

Metrics, trends and capabilities for evaluating hydrogen effects in metals

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H-Mat Kick-off Meeting

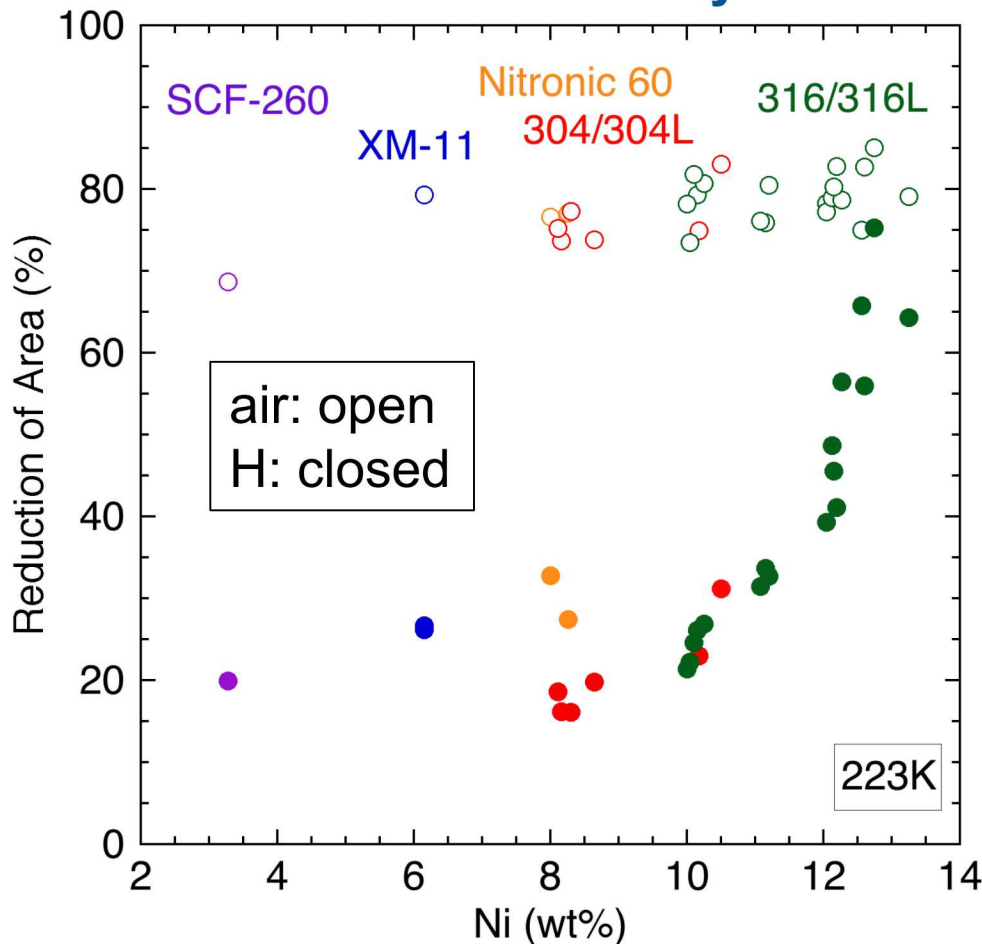
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Outline

- **Metrics and Targets**
 - Why do we need them?
 - What does ‘better than’ mean?
 - What is a meaningful metric/target?
- **Demonstrate importance of quantitative metrics with data trends**
- **Describe high-pressure capabilities at Sandia**

Extensive database exists for tensile behavior of γ -stainless steels in hydrogen environments

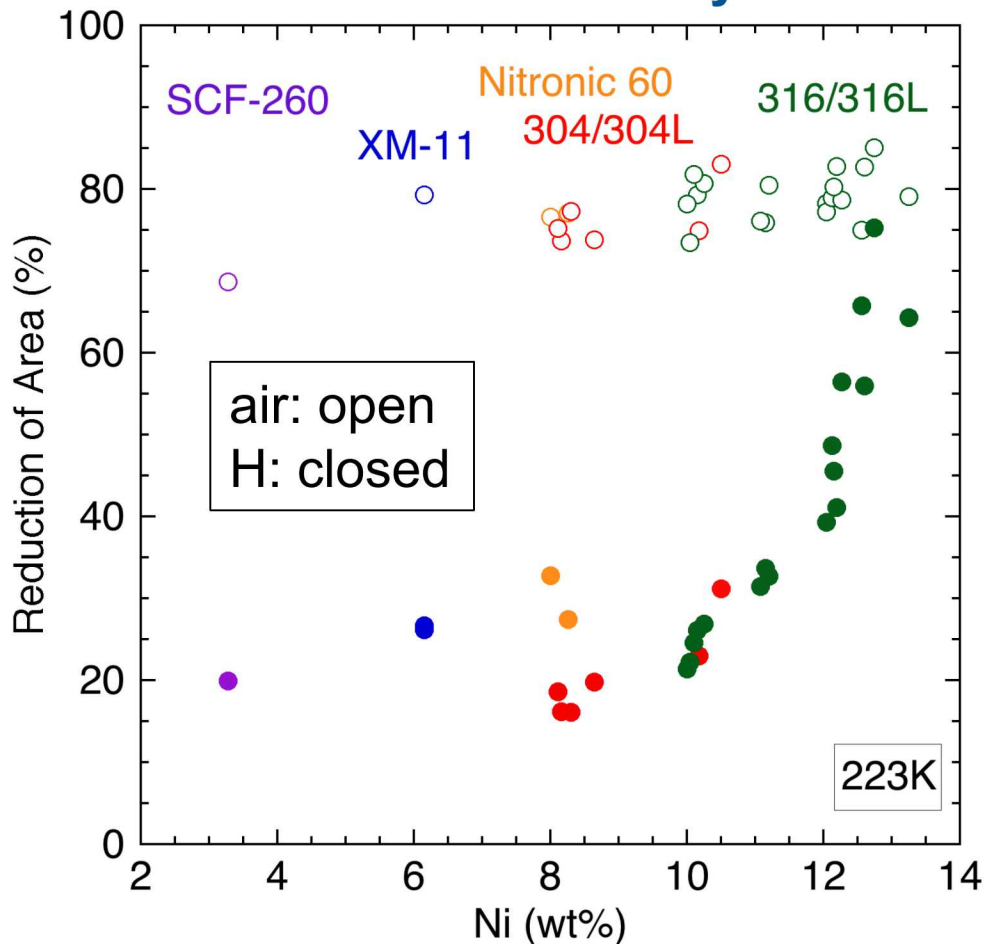
Tensile ductility



- Strength properties are generally not affected by hydrogen
- Nickel correlates with ductility in hydrogen as well as any other indicator
- Austenite stability is not as good an indicator when nitrogen-strengthened alloys are considered

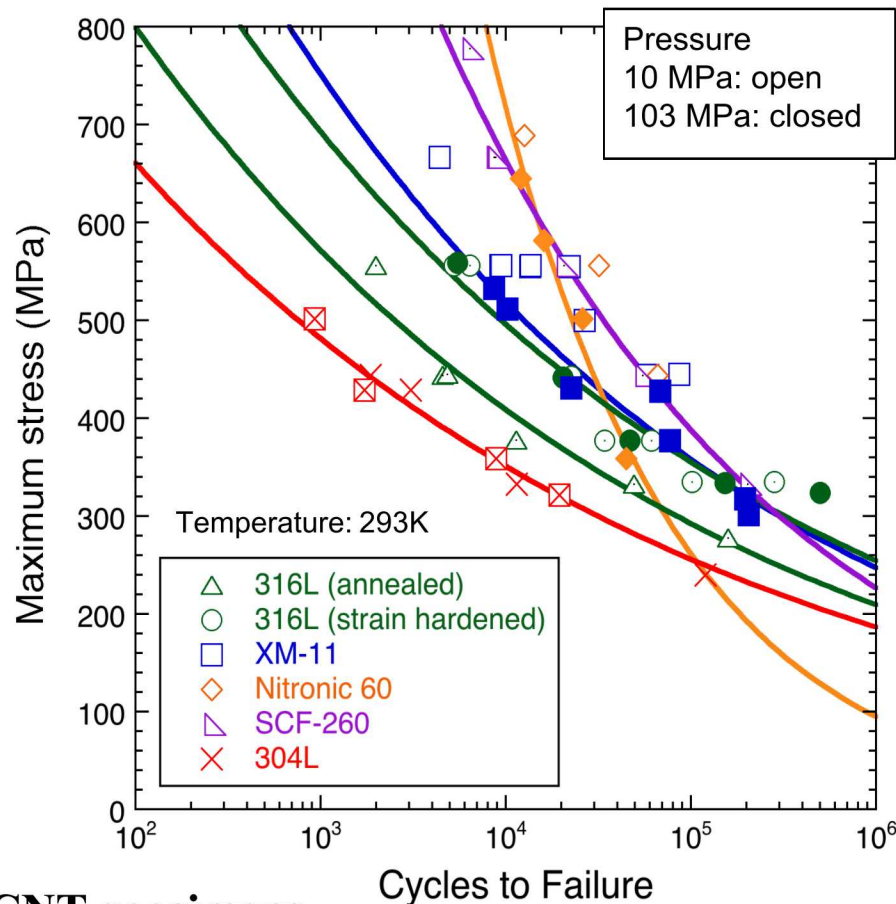
Is tensile ductility a meaningful metric for evaluating hydrogen effects?

Tensile ductility



- RA can be useful screening and comparative measure
 - eg, verification of the materials pedigree
- RA is not a useful design parameter
 - RA for high-strength aluminum can be <20%
- Therefore, RA is not a sufficient general metric for materials selection

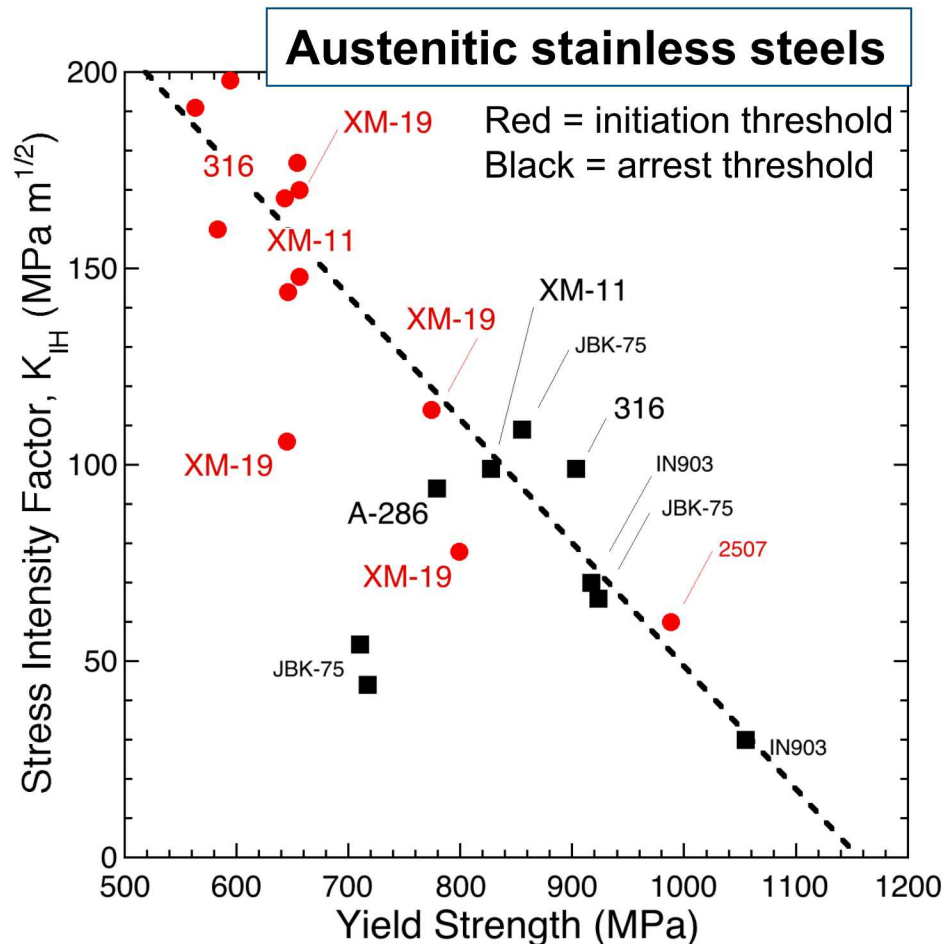
Fatigue life data shows less dramatic effects from hydrogen than tensile data



- Fatigue life data are used in design and can be a meaningful metric
- *For example:* automotive uses performance metric for materials selection in hydrogen systems:
 - 10^5 cycles to failure at 1/3 tensile strength
- Other metrics can be just as meaningful

CNT specimens
 $R = 0.1, f = 1\text{Hz}$

Typical austenitic stainless steel maintain high fracture threshold in hydrogen environments



- Fracture threshold in gaseous hydrogen is reduced by >50% for all steels on this plot
- General trend of lower fracture threshold with higher strength
- More highly alloyed and/or complex alloys can have lower fracture threshold

Diverse range of austenitic stainless steels show exceptional properties in hydrogen

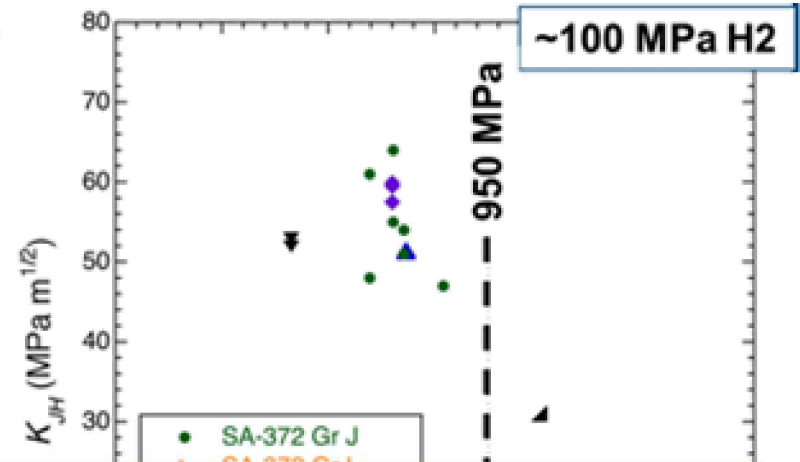
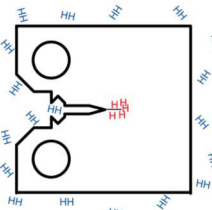
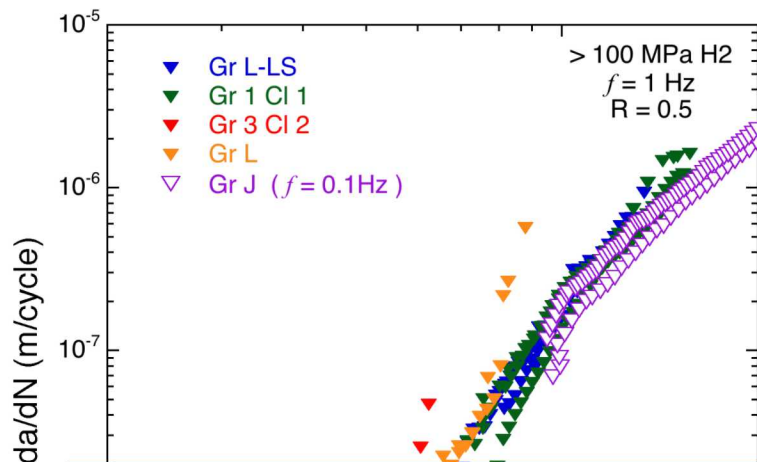
material	Yield (MPa)	Tensile (MPa)	Tension RA (%)	Fracture K_{JH} (MPa m ^{1/2})	Fatigue S_{fH}^{\dagger} (MPa)
316L	280	562	57	—	295
CW 316L	573	731	60	—	355
	563	735	66	190	—
304L	497	721	25	—	255
	452	674	49	220	—
XM-11	539	881	42	—	355
	643	816	51	225	—
Nitronic 60	880	1018	36	—	260
	499	857	53	—	—
SCF-260	1083	1175	50	—	390

[†] defined as the stress for with notched fatigue life $\sim 10^5$ cycles in H₂
(100 MPa, R = 0.1, f = 1Hz)

- **Strength reflects allowable stresses and wall thickness**
- **Composition is related to cost (but not only factor)**

Fatigue and fracture of ferritic steels

- Fatigue crack growth is similar for typical pressure vessel and linepipe steels (deviations relate to fracture toughness)
- Fracture resistance is consistent and acceptable for low strength – fracture resistance of steels with tensile strength > 900-950 MPa is unacceptable for PVs ($\sim 20 \text{ MPa m}^{1/2}$)



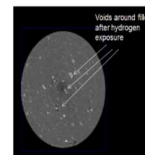
For PV applications, we identified the following metric:

- fracture resistance of $50 \text{ MPa m}^{1/2}$ for steel with tensile strength > 950 MPa

Sandia maintains unique capabilities to support research on *Hydrogen Materials Compatibility*

Hydrogen Effects on Materials Laboratory

- In situ mechanical testing ($P > 100 \text{ MPa}$ and $230\text{K} < T < 400\text{K}$)
- Long-term, high-pressure H_2 exposure
- Pressure cycling at controlled temperature



Environment

Materials

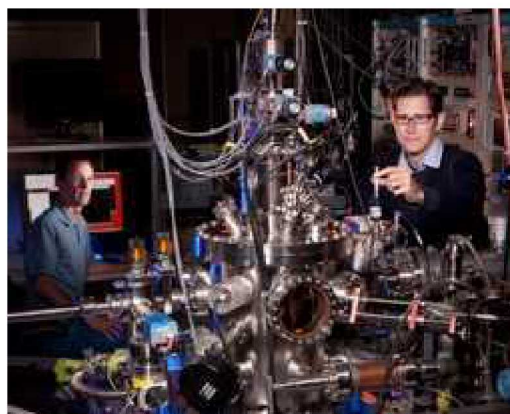
Stress / Mechanics

Active materials science community

- Computational materials science expertise
- Full-suite of state-of-the-art materials characterization tools
- Joining laboratory (austenitic steels, non-ferrous materials)

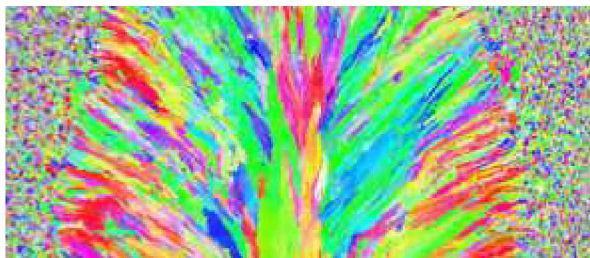
Hydrogen Transport and Trapping Laboratory

- Diffusion and permeation
- Thermal desorption spectroscopy



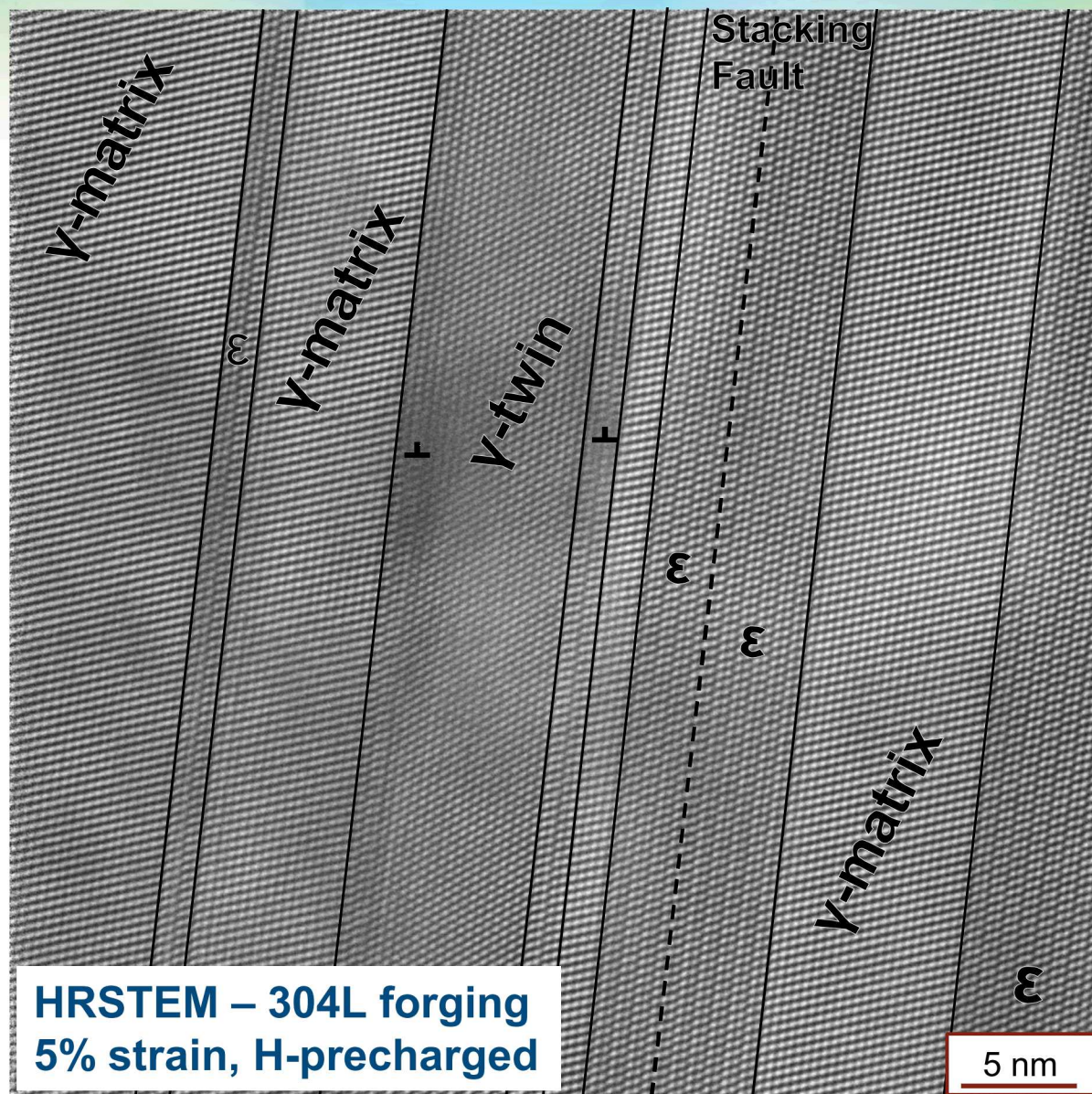
Hydrogen-Surface Interactions Laboratory

- Low-energy ion spectroscopy
- Ambient pressure x-ray photoelectron spectroscopy
- Kelvin probe atomic force microscopy



Example of characterization at the nanometer length scale

- HR-STEM shows some interface dislocations ($\frac{1}{6}\langle 112 \rangle$ and $\frac{1}{3}\langle 111 \rangle$) with no dislocations observable within twins, matrix, or ϵ -martensite
- Martensite is more common here than twinning (typical for H-precharged samples)
- Twins and ϵ -martensite are generally very thin (less than $\sim 20 \{111\}$ planes) while spanning through most of the grain. With twins appearing as faulted ϵ -martensite



H-precharging is used to simulate hydrogen service environment for some materials systems

- Exposure to gaseous H_2 until saturated with hydrogen
 - ~10 days for 4 mm round bar
 - Pressure: 138 MPa
 - Temperature: 300°C
 - For stainless: hydrogen content ~140 wt ppm (0.8% H/M)



- Testing in air after H-precharging

- Mechanical testing in H-precharged condition is similar to *in situ* testing in high-pressure gaseous hydrogen for tension, fatigue and fracture

- *Must consider the H-solute hardening: strength increase of 10-20%*



General trends in hydrogen transport

- **Ferritic steels**

- Diffusivity: $10^{-8} \text{ m}^2/\text{s}$
- Solubility: $10^{-8} \text{ H/M MPa}^{-1/2}$
 - Lattice concentration ($P=100 \text{ MPa}$): 0.3 ppm H/M
 - Trapping concentration: 100x greater than lattice concentration
- *Not amenable to gas-phase precharging*

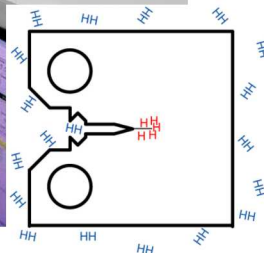
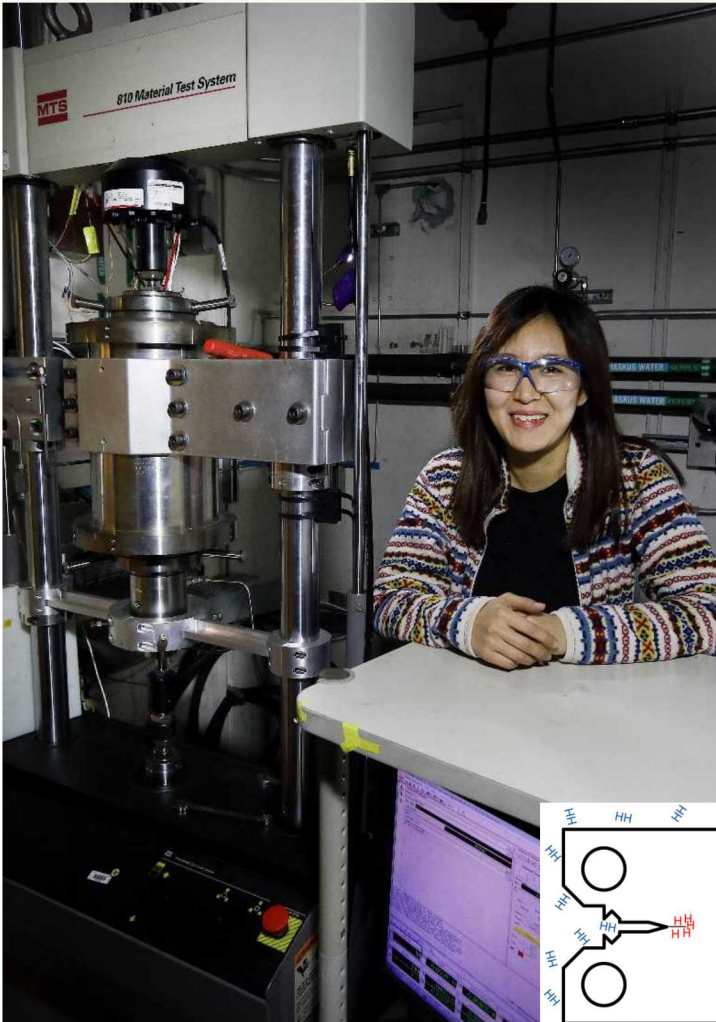
- **Austenitic stainless steels**

- Diffusivity: $10^{-15} \text{ m}^2/\text{s}$
- Solubility: $10^{-4} \text{ H/M MPa}^{-1/2}$
 - Lattice concentration ($P=100 \text{ MPa}$): 0.2% H/M
 - Trapping concentration: $\ll 1$ x lattice concentration
- *Gas-phase precharging is a well-developed technology*
 - Specimens can be shipped anywhere on dry ice and stored for extended time (months) at low temperature (-50°C)
 - Precharging time weeks to months depending on specimen size

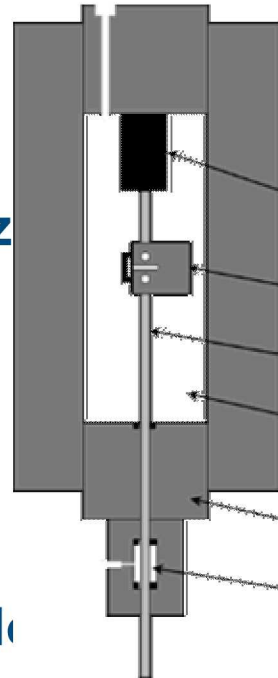
Solubility
(ideal gas)

$$K = \frac{c_L}{\sqrt{P}}$$

Fatigue and fracture measurements in high-pressure gaseous hydrogen



- Instrumentation
 - Internal load cell (w/ feedback)
 - Displacement measured on sample using LVDT or clip gauge
 - DCPD measurements possible
- Mechanical loading
 - Cyclic / monotonic
 - Load-ratio = 0.1 to 0.8
 - Frequency = 0.002 to 10 Hz
 - Loads: 1–15 kN
 - ASTM E1820, E647, etc
- Environment
 - Gaseous environment
 - Pressure ≤ 120 MPa
 - Room temperature (some have temperature capability)

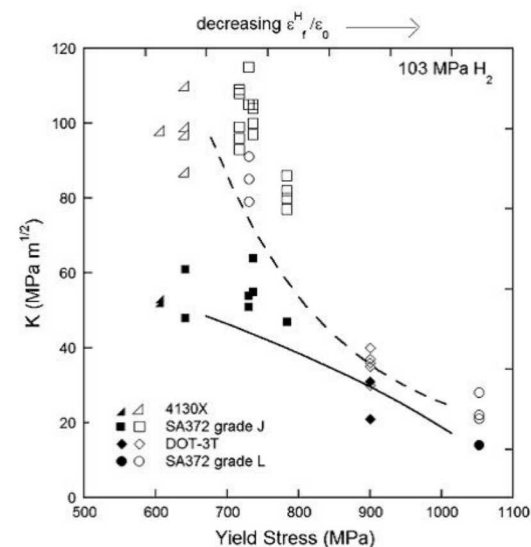


Constant displacement fracture tests in gaseous hydrogen environments

- Constant displacement fracture testing (ASTM E1681)
 - exposed to high pressure hydrogen to evaluate fracture thresholds



- Relatively easy to load and leave specimens
- Test methods often require 1000s of hours
- Linear elastic method
- Requires large specimens for ductile metals



Summary

- **It is important to think critically about quantitative measures of success**
 - What are we trying to achieve?
(cost, strength, fatigue behavior, fracture resistance, and/or other)
 - On what length scale?
 - What are the requirements of the application, standards and codes? (is better the enemy of good enough...)
- **National laboratories have numerous H-related capabilities**
 - Thermal (gas-phase) H-precharging
 - Fatigue and fracture in high-pressure gaseous hydrogen
 - Hydrogen transport (TDS, diffusion/permeation)
 - Static loading/displacement testing
- **Should not overlook other capabilities and expertise, such as**
 - Expert materials science characterization
 - Computational materials science