

SAND2020-

# **Metrics, trends and capabilities for evaluating hydrogen effects in metals**

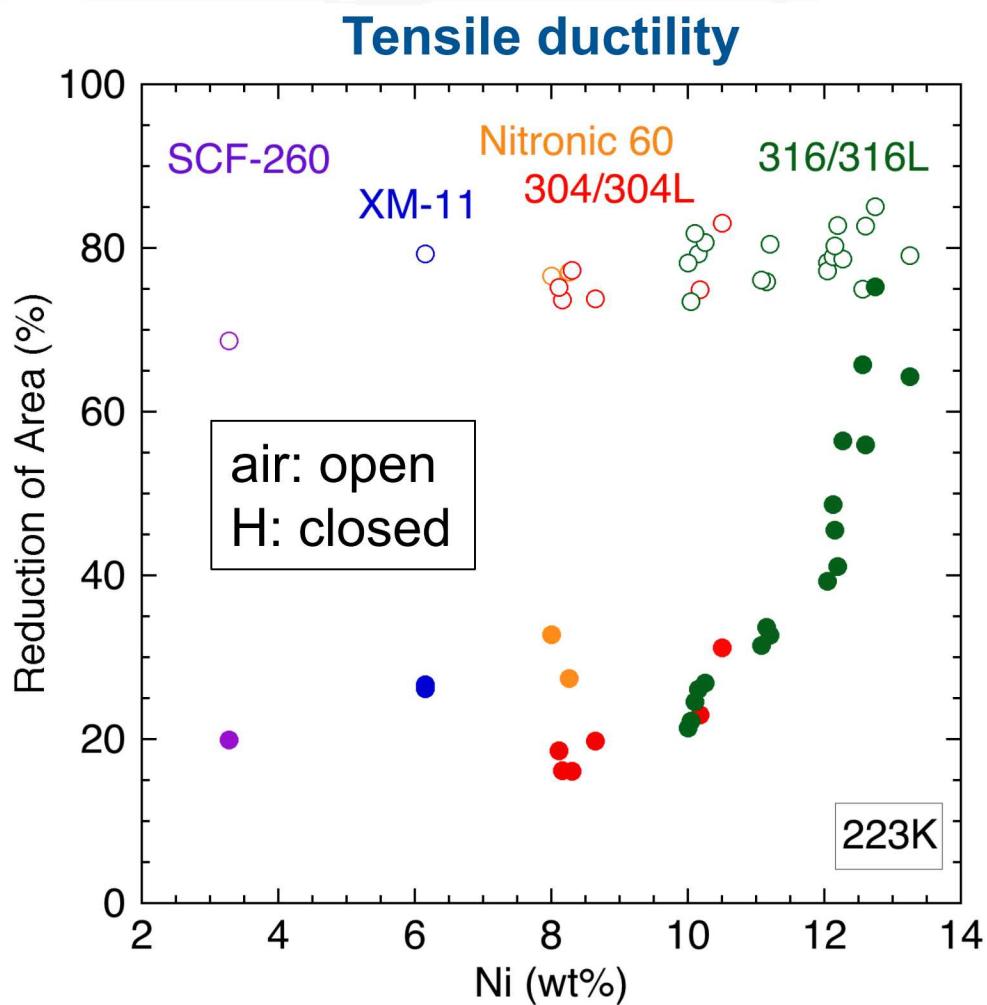
**Chris San Marchi and Joe Ronevich**

**H-Mat Kick-off Meeting**  
**March 25, 2020**

# Outline

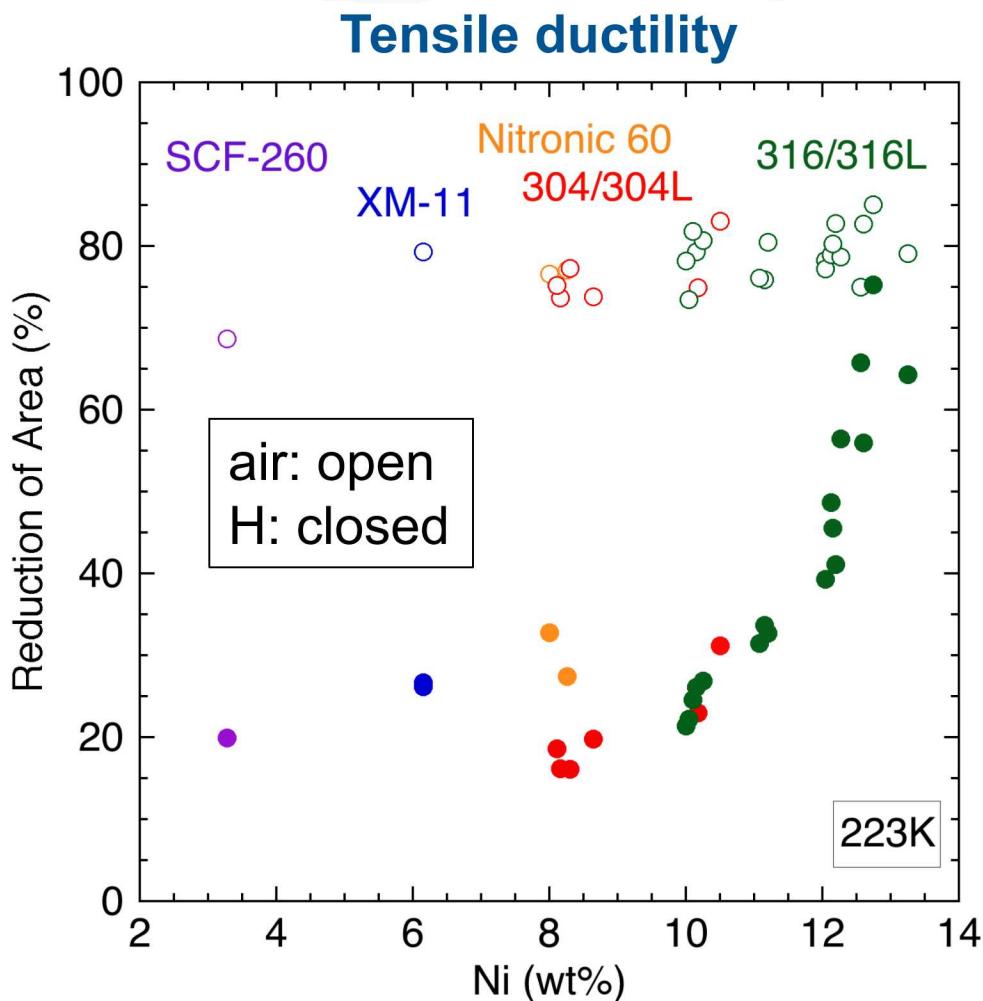
- Metrics and Targets
  - Why do we need them?
  - What does 'better than' mean?
  - What is a meaningful metric/target?
- Demonstrate importance of quantitative metrics with data trends
- Describe high-pressure capabilities at Sandia

# Extensive database exists for tensile behavior of $\gamma$ -stainless steels in hydrogen environments



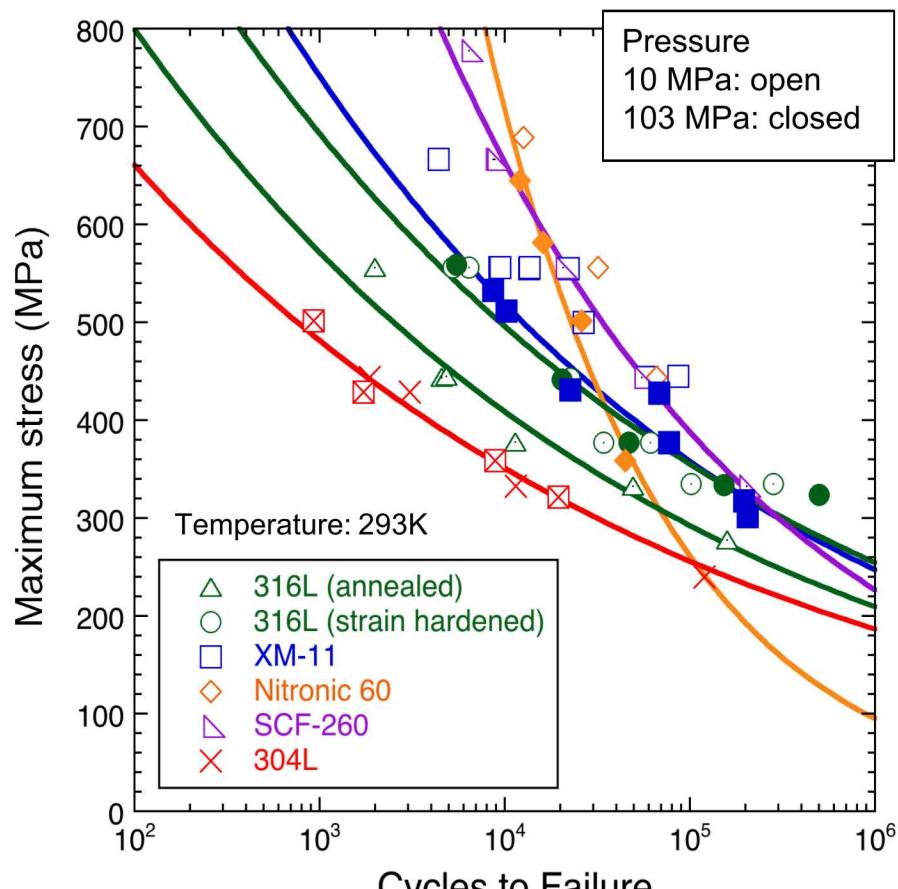
- Strength properties are generally not affected by hydrogen
- Nickel correlates with ductility in hydrogen as well as any other indicator
- Austenite stability is not as good an indicator when nitrogen-strengthened alloys are considered

# Is tensile ductility a meaningful metric for evaluating hydrogen effects?



- **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**

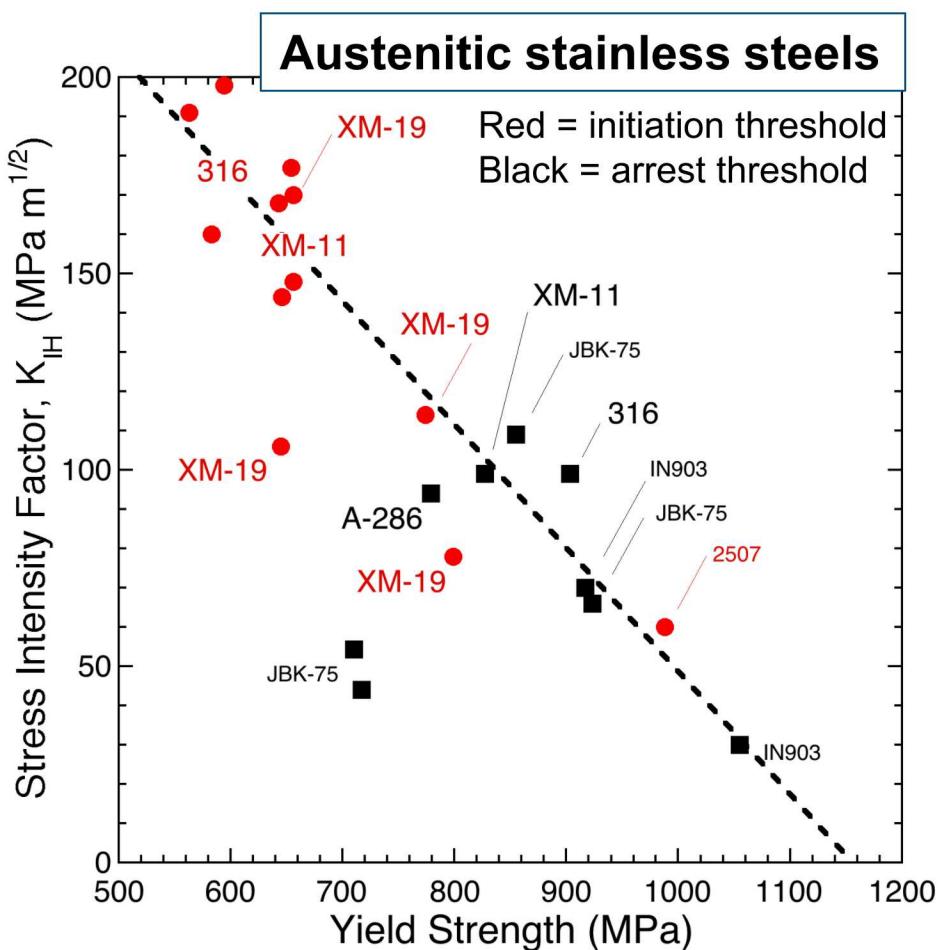
# Fatigue life data shows less dramatic effects from hydrogen than tensile data



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

- 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

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

<sup>†</sup> defined as the stress for with notched fatigue life  $\sim 10^5$  cycles in  $H_2$   
(100 MPa, R = 0.1, f = 1Hz)

# Strength and composition can be relevant metrics

material	Yield (MPa)	Tensile (MPa)	Cr	Ni	Mn	N	Typical allowable stress (MPa)
316L	280	562	17.5	12	1.2	0.04	115
CW 316L	573	731	17.5	12	1.2	0.04	218
304L	497	721	18.3	8.2	1.8	0.56	195
XM-11	539	881	20.4	6.2	9.6	0.26	207
Nitronic 60	880	1018	16.6	8.3	8.0	0.16	218
SCF-260	1083	1175	19.1	3.3	17.4	0.64	333

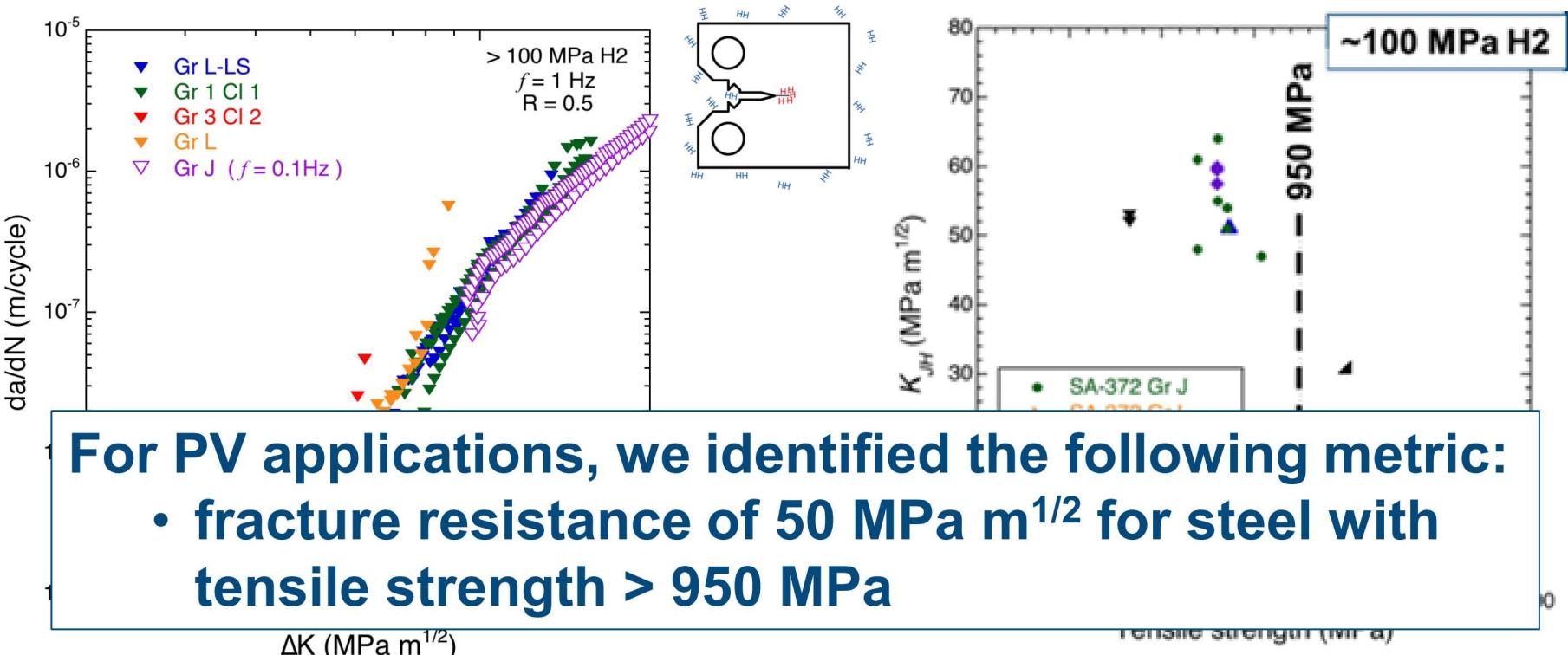
*Wide range of strength*

*Wide range of Ni/Mn content*

- 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 ( $\sim 20$  MPa  $m^{1/2}$ )



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



## Hydrogen Effects on Materials Laboratory

- In situ mechanical testing ( $P > 100$  MPa and  $230K < T < 400K$ )
- Long-term, high-pressure H<sub>2</sub> exposure
- Pressure cycling at controlled temperature

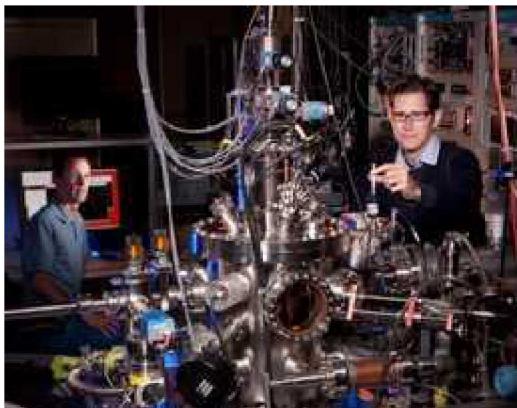


## Active materials science community

- 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

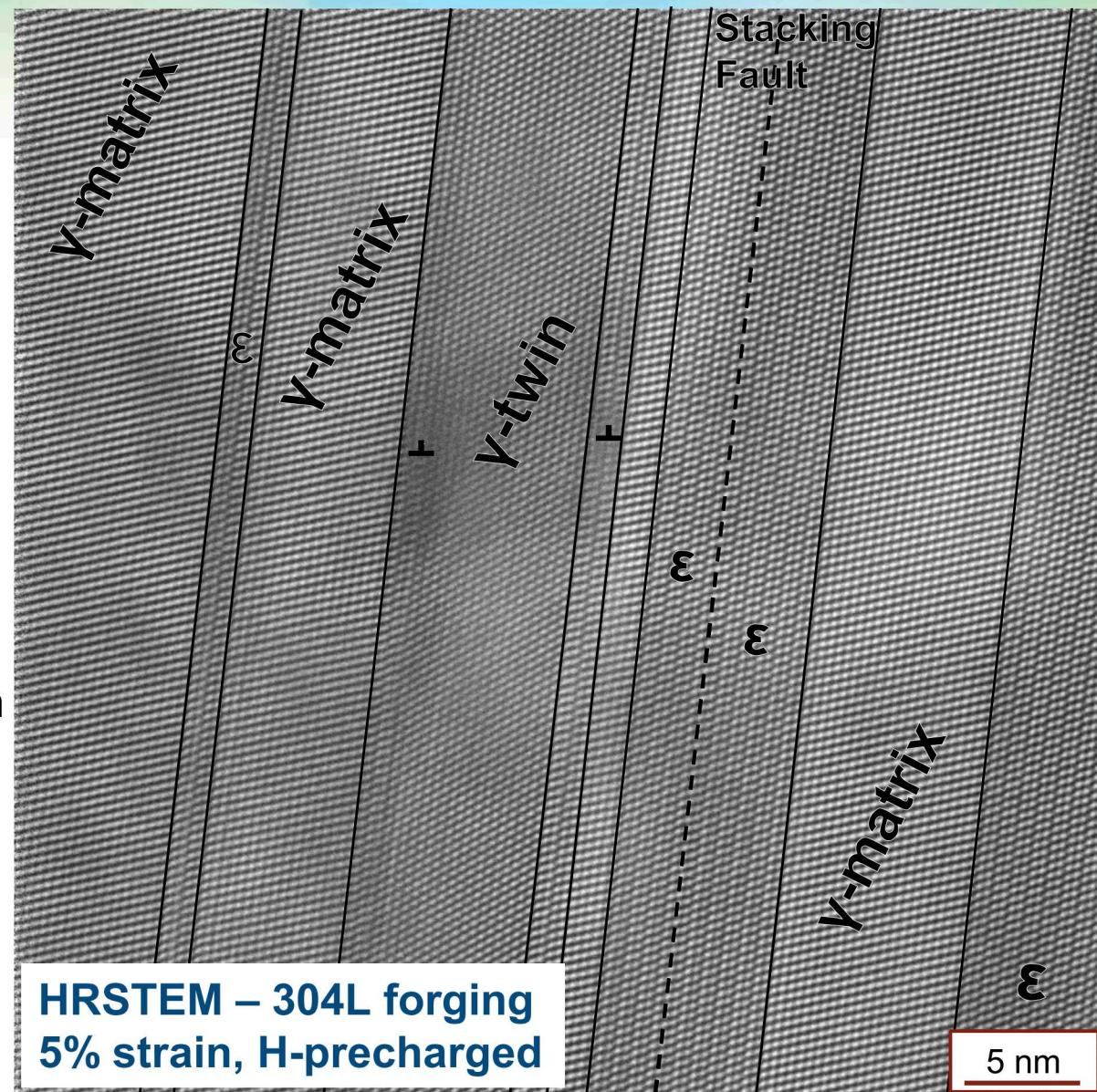


## Hydrogen-Surface Interactions Laboratory

- 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  $\epsilon$ -martensite
- Martensite is more common here than twinning (typical for H-precharged samples)
- Twins and  $\epsilon$ -martensite are generally very thin (less than  $\sim 20 \{111\}$  planes) while spanning through most of the grain. With twins appearing as faulted  $\epsilon$ -martensite



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

- **Exposure to gaseous H<sub>2</sub> 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%*



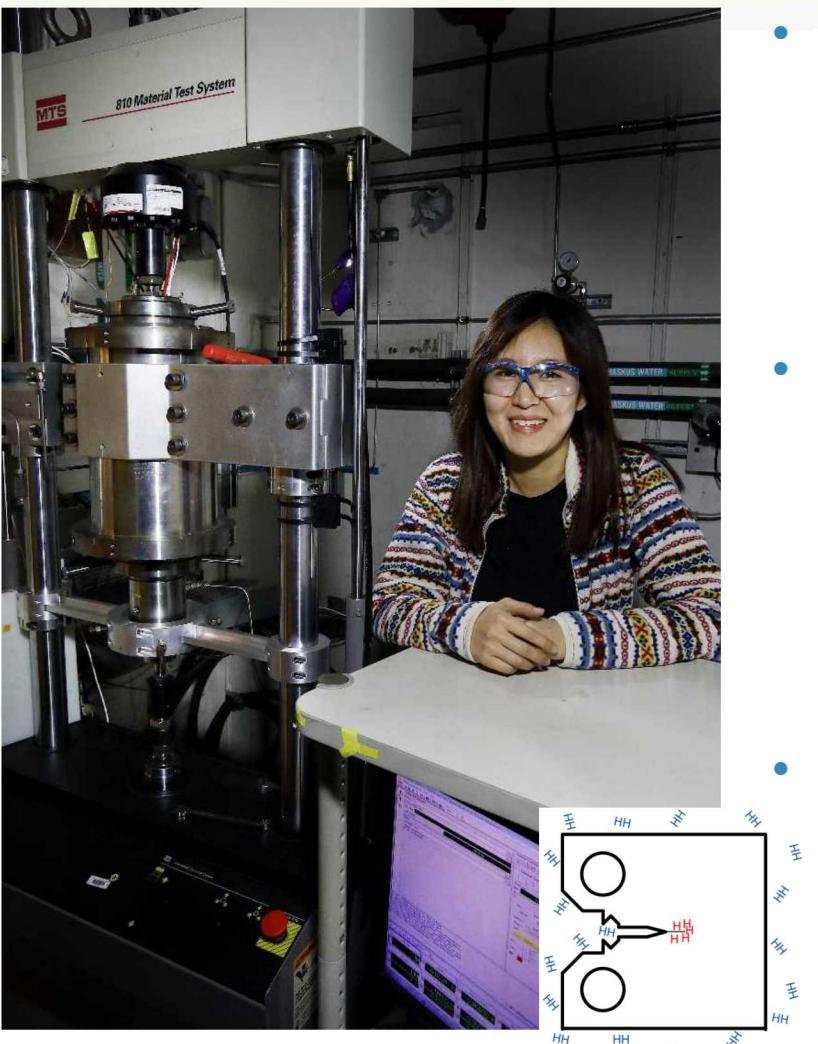
# General trends in hydrogen transport

- **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: <<1x 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

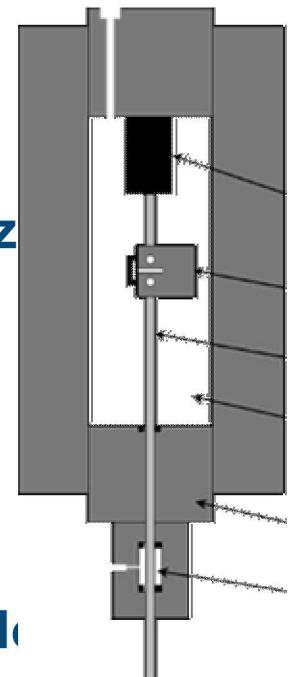
Solubility  
(ideal gas)

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

# 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  $\leq$  120 MPa
  - Room temperature (some low temperature capability)

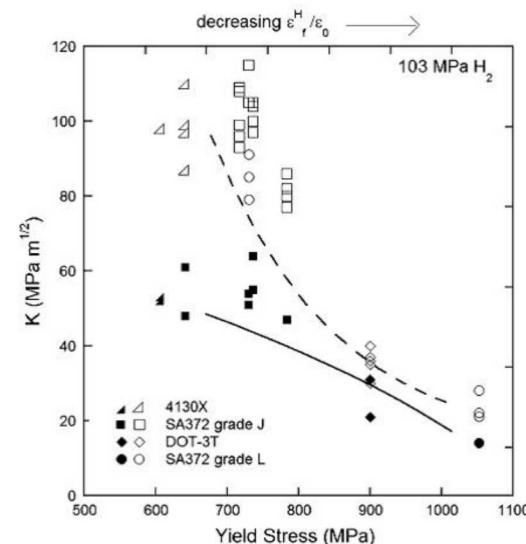


# Constant displacement fracture tests in gaseous hydrogen environments

- 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