H-Mat Overview: Metals

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Lab Partners: ANL, ORNL, SRNL

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H-Mat Hydrogen Materials Compatibility Consortium

2024 Annual Merit Review & Peer Evaluation Meeting

Sandia National Laboratories

Oak Ridge National Laboratory

Pacific Northwest National Laboratory

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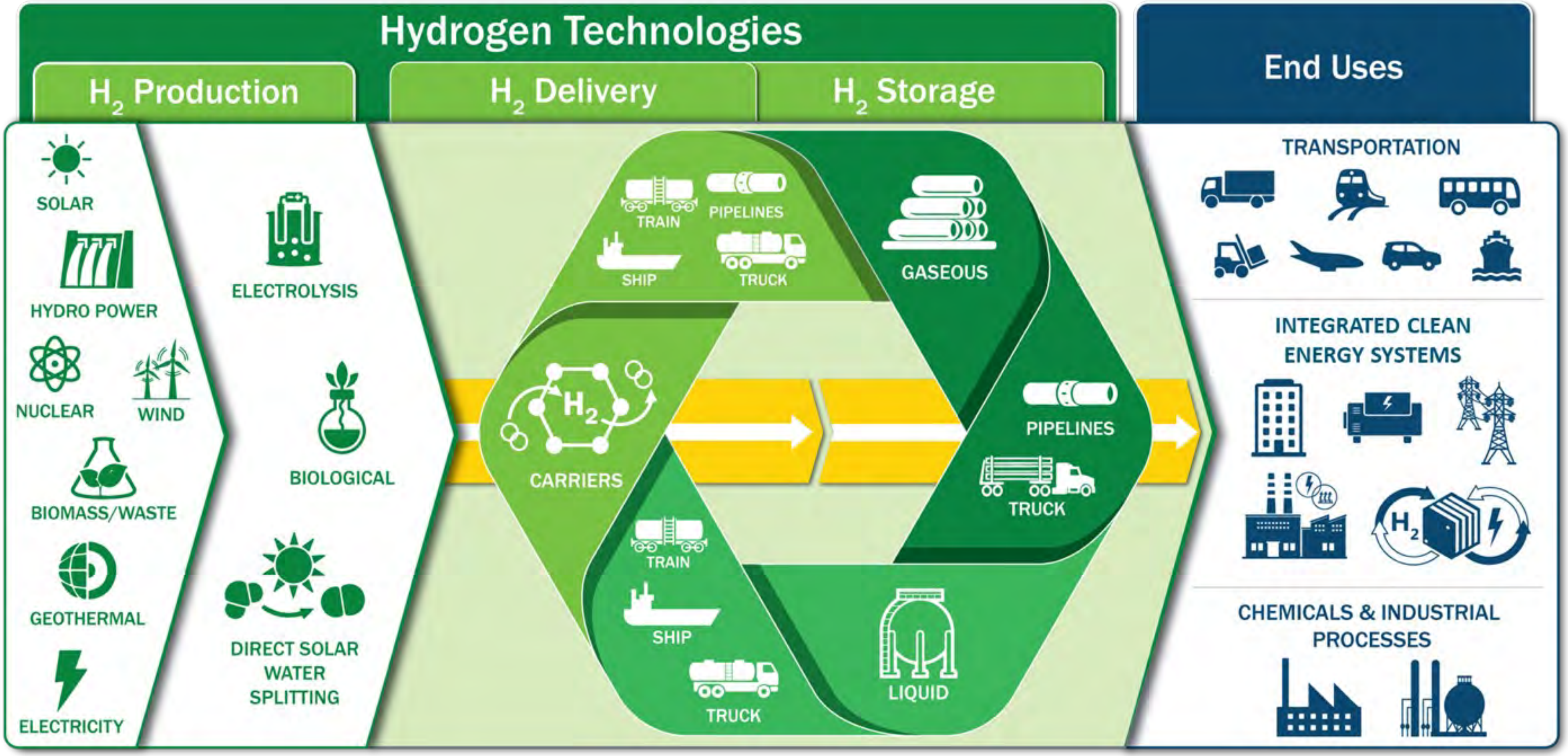
DOE program addresses challenges of the H2@Scale vision

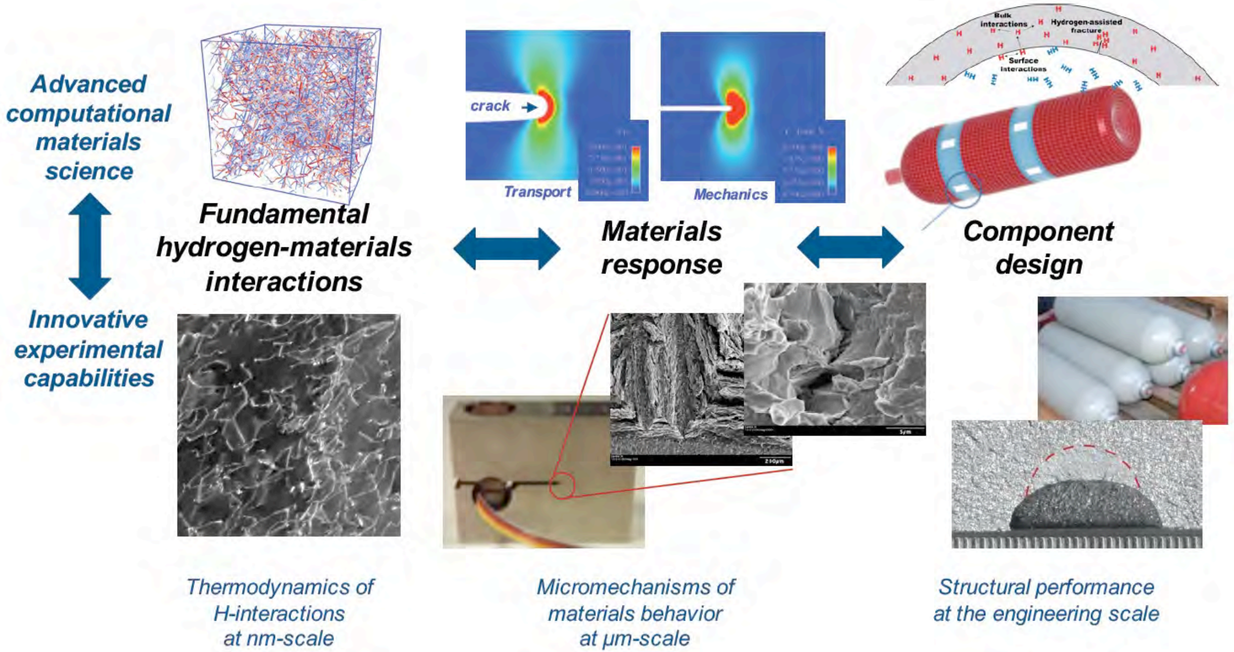


Source: Ned Stetson 2022 Annual Merit Review HFTO

Project Goal

Elucidate the mechanisms of hydrogen-materials interactions to inform science-based strategies to design the microstructure of metals with improved resistance to hydrogen degradation

- Hydrogen interactions at elevated temperature
- Surface phenomena, hydrogen uptake and transport
- Advanced high-strength alloy
- Similitude between accelerated laboratory tests and real-world
- Mechanisms of hydrogen degradation



Integrate innovative computational & experimental activities across length scales to inform mechanistic understanding at nanometer length scales and to engineer performance at the component scale

Overview

Timeline & Budget

- Phase 1 start: Oct 2018
  end: Sept 2023
  Budget: $12MM
- Phase 2 start: Oct 2023
  end: Sept 2027*
  Budget: $19.5MM

* Project continuation and direction determined by DOE annually

- FY24 DOE Funding
  - SNL (both metals and polymers): $2,780K

Any proposed future work is subject to change based on funding levels

Barriers

B. Reliability and Costs of Gaseous Hydrogen Compression

E. Gaseous Hydrogen Storage and Tube Trailer Delivery Costs

I. Other Fueling Site/Terminal Operation

Partners

Sandia National Laboratories

Pacific Northwest National Laboratory

Oak Ridge National Laboratory

- **Other projects**
  - eXtreme Materials (X-MAT)
  - Pipeline Blending CRADA (HyBlend)
- **Industry**
  - Swagelok, Siemens
- **FOA projects**
  - Colorado School of Mines
  - HyPerformance Materials Testing, LLC
  - MIT
  - Univ Alabama
  - Univ Illinois Urbana-Champaign

Relevance and Impact

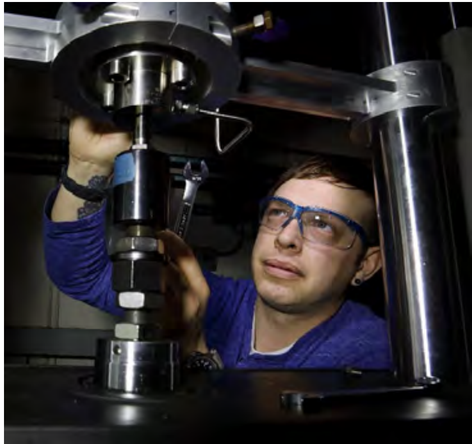
H-Mat goal enhanced performance and safety through improved understanding of materials compatibility and comprehensive materials data

Tasks	*Objectives*
Hydrogen interactions at elevated temperature	Establish basic trends on deformation and fracture for materials classes relevant to clean energy technology
Surface phenomena, uptake and transport	Provide a theoretical framework with experimental validation to qualify surface phenomena (eg, role of oxides)
Advanced high-strength alloys	Quantify trends for high-strength engineering alloys in hydrogen-exposed, non-pressure containing applications
Similitude between lab and real-world	Identify and address gaps in materials understanding and test methods to promote robust testing for hydrogen service
Mechanisms of hydrogen degradation	Advance microstructural understanding of hydrogen's influence on deformation and damage

Approach: Safety Planning and Culture

This project was not required to submit a safety plan for review by the HSP.

- **National Laboratories have over 2 decades of experience in hydrogen R&D**
  - DOE labs have extensive corporate requirements based on state and DOE requirements
  - Dedicated full-time staff to operate high-pressure experiments
- **Weekly safety, planning and discussion meetings**
  - Lab experimental teams meet every week to discussion safety concerns and plan activities for the week as well as share best practices and results
- **Layered safety approach**
  - Gas storage and handling outside building
  - Closed systems (designed with redundant seals and for venting above roof line)
  - Minimized gas volumes
  - Flammable gas sensors integrated with fire alarm system
  - Remote experimental operations (whenever feasible)



Approach

- Evaluate materials properties of high-priority alloys
  - focus on ductility and fracture
- Utilize H-precharging, when possible
- Refine framework to compare internal and external hydrogen
  - Targeted in situ testing
- Leverage outcomes from eXtremeMAT where feasible
  - Elevated vs high temp.

Hydrogen interactions at elevated temperature

(e.g., austenitic stainless steels, iron-based superalloys, and nickel-based alloys)

Science question:

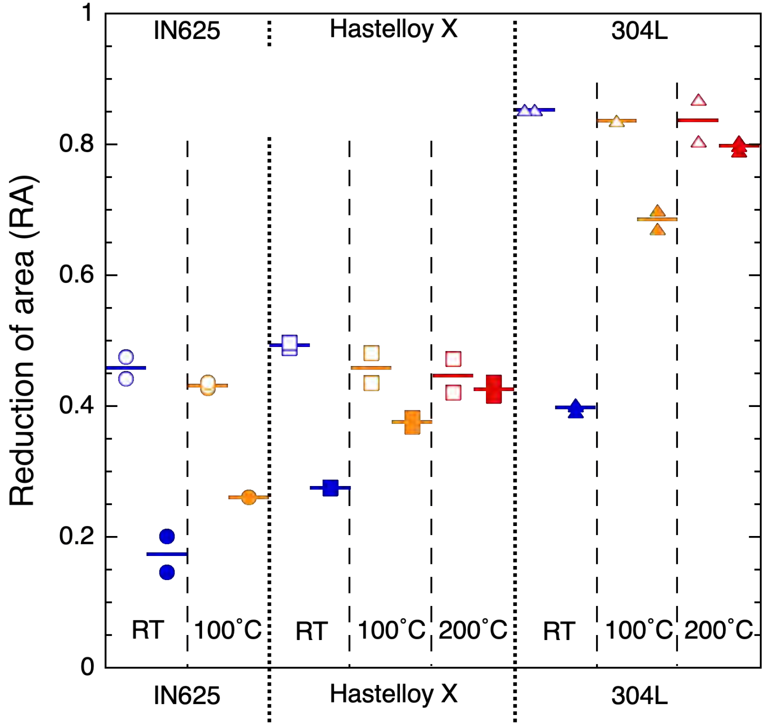
- **How do hydrogen effects depend on materials, environmental, and mechanics variables in applications at elevated temperature?**

Engineering goals:

- **Establish engineering relationship between temperature and ductility/fracture properties**
- **Compare and contrast properties of conventional wrought material and additively manufactured nickel-based alloys**

Accomplishments - Progress

Hydrogen interactions at elevated temperature



Ref.: Ronevich et al, PVP2024-83915

- **The effects of internal hydrogen on tensile ductility diminish at elevated temperature for 304L (not shown), IN625 and Hastelloy X**
  - **Almost no degradation of RA is apparent at temperature of 200˚C**
  - **Literature data, however, show an effect on creep at much higher temperature**
- **Fracture experiments are underway between room temperature and 200˚C**

Hypothesis: **At elevated temperature, hydrogen is more mobile and the 'strength' of the interaction with the microstructure is reduced**

Approach

- Use first principles to evaluate interactions between O_2 and H_2 on metal and oxide surfaces
- Use experimental studies of surface interactions to direct thermodynamic calculations (e.g., XPS)
- Develop *in situ* capability to measure impurities during long-term fracture experiments
- Consider additional tools to quantify kinetics (e.g. gas-phase permeation)

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Surface phenomena, uptake and transport

(emphasis on ferritic steels)

Science questions:

- **How do gas and surface impurities affect hydrogen dissociation and uptake?**
- **Can surface condition be controlled to achieve a thermodynamic barrier to hydrogen?**

Engineering goals:

- **Quantify long-term (100-1,000 hours) behavior of impurities on hydrogen-assisted fracture**
- **Provide quantitative guidance on 'credit' (if any) for oxidized metal surfaces to mitigate hydrogen-assisted fracture**

Accomplishments - Progress

Surface phenomena, uptake and transport

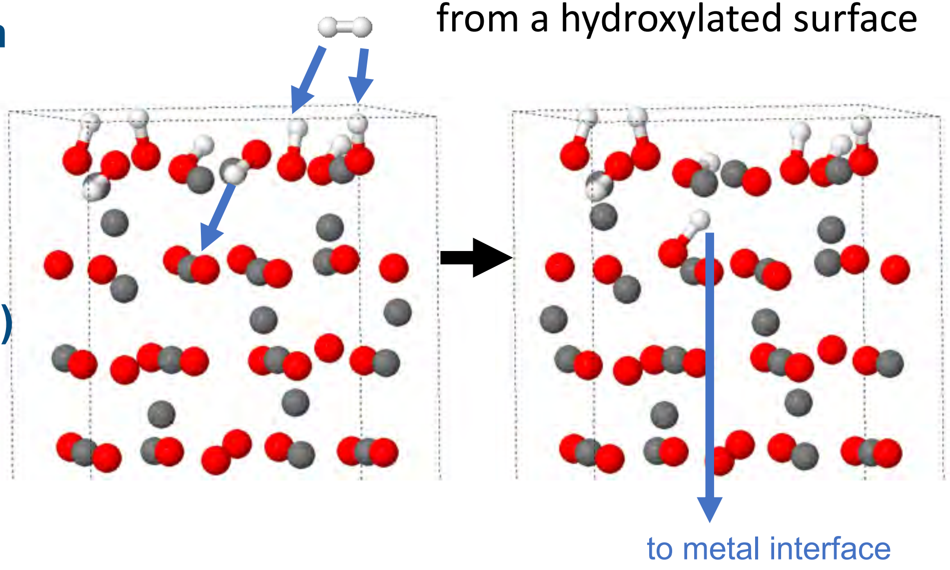
Experiments:

- Hydrogen-assisted fracture in pipe even for undisturbed native oxides
- Oxides form rapidly on clean steel surfaces (XPS)
- Hydroxyls form rapidly when oxide surfaces are exposed to hydrogen (XPS)

Modeling:

- First principle calculations suggest hydrogen atoms can diffuse through oxides (DFT simulations, right)

H atom diffusing into Fe_3O_4 from a hydroxylated surface



Experimental and computational observations consistently show oxides can impede but not prevent hydrogen-assisted fracture, especially on long time scales (> hours)

Approach

- Use internal hydrogen to evaluate ductility, fatigue and fracture properties of high-strength alloys for hydrogen service
- Evaluate hydrogen-assisted fracture of precipitation-strengthened stainless steels as a function of strength
- Explore role of microstructure in nickel-based alloys by comparing wrought and additively manufactured materials

Advanced high-strength alloys

(especially for internal components and subassemblies)

Science questions:

- **How does the mode of hydrogen-assisted fracture change in precipitation-strengthened stainless steels with strength?**
- **Can hydrogen-assisted fatigue in nickel alloys be managed through advanced processing?**

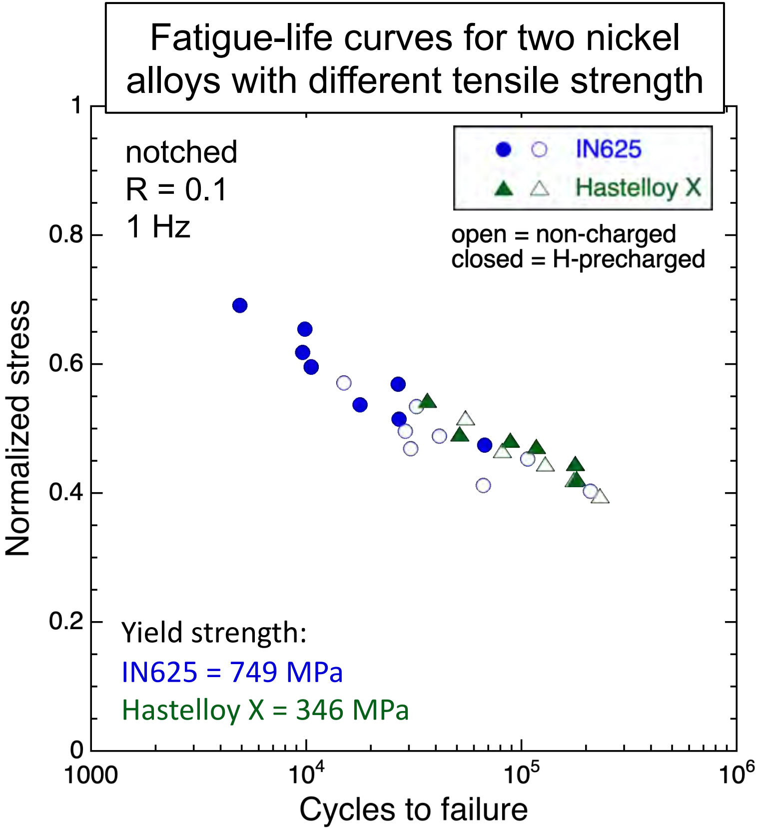
Engineering goals:

- **Identify practical bounds on strength (heat treatment) of precipitation-strengthened stainless steels to achieve fracture resistance > 50 MPa $m^{1/2}$**
- **Compare fracture resistance of wrought and additively manufactured nickel-based alloy**

Accomplishments - Progress

Advanced high-strength alloys

- **Fatigue life response of two nickel-based alloys show consistent response when normalized by the tensile strength**
  - **Internal H quantified by normalization**
  - **Targeted tests in gaseous hydrogen are underway**
  - **Fracture testing from task 1 will complement**
- **Fatigue response is quite different from tensile and fracture response (task 1)**



- **Initial results suggest H does not significantly degrade fatigue life of nickel-based engineering alloys**
  - **Testing of additively manufactured companion alloys will aid investigation of microstructure**

Approach

- Use unconventional fatigue wave forms and load holds to evaluate sub-critical crack growth in gaseous hydrogen
- Develop in situ gas monitoring capability and use mixed gases to quantitatively evaluate the influence of impurities at both long and short time scales
- Exploit pressure cycling to validate concepts in idealized component structures

Similitude between lab and real-world

Science questions:

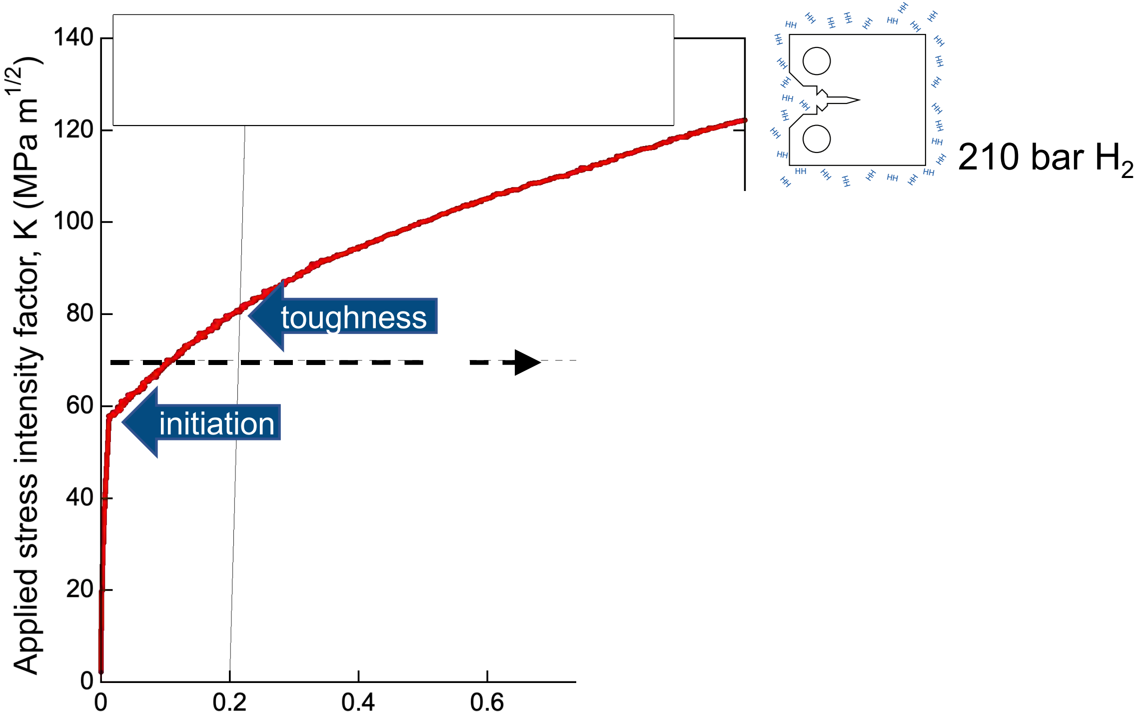
- **Can unstable crack propagation occur at stress intensity factor less than the initiation threshold from a fracture test?**
- **What is the relationship between partial pressure and oxygen concentration in crack initiation and propagation, respectively?**

Engineering goals:

- **Demonstrate threshold testing rate for hydrogen-assisted fracture in ferritic steels**
- **Identify best practices for hydrogen-assisted fatigue and fracture of ferritic steels (e.g., frequency, strain rate, hydrogen purity, etc)**

Accomplishments - Progress

Similitude between lab and real-world



Question:
Can unstable crack growth occur at stress intensity factor (K) less than measured fracture resistance?

- **Constant load testing shows very slow crack extension for K less than conventional 0.2 mm offset value**
- **Crack extension may be difficult to assess by proposed step loading methods**
- **Stability of crack is still unclear**

Additional testing is needed to verify conservative methodology to measure fracture resistance in gaseous hydrogen

Approach

- Advance novel analytical model of dislocations to predict effect of hydrogen on dislocation reactions
- Advance new concepts for MD configurations to quantify influence of hydrogen on energy barrier for relevant dislocation reactions
- Develop small-scale experimental methodology using advanced microscopy techniques

Mechanisms of hydrogen degradation

Science questions:

- **Can analytical models of dislocation reactions be adapted to incorporate effects of hydrogen?**
- **How and how much does hydrogen affect the energy barrier for cross slip?**

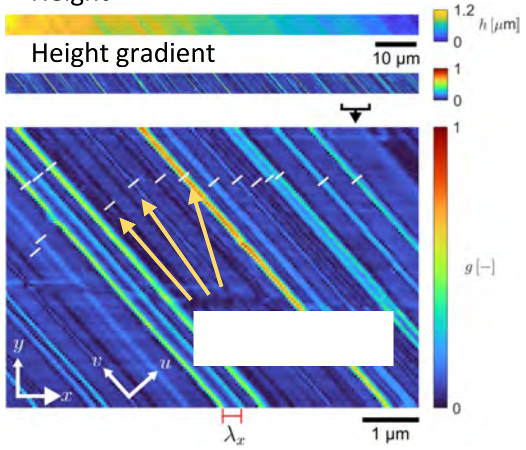
Engineering goal:

- **Identify testing configurations to validate modeling interpretations and provide direct evidence for hydrogen-induced damage in model alloy system**

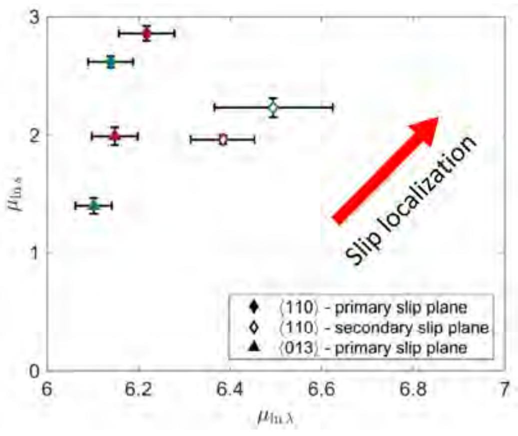
Accomplishments - Progress

Mechanisms of hydrogen degradation

Quantitative characterization of slip distribution via Atomic Force Microscopy (AFM)



6,331 surface steps identified over 4 specimens



Log-normal mean of slip band shear length and spacing

- **Tensile testing of H-precharged 316L single crystals reveal an increase in the critical resolved shear stress without deviation from Schmid's Law (i.e., conventional mechanics)**
- **Comprehensive analysis of slip steps using AFM demonstrates hydrogen-enhanced slip localization for both single- and multiple-slip configurations**

Internal H increases slip localization in single crystal 316L, likely due to cross-slip suppression

Response to Reviewer's Comments

comment:	response:
The project should consider how many times [valves] can be opened and closed… consider adding various materials' impacts on system weight … consider adding an inventory project	These are important considerations for industry. However, such activities are out of scope for this project. H-Mat is focused on the materials and their behavior. Valve operation, for example, will depend on the valve design, installation, maintenance etc, thus activities like this are arguably specific engineering considerations, and do not represent general materials behavior.
"The project should drop all the aluminum alloys, except AA6XXX…" "The project would benefit from additional experiments exploring the aluminum alloy behavior"	These comments on aluminum appear contradictory (from different reviewers). In any case, the aluminum work was motivated by exploring alternatives to 6000-series alloys and determining whether other factors (e.g., moisture) could enable hydrogen degradation. We believe that H-Mat has achieved this goal by providing foundational information that enables industry to consider higher performance aluminum alloys.
"The initiation work is weak."	The initiation work was a stretch goal for the project and has been as challenging as we expected. While the efforts did not result in a framework to design for crack initiation, we've established a method for measurement of crack initiation that we believe could be generalized (but would likely require broader community engagement). We'd love to hear actionable criticism.
"The project(s) need more specific partners with more experience with certain materials and scientific fields to help guide the testing and research."	The H-Mat team values partnership and participation from interested parties – and the team engages whenever possible (tasks are motivated by input from industry partners). However, the lab team(s) do not control funding for other groups, which limits the extent of engagement. H-Mat labs do support other DOE-funded projects, but we leave reporting on that work to the PIs of those projects. Otherwise, the H-Mat team can only dedicate resources to the milestones agreed upon with DOE.

Collaboration and Coordination

H-Mat Hydrogen Materials Compatibility Consortium

Core Team:	Project Roles (metals):
Sandia National Laboratories	Project co-lead (metals); testing in gaseous hydrogen; hydrogen precharging; advanced characterization; high-performance computing
Pacific Northwest National Laboratory	Project co-lead (polymers); cryogenic testing; H-Mat website and DataHUB
Oak Ridge National Laboratory	Microstructural characterization, development and production of advanced microstructures

- **Academic partners**
  - *Colorado School of Mines*: identification and custom heat treatment of high-strength ferritic steels
  - *Rutgers University*: atomistic simulation of defects
- **Independent H-Mat projects**
  - *Colorado School of Mines, Hy-Performance Materials Testing LLC, Univ Alabama, Univ Illinois (UIUC)*
- **Industry**
  - *Swagelok, Siemens*

Remaining Challenges

- Hydrogen degrades mechanical properties of all metals, but the degree of degradation remains a knowledge gap for most materials
- Mechanistic understanding requires multiscale simulation and novel 'imaging' techniques
- Existing modeling frameworks are largely inadequate to capture the behavior of hydrogen in metals

Associated Barriers

- **While some superficial trends are known for some materials, detailed design information is often lacking**
  - Austenitic stainless steels have been extensively studied, but remarkably little fatigue and fracture design data are available
  - Fatigue and fracture data are available for narrow range of construction steels, but compositional variables remain limited
- **Hydrogen's influence on deformation, damage and failure is difficult to characterize**
  - Characterization techniques are hampered by the unique characters of hydrogen: small and highly mobile, most common element – therefore, background is high
- **Modeling at the atomic scale is necessary to understand the mechanisms, but most tools are insufficient**
  - Limited time scales of atomistic models lead to mis-interpretations of observed phenomena
  - Many degrees of freedom in steel microstructures challenge multiscale modeling efforts

Proposed future work for FY24-25

Deliverables and milestones

Hydrogen interactions at elevated temperature	• Present initial characterization of 3 alloys at elevated temperature at ASME conference (associated manuscript nearing completion) • Establish baseline fatigue life curves for high-temperature nickel-based alloys, including characterization of crack initiation
Surface phenomena, uptake and transport	• Provide critical thermodynamic and kinetic assessments of hydrogen interactions with metal and oxide surfaces to inform mechanisms of hydrogen uptake
Advanced high-strength alloys	• Quantify role of strength in precipitation-hardened stainless steel for hydrogen-exposed, non-pressure containing applications
Similitude between lab and real-world	• Evaluate fracture resistance of high-strength and low-strength steels at strain rates over 3 orders of magnitude (journal submission planned) • Define best practices in hydrogen-assisted fracture testing
Mechanisms of hydrogen degradation	• Develop framework to explain the influence of hydrogen on cross slip and implications for hydrogen-assisted degradation of FCC metals • Formulate concepts into a manuscript for journal submission

Summary

- H-Mat is a consortium of national laboratories formulated to address the **materials science of hydrogen-induced degradation** of materials
  - ***Motivation***: enable **science-based decision making** for design optimization of hydrogen technologies
  - ***Approach***: establish similitude between **laboratory, computational studies, and real-world applications** utilizing state-of-the-art laboratory capabilities

Hydrogen interactions at elevated temperature	• **Hypothesize that mobility of hydrogen is increased at elevated temperature, reducing interactions between hydrogen atoms and dislocations**
Surface phenomena, uptake and transport	• **Oxides increase the time scale for hydrogen-assisted fracture but do not prevent the effects of hydrogen**
Advanced high-strength alloys	• **Two nickel-based alloys show loss of tensile ductility and fracture resistance with internal hydrogen, but little change in fatigue life**
Similitude between lab and real-world	• **Fracture specimens subjected to constant load show slow crack extension at stress intensity factor less than conventional measures of fracture resistance**
Mechanisms of hydrogen degradation	• **Fundamental mechanics of deformation in single crystals of 316L are similar to observations of deformation in polycrystalline material**

Thank You!

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