SAND2019- 3279 C

H-Mat Overview: Steels

Science-based advancement of materials for hydrogen technologies

PI: Chris San Marchi (SNL) and Kevin Simmons (PNNL)

Lab Partners: SRNL, ORNL, ANL

2019 DOE Hydrogen and Fuel Cells Annual Merit Review

May 1, 2019

Project ID# IN001

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525.

Overview

Timeline

- Project start date: Oct 2018
- Project end date: Sept 2022*

* Project continuation and direction determined by DOE annually

Technical Barriers

B. Reliability and Costs of Gaseous Hydrogen Compression
E. Gaseous Hydrogen Storage and Tube Trailer Delivery Costs
I. Other Fueling Site/Terminal Operation

Budget (metals only)

- Total FY19 Budget: $2.2M
  - SNL: 1,750K
  - PNNL: 100K
  - ORNL: 200K
  - SRNL: 150K
- Planned FY20 Funding: $2M

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

Partners

- **Academia:**
  - Colorado School of Mines (not funded)
  - University of California Davis (not funded)
- **Industry:**
  - Swagelok (not funded)

Additional partnerships to be added through DOE solicitations

H-Mat addresses materials-compatibility science questions

Metals

Task M1
High-strength ferritic steel microstructures

Task M2
High-strength aluminum alloys

Task M3
Transferability of damage and crack nucleation

Task M4
Microstructure of austenitic stainless steels

Task C1
Materials for cryogenic hydrogen service

Polymers

Task P1
Mechanisms of degradation

Task P2
Multiscale modeling

Task P3
Hydrogen-resistant polymeric formulations

Relevance and Objectives

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

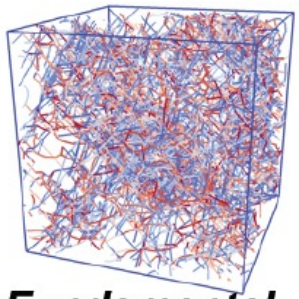
Task	Relevance and Objective
High-strength ferritic steel microstructures	Develop a mechanistic understanding of hydrogen-induced fracture processes in ferritic steel microstructures to improve fracture resistance of low-cost steels with tensile strength >950 MPa
High-strength aluminum alloys	Elucidate 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 deformation and damage in fatigue environments at multiple length scales toward a framework to implement 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

Relevance: Engineering performance depends on mechanisms manifest at nanometer length scales

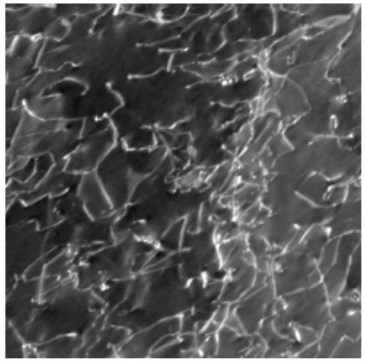
Approach: Integrate innovative computational & experimental activities across length scales

Advanced computational materials science

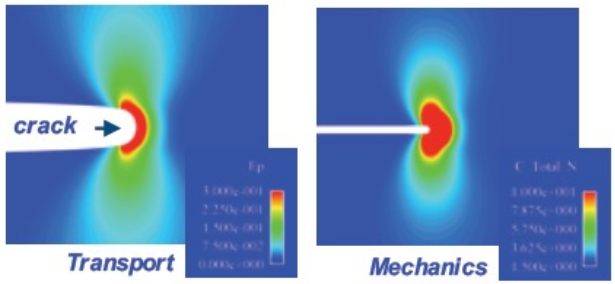
Innovative experimental capabilities



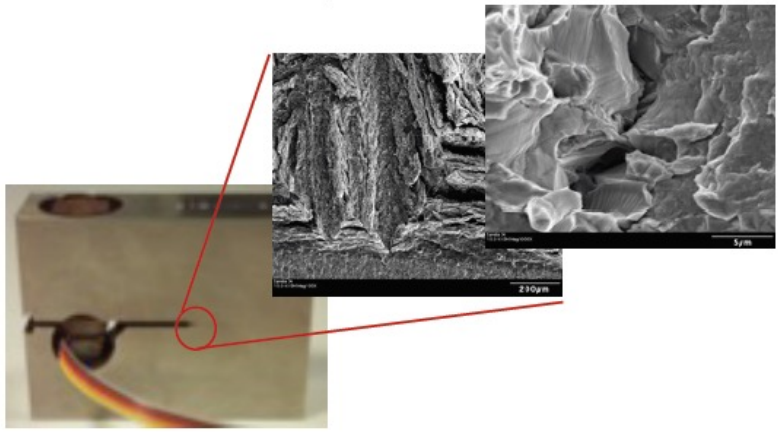
Fundamental hydrogen-materials interactions



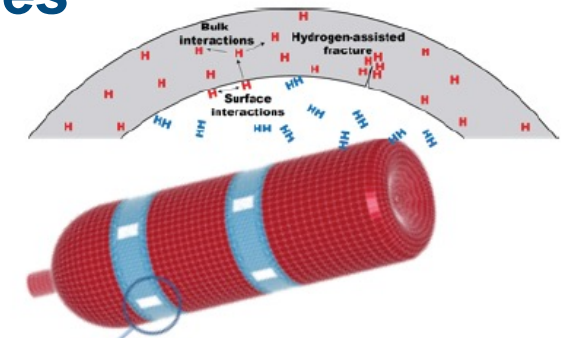
Thermodynamics of H-interactions at nm-scale



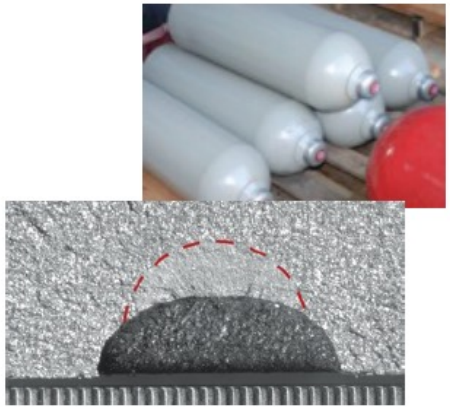
Materials response



Micromechanisms of materials behavior at μm-scale

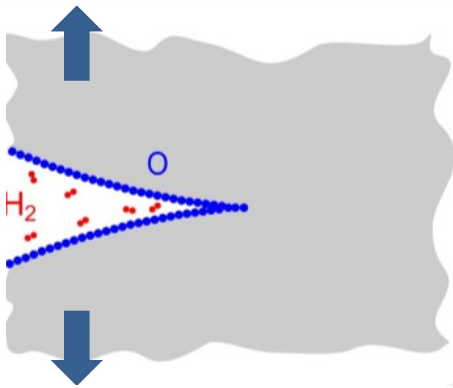


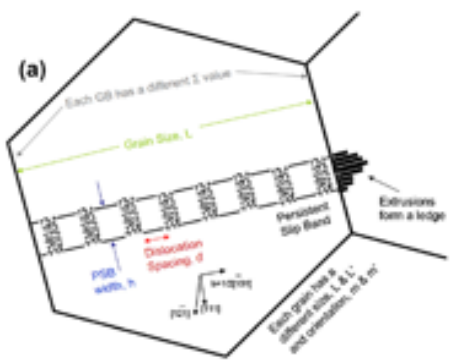
Component design

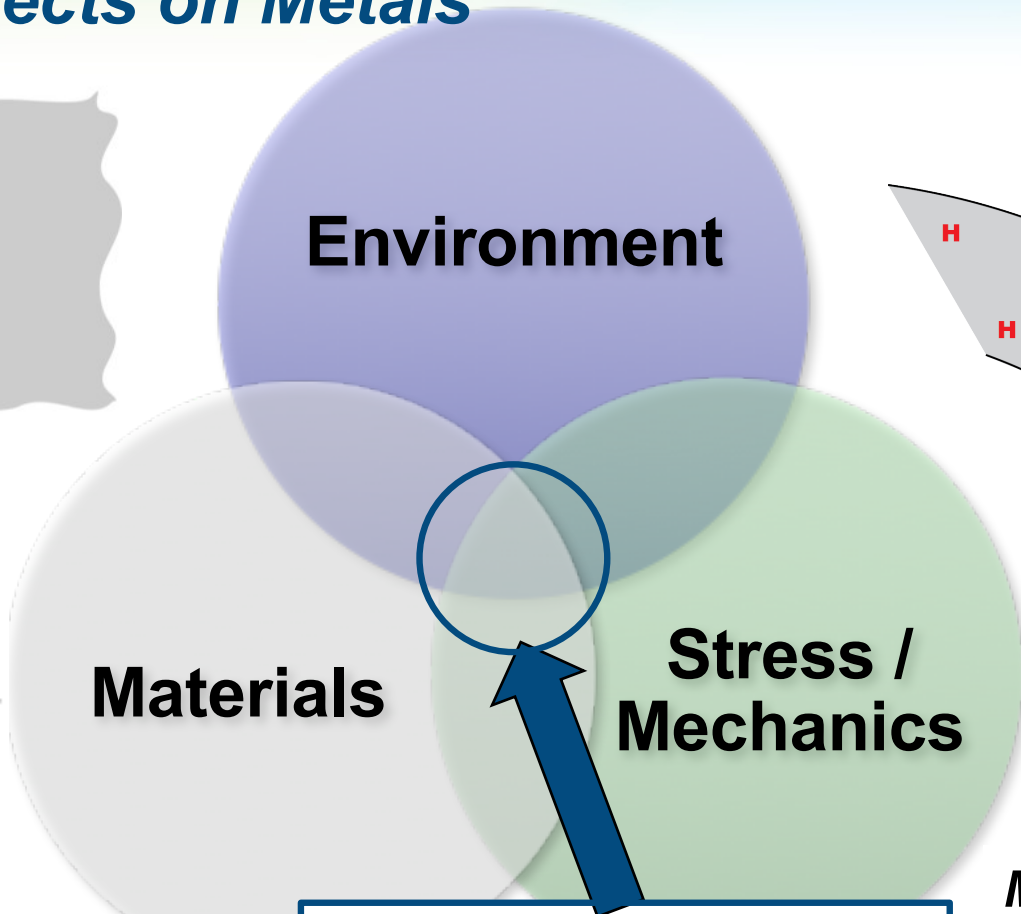


Structural performance at the engineering scale

Approach: Consider the intersection of *environmental*, *mechanics* and *materials* variables to understand *Hydrogen Effects on Metals*



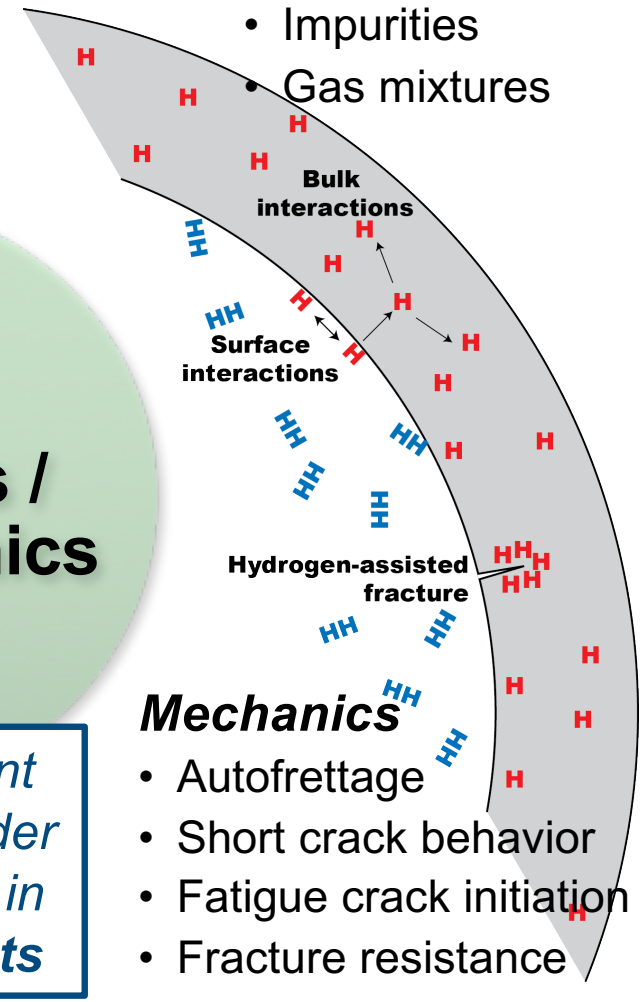




*Hydrogen embrittlement occurs in **materials** under the influence of **stress** in hydrogen **environments***

Environment

- Low temperature
- High pressure
- Impurities
- Gas mixtures



Materials

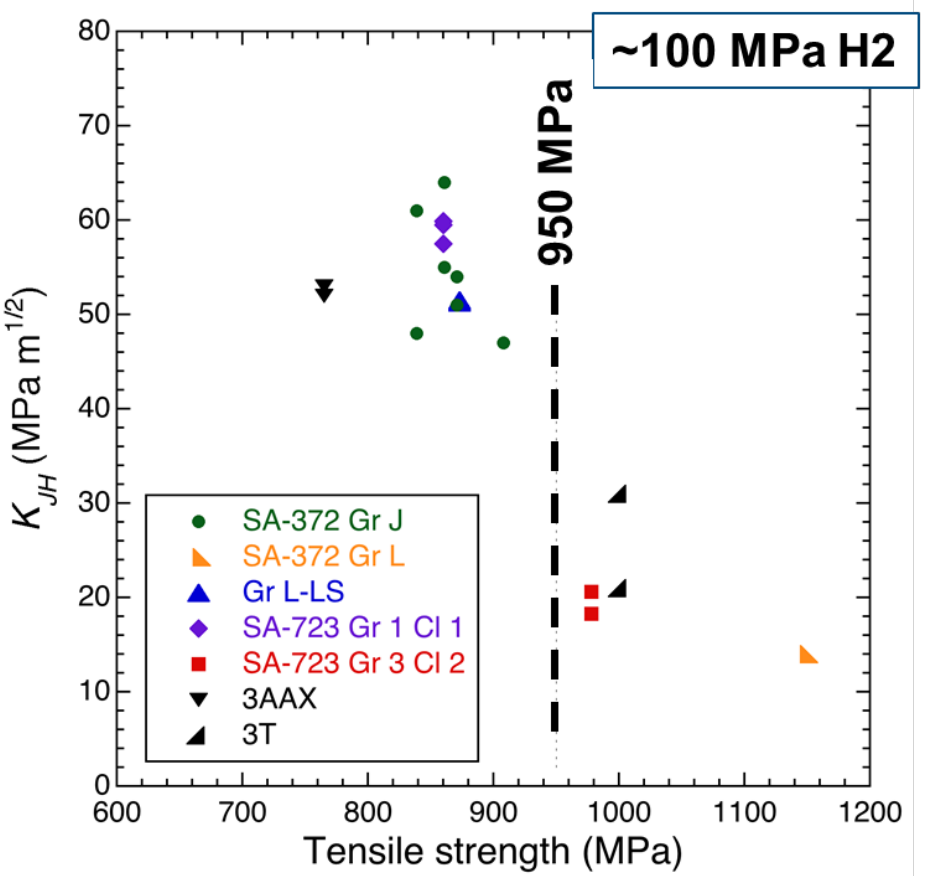
- High-strength
- Hydrogen-enhanced plasticity
- Boundary cracking
- Surface passivation

Mechanics

- Autofrettage
- Short crack behavior
- Fatigue crack initiation
- Fracture resistance

Approach: 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 hydrogen
- Development of unique microstructures (e.g., austempering)
- Kelvin Probe Force Microscopy to investigate hydrogen distribution
- Modeling of Fe-C-H (DFT and MD) to explore microstructure-hydrogen interactions

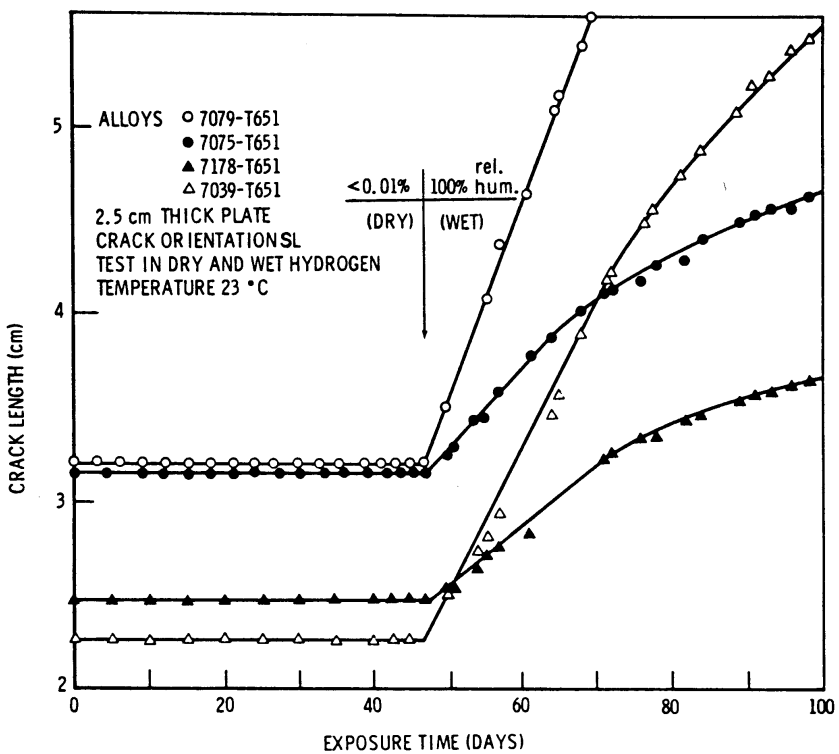
Engineering goals:

- **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 H2**

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
- Mechanisms of H on Al surfaces (DFT) and H-microstructure interactions (MD)

Engineering goals:

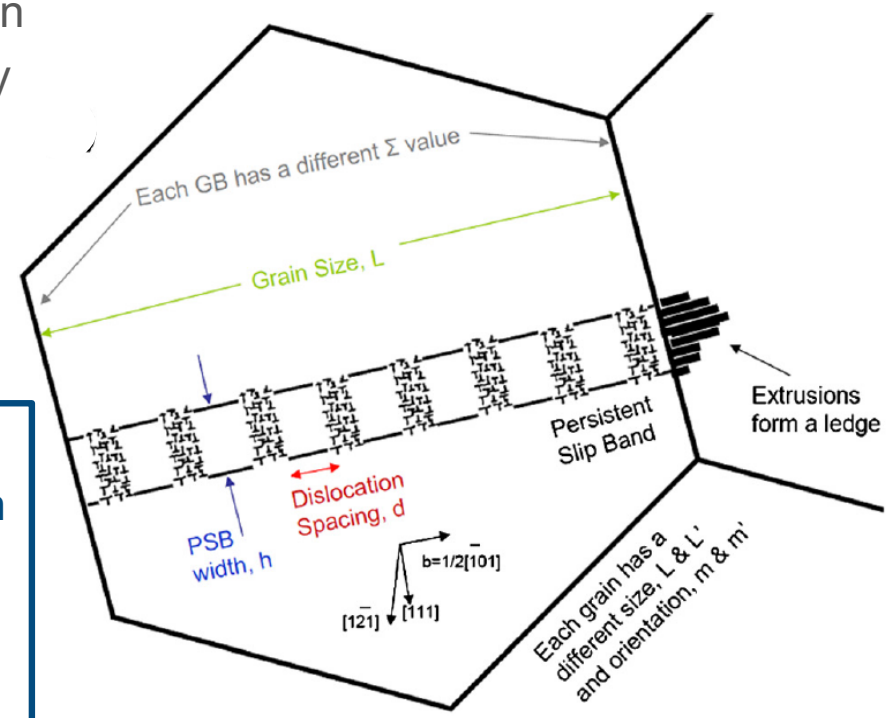
- **Aluminum alloys with yield strength >350 MPa that are insensitive to standardized moisture limits for fuel-grade hydrogen (5ppm H_2O)**
- **Specification of environmental conditions under which aluminum is not degraded in gaseous (and liquid) hydrogen environments**

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

Science questions:

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

- Atomistic modeling of defect structures to rank-order the effects of hydrogen on defect evolution
- Continuum modeling of test specimen geometry to develop normalization schemes correlating material evolution to fatigue crack nucleation
- Experimental evaluation and microstructural quantification of hydrogen-affected cyclic deformation and fatigue crack nucleation



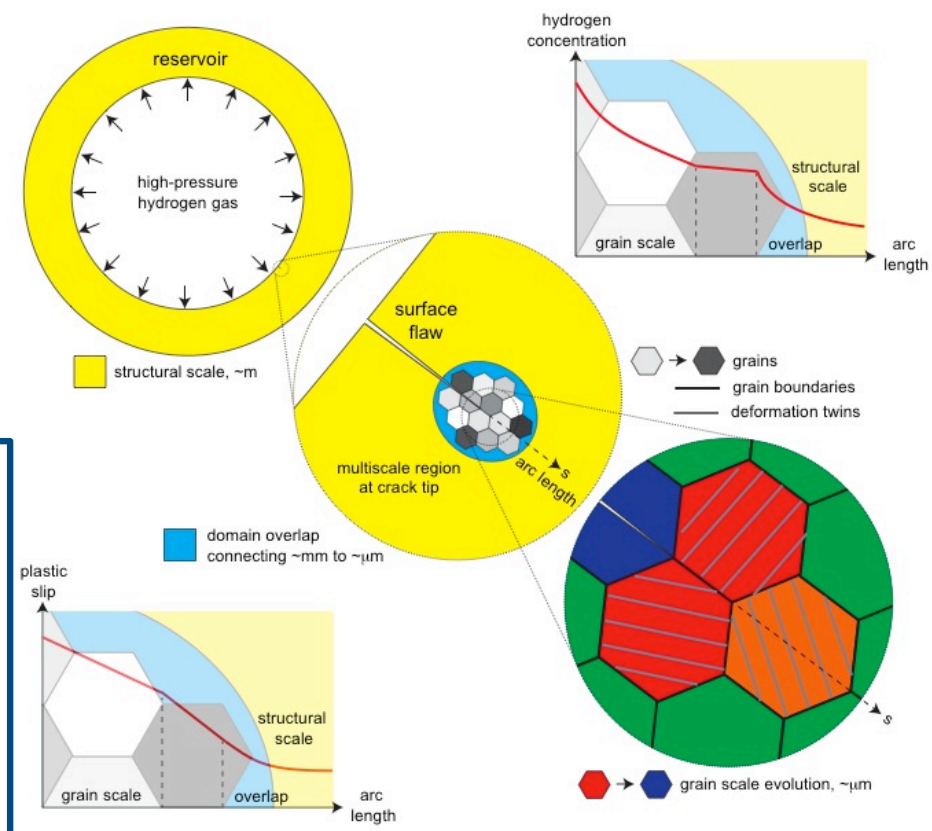
Engineering goals:

- **Framework for quantification of crack initiation to increase design life by 50% compared to conventional fracture mechanics approach**
- **Microstructural requirements that minimize effects of hydrogen**

Approach: 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 oligocrystals of austenitic stainless steels
- In situ testing and local characterization of strain and damage accumulation
- Micromechanical modeling (CP) of oligocrystals to illuminate mechanisms of hydrogen-microstructure interactions

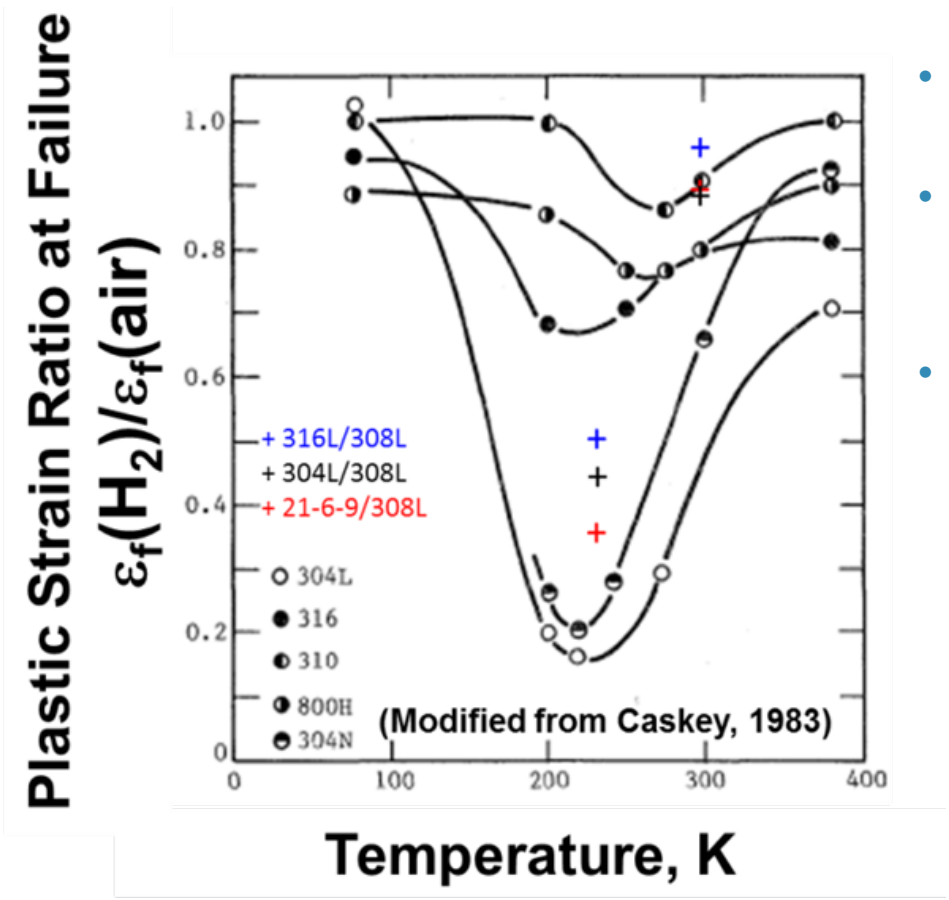


Engineering goals:

- **Microstructural design concepts that mitigate H-assisted fracture of austenitic stainless steels**
- **Micromechanical modeling tools (CP) sensitive to hydrogen transients, local microstructure, and phase transformations**

Approach: Metals for cryogenic applications in hydrogen service (task C1)

Science question:
At cryogenic temperature, what are the kinetic versus mechanistic limitations to the manifestation of degradation in hydrogen environments?



- Identify effects of hydrogen-induced cracking at LH2 temperature
- Design of mechanical tests to elucidate kinetic factors on testing results (such as test rate)
- Evaluate weld microstructures at low-temperature with high hydrogen concentration

Engineering goals:
- **Guidance for long-term performance of materials in cryogenic environments**
- **Performance metrics (e.g., fatigue) for structural welds in cryogenic hydrogen applications**

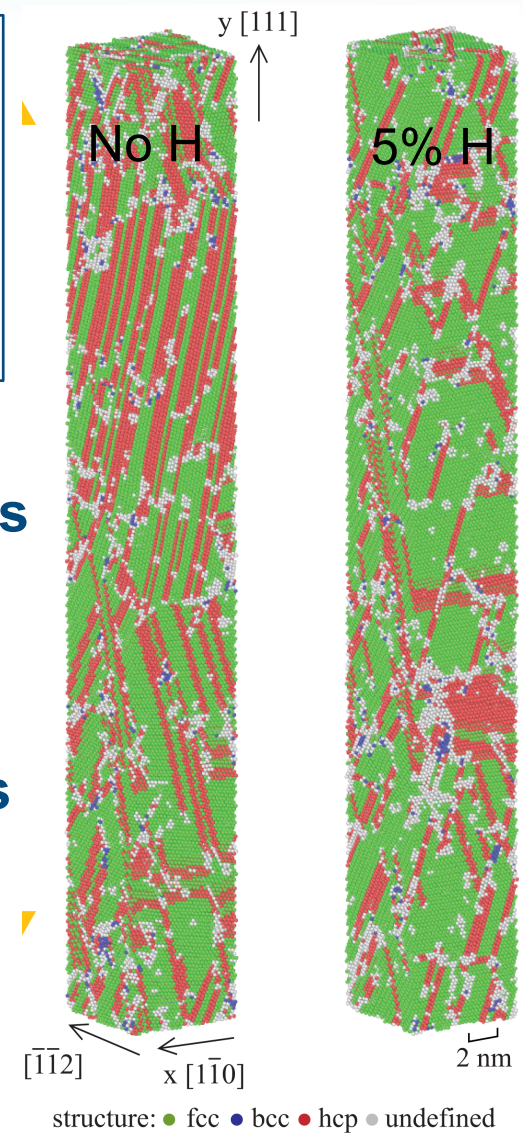
Accomplishments: High-strength ferritic steel microstructures (M1)

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



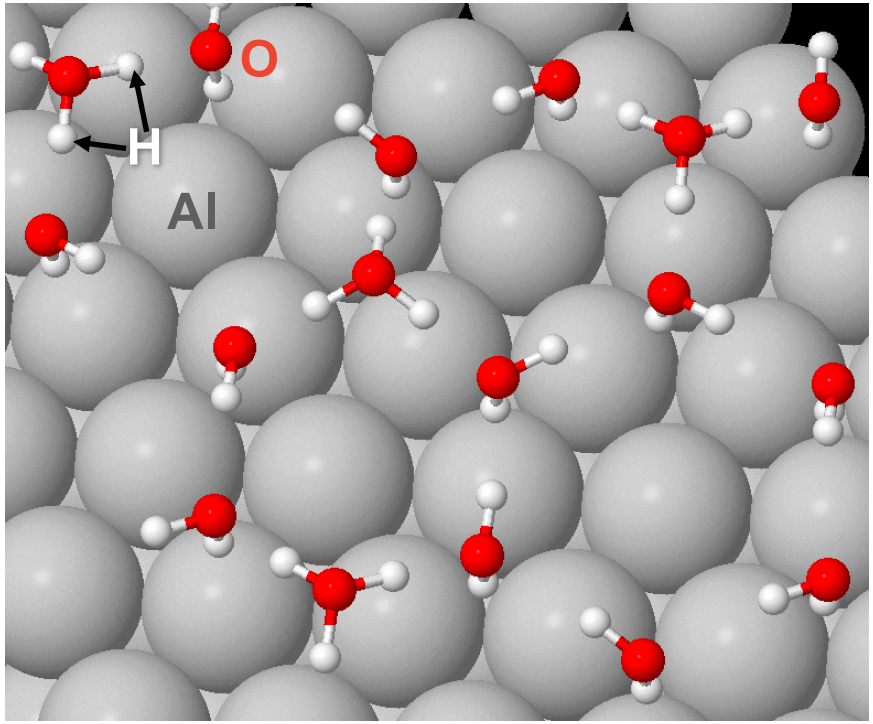
Accomplishments: High-strength aluminum alloys (M2)

First principles calculations are illuminating of the role of moisture in metal-hydrogen interactions

Initial DFT results suggest the presence of water might affect the kinetics of hydrogen absorption

In progress

- MD simulations to evaluate the effect of hydrogen on dislocation mobility
  - hypothesized role on fracture
- Kelvin probe force microscopy (KPFM) techniques
  - measure local hydrogen relative to microstructure
- Fracture tests in hydrogen-water gas mixtures
  - experimental evidence of hydrogen-induced fracture

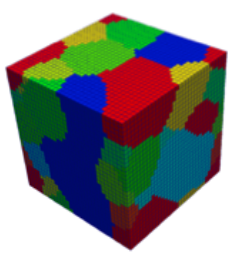


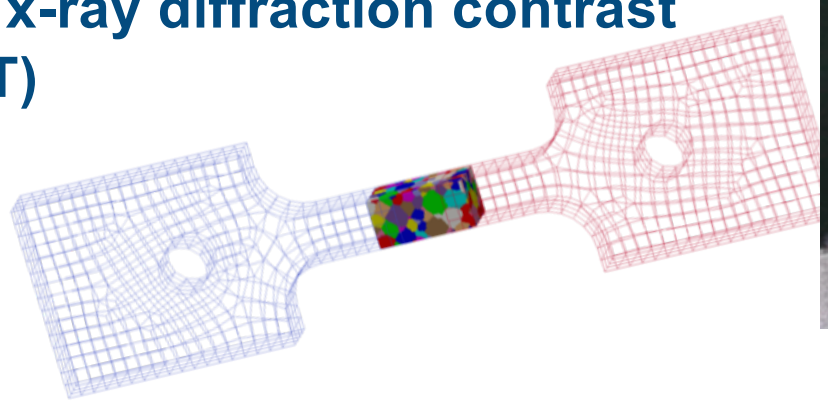
DFT calculations of Al(111) surface show hydrogen is more strongly bound in mixed water-hydrogen layer than in the absence of water.

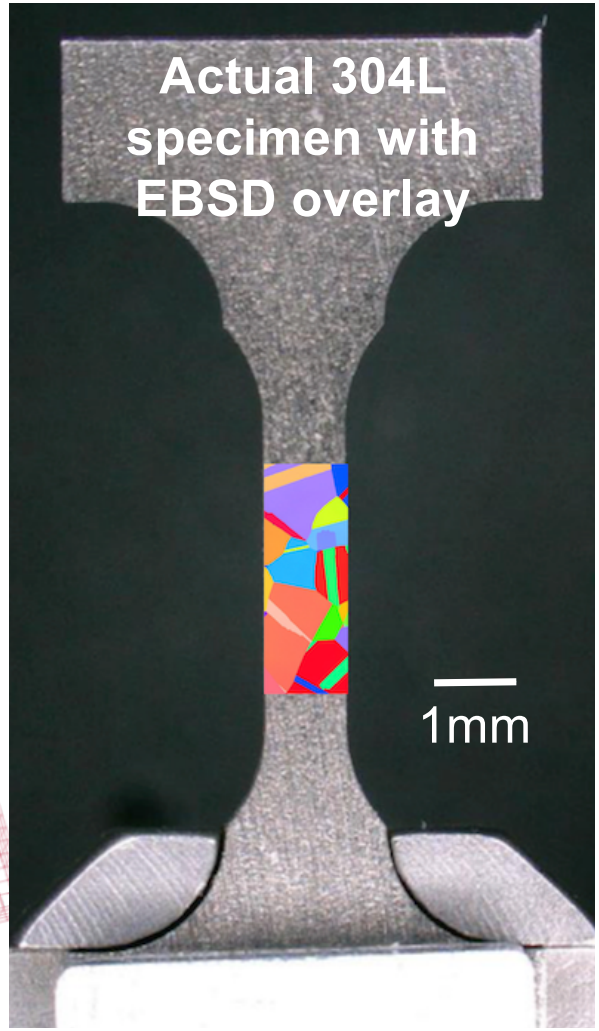
Accomplishments: Hydrogen-deformation interactions in stainless steels (M4)

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)







Project Milestones

Task	FY19 Objective	Status
High-strength ferritic steels	Document literature survey of Fe-C interatomic potentials as basis for steel microstructure MD simulations	***Complete***: Created Fe-C-H interatomic potential and implemented in LAMMPS
High-strength aluminum alloys	Generate quantitative experimental evidence that hydrogen/water mixtures negatively affect Al	New insights on role of hydrogen uptake in presence of water (DFT calculations)
Damage and crack nucleation	Experimentally quantify crack nucleation in model system and computationally predict mechanical fields for tested configuration	Leveraging previous work on notched fatigue specimen, identified hole-drilled tubular specimen for comparison
Austenitic stainless steels	Compare local strain history in experimental and computational tensile tests of oligocrystals	Oligocrystals manufactured, specimen geometry tested, specimen prep demonstrated
Cryogenic hydrogen service	Develop representative welded configuration and specimen geometry for testing at cryogenic temperature	Adopted GTA welded stainless steel, specimen geometries being evaluated

Response to Previous Year Reviewers' Comments

- ***This project was not reviewed in FY18***

Comments from proposal reviewers:

- "Current designs (i.e., wall thickness) of steel storage vessels are not dictated by fracture resistance but rather hydrogen-accelerated fatigue crack growth."
  - There is clear evidence that low fracture resistance promotes hydrogen-accelerated fatigue crack growth. Moreover, the low fracture resistance of high strength steels (eg, <20 MPa $m^{1/2}$) limits defects to impractically small size.
- "The most significant threat to aluminum components is not the relatively low water vapor (RH) levels in hydrogen gas" … "there should be less attention paid to the HS aluminum alloys (Task M2) as it would less impact with respect to infrastructure"
  - High-strength aluminum alloys are excluded from use precisely due to concerns about moisture in the gaseous hydrogen (SAE/GTR).
  - Aluminum has good cryogenic properties and could find greater use as cryogenic applications grow.
- "Austenitic steels should also be included since they are commonly used"
  - A task on austenitic stainless steels seeks to improve our understanding of hydrogen-assisted fracture in this class of materials.

Collaborations

Consortium initiated as national laboratory-focused research with the expectation of broader partnership with academia and industry through DOE solicitations

- National Laboratories
  - Task teams integrated across laboratories, leveraging expertise at individual labs
- Academic partners
  - *Colorado School of Mines*: identification and custom heat treatment of high-strength ferritic steels
  - *University of California Davis*: fatigue behavior of austenitic stainless steels
- Industry partners
  - *Swagelok*: letter of support and interest in high-strength microstructure
- International research institutions (informal)
  - *Kyushu University, University of Stuttgart, Korea Research Institute of Standards and Science*: regular communications on capabilities, data sharing and research activities

Remaining Challenges and Barriers

- The only obvious steel microstructure that displays high fracture resistance in high-pressure hydrogen is austenite
  - It many not be possible to identify a high-strength ferritic microstructure with sufficient fracture resistance in hydrogen
  - Computational tools are essential to leading us to candidates
- Moisture is known to affect high-strength aluminum alloys
  - Mechanistic understanding of the hydrogen requires multiscale simulation and novel imaging techniques to “observe” mechanisms of degradation
- A generally accepted methodology to account for crack nucleation in damage tolerant design does not exist
  - A quantitative framework to predict crack nucleation has proven to be challenging
  - The first step to developing a framework to account for nucleation is quantification of the phenomena

Proposed Future Work

Remainder of FY19

- ***Fracture resistance of high-strength ferritic steel microstructures***
  - Demonstrate utility of Fe-C-H interatomic potential for clarifying hydrogen-microstructure interactions in steel microstructures
  - Identify high-strength steel microstructure for experimental assessment in high-pressure gaseous hydrogen
- ***Role of gaseous mixtures containing hydrogen and water on fracture resistance of high-strength aluminum alloys***
  - Demonstrate moisture-induced cracking in high-strength aluminum alloys
  - Clarify role of water in aluminum-hydrogen surface interactions using first principle calculations

FY20 (project continuation and direction determined by DOE annually)

- ***Identify reduced-order metric to characterize crack nucleation***
  - Experimental and computational comparison of mechanics leading to crack nucleation in structurally unique configurations
- ***In situ observation of deformation in oligocrystal specimens***
  - Perform in situ studies to distinguish role of hydrogen on deformation at sub-millimeter length scales and calibrate CP models with and without hydrogen

Summary

- **H-Mat** is a consortium of national laboratories formulated to address the **materials science of hydrogen-induced degradation** of materials
  - *Motivation*: develop **science-based strategies** to design the microstructure of materials for improved resistance to degradation in high-pressure hydrogen
- **H-Mat** integrates advanced **computational materials science** and innovative experimental capabilities across microstructural length scales
  - *Approach*: consideration of the intersection of **environmental, mechanics and materials variables** associated with hydrogen effects in materials
- **H-Mat** tasks are formulated around **high-value materials and physical phenomena**
  - High-strength ferritic steels: MD simulations in the Fe-C-H system will inform microstructural development and materials evaluation in high-pressure H2
  - High-strength aluminum alloys: new understanding evolving from DFT simulations of the effects of moisture on hydrogen uptake
  - Austenitic stainless steels: oligocrystals provide framework for understanding fundamental behavior of hydrogen effects on deformation and fracture
- **H-Mat** seeks to provide the foundational knowledge necessary to **design materials microstructures** for resistance to hydrogen-assisted fracture

Acknowledgments

Task	Lead	Principal Contributors
High-strength ferritic steels	Joe Ronevich	• Xiaowang Zhou, Catalin Spataru (computational) • Zhili Feng, Yanli Wang (material/microstructure) • Don Anton, Joy McNamara, Andy Duncan (KPFM) • Eun Ju Song, Chris San Marchi (experimental)
High-strength aluminum alloys	Chris San Marchi	• Norm Bartelt, Xiaowang Zhou (computational) • Don Anton, Joy McNamara, Andy Duncan (KPFM) • Joe Ronevich (experimental)
Damage and crack nucleation	Jay Foulk	• Ryan Sills (computational) • Joe Ronevich, Chris San Marchi (experimental)
Austenitic stainless steels	Coleman Alleman	• Jay Foulk (computational) • Thale Smtih (characterization/experimental) • Chris San Marchi, Joe Ronevich (experimental)
Cryogenic hydrogen service	Aashish Rohatgi	• Daniel Merkel (experimental) • Chris San Marchi (materials)

Technical Back-Up Slides

Acronyms

- DFT = density functional theory
  - First principles (quantum mechanical) calculation of energy states
- MD = molecular dynamics
  - Computational simulation of atomic/molecular interactions
- LAMMPS = Large-scale Atomic/Molecular Massively Parallel Simulator
  - Free, open-source MD software
- CP = crystal plasticity
  - Finite-element simulation methodology accounting for anisotropic behavior of individual grains