H-Mat Hydrogen Materials Compatibility Consortium SM

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H-Mat Overview: Metals

Science-based advancement of materials for hydrogen technologies

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Lab Partners: SRNL, ORNL, ANL

Joint Hydrogen Delivery, Codes & Standards, Storage Tech Team
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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

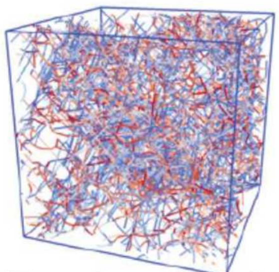
Task	Relevance and Objective
High-strength ferritic steel microstructures	Develop a mechanistic understanding of hydrogen-induced fracture processes in ferritic steel microstructures to improve fracture resistance of low-cost steels with tensile strength >950 MPa
High-strength aluminum alloys	Elucidate 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

Engineering performance depends on mechanisms manifest at nanometer length scales

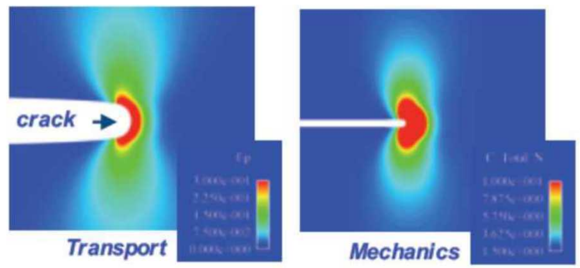
***Approach*: Integrate innovative computational & experimental activities across length scales**

Advanced computational materials science

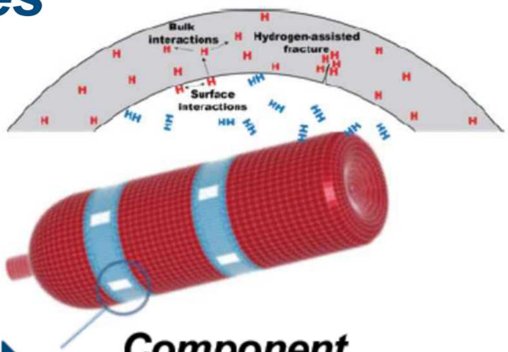
Innovative experimental capabilities



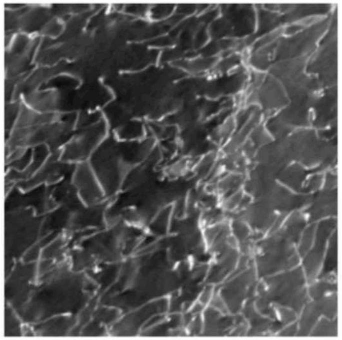
Fundamental hydrogen-materials interactions

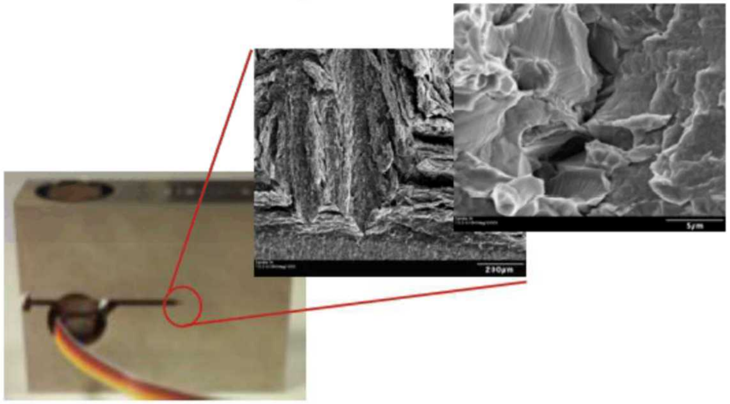


Materials response



Component design



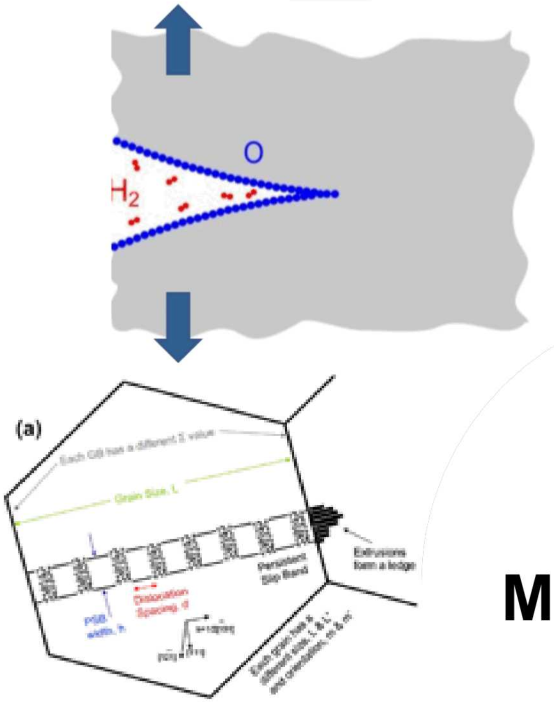


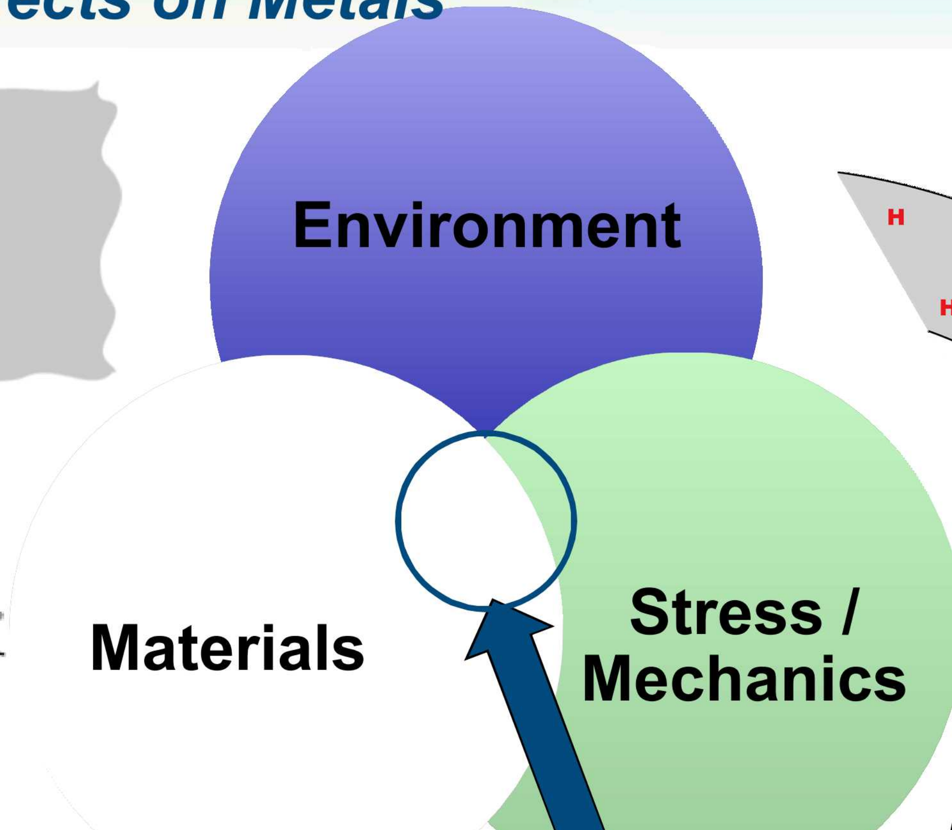
Thermodynamics of H-interactions at nm-scale

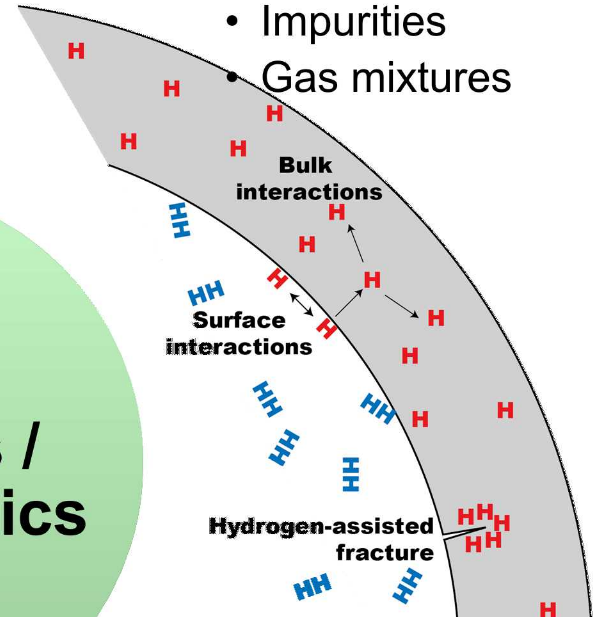
Micromechanisms of materials behavior at µm-scale

Structural performance at the engineering scale

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







Environment

- Low temperature
- High pressure
- Impurities
- Gas mixtures

Materials

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

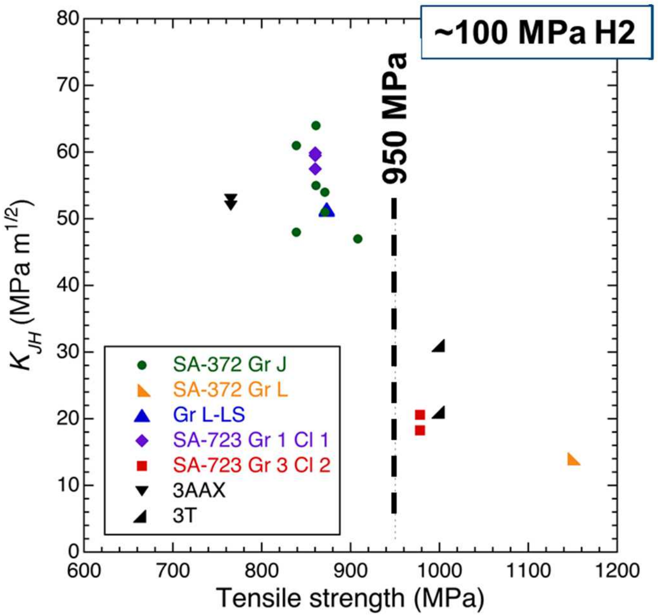
Hydrogen embrittlement occurs in ***materials*** *under the influence of* ***stress*** *in hydrogen* ***environments***

Mechanics

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

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

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



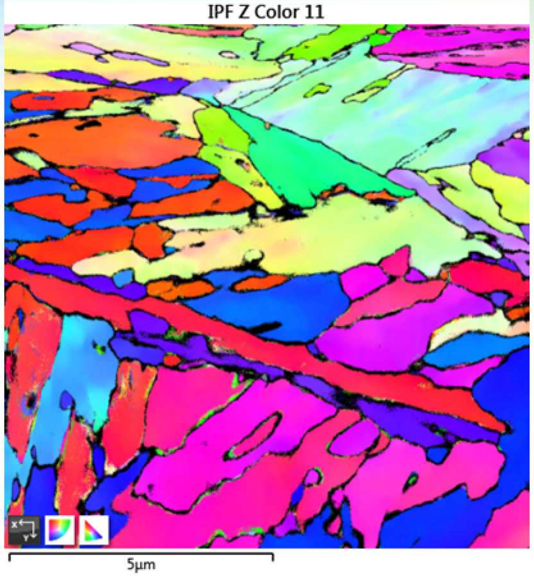
- Mechanical testing of steels in high pressure H_2
- Development of unique microstructures (e.g., austempering)
- Microstructural and fracture characterization
- Kelvin Probe Force Microscopy to investigate hydrogen distribution in different microstructures
- Modeling of Fe-C-H (DFT and MD) to explore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

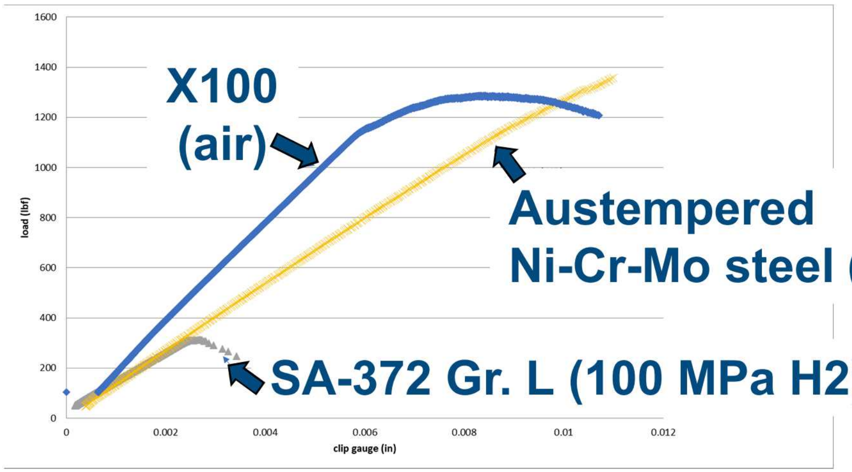
Engineering goals:
- **Achieve K_{JH} > 50 MPa m$^{1/2}$ for steels with UTS > 950 MPa**
- **Ferritic steel microstructures with tensile strength up to 1100 MPa and 50% increase of fracture resistance in high-pressure hydrogen**

High-strength ferritic steel microstructures (task M1)

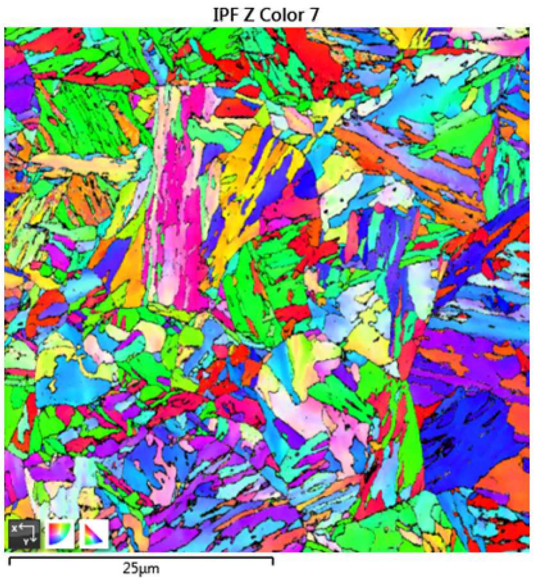
Considering austempered Ni-Cr-Mo steel

- **Conventional quench and tempered steel microstructure**
  - Tensile strength ~1000 MPa
  - Fracture toughness > 100 MPa $m^{1/2}$





- **Austempered steel microstructure**
  - Tensile strength ~1300 MPa
  - Fracture toughness = 64 MPa $m^{1/2}$



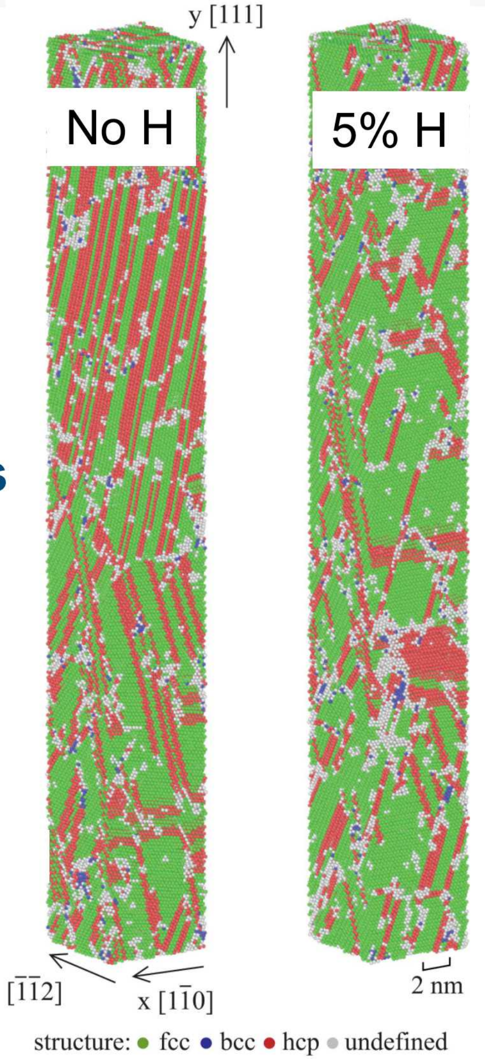
High-strength ferritic steel microstructures (task M1)

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

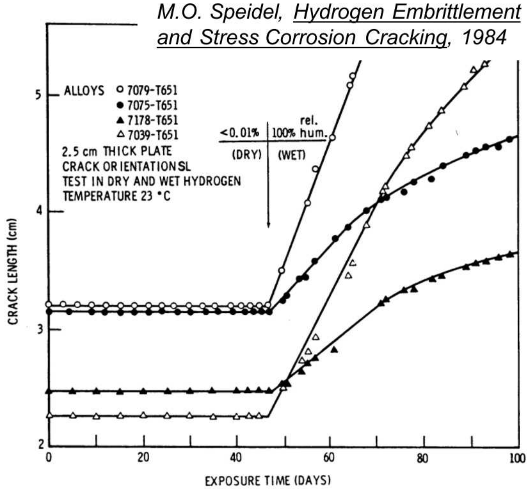


High-strength aluminum alloys (task M2)

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**

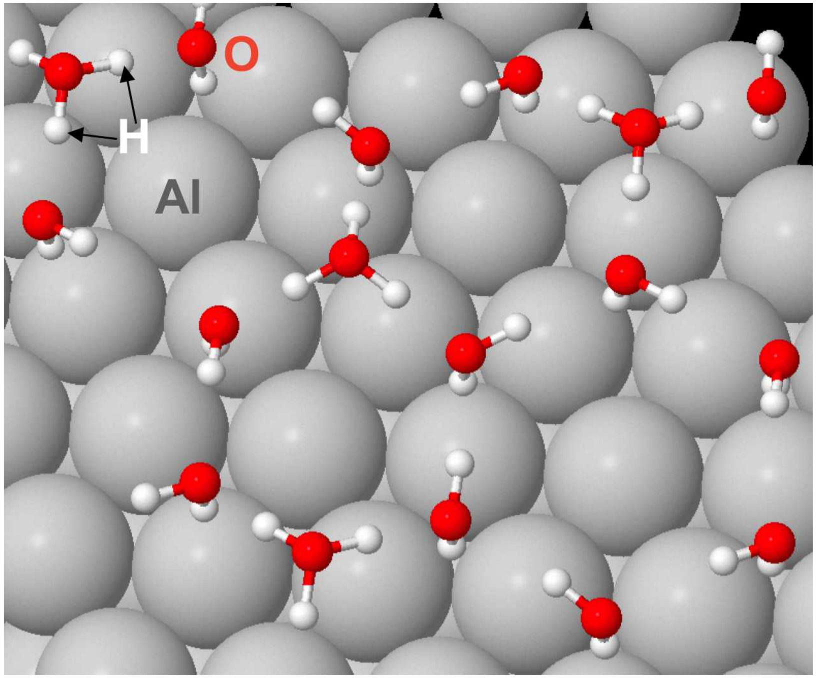
High-strength aluminum alloys (task M2)

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

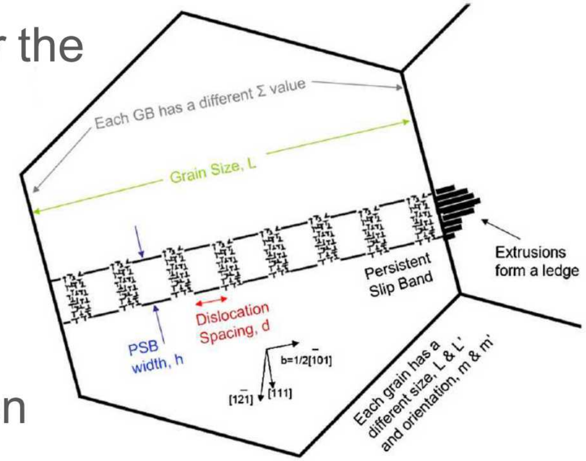


DFT calculations of Al(111) surface show hydrogen is more strongly bound in mixed water-hydrogen layer than in the absence of water.

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

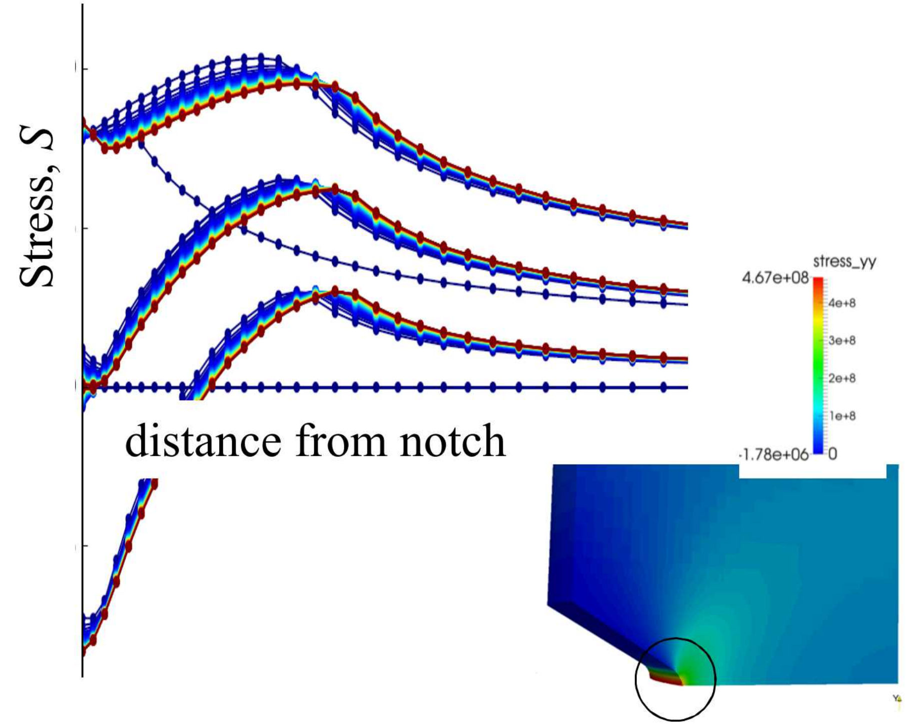


Engineering goals:
- **Framework for quantification of damage and crack nucleation that can be implemented in design to increase lifetime assessment by 50% compared to conventional fracture mechanics approach**
- **Microstructural requirements that minimize effects of hydrogen**

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

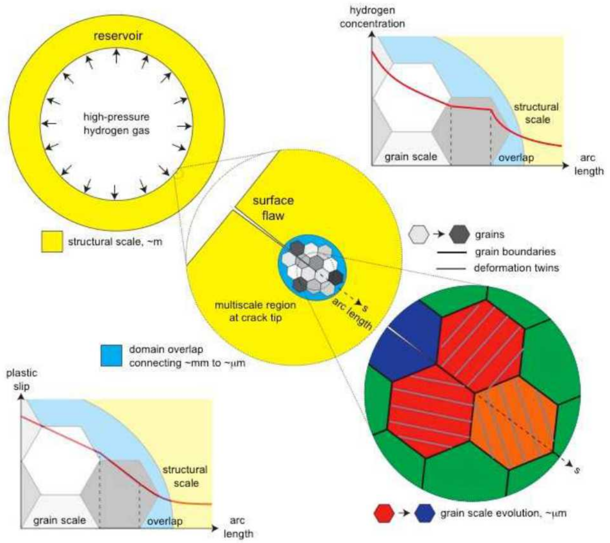


Solid mechanics modeling coupled with measurement of crack initiation provides new strategy to quantify nucleation

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 (leveraged) 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

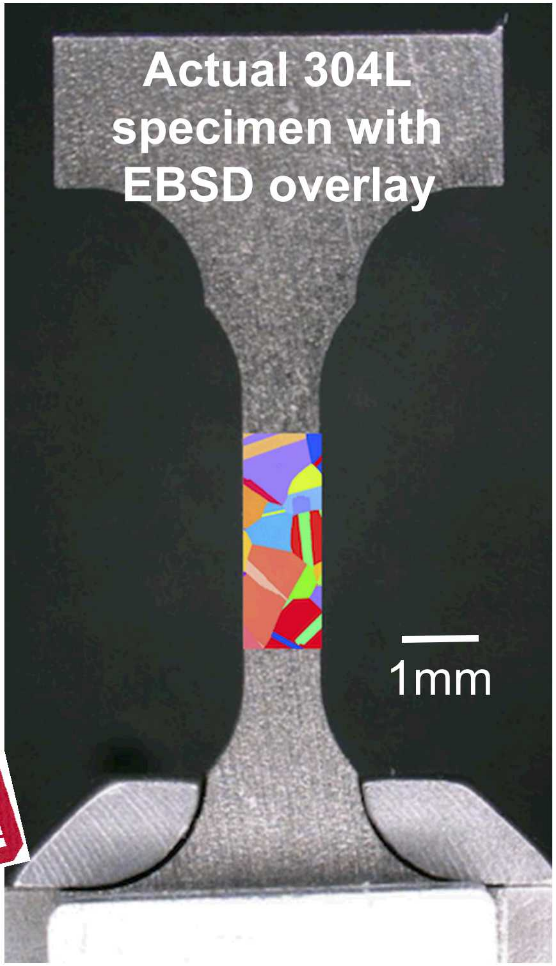


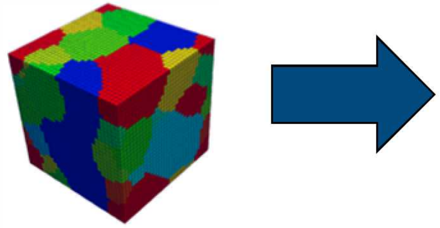
Engineering goals:
- **Microstructural design concepts that improve ductility of austenitic stainless steels in high concentration of hydrogen**
- **Accessible micromechanical modeling tools (CP) sensitive to hydrogen transients, local microstructure, and phase transformations**

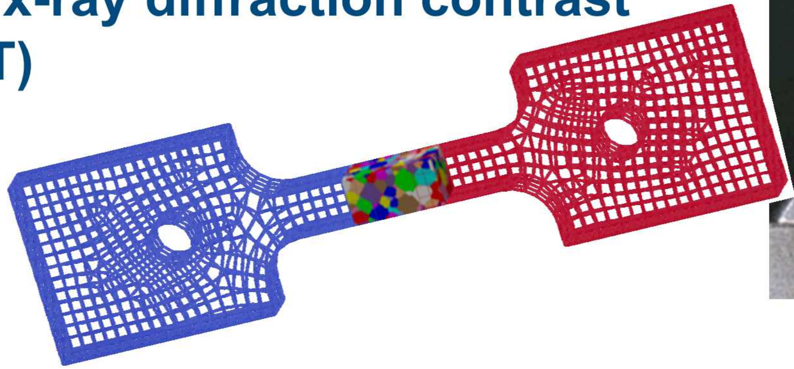
Hydrogen-deformation interactions in stainless steels (task M4)

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)

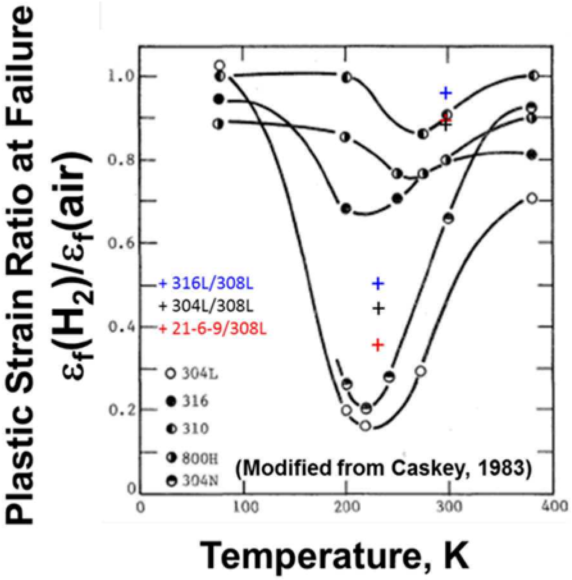






Metals for cryogenic applications in hydrogen service (task C1)

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

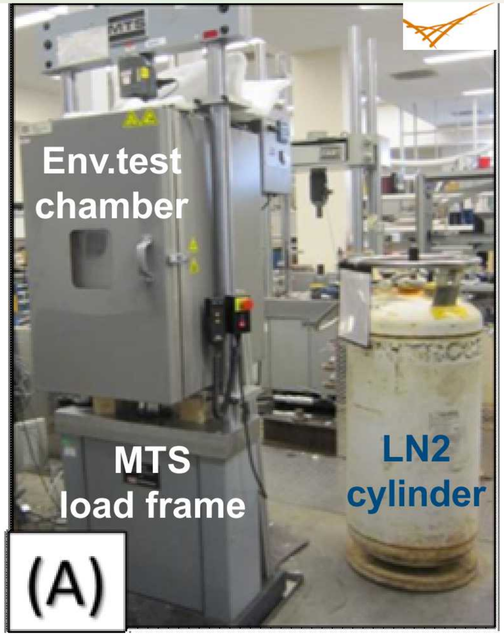


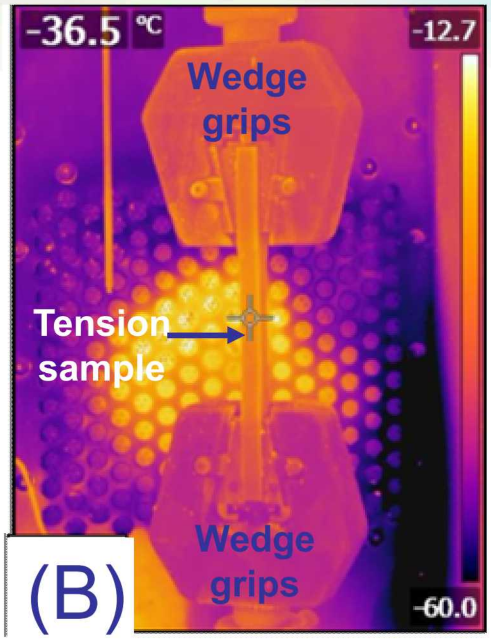
- Identify effects of hydrogen-induced cracking at LH2 temperature
- Design of mechanical tests to elucidate kinetic factors on testing results (such as test rate)
- Evaluate weld microstructures at low-temperature with high hydrogen concentration

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

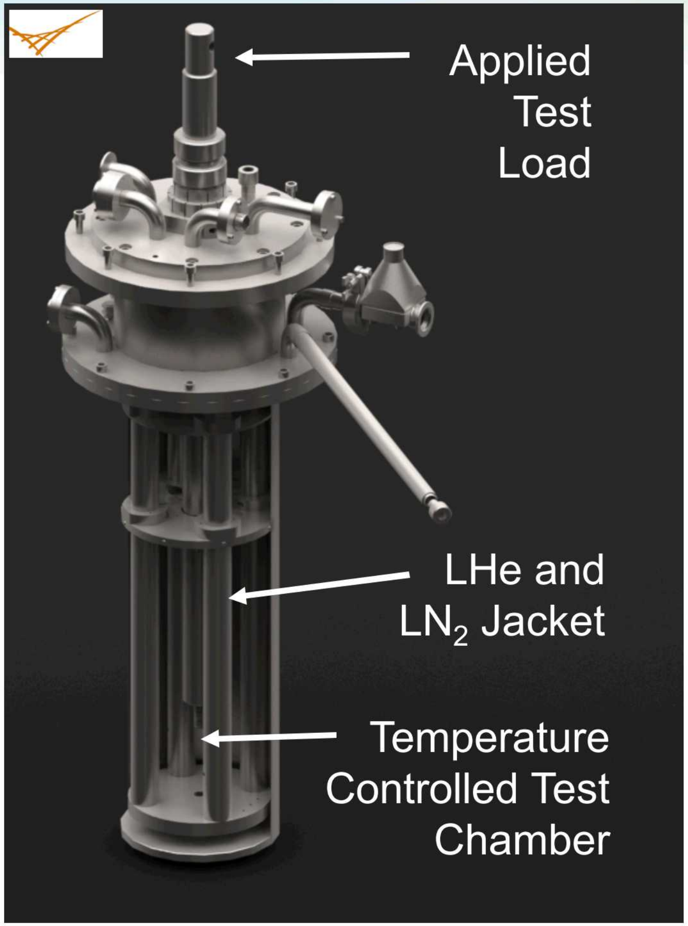
Metals for cryogenic applications in hydrogen service (task C1)

Cold/Cryo-temperature mechanical testing capabilities





- **MTS load frame with environmental chamber for heating or liquid nitrogen: -130 to +315˚C**
- **Strain measurement**
  - **Extensometer capabilities to -253˚C**
  - **Digital image correlation (DIC)**



Schematic of liquid helium-cooled Janis Research dewar

Metals for cryogenic applications in hydrogen service (task C1)
Challenges: Sample design for low-temperature

- Sample handling
  - Limited maneuverability due to use of gloves/tongs etc. to handle samples at sub-zero temperature
- Sample gripping →
  - Threaded ends can seize in the grips
  - Replace threaded end design with a button-head design
- Load-frame capacity
  - Failure load of 304L (0.16” gauge dia.) <4000 lbf at -130˚C
  - PNNL’s load frames can handle up to 20,000 lbf

Threaded specimen (SNL Design)

Button-head specimen (Proposed PNNL Design)

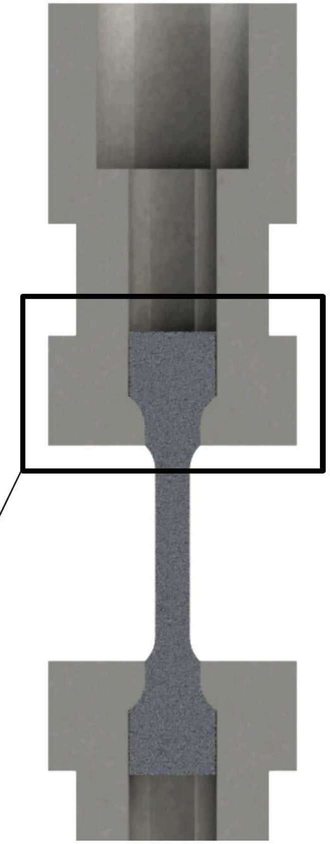
Same gauge design in both cases

- 4mm diameter (0.16”)
- 19 mm length (0.75”)

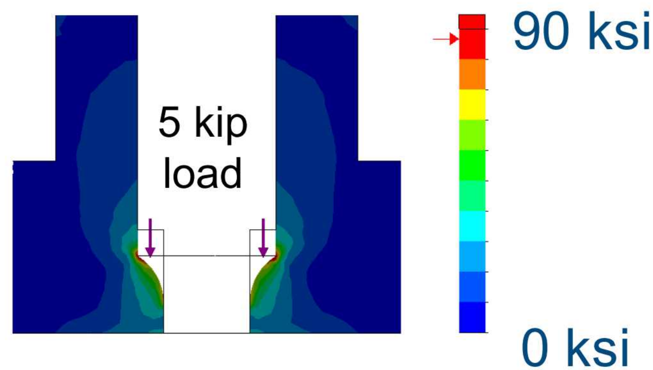
Metals for cryogenic applications in hydrogen service (C1)

Challenges: Grip design for low-temperature

- Button-head for rapid specimen fixturing between tests
- Grip material: Nitronic 60
  - $\sigma_y = 58\ \mathrm{ksi}$ at 25˚C
  - $\sigma_y = 85\ \mathrm{ksi}$ at -130˚C
  - Maintains ductility at -253˚C



Stress Analysis of the Grip



Schedule

- Grip fabrication: March end
- Trial tension testing (-130˚C, 304L): March/April
- LHe dewar delivery: March/April

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

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)