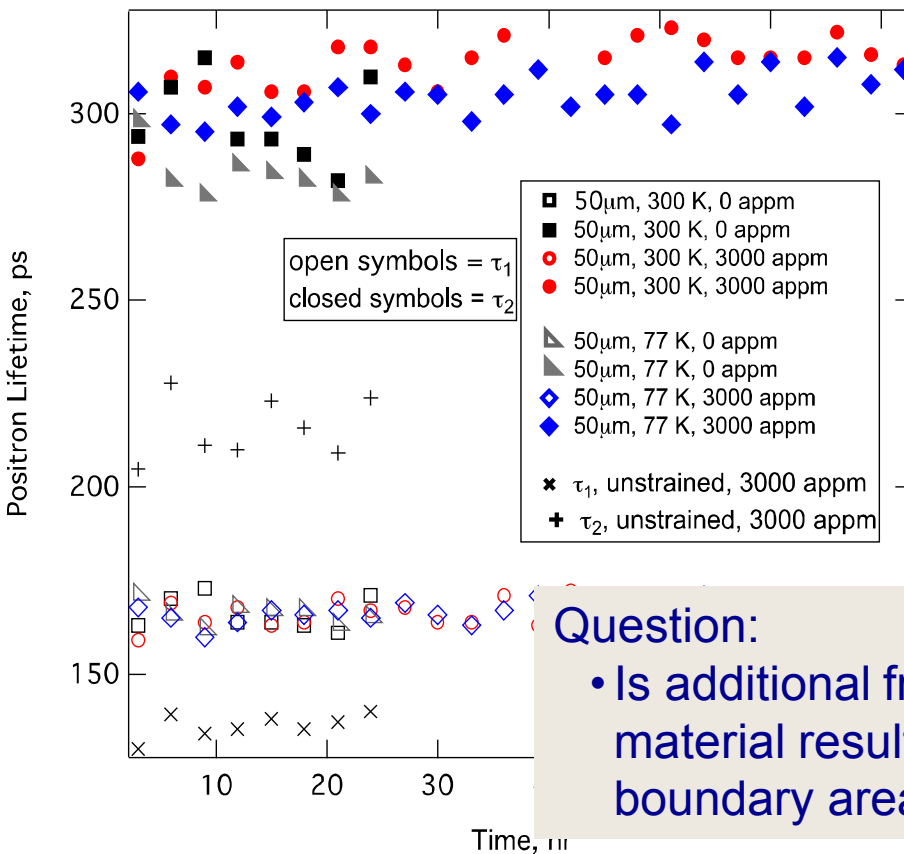
Statistical analysis suggests:

- Both strain and H-charging independently induce additional free volume in microstructure
- Induced defects are not recovered in the absence of annealing
- Grain size and deformation temperature affect τ values independently
- τ values and rate of increase tend to be higher for 50 μ m 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 PAS Data



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

Summary & Conclusions

- Ni-201 exhibits higher yield strength and increased work hardening when hydrogen-charged, particularly when the hydrogen is immobile, suggesting solute H is not responsible for increased flow stress. Other microstructural modifications are governing factors.
- Thermal precharging and precharging+straining of Ni-201 exacerbates the generation and coalescence of large vacancy clusters or voids.
- Larger grain boundary area (smaller grain size) magnifies the effect, suggesting grain boundaries are sites for free volume nucleation.

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

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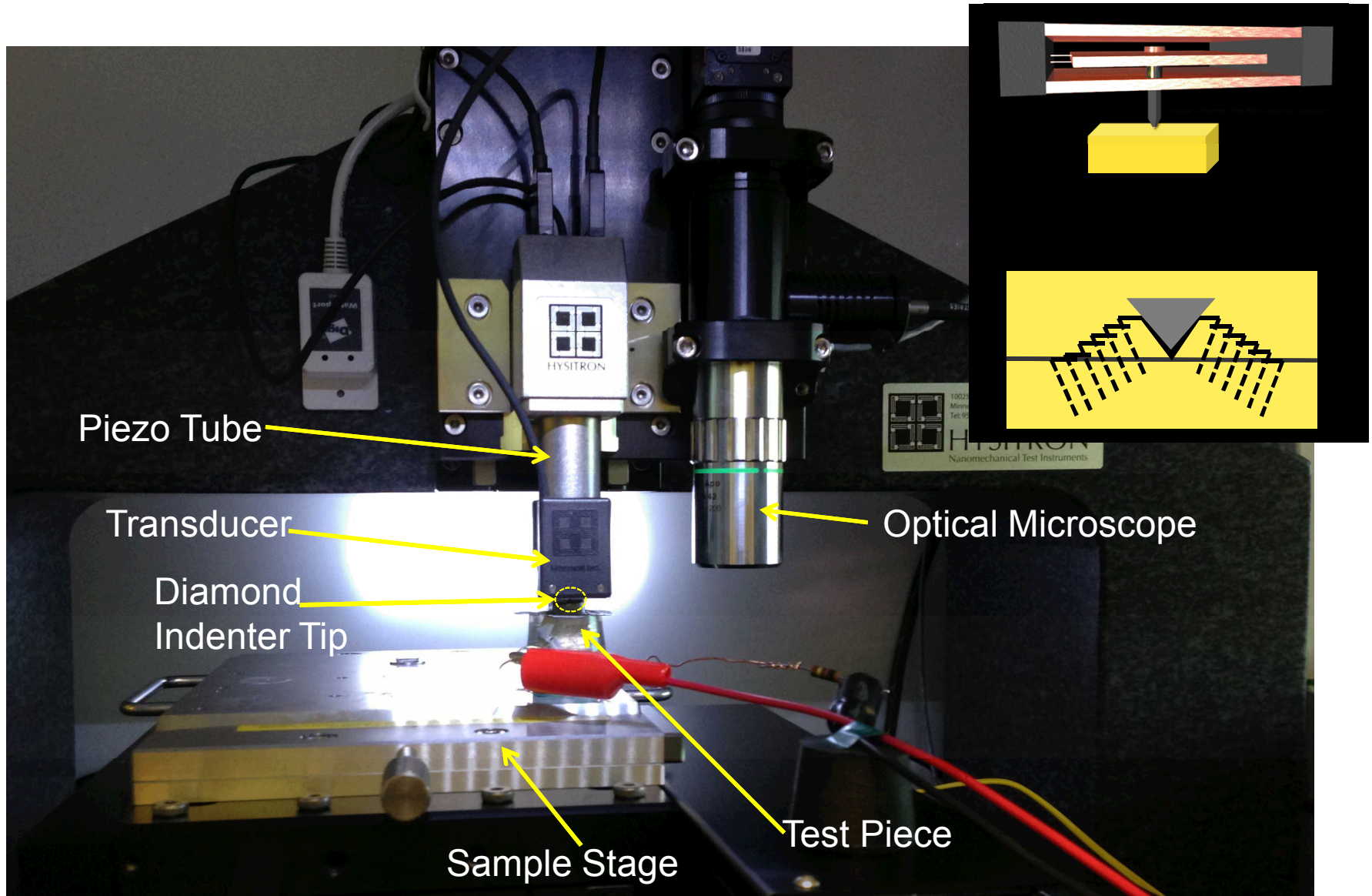
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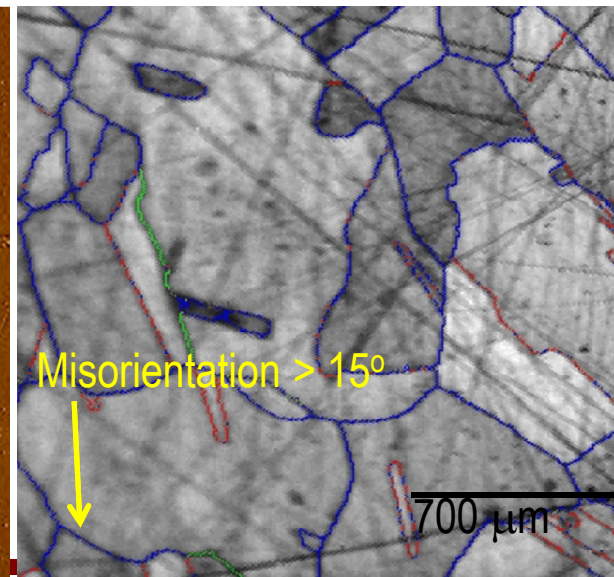
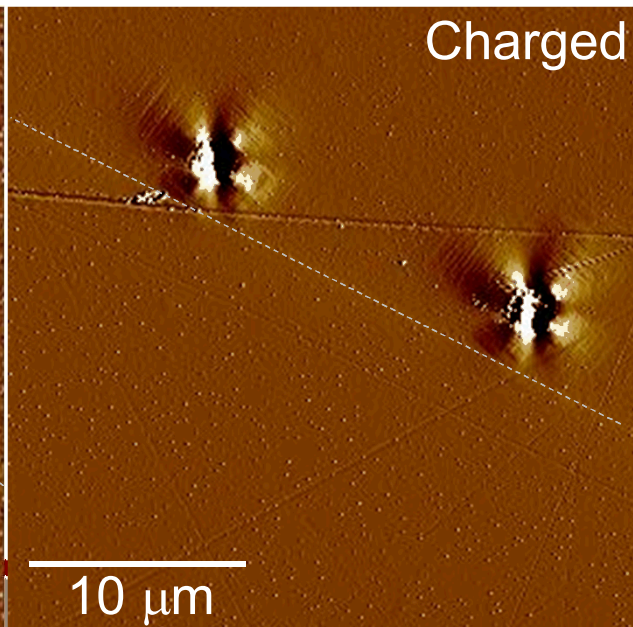
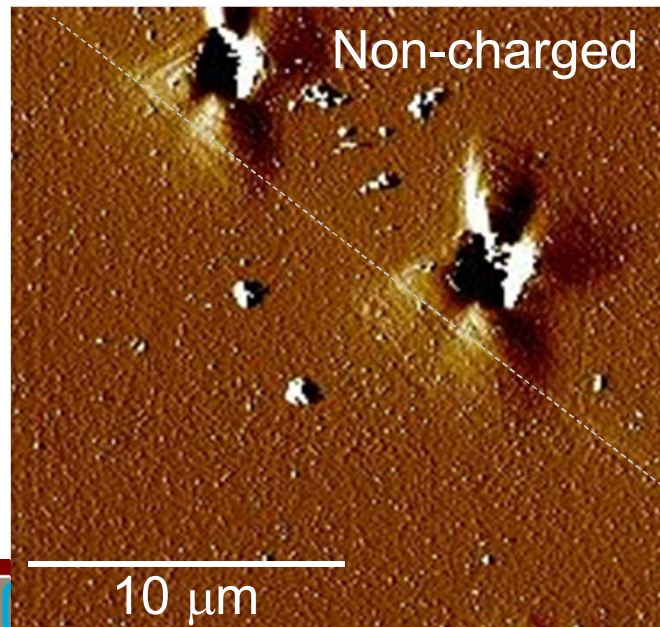
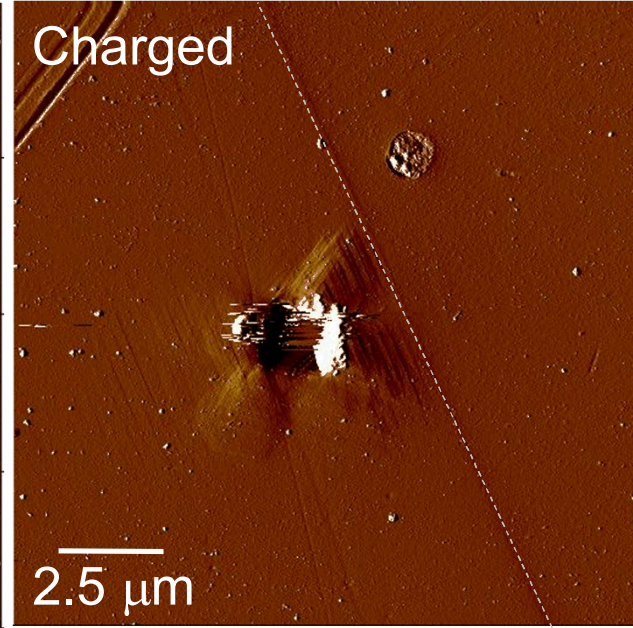
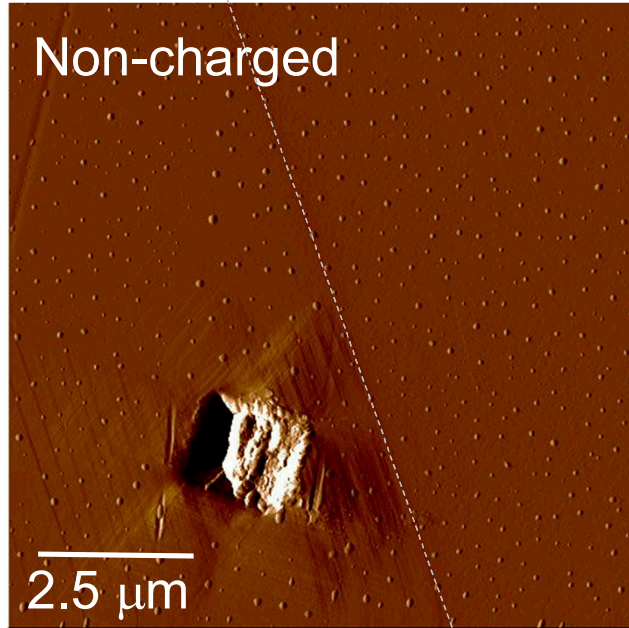
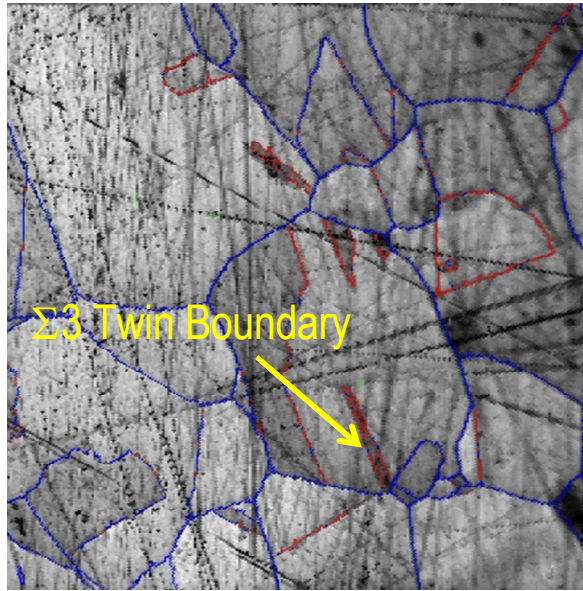
Results confirm hydrogen enhances free volume formation: does this free volume contribute to IG failure?

Backup Slides

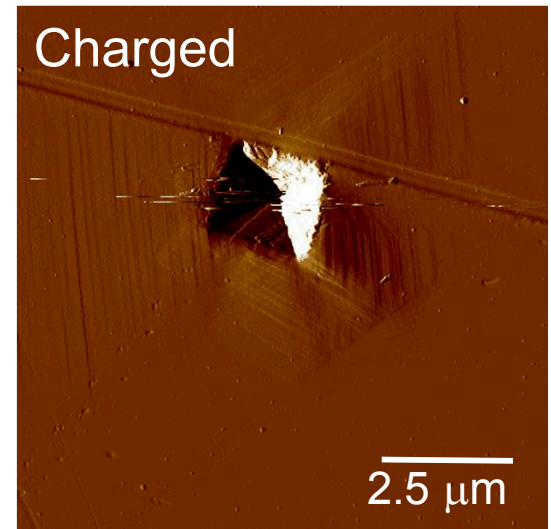
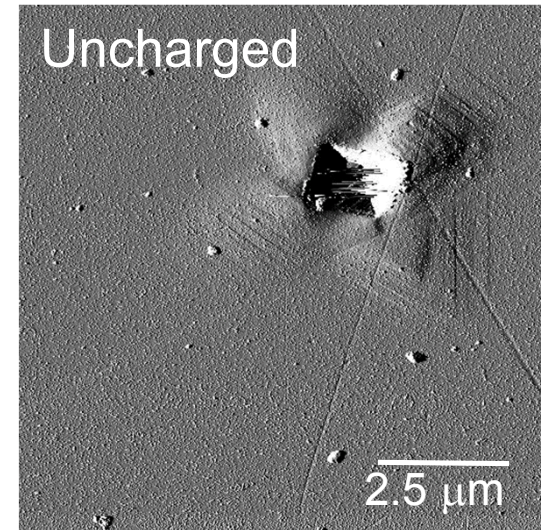
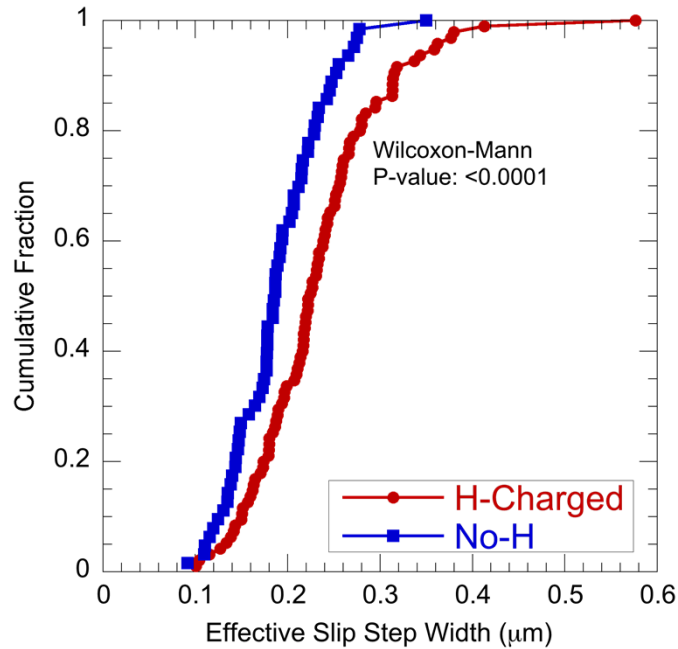
Nanoindentation: Background



Boundary misorientation affects slip transmission

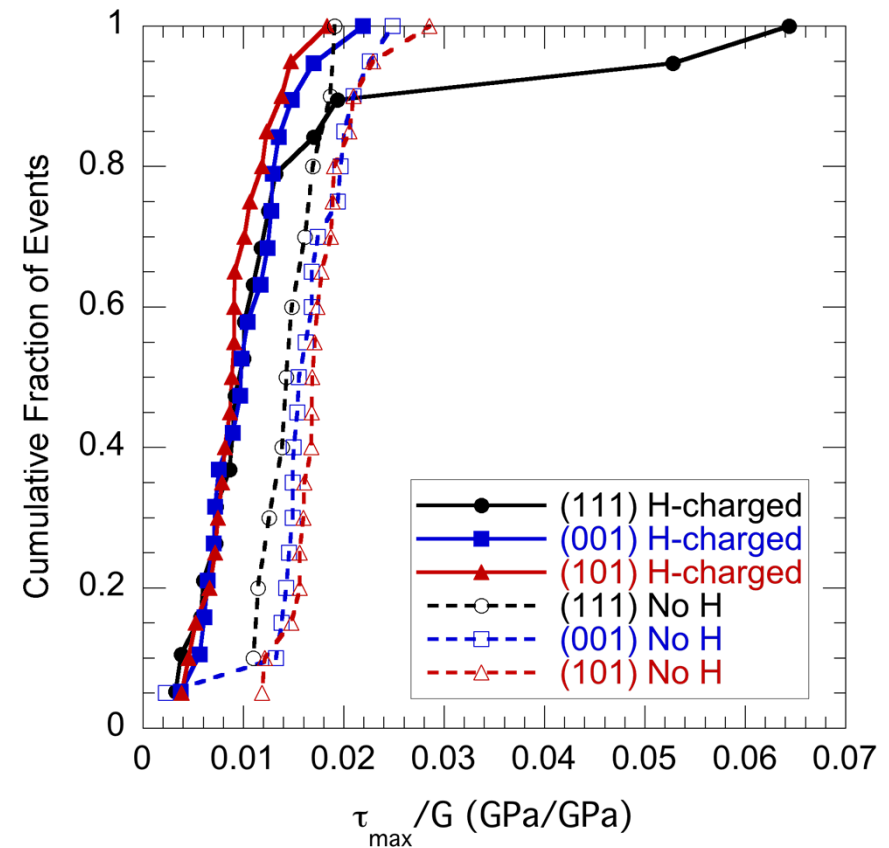
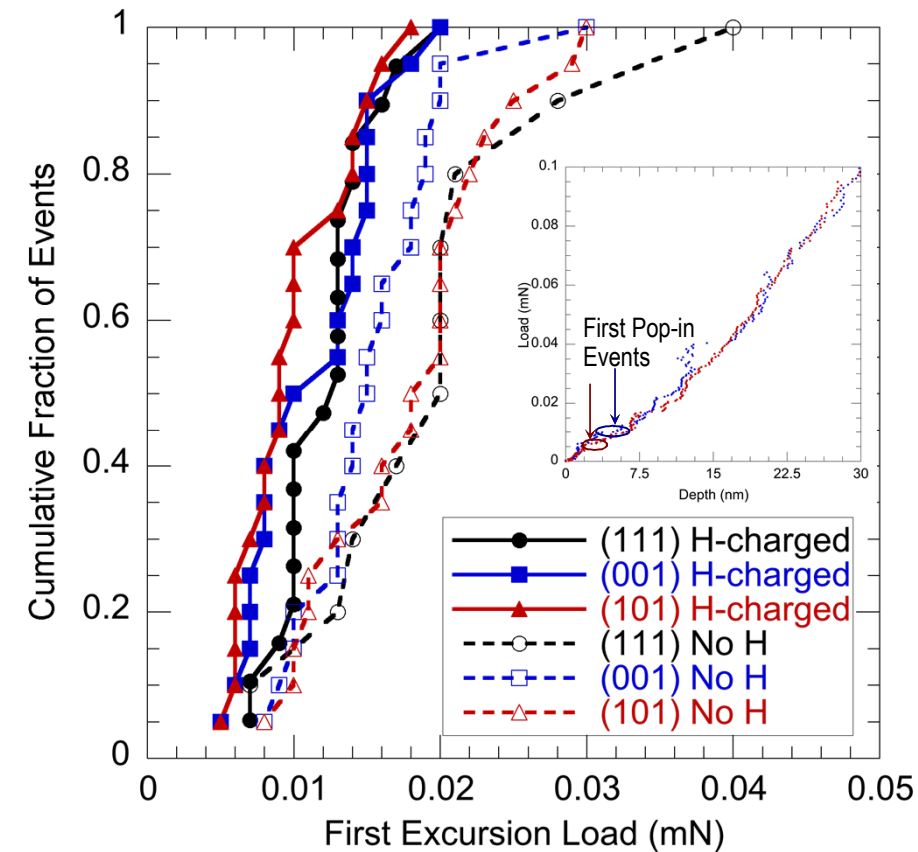


Hydrogen localizes slip induced by nanoindentation



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

Shear stress to initiate plasticity decreases with H

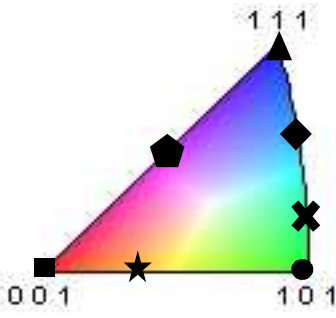
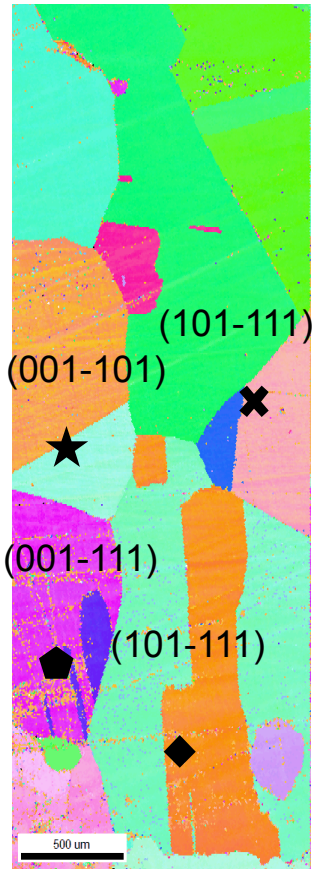
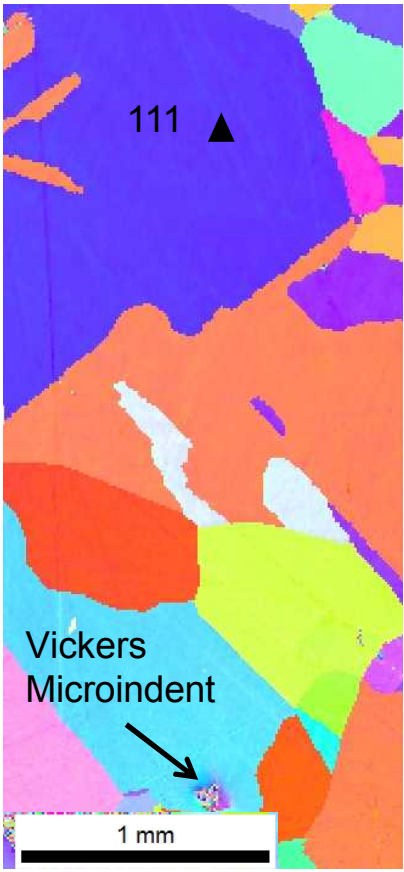


$$\tau_{max} = 0.31 \left(\frac{6PE^*}{\pi^3 R^2} \right)^{1/3}$$

$$R = \frac{9P^2}{\delta^3 16E^{*2}} \quad \frac{1}{E^*} = \frac{(1-\nu^2)}{E} + \frac{(1-\nu_i^2)}{E_i}$$

- G decreases $\sim 26\%$ 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)	
	<i>Calculated</i>	<i>Non-charged</i>	<i>H-charged</i>	<i>Non-charged</i>	<i>H-charged</i>
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:

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