SAND2019-3693PE

Sandia's Hydrogen Program: Understanding Hydrogen-Materials Compatibility

ASPPRC Spring Meetings
Golden, CO
March 18, 2019

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Sandia National Laboratories

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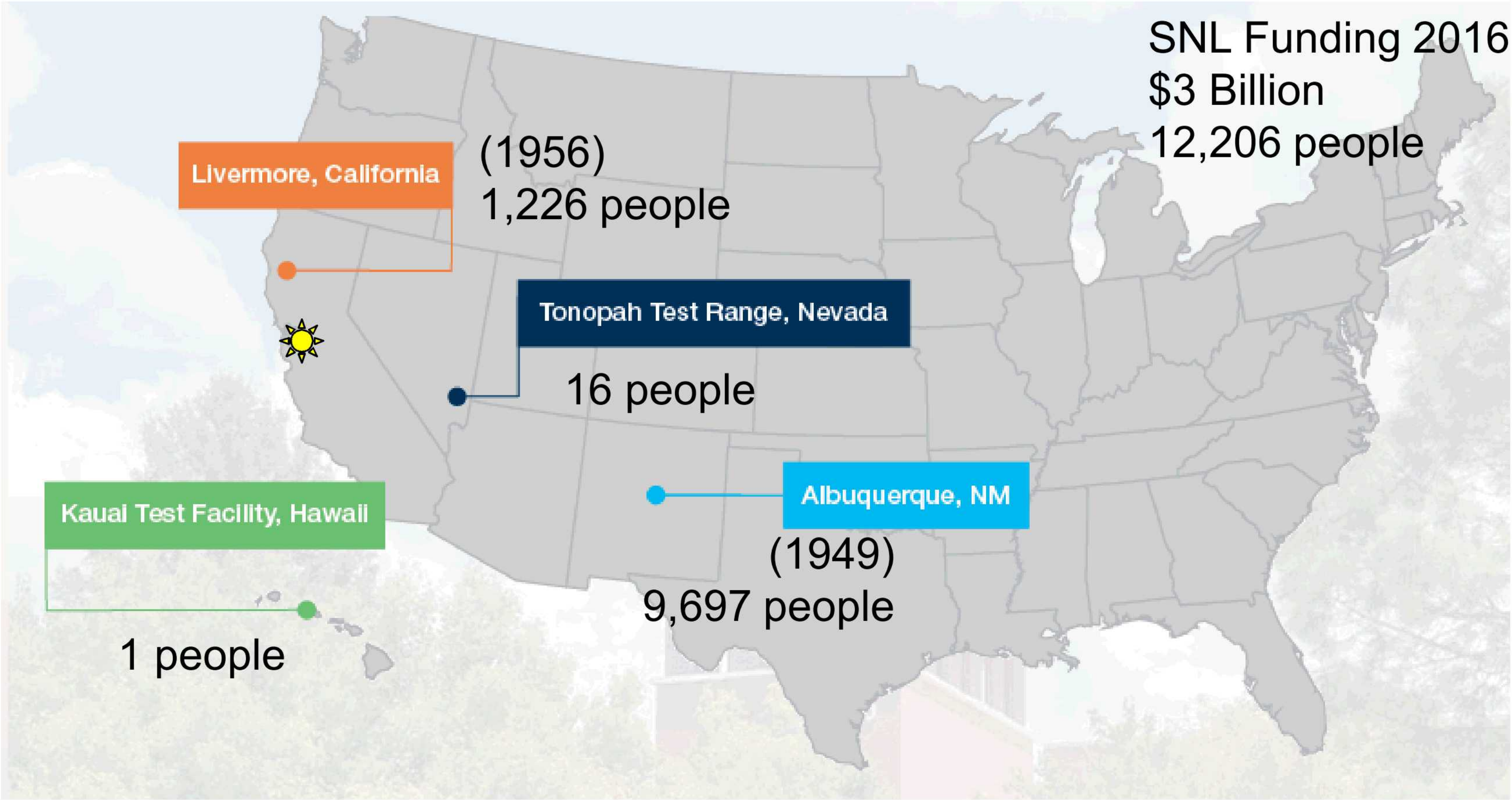
Outline

- Sandia's current capabilities (Hydrogen Effects on Materials Laboratory – HEML)
- Hydrogen-materials exemplar projects
  1) Evaluated pressure vessels for H_2 fuel cell fork lift trucks
  2) Investigated oxygen impurity effects on mitigating hydrogen embrittlement
  3) Residual stress effects on high strength pipeline steel welds
- HMat Program Overview
  – Current funded projects

Stats: Sandia National Laboratories

Our unique mission responsibilities in the nuclear weapons (NW) program create a foundation from which we leverage capabilities, enabling us to solve complex national security problems.



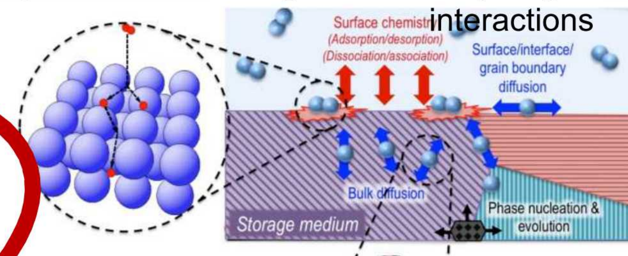
Sandia's Current Hydrogen Program

Hydrogen Production

Develop concentrated solar power for large-scale, renewable production of hydrogen

Hydrogen Storage

Provide fundamental understanding of the phenomena limiting solid-state hydrogen interactions

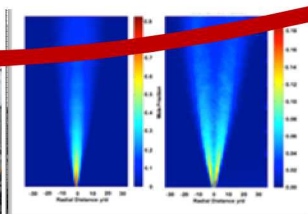


Hydrogen Delivery

Identify pathways for reducing cost of steel hydrogen pipelines without compromising reliability and integrity

Safety, Codes and Standards

Facilitate safe deployment of hydrogen technologies with science-based codes and standards

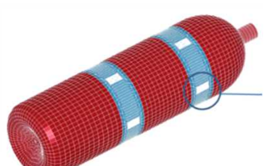


Fuel Cells

Develop new membrane systems for enhanced electrochemical performance

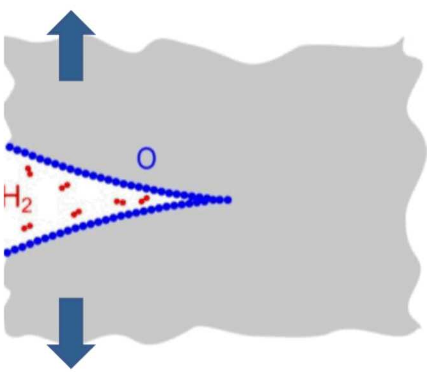
Systems Engineering

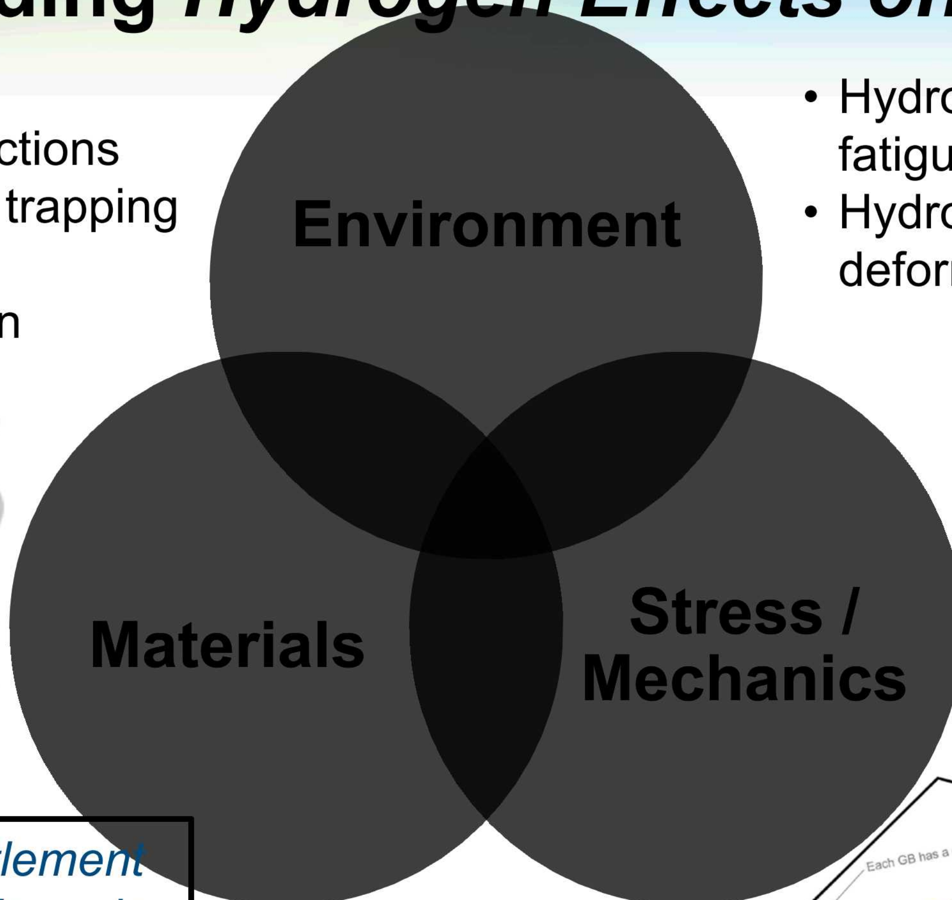
Demonstrate innovative engineering solutions to harness clean energy technologies



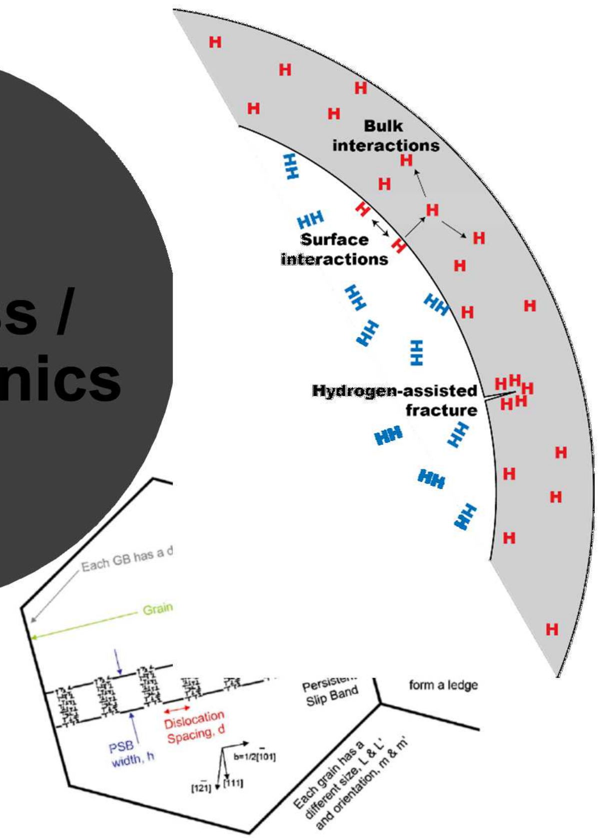
Sandia program(s) take a holistic approach to understanding *Hydrogen Effects on Materials*

- Surface interactions
- Transport and trapping
- Rapid gas decompression





- Hydrogen-assisted fatigue and fracture
- Hydrogen effects on deformation

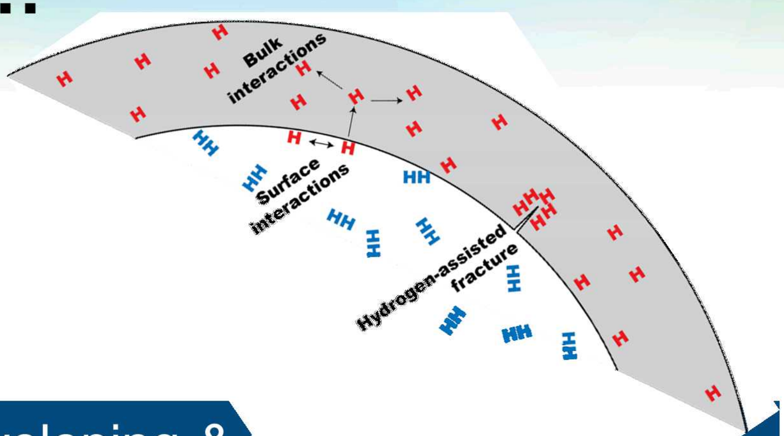


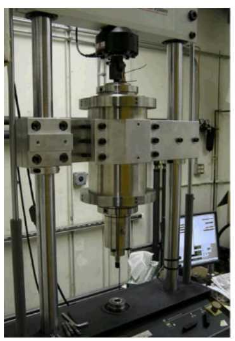
Hydrogen embrittlement occurs in ***materials*** *under the influence of* ***stress*** *in hydrogen* ***environments***

- Mechanisms of fatigue and fracture
- Evolution of damage

Sandia's hydrogen program contributes to foundational knowledge by…

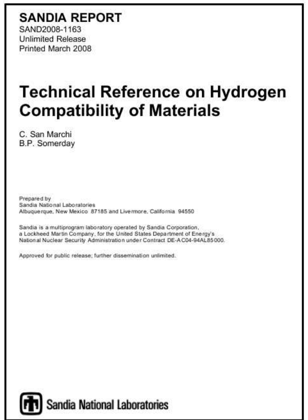
Developing fundamental understanding of materials compatibility with H_2





Developing & maintaining unique capabilities that can be used to probe mechanisms and physics of behavior

Effectively communicating our understandings to broader community including industry, government, and Codes & Standards


SANDIA REPORT
SAND2008-1163
Unlimited Release
Printed March 2008

Technical Reference on Hydrogen Compatibility of Materials

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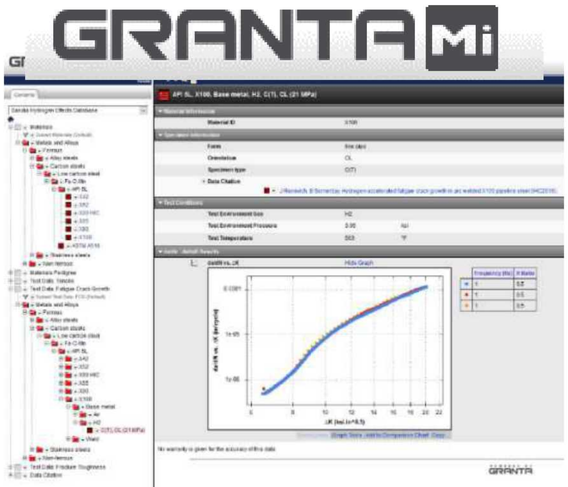
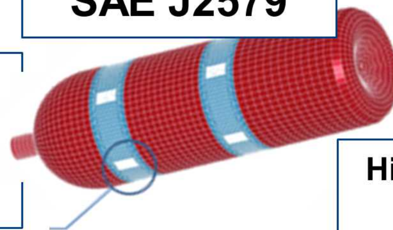


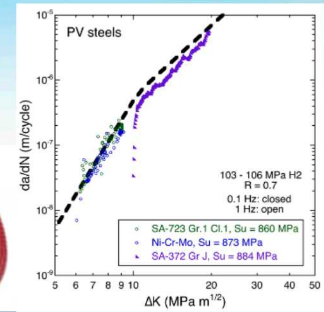
Evaluation of *Materials Compatibility with H_2* enables materials innovation

ASME article KD-10 input on test methodology

First qualification data for high-pressure ASME vessels

Full-scale tank testing CSA HPIT1 SAE J2579



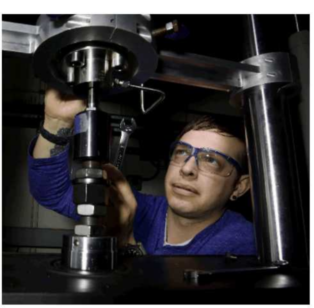


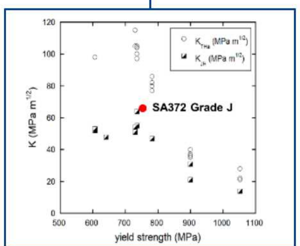
Platform for pressure cycling of polymers in GH2 (up to 400 C)

High-hardenability pressure vessel steel results presented to ASME KD-10 for acceptance of curve fits based on data

2006	2008	2010	2012	2014	2016	2018

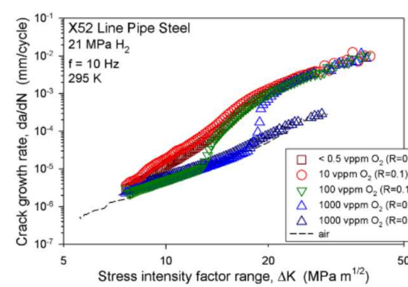
Platform for matls testing in GH2 at high pressure





Critical assessment of statically loaded cracks

Modeled H_2 embrittlement mitigation through O_2 gas impurities

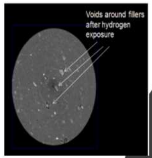


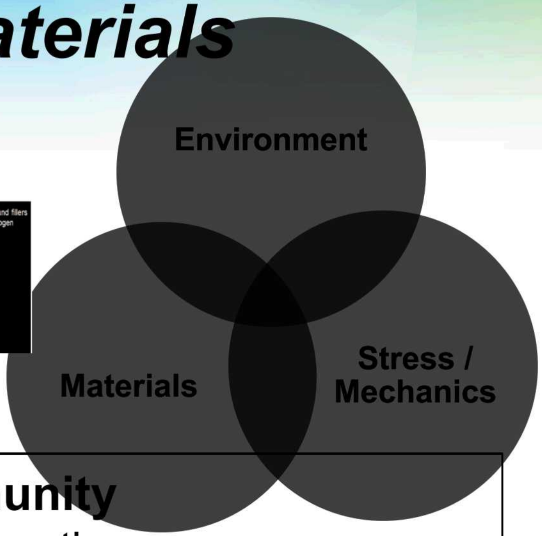
Platform for high-pressure GH2 over temperature range (-40˚C to +85˚C)

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

Hydrogen Effects on Materials Laboratory

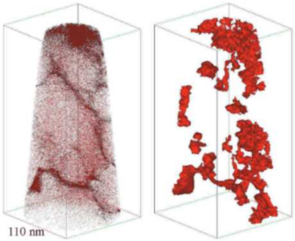
- In situ mechanical testing
  (P >100 MPa and 230K < T < 400K)
- Long-term, high-pressure H2 exposure
- Pressure cycling at controlled temperature





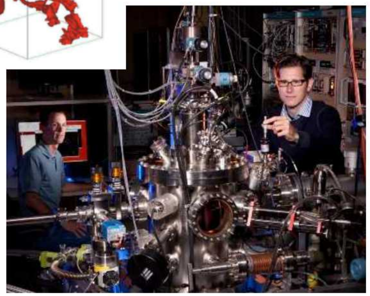
Active materials science community

- 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
- Local-electrode atom probe tomography

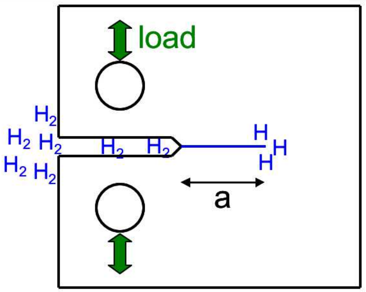


Hydrogen-Surface Interactions Laboratory

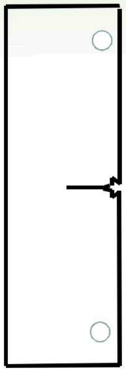
- Low-energy ion spectroscopy
- Ambient pressure x-ray photoelectron spectroscopy
- Kelvin probe atomic force microscopy

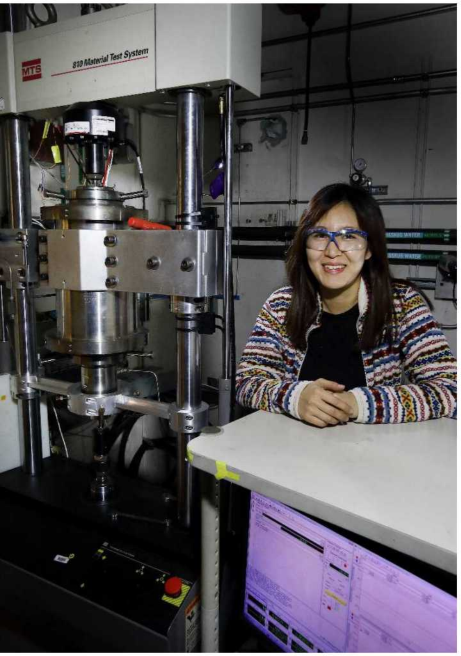
Fatigue & Fracture measured in service environment, i.e. high-pressure H_2 gas at ambient temperatures (Cell 3)

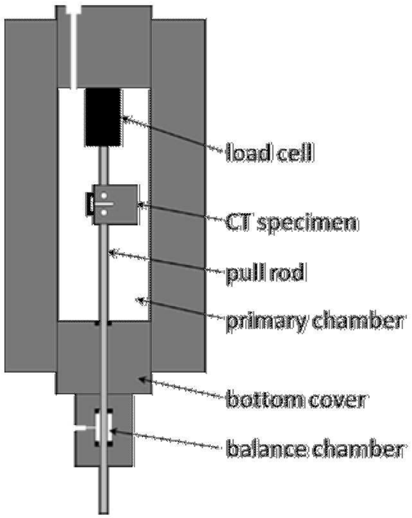
Compact Tension (C(T))



ESE(T)







- Instrumentation
  - Internal load cell in feedback loop
  - COD measured internally using LVDT or clip gauge
  - Crack length calculated from compliance
- Mechanical loading
  - Quasi-static
  - Cyclic
  - R-ratios (0.1 to 0.8)
  - Frequencies (0.002 to 10 Hz)

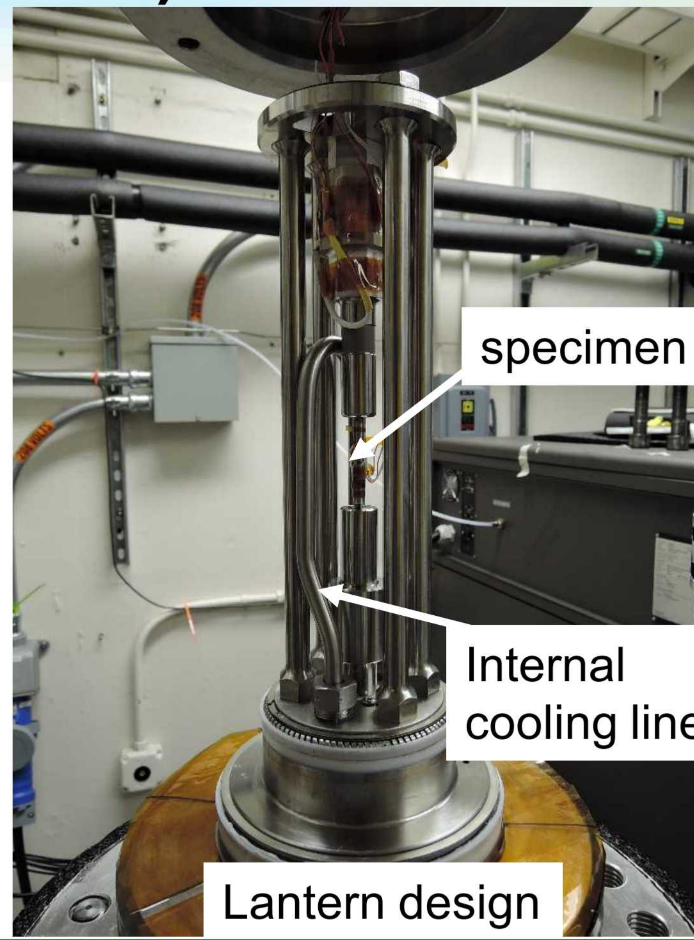
Environment
  - Supply gas:
    - 99.9999% H_2
    - Mixed gas
  - Max Pressure = 138 MPa (20 ksi)
  - Room temperature

Dynamic testing in high pressure hydrogen at sub-ambient temperatures (Cell 2)

Temperature
-50C to 150C

Pressure
Up to 106 MPa

Mechanical Test
Quasi-static
or
Cyclic loading

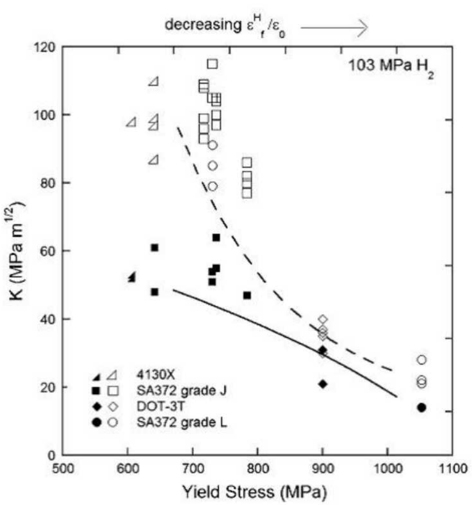


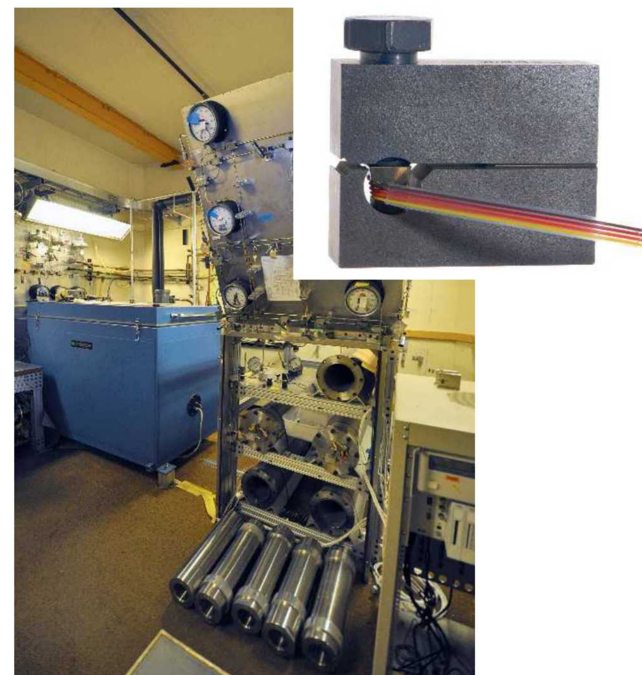
Hydrogen refueling stations pre-chill gas and components experience temperatures from -40C to +85C

High temperature hydrogen pre-charging or statically loaded tests in hydrogen environment (Cell 5)

- Thermally pre-charge test specimens up to 138 MPa H_2 at 300C
- For austenitic stainless steel, results in approximately 1 at% hydrogen
    - 140 wppm in 300 series

- Statically loaded specimens (ASTM E1681) exposed to high pressure hydrogen to evaluate fracture thresholds





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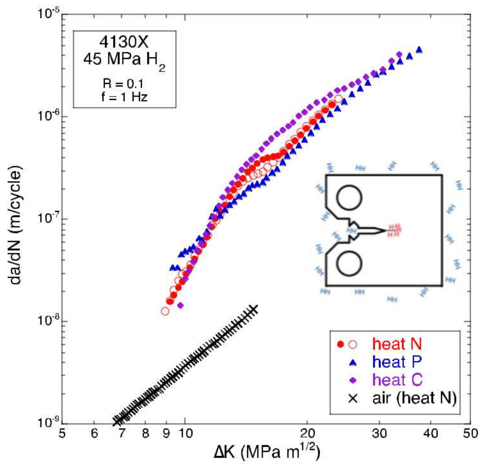
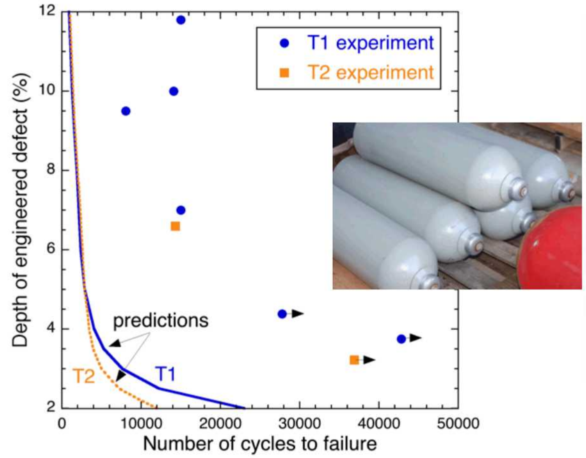
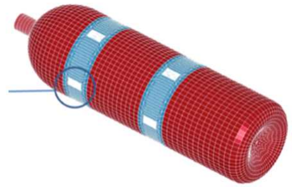
1) Full-scale testing of pressure vessels enabled deployment of safe, low-cost fuel cell forklift fuel systems

Materials testing and evaluation → *Component testing* → *Lifetime prediction and SCS development*







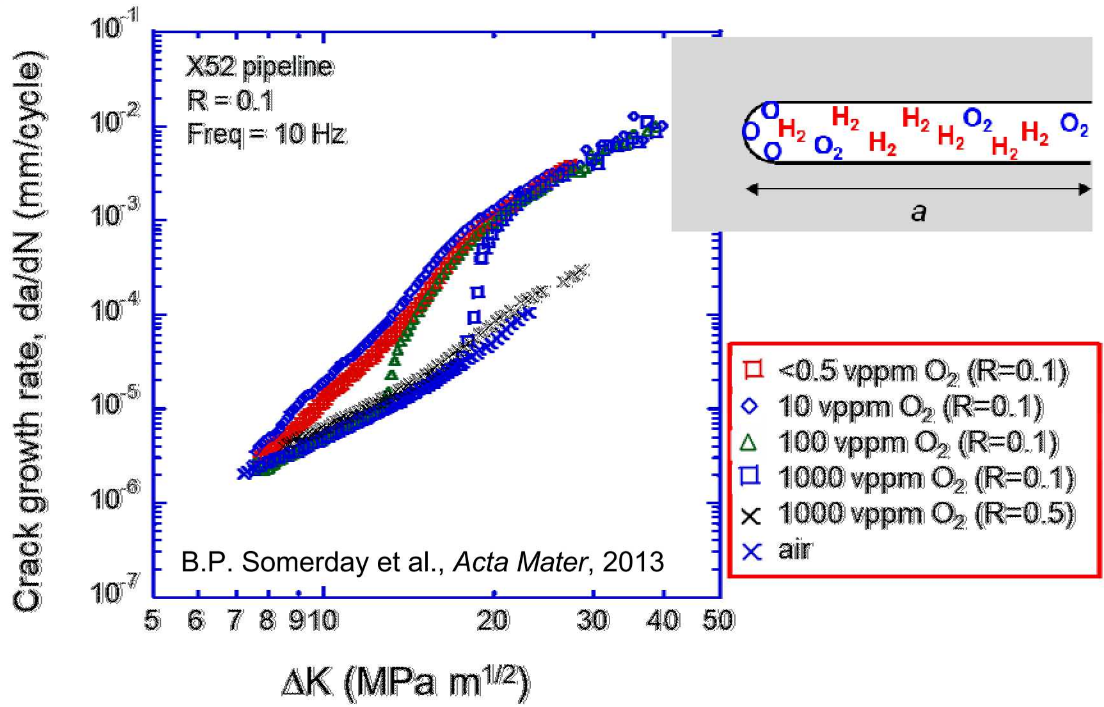
- **Quantified uncertainties in the cycle life of hydrogen storage tanks for the lift-truck application**
- Enhanced safety and market growth enabled through standards development (CSA HPIT1)
- Today, there are >23,000 clean and efficient fuel cell forklifts in service (and growing!)

plug power
NUVERA FUEL CELLS
NORRIS CYLINDER
CSA

Enabled H_2 fueled forklifts through combined full-scale & laboratory materials testing

2) Oxygen impurities can mitigate hydrogen assisted fatigue

- X52 pipeline steel exhibited delayed or in some conditions suppression of hydrogen assisted fatigue (Somerday *et al.* 2013)
- Combination of loading conditions and environment
  - Oxygen partial pressure
  - Frequency, R-ratio, da/dN_{inert}
- Analytical model to describe critical da/dN



$$\left[\frac{da}{dN}f\right]_{crit} = \frac{0.3\chi D p_{tot}(1-\nu^2)}{\pi z_{pass}\theta_O R_g T E \sigma_0}\left(\frac{\Delta K}{\sqrt{a^*}(1-R)}\right)^2$$

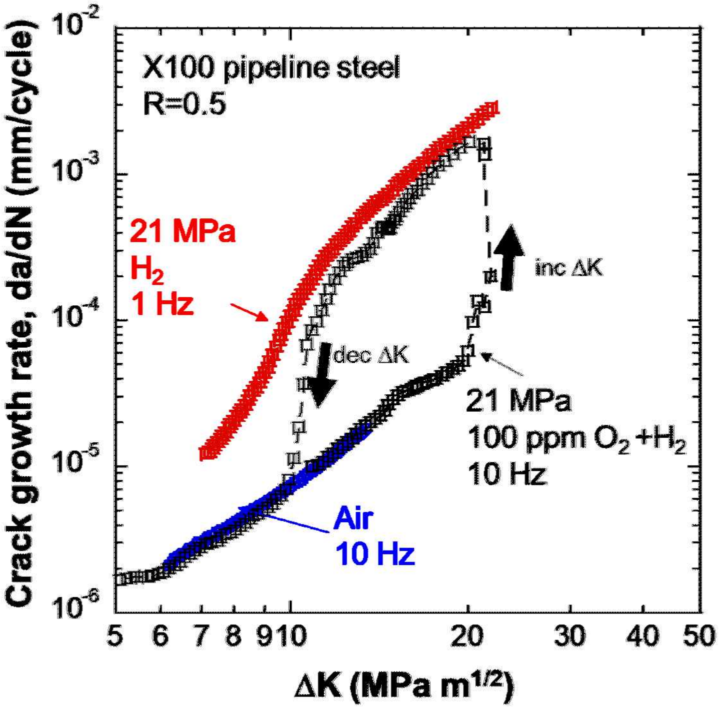
da/dN = inert crack growth rate
f = frequency
χ = oxygen concentration
ν = Poisson's ratio = 0.3
T = temperature
z_{pass} = number of oxygen layers required to passivate surface
θ_O = density of oxygen atoms in FeO layer
a^* = crack length extending from precrack start notch

E = elastic modulus
s_o = yield strength
R = load ratio
R_g = gas constant

Can analytical model be improved? What about different materials and different loading environments?

Designed experiments to assess the dependence on da/dN_{crit} (e.g. freshly created crack surface)

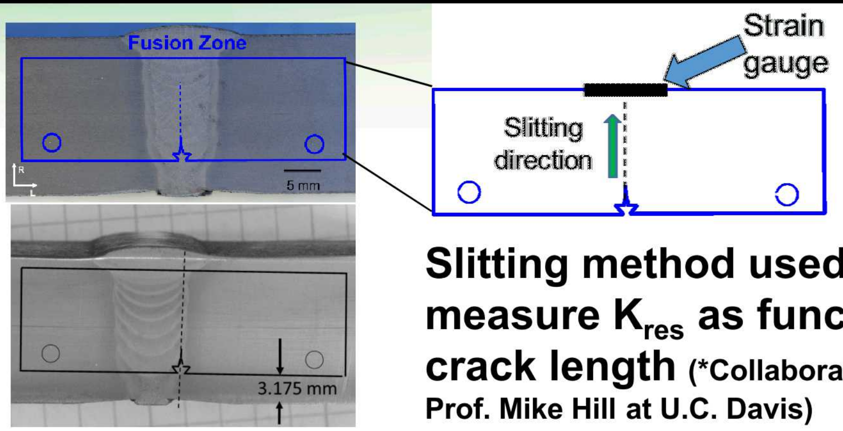
- In pure H_2, accelerated fatigue at onset of test
- In mixed gas (100 ppm O_2) R=0.5, f=10 Hz, onset of HA-FCG delayed to 5.3E-5 mm/cycle during K-increasing test
- Decreasing K used to explore onset of hydrogen-accelerated fatigue crack growth (HA-FCG)
- During K-decreasing, return of FCGR towards inert condition occurs at approximately the same da/dN



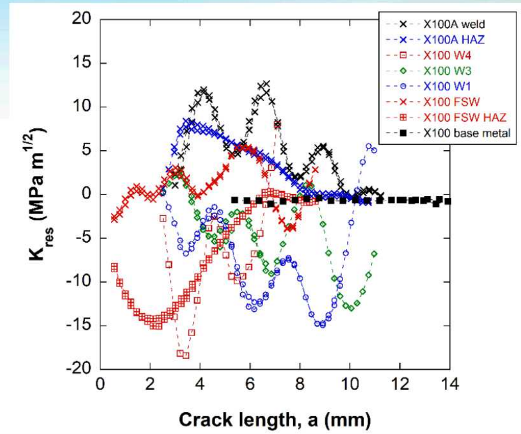
Ronevich, J.A. *et al.*, ASME PVP 2018

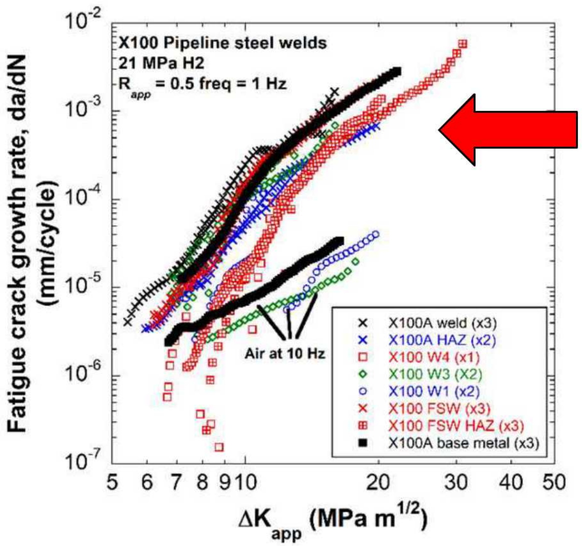
- **Clear dependence on da/dN not ΔK**
- **Verified applicability of phenomenon & model to higher strength pipe**

3) Fundamental understanding of hydrogen-assisted fatigue behavior of pipeline welds through measurements & correction for residual stress



Slitting method used to measure K_{res} as function of crack length (*Collaboration with Prof. Mike Hill at U.C. Davis)





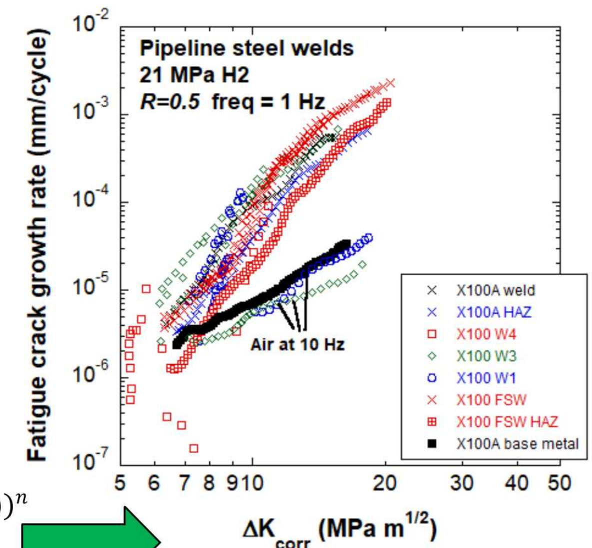
Data *not corrected* yield FCGR curves of varying R-ratios

$$R_{tot}(a) = (K_{min\text{-}app}(a) + K_{res}(a))/(K_{max\text{-}app}(a) + K_{res}(a))$$

Corrected data normalizes FCGR curves to single R-ratio = 0.5 providing better utility and fidelity

$$K_{norm}(a) = (\Delta K(a))^{1-n} * (K_{max-app}(a) + K_{res}(a))^n$$

$$\Delta K_{corr} = K_{norm} * (1 - \bar{R})^n$$



Removal of residual stress provides neutral starting ground for comparison and design guidance

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H-Mat℠ Hydrogen Materials Compatibility Consortium

Science-based advancement of materials for hydrogen technologies

Metals

Polymers

Sandia National Laboratories

Pacific Northwest National Laboratory

Oak Ridge National Laboratory

SRNL

Argonne National Laboratory

Initiated Fall of 2018

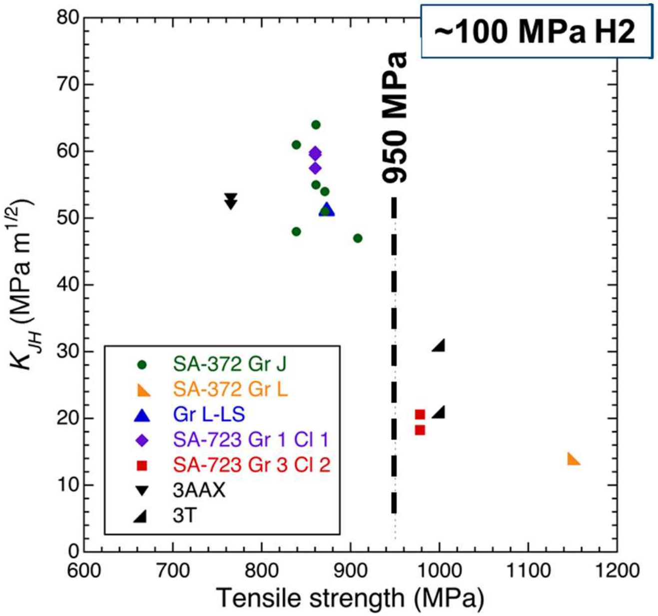
Objectives of Metals Tasks

Motivation: elucidate the mechanisms of hydrogen-materials interactions to inform **science-based strategies to design the microstructure** of metals with improved resistance to hydrogen degradation

Task	Relevance and Objective
High-strength ferritic steel microstructures	Develop a mechanistic understanding of hydrogen-induced fracture processes in ferritic steel microstructures to improve fracture resistance of low-cost steels with tensile strength >950 MPa
High-strength aluminum alloys	Elucidate mechanisms of hydrogen embrittlement in high-strength aluminum alloys and the role of moisture in hydrogen surface interactions in this class of materials
Transferability of damage and crack nucleation	Understand the mechanics of hydrogen-induced damage leading to crack nucleation in metals and develop a framework that can quantify the cycles required for crack nucleation in structural design
Microstructure of austenitic stainless steels	Identify governing physical processes of hydrogen embrittlement in austenitic stainless steels to design microstructures that mitigate the adverse effects of hydrogen environments
Materials for cryogenic hydrogen service	Identify materials for cryo-compressed hydrogen storage onboard vehicles, and develop key technical metrics for viable structural materials in this application

Hydrogen-resistant, high-strength ferritic steel microstructures (task M1)

Science question:
Are there high-strength steel microstructures that can be resistant to hydrogen effects?



- Mechanical testing of steels in high pressure H_2
- Development of unique microstructures (e.g., austempering)
- Microstructural and fracture characterization
- Kelvin Probe Force Microscopy to investigate hydrogen distribution in different microstructures
- Modeling of Fe-C-H (DFT and MD) to explore preferential locations for hydrogen in microstructure from physics standpoint

Engineering goals:
- **Achieve K_{JH} > 50 MPa m$^{1/2}$ for steels with UTS > 950 MPa**
- **Ferritic steel microstructures with tensile strength up to 1100 MPa and 50% increase of fracture resistance in high-pressure hydrogen**

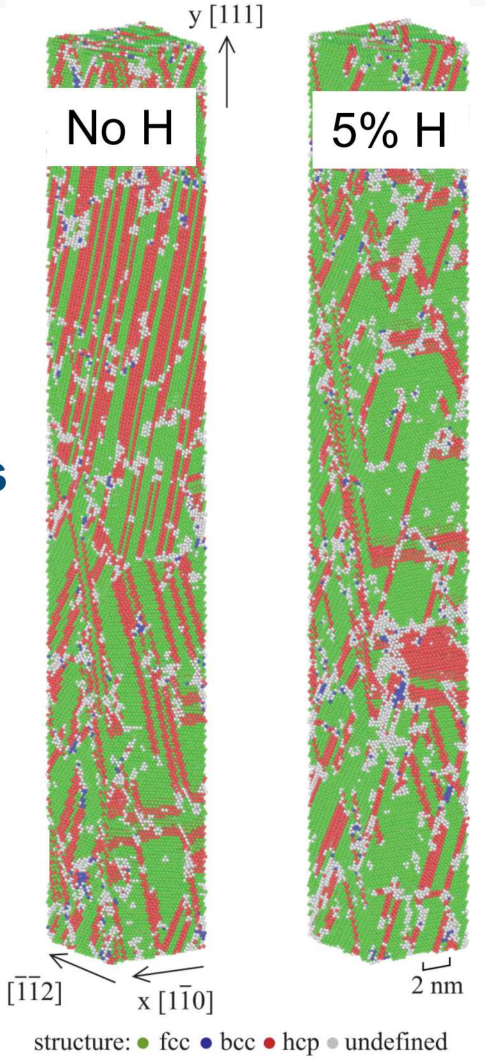
High-strength ferritic steel microstructures (task M1)

Fe-C-H interatomic potential has been implemented into LAMMPS and provides platform for microstructural studies

- **Comparison of predicted deformation structures with/without hydrogen identifies potential sites of damage accumulation and fracture initiation**
- **Novel microstructures identified in collaboration with partners (future iterations planned)**

In progress

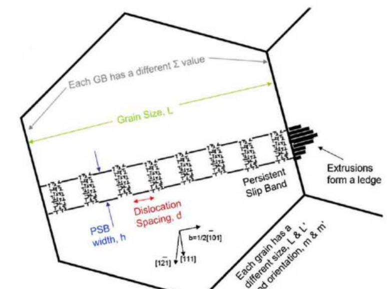
- **MD simulations will evaluate hydrogen interactions with different ferritic steels microstructure**
  - **provide insights to interactions of hydrogen with microstructure**
- **Kelvin probe force microscopy (KPFM) techniques**
  - **measure local hydrogen relative to microstructure**
- **Fatigue and fracture tests in high-pressure H2**
  - **demonstrate resistance to hydrogen-induced fracture**



Transferability of damage and crack nucleation in hydrogen environments (task M3)

Science questions:
- **Can the mechanics of damage be generalized such that crack activation can be predicted in the context of design lifetimes?**
- **What are the mechanisms of hydrogen-defect interactions that lead to damage accumulation?**

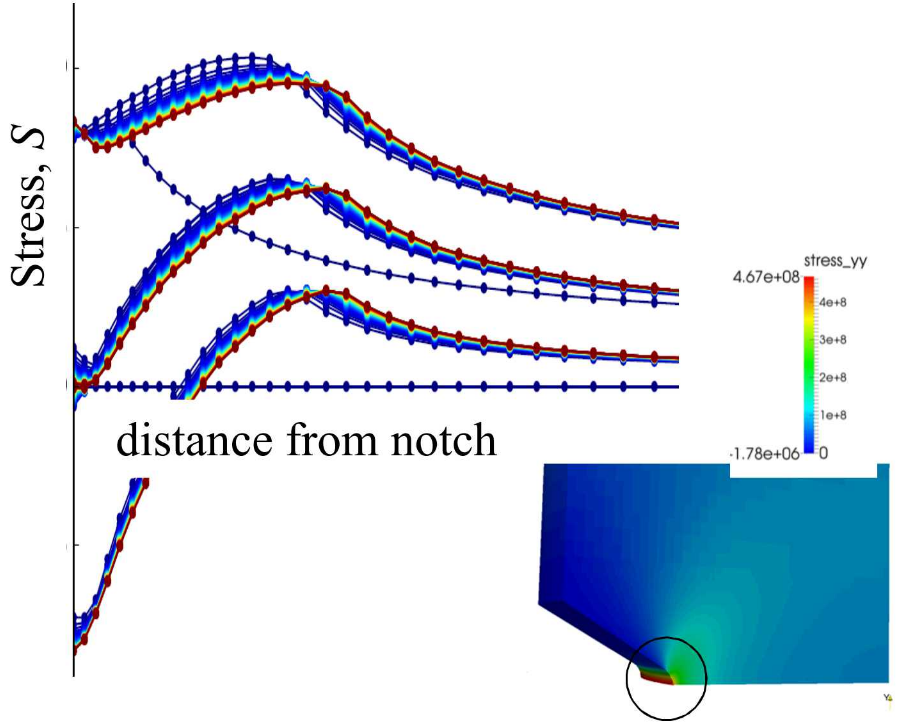
- Micromechanical modeling of defect initiation/growth in the presence of hydrogen through MD simulations
- Continuum modeling of test specimen geometry to develop normalization schemes to account for materials characteristics
- Experimental evaluation of crack nucleation to identify microstructural dependencies



Engineering goals:
- **Framework for quantification of damage and crack nucleation that can be implemented in design to increase lifetime assessment by 50% compared to conventional fracture mechanics approach**
- **Microstructural requirements that minimize effects of hydrogen**

Damage and crack nucleation (task M3)

Develop and utilize techniques to identify and monitor crack formation, coupled with mechanics modeling



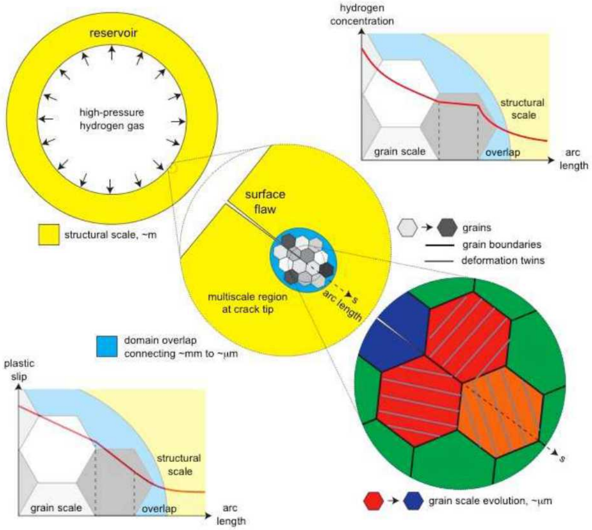
4-point probe provides very sensitive measure of crack initiation and advance

Solid mechanics modeling coupled with measurement of crack initiation provides new strategy to quantify nucleation

Mechanisms of hydrogen-deformation interactions in austenitic stainless steels (task M4)

Science question:
How does hydrogen change deformation and fundamental boundary interactions in austenitic stainless steels?

- Develop methods to test and evaluate single crystals and oligocrystals of austenitic stainless steels
- In situ testing and local characterization of strain and damage accumulation
- Micromechanical modeling of oligocrystals with internal hydrogen (CP) to illuminate mechanisms of hydrogen-microstructure interactions

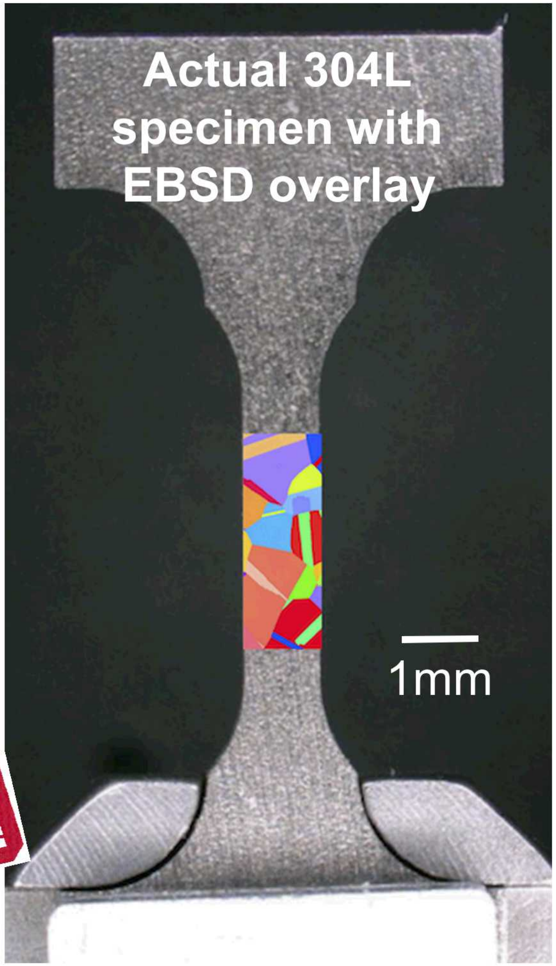


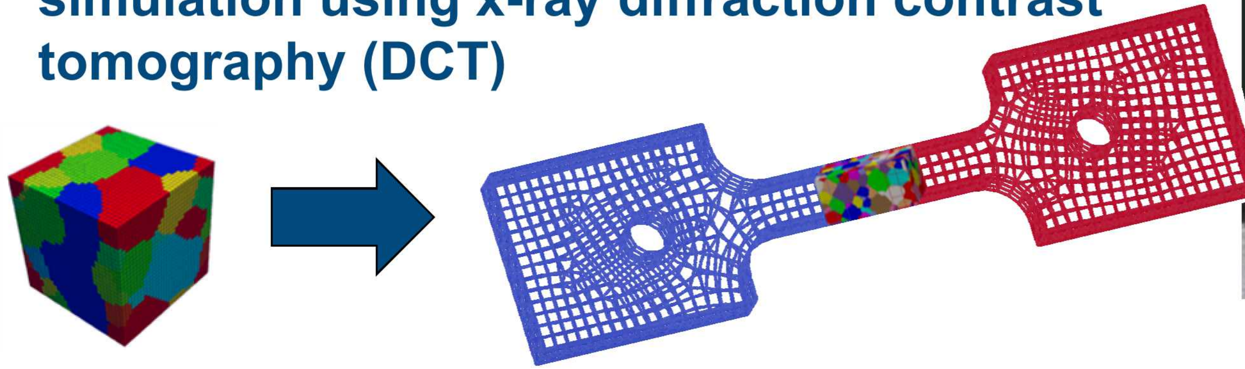
Engineering goals:
- **Microstructural design concepts that improve ductility of austenitic stainless steels in high concentration of hydrogen**
- **Accessible micromechanical modeling tools (CP) sensitive to hydrogen transients, local microstructure, and phase transformations**

Hydrogen-deformation interactions in stainless steels (task M4)

Techniques to manufacture, characterize and simulate deformation of oligocrystal microstructures are developing

- Test geometry suitable for in situ characterization and testing of small ensembles of grains (<100), including
  - local (in situ) measurements of strain using digital image correlation (DIC)
  - grain mapping and in situ deformation character with electron backscattered diffraction (EBSD)
- Working toward 3D non-destructive characterization of grain structure for direct simulation using x-ray diffraction contrast tomography (DCT)





Summary

The materials compatibility with hydrogen program is focused on:

- Advancing technology by developing fundamental understanding of damage mechanisms
- Developing & fostering collaborations to leverage expertise
- Communicating results to develop safer, lower cost materials for hydrogen infrastructure

H-Mat seeks to provide the foundational knowledge necessary to **design materials microstructures** for resistance to hydrogen-assisted fracture

H-Mat℠ Hydrogen Materials Compatibility Consortium

Acknowledgements

FCTO for funding much of this research

Hydrogen Effects on Materials Laboratory Team

- Chris San Marchi, Joe Ronevich, Jeff Campbell, Brendan Davis, Thale Smith, Eun Ju Song

Microscopy

- Josh Sugar, Doug Medlin, Julian Sabisch

Modeling

- Jay Foulk, Coleman Alleman, Ryan Sills, Xiaowang Zhou, Norm Bartelt

Surface Science

- Farid El Gabaly, Rob Kolasinski, Konrad Thurmer

Trapping and Transport Lab

- Rick Karnesky, Dean Buchenauer

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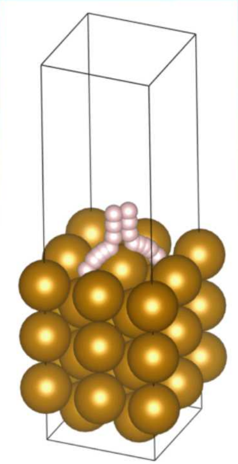
Back up slides

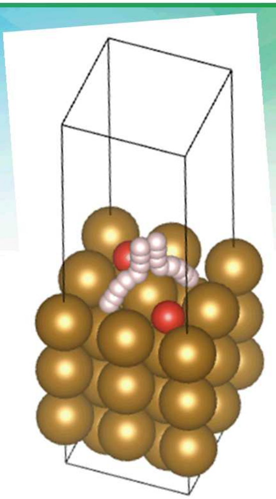
Potential energy surface scan for H_2 approaching Fe(100) surface

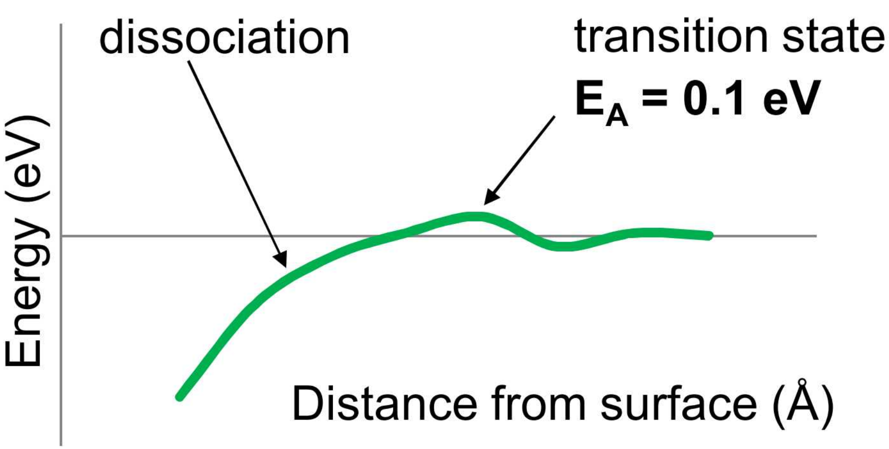
H_2 molecule approaches directly on top Fe atom

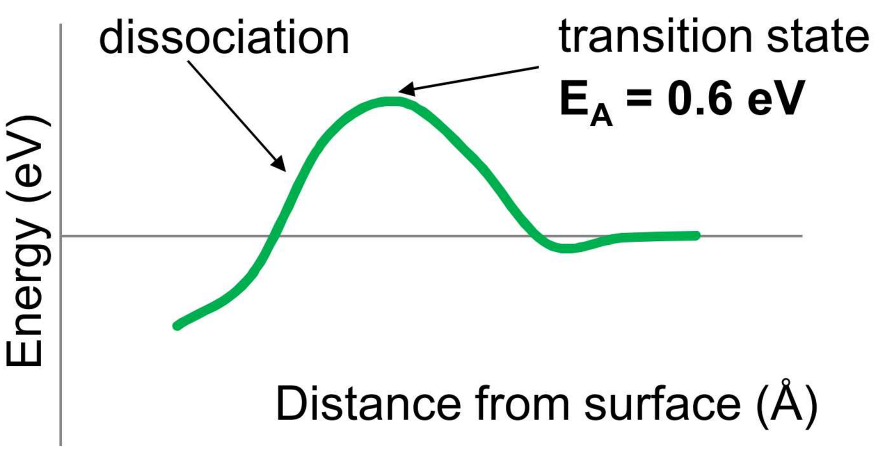


Potential energy surface scan for H_2 approaching Fe(100) surface with preadsorbed O atoms

H_2 molecule approaches directly on top Fe atom







Staykov et al., *Int J Quantum Chemistry*, 2014

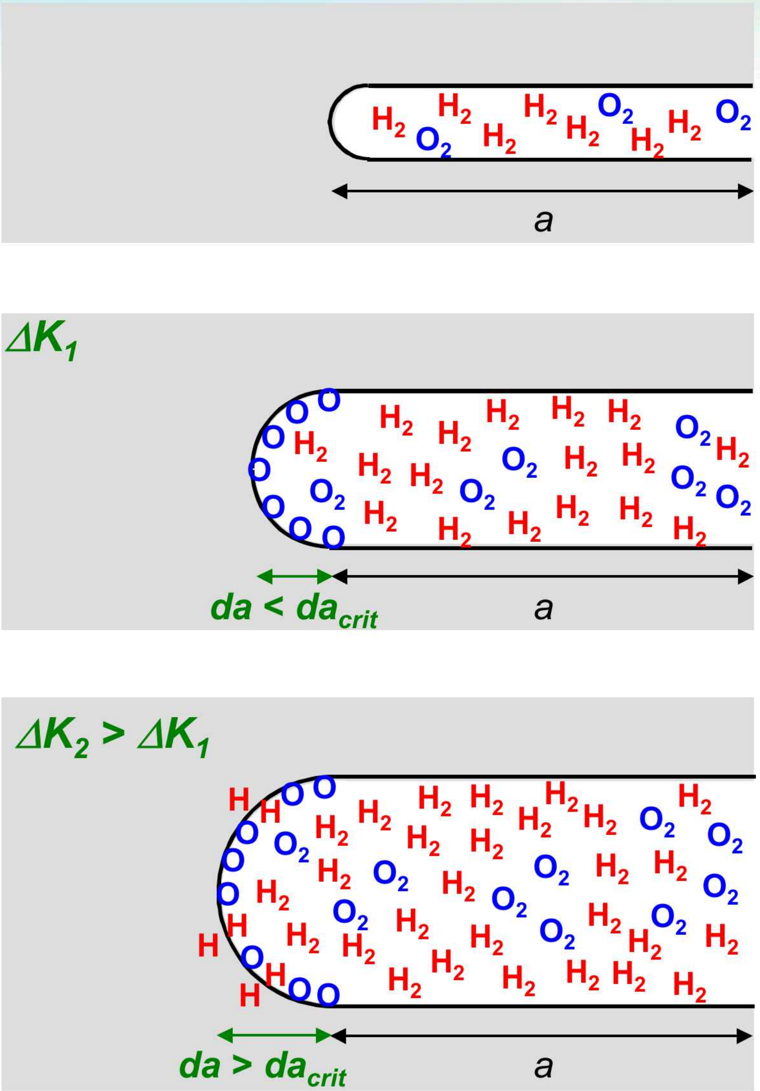
DFT simulations show that pre-adsorbed oxygen inhibits H_2 dissociation.

Related Research: Modeling H2 Embrittlement with Oxygen Impurities

B. Somerday et al., *Acta Mater*, 2013

Assumptions

- Initial inert-environment crack growth modeled by blunting-resharpening
- Oxygen out-competes hydrogen for adsorption sites on freshly exposed crack-tip surface
- Extent of oxygen adsorption depends on crack-tip area, proportional to crack-growth increment (*da*)
  - when $da < da_{crit}$, crack tip *fully passivated* by oxygen
  - when $da > da_{crit}$, crack tip *not fully passivated* → H uptake

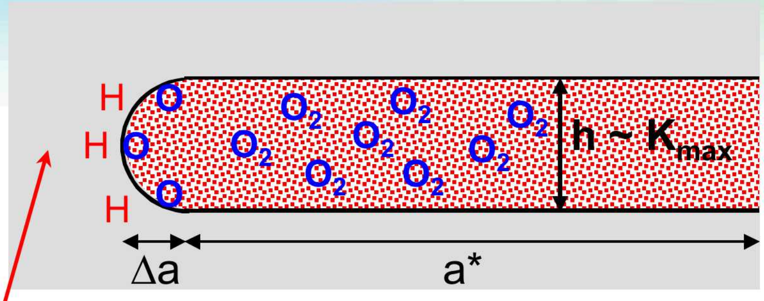


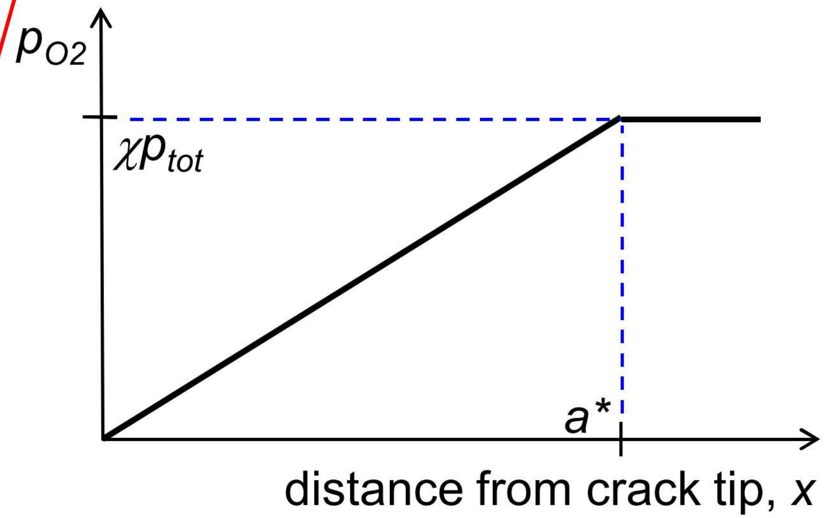
Developed model that relates oxygen adsorption to hydrogen uptake.

Model developed based on idealized crack geometry and diffusion-limited oxygen adsorption

Somerday et al., *Acta Mater*, 2013

- *Goal:* quantify amount of adsorbed oxygen (n) during load-cycle time (Δt)
- *Key assumption: adsorption rate-limited by O_2 diffusion in crack channel*
  - constant crack-channel height (h) during diffusion
  - steady state p_{O2} profile
- Model foundation: oxygen delivered to crack tip ($Jh\Delta t$) = oxygen adsorbed on crack tip ($S\theta\pi\Delta a$)





$$J = \text{flux} = D\frac{\chi p_{tot}}{R_g T a^*}$$

$$h = \text{channel height} = 0.6(1-\nu^2)\frac{\sigma_0}{E}\left(\frac{\Delta K}{\sigma_0(1-R)}\right)^2$$

$$\Delta t = 1/f$$

$$\theta = \text{oxygen coverage}$$

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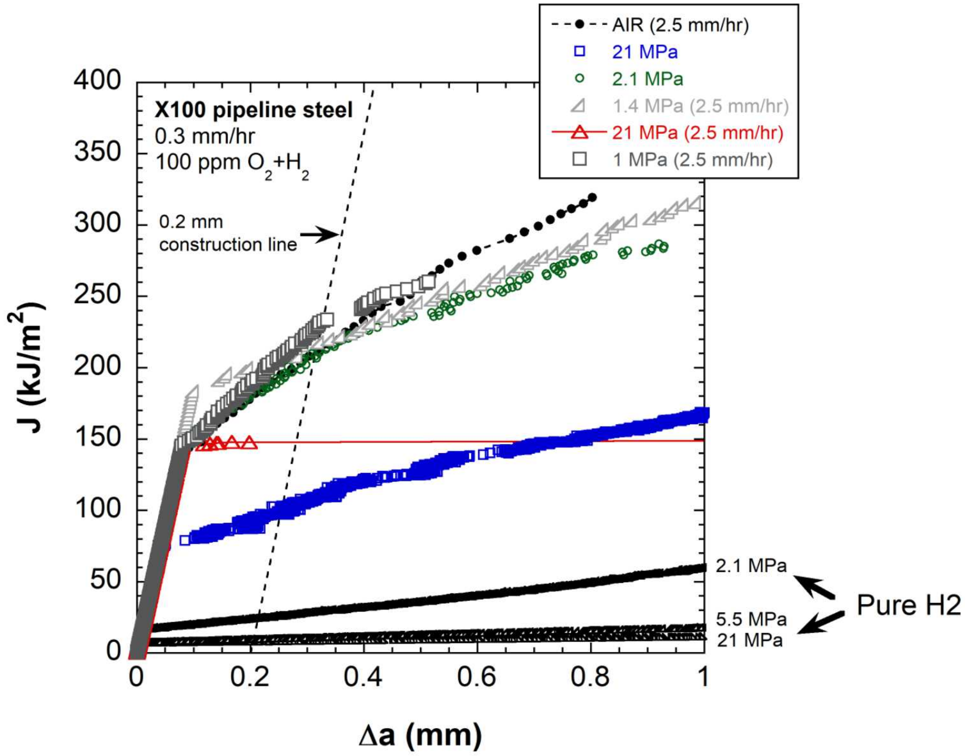
H uptake and accelerated crack growth when $\theta = \theta_{crit}$

$$\theta = \frac{0.3\chi D p_{tot}(1-\nu^2)}{\Delta a f \pi S R_g T E \sigma_0}\left(\frac{\Delta K}{\sqrt{a^*}(1-R)}\right)^2$$

Oxygen moderated hydrogen-assisted fracture (J-R curves ASTM E1820)

- In 21 MPa pure H_2, fracture toughness K_{JIH} values decreased by 80%.
- In 21 MPa mixed gas, fracture toughness decreased by only 30%.
- At lower pressures (1 - 2.1 MPa) in mixed gas, no effect of hydrogen was measured
  →(K_{JIH} in air ~ K_{JIH} in mixed gas)
- At lower pressure, test rates of 0.3 and 2.5 mm/hr resulted in similar K_{JIH} ~ air



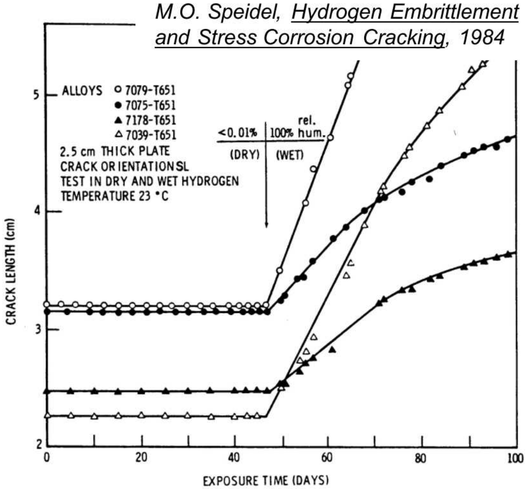
Fracture toughness at lower pressure similar to tests in air

Approach: High-strength aluminum alloys (task M2)

Science question:

What are the mechanisms of environmental embrittlement of high-strength aluminum alloys in high-pressure hydrogen? (in particular, what is role of moisture?)

M.O. Speidel, Hydrogen Embrittlement and Stress Corrosion Cracking, 1984



- Mechanical testing of aluminum in mixed gases (H_2 + H_2O) at high pressure
- Kelvin Probe Force Microscopy to investigate moisture on Al surfaces
- Modeling of moisture on Al surfaces to identify and quantify mechanisms of H uptake (DFT) and microstructural interactions of dissolved H (MD)

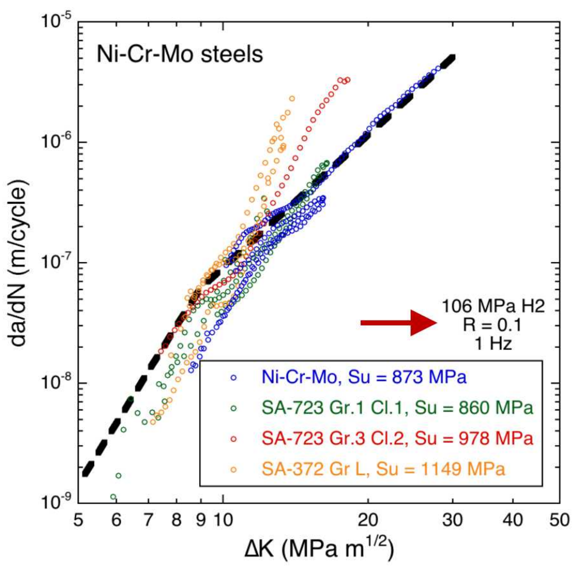
Engineering goals:

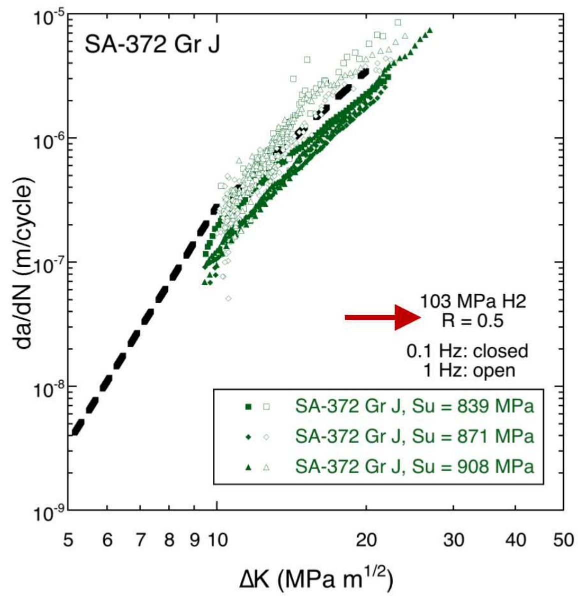
- **Hydrogen-compatible microstructures of aluminum alloys with yield strength >350 MPa that are insensitive to standardized moisture limits for fuel-grade hydrogen (5ppm H_2O)**
- **Specification of environmental conditions under which aluminum is not degraded in gaseous (and liquid) hydrogen environments**

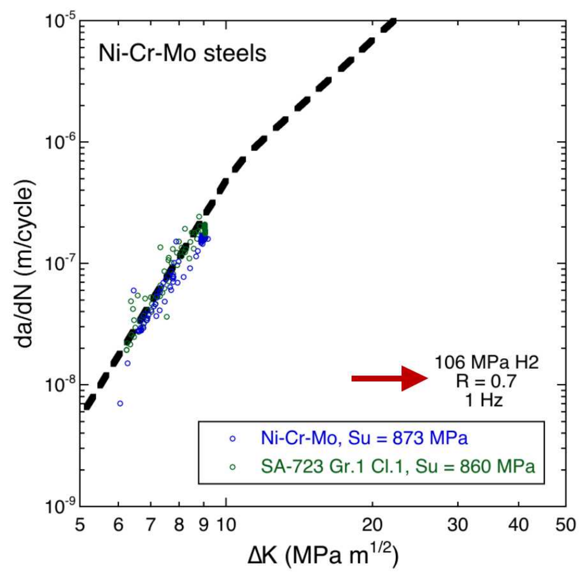
Accomplishment: stationary pressure vessels

ASME Code Case 2938 approved

"Technical basis for proposed master curve for fatigue crack growth of ferritic steels in high-pressure gaseous hydrogen in ASME section VIII-3 code" (PVP2019-93907), Proceedings of the 2019 ASME Pressure Vessels & Piping Conference, 14-19 July 2019, San Antonio TX. (manuscript in review)



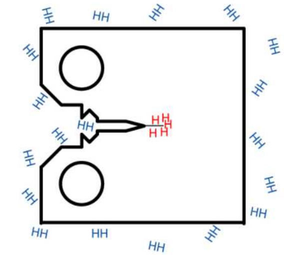




- **Provides design curve**

$$\frac{da}{dN} = C\left[\frac{1 + C_H R}{1 - R}\right]\Delta K^m$$

based on data and analysis from this program



Accomplishment: stationary pressure vessels

Design curves based on best available data, however a few questions remain (in progress)

- **High-strength steels show low fracture resistance in H2**
  - Fracture resistance becomes uncomfortably low, when tensile strength is >950 MPa
  - CC limits TS ≤ 915 MPa

> - *Steels with TS between 915-950 MPa are being re-evaluated*
> - *High-strength steels considered in H-Mat*

- **Fatigue behavior is pressure sensitive**
  - Empirical pressure term fits data for pipeline steels at low pressure

> *Testing is being considered to evaluate broader applicability of design curves*

- **Fatigue behavior near threshold and with negative load ratio are not well documented**
  - CC assumes that a fatigue threshold does not exist in H2
  - CC allows assumption that for $R < 0$, $K_{min} = 0$

> *Hardware and methods are being developed for high-pressure testing at low K_{max} and negative K_{min}*