SAND2020-5518 PE

H-Mat Overview: Metals

Science-based advancement of materials for hydrogen technologies

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

Lab Partners: SRNL, ORNL, ANL

2020 DOE Hydrogen and Fuel Cells Annual Merit Review

May 21st, 2020

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 Project Budget: $9.2M
- FY20 DOE Funding
  - SNL: 2,090K
  - PNNL: 100K
  - ORNL: 200K
  - SRNL: 150K
- Planned FY21 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)
- **FOA projects:**
  - Colorado School of Mines
  - HyPerformance Materials Testing, LLC
  - MIT
  - Univ Alabama
  - UIUC

H-Mat addresses materials-compatibility science questions

Metals

Task M1
High-strength ferritic steel microstructures

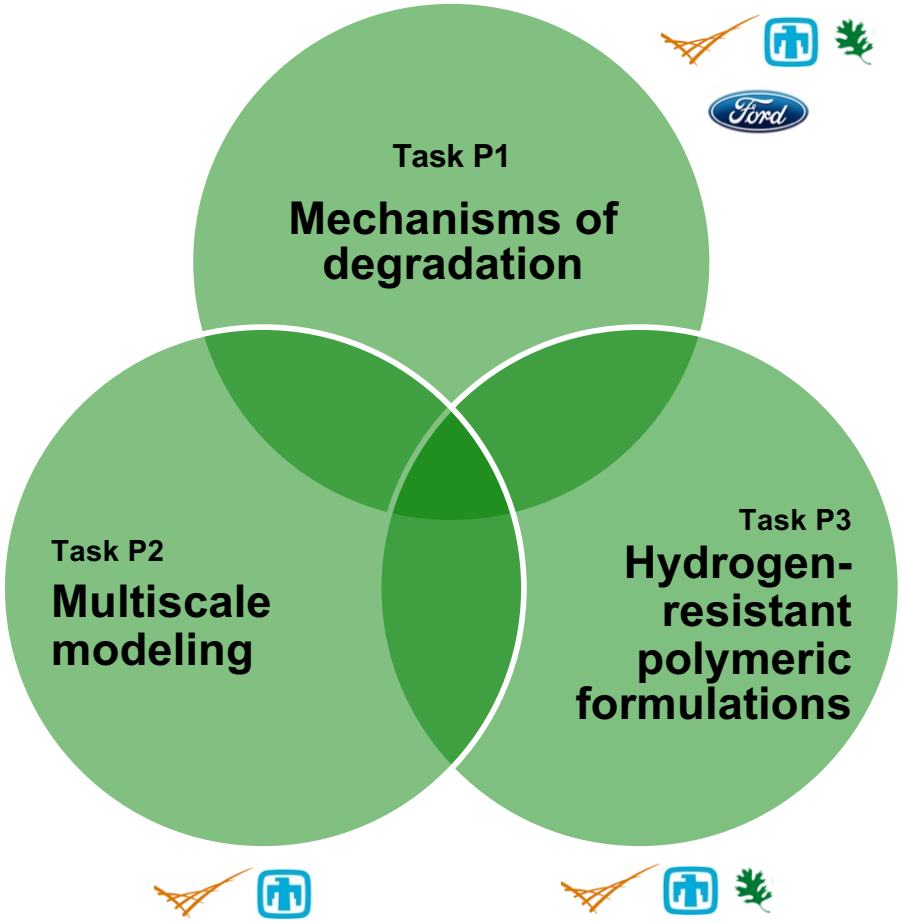
Task M2
High-strength aluminum alloys

Task M3
Transferability of damage and crack nucleation

Task M4
Microstructure of austenitic stainless steels

Task C1
Materials for cryogenic hydrogen service

Polymers



Relevance and Objectives

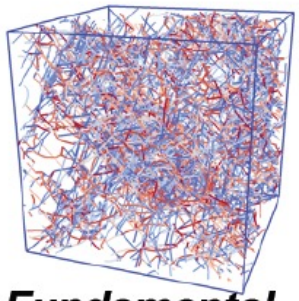
Motivation: elucidate the mechanisms of hydrogen-materials interactions to inform **science-based strategies to design the microstructure** of metals with improved resistance to hydrogen degradation

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

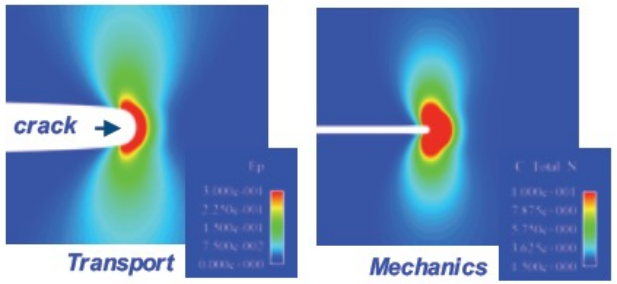
Relevance: Engineering performance depends on mechanisms manifest at nanometer length scales

Approach: Integrate innovative computational & experimental activities across length scales

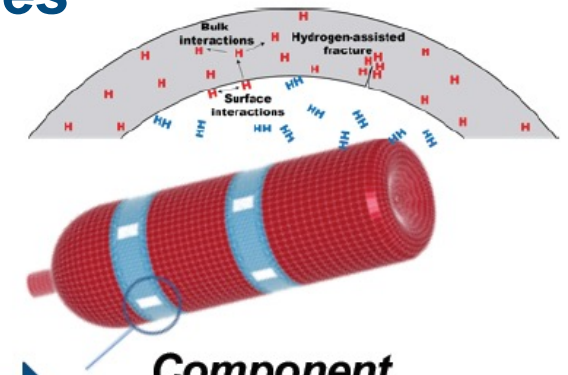
Advanced computational materials science



Fundamental hydrogen-materials interactions

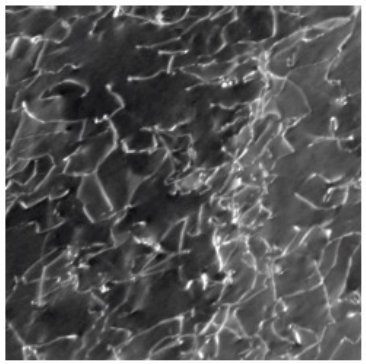


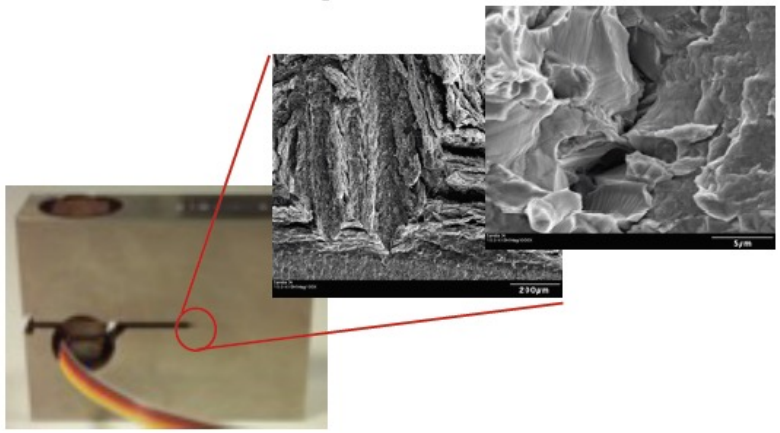
Materials response

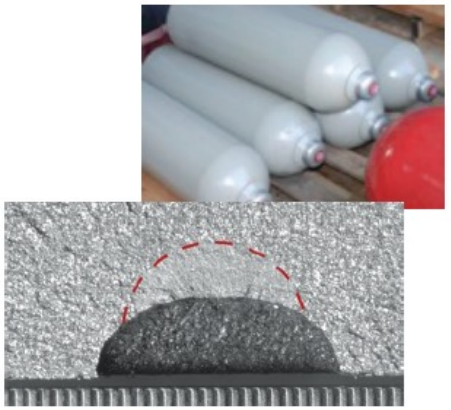


Component design

Innovative experimental capabilities





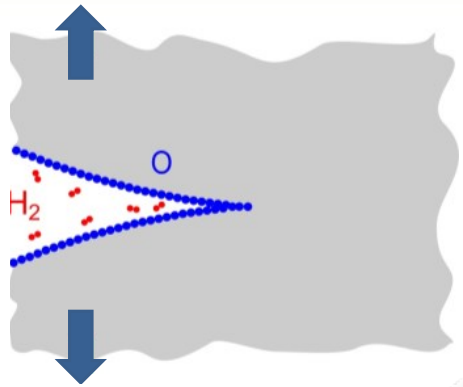


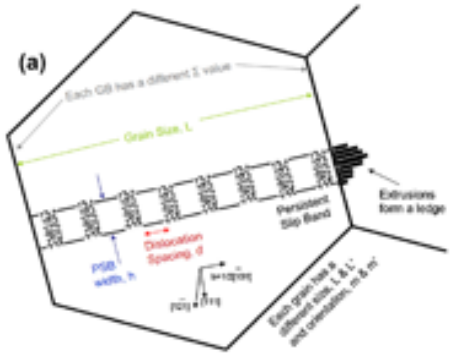
Thermodynamics of H-interactions at nm-scale

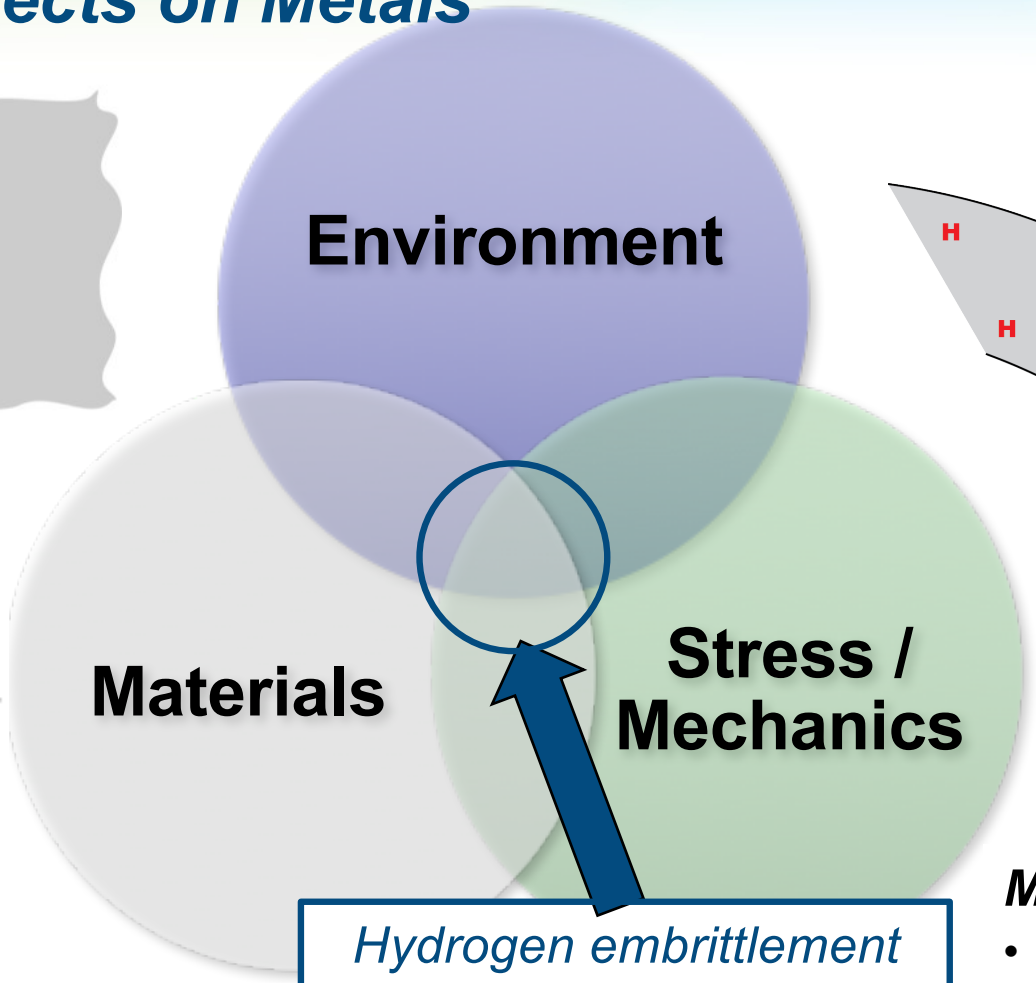
Micromechanisms of materials behavior at μm-scale

Structural performance at the engineering scale

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

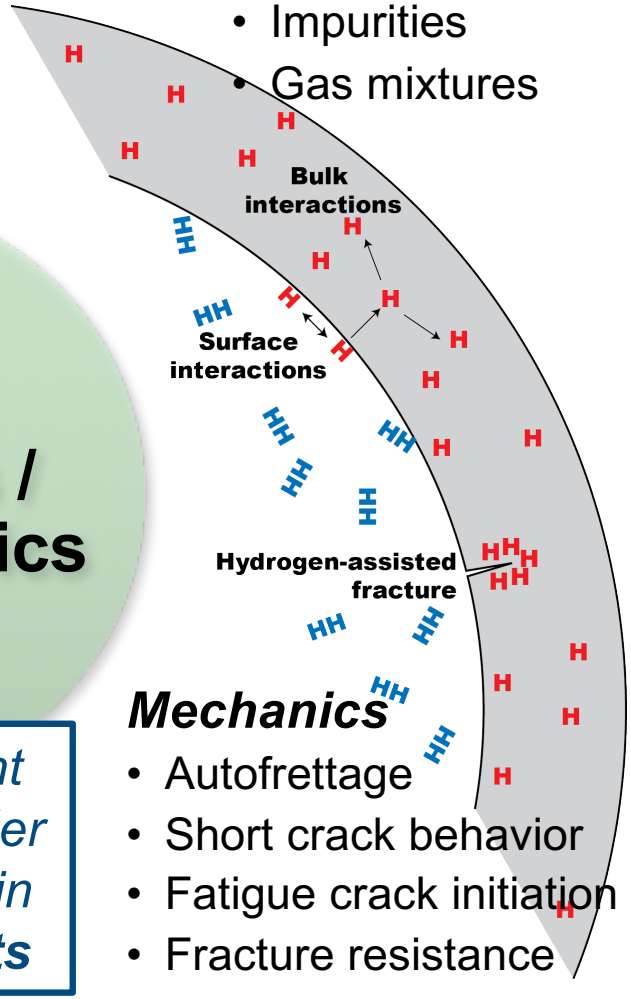






Environment

- Low temperature
- High pressure
- Impurities
- Gas mixtures



Materials

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

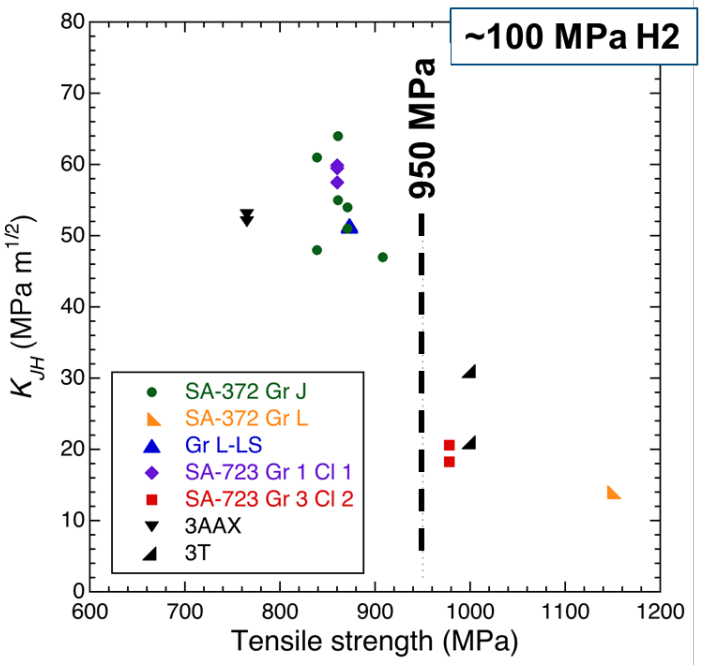
*Hydrogen embrittlement occurs in **materials** under the influence of **stress** in hydrogen **environments***

Mechanics

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

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?



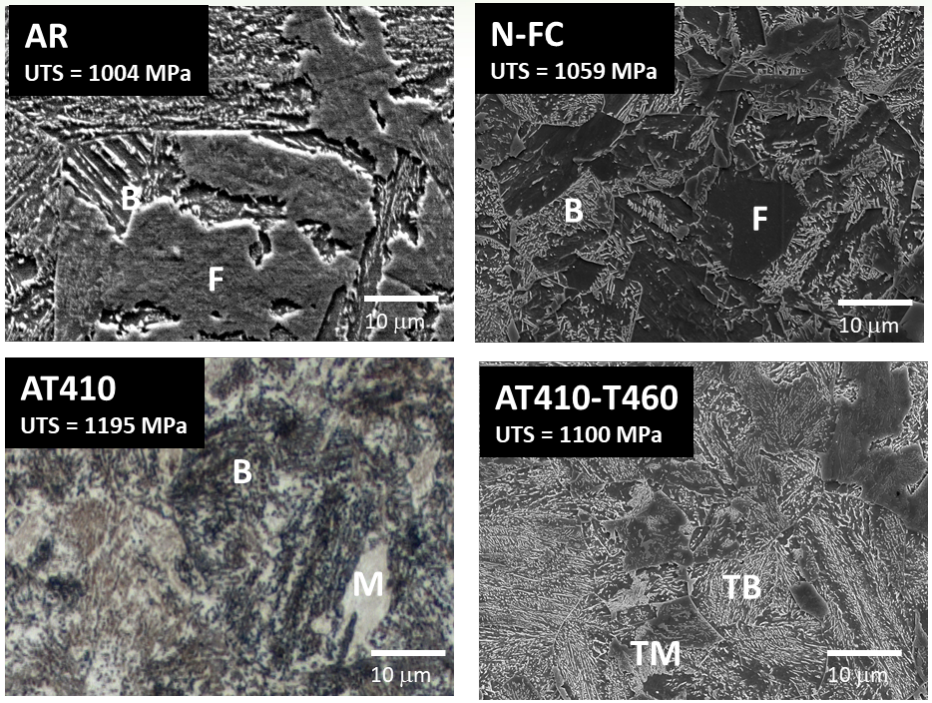
- Mechanical testing of steels in high pressure H_2
- Development of unique microstructures (e.g., austempering)
- Microstructural and fracture characterization
- Kelvin Probe Force Microscopy to investigate hydrogen distribution in different microstructures
- Modeling of Fe-C-H (DFT and MD) to explore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

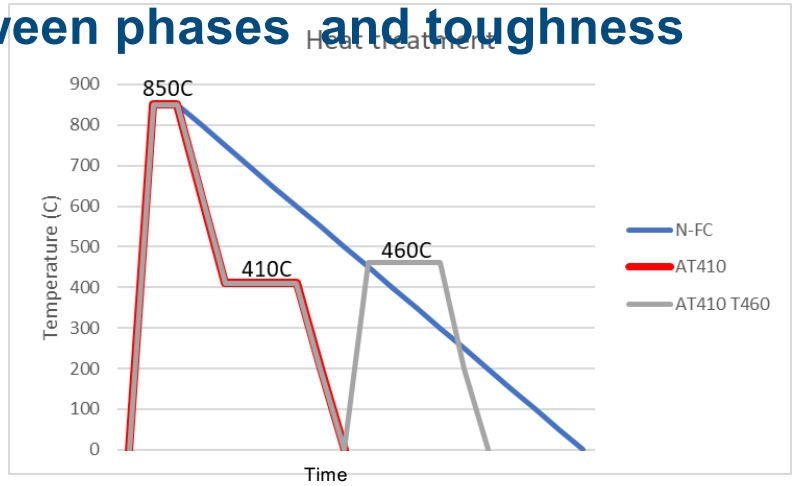
Accomplishments: High-strength ferritic steel microstructures (task M1)

Microstructure variants produced from single 4340 alloy



Established multiple microstructures consisting of
F: ferrite
B: bainite, TB: tempered bainite
M: martensite, TM: tempered martensite

Controlled microstructural variations enable evaluation of relationship between phases and toughness



- Fracture toughness of AR measured in 100 MPa H_2 (K_{IH} = 24 MPa $m^{1/2}$)
- Measurements planned for additional 3 microstructures

In progress: **Two pathways being pursued to obtain improved toughness**

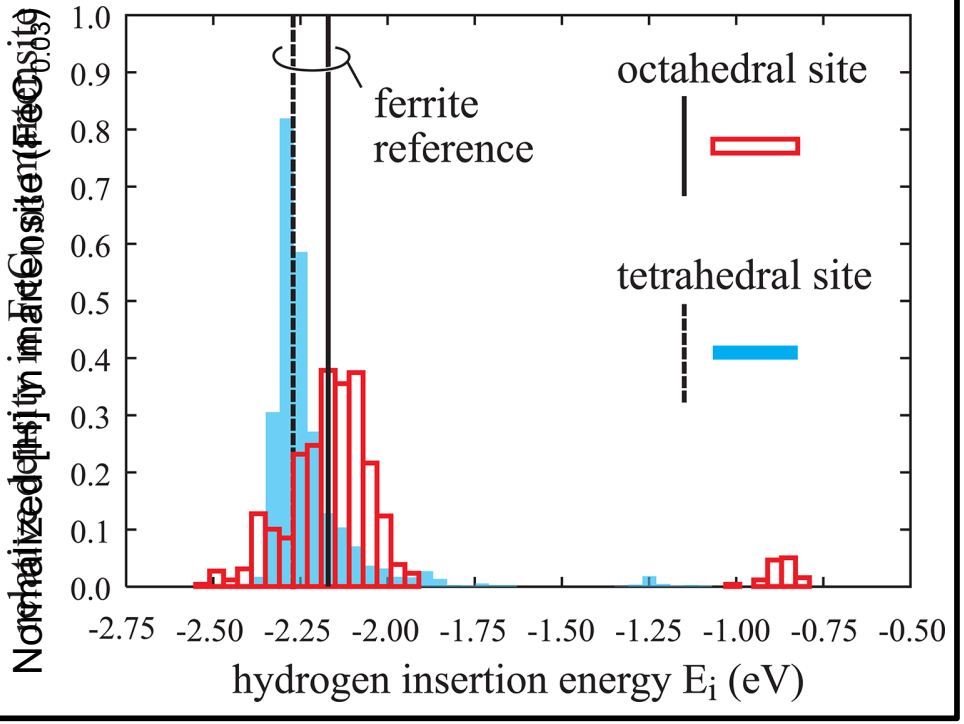
1) **Examining role of grain boundaries in fracture resistance (impurities, prior austenite grain size). Can we reduce intergranular fracture?**
2) **Alter plasticity through incorporating more crack resistant phases (F, γ)**

Accomplishments: High-strength ferritic steel microstructures (M1)

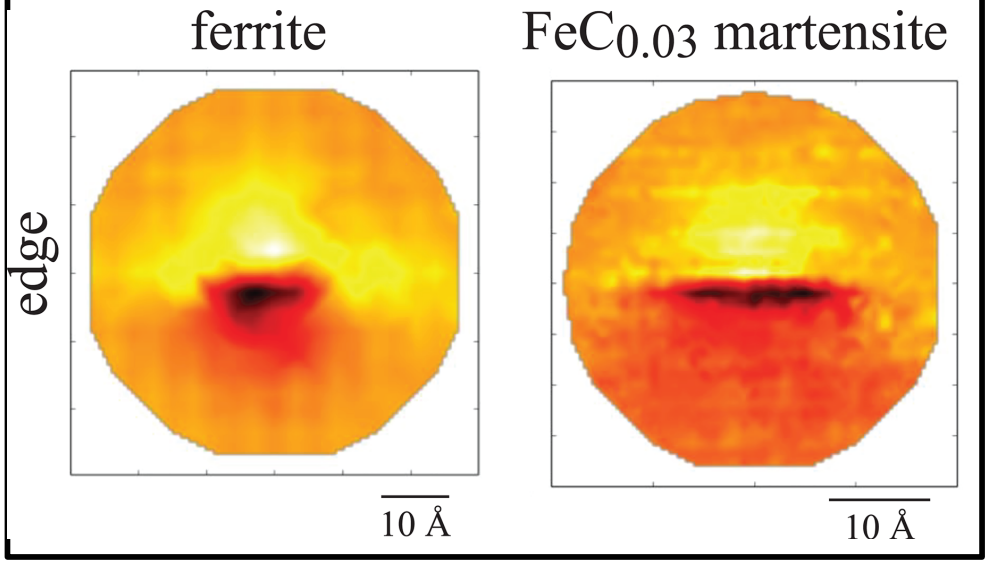
Our Fe-C-H interatomic potential has revealed preferences of hydrogen in high strength steel microstructures

H prefer martensite to ferrite without dislocations:

- Ferrite have single insertion energy E_i for tetrahedral and octahedral sites.
- Martensite have a distribution of E_i lower than ferrite.



Dislocations segregation further supports martensite preference:



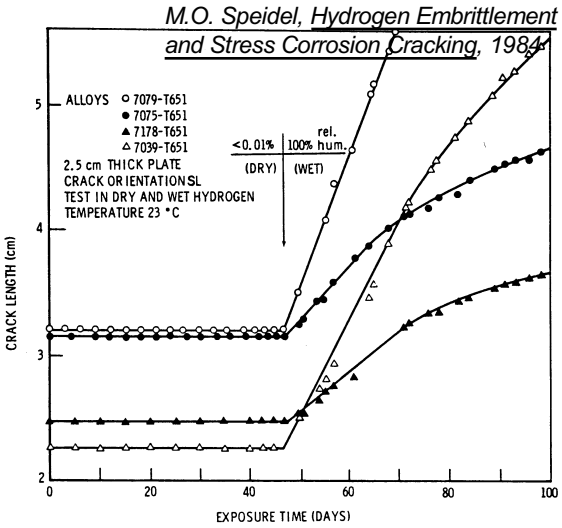
In progress:

- **H interactions with interfaces (martensite/cementite, prior γ GBs)**
- **Strain fields effects at interfaces**
- **Developing KPFM methods (SRNL) to visualize location of H**

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?)



- 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:

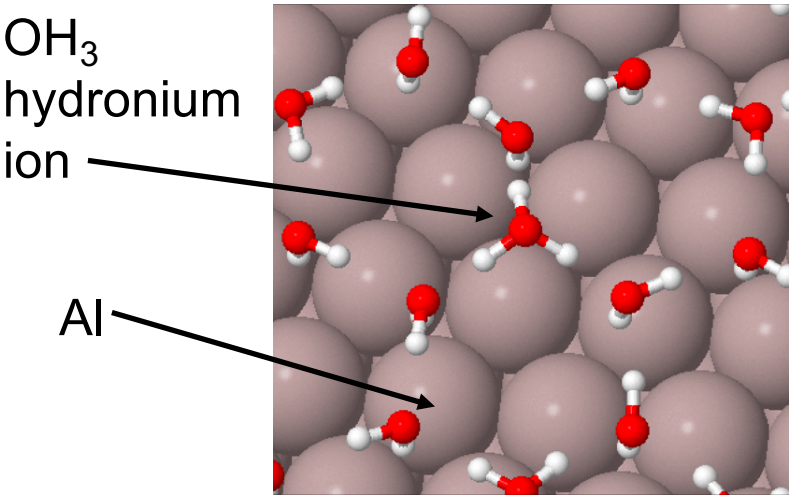
- **Hydrogen-compatible microstructures of aluminum alloys with yield strength >350 MPa that are insensitive to standardized moisture limits for fuel-grade hydrogen (5ppm H_2O)**
- **Specification of environmental conditions under which aluminum is not degraded in gaseous (and liquid) hydrogen environments**

Accomplishments: High-strength aluminum alloys (task M2)

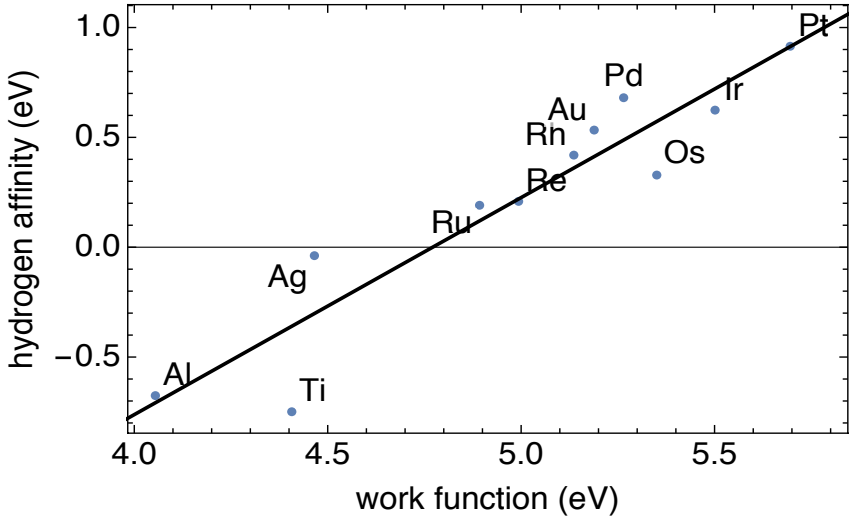
First principles calculations are illuminating of the role of moisture in metal-hydrogen interactions

Using DFT, we have discovered that the presence of water can enhance the kinetics of hydrogen absorption for metal surfaces with high electronic work functions.

H forms OH_3 ions on water layers:



High electronic work function favors these ions:



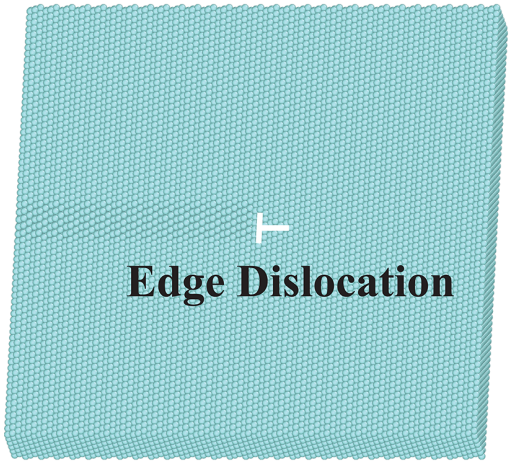
Clean, unalloyed and unoxidized Al has a low work function and adsorbed water does not enhance H uptake.

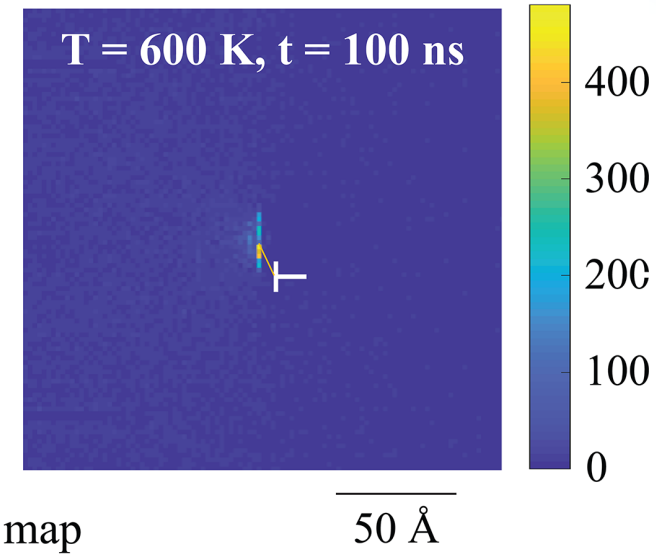
In progress: **H_2O-H_2 interactions on oxidized Al surfaces are being explored.**

Accomplishments: High-strength aluminum alloys (task M2)

Atomistic simulations are illuminating the role of hydrogen on friction stresses in aluminum

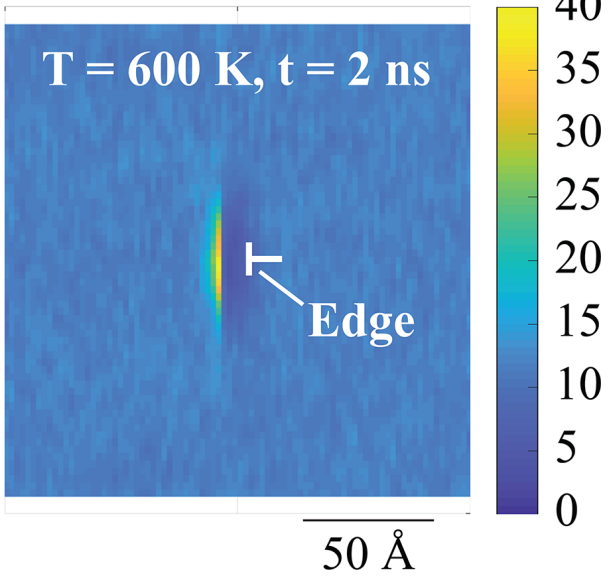
MS Progress





MS simulations => H energy map
Continuum + energy map => H concentration map at T and t
Energy + concentration maps => friction stress

MD Progress



Time-averaged MD reveals H atmosphere at dislocation

- **MS simulations reveal H insertion energies around edge dislocation**
- **Energy map is used to predict concentration map and friction stress**
  - **Paper submitted to JOM**

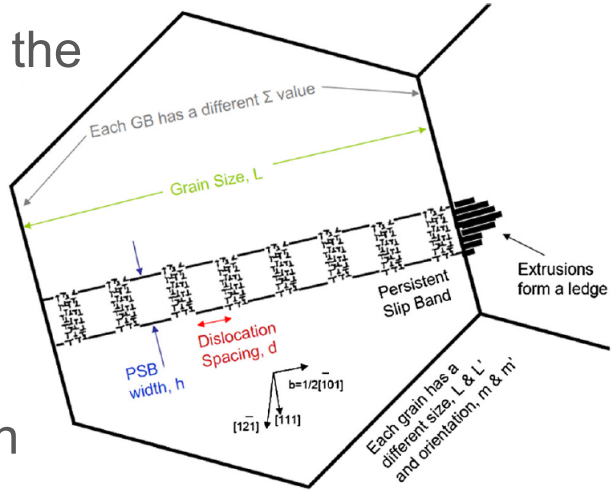
In progress: **Time-averaged MD is being used to study kinetics of H atmosphere formation with preliminary success**

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

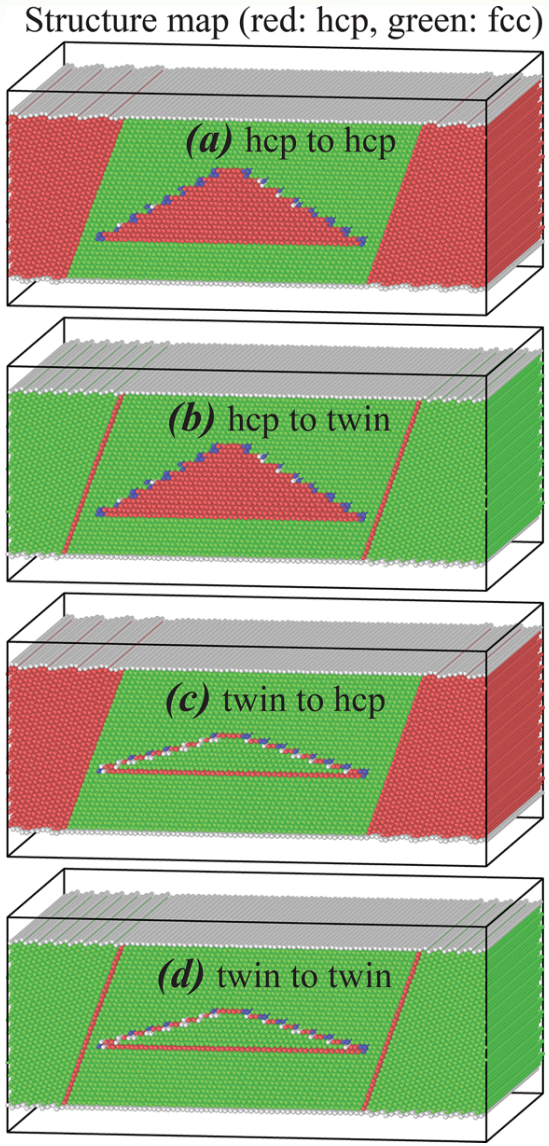


Engineering goals:

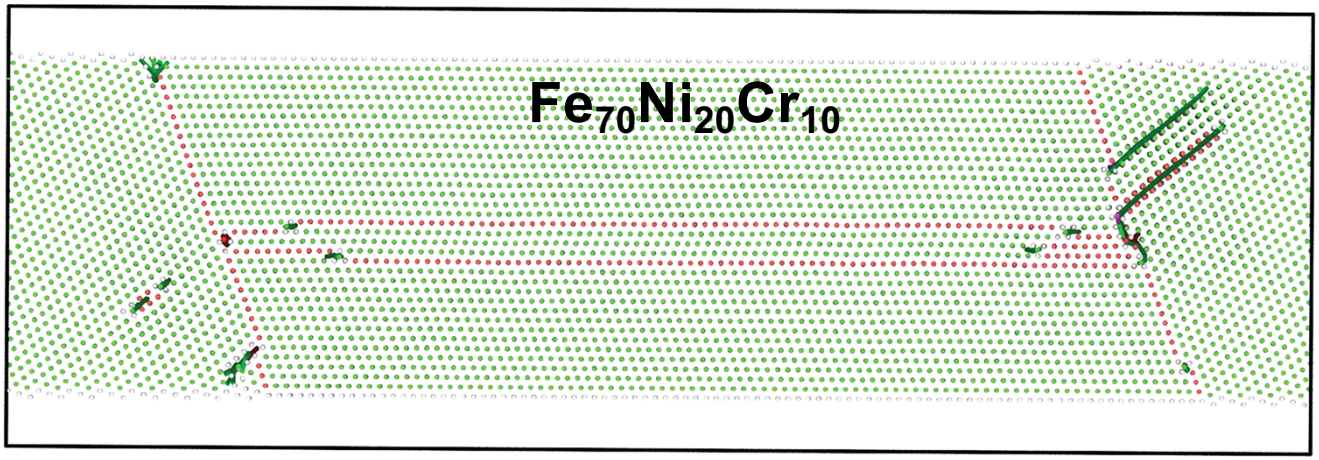
- **Framework for quantification of damage and crack nucleation that can be implemented in design to increase lifetime assessment by 50% compared to conventional fracture mechanics approach**
- **Microstructural requirements that minimize effects of hydrogen**

Accomplishments: Crack nucleation in stainless steels (task M3)

Methodology developed to explore defect interactions at the atomistic scale in the presence of hydrogen



- Capability developed to seed defects among deformation structures in MD framework
- Simulations enable identification of damage structures to inform evolution of damage models at higher length scales



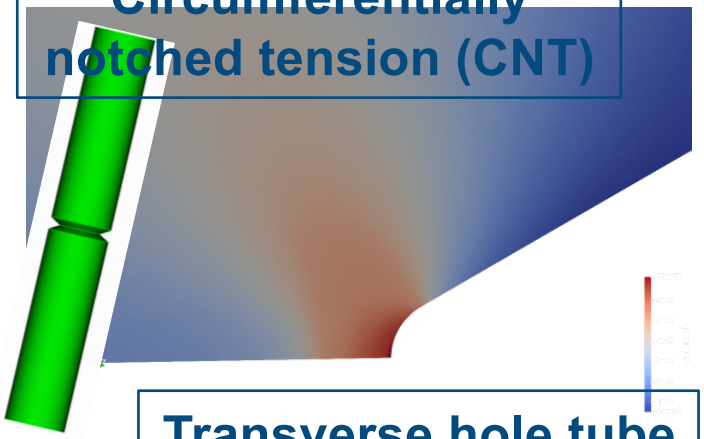
In progress:

- MD is being used to study behavior of defect-defect interactions in Fe-Cr-Ni-H system

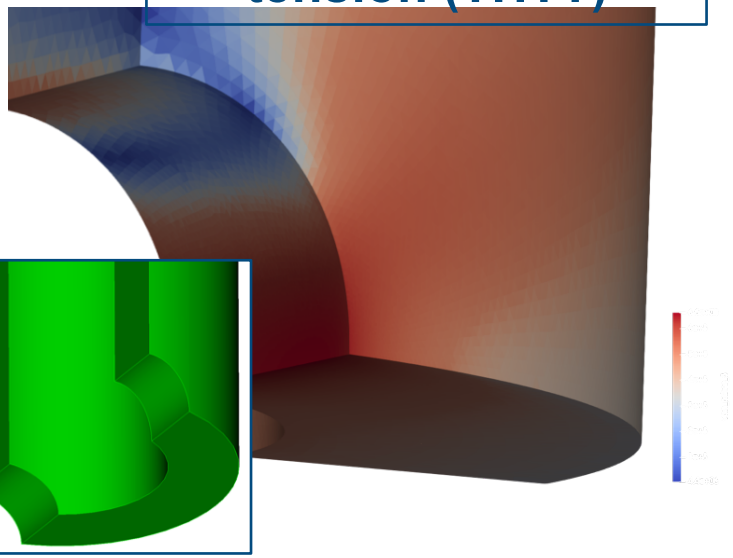
Accomplishments: Crack nucleation and role of geometry (task M3)

FEA of several geometries reveals significant differences in the mechanics of the specimens

Circumferentially notched tension (CNT)



Transverse hole tube tension (THTT)



- Experimental findings indicate that crack initiation is similar for the CNT and THTT geometries both in the as-received and H-precharged conditions
  - Similar behavior is also noted for materials with different strength (with normalization)
- Solid mechanics modeling, however, illustrates that the character of the stress concentration is quite different in these geometries

In progress:

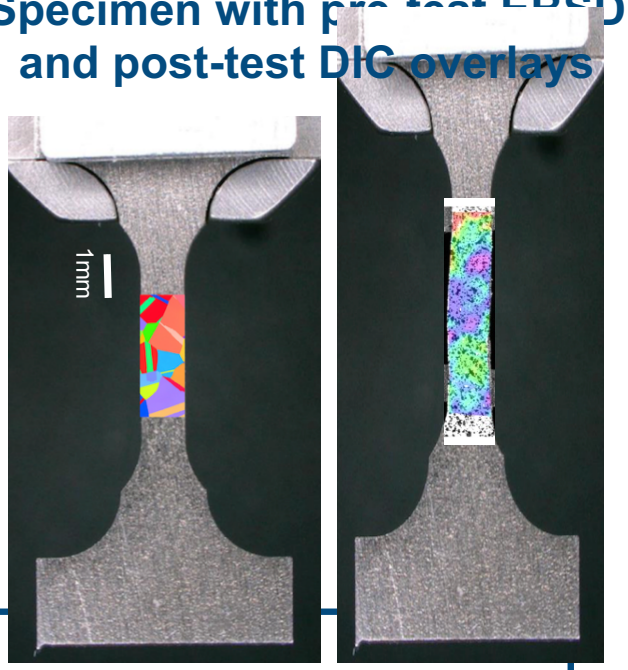
- Results are being analyzed to identify field quantities and characteristic length scales that quantify crack initiation

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 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

Specimen with pre-test EBSD and post-test DIC overlays



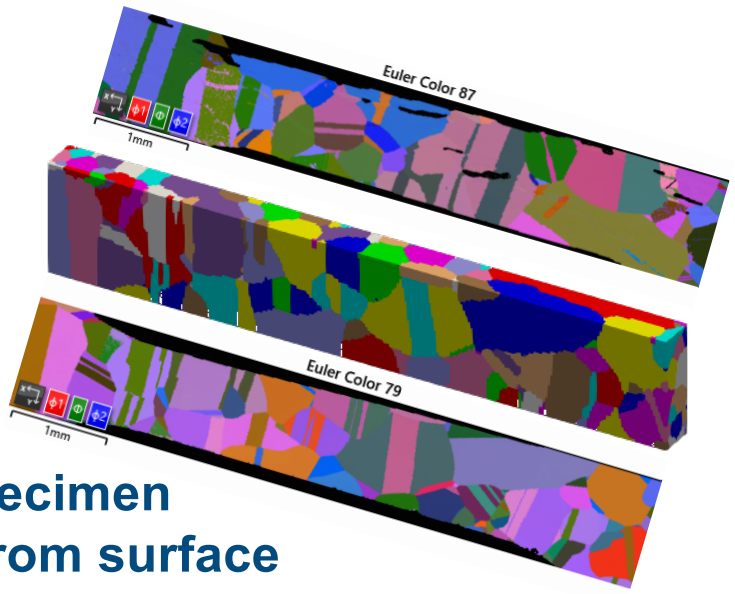
Engineering goals:

- **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**

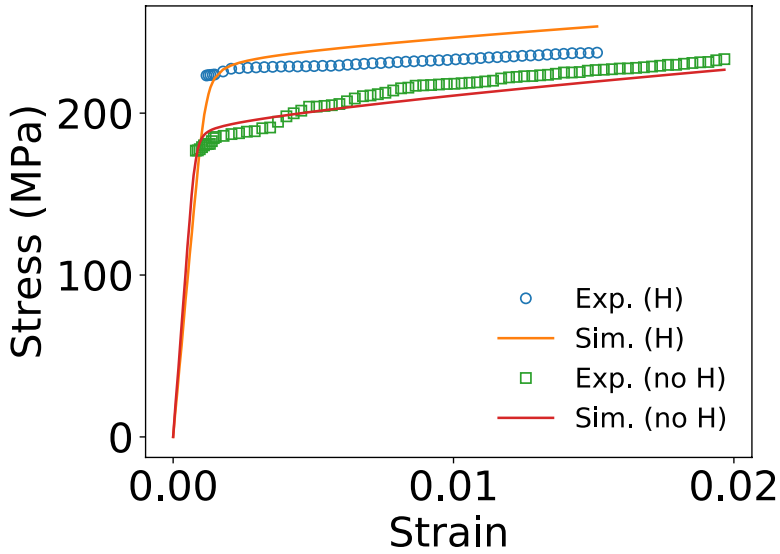
Accomplishments: Hydrogen-deformation interactions in stainless steels (M4)

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

- Specimen suitable for characterization and testing of small ensembles of grains (~100)
  - Digital image correlation (DIC) measures local (in situ) strain
  - Electron backscattered diffraction (EBSD) provides grain mapping and evolution of local deformation character with applied strain
  - Model reproduces specimen microstructure, simulates mechanical behavior



Model specimen created from surface EBSD measurements

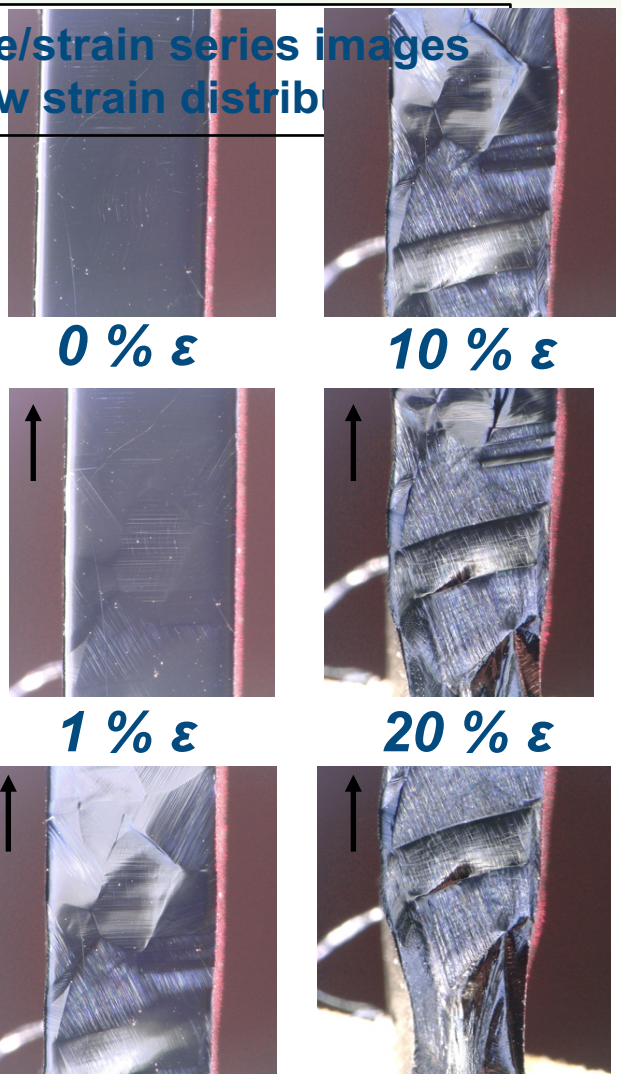


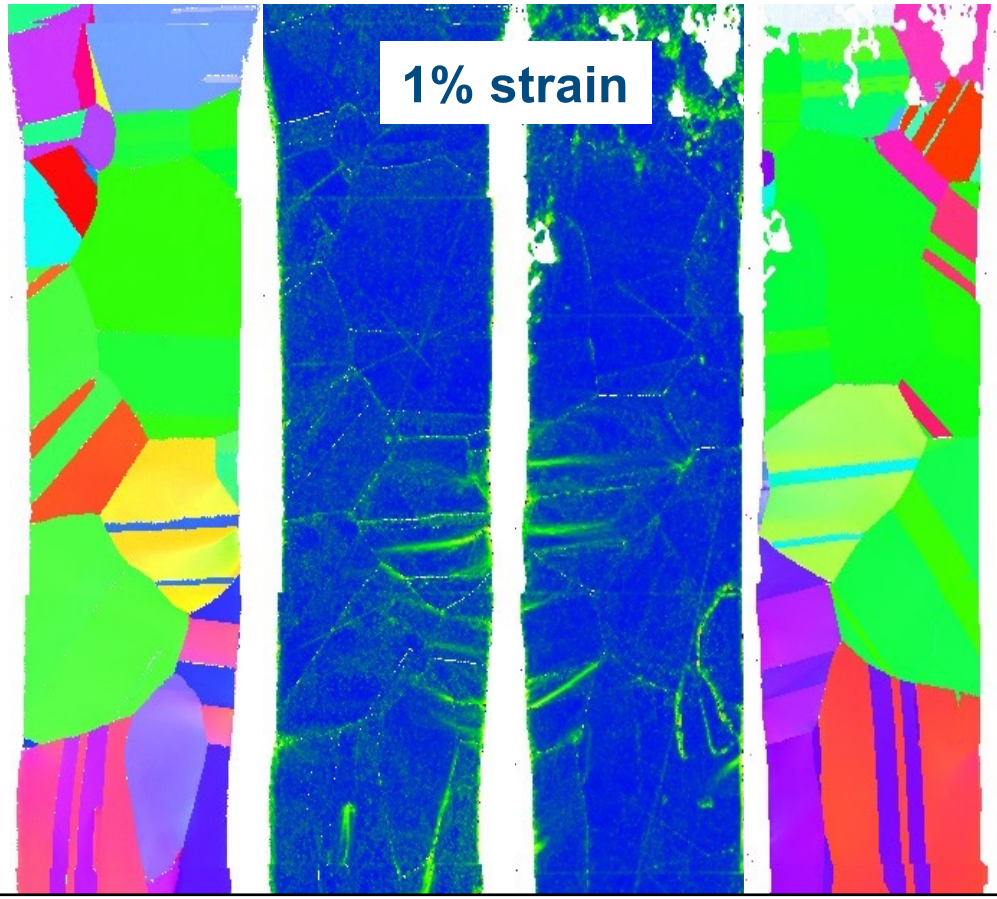
Results of experiment and simulation compare well in global measures

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

Tracking hydrogen-induced deformation changes

Time/strain series images show strain distribu





EBSD characterization of tensile specimens (front and back): inverse pole figures show grain orientations and misorientation mapping shows strain accumulation

Project Milestones

Task	FY20 Objective	Status
High-strength ferritic steels	Measure fracture resistance of ferrite-bainite microstructure with strength level ~ 1000 MPa in 106 MPa H2	One alloy tested (ferrite + bainite): fracture resistance = 24 MPa $m^{1/2}$, 3 additional alloys to be tested in FY20
High-strength aluminum alloys	Generate evidence that hydrogen/water mixtures negatively affect the structural integrity of high-strength aluminum alloys	DFT calculations indicate that H_2O on low work function metal surfaces (like clean Al) does not enhance H uptake
Damage and crack nucleation	Compare plasticity subjected to varying constraint (notches in bars, holes in cylinders, notches in plates) with a focus on crack initiation	Initial simulation results show very different strain fields, whereas experiments show similar crack initiation
Austenitic stainless steels	Compare experiment & simulation of oligocrystal, both with and without internal hydrogen	Comparison reveals potential hydrogen effects: decreased rate sensitivity, dislocation multiplication

Response to Previous Year Reviewers' Comments

Comments from reviewers:

- "The project's collaborations are somewhat limited. It is likely that this limitation is a function of the new project and that collaboration is anticipated to grow."
  - The collaborations have, in principle, grown through the FOA projects. However, the FOA projects are independent projects. The Sandia team has regular discussion with many stakeholders, the ones listed here are those that provide resources to the H-Mat project. Funding is the main limitation to expansion of collaborations.
- "While each of the project tasks have finite and achievable goals, in aggregate, there is a good deal of proposed work. The total effort is ambitious."
  - Thank you for the comment. We developed this program to be ambitious. Our goals are to elucidate some of the basic character of hydrogen-induced phenomena so that the community can move beyond simple tensile testing of materials in hydrogen environments toward deeper understanding of microstructural-property relationships. With a science-based understanding of relevant engineering materials, we believe materials processing strategies can be implemented to improve resistance to hydrogen's detrimental effects.
- "Specifics plans should be clarified for how the information and results will be disseminated and made available to industry working on component or system design and development. It is unclear whether the project team expects that the work will lead to any specific test protocol recommendations, similar to the polymers project."
  - Test method development occurs in the SCS program and is a strong leverage point for this program. Tools are in place for public access to engineering information, such as the Technical Reference and the H-compatibility database. In H-Mat, we are focused on the materials science. PNNL is taking the lead on additional data management tools associated with H-Mat.

Collaborations

- **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
  - *Rutgers University*: atomistic simulation of defects
- **New H-Mat partners**
  - *Colorado School of Mines, Hy-Performance Materials Testing LLC, MIT, Univ Alabama, Univ Illinois (UIUC)*
- **Industry partners**
  - *Swagelok*: letter of support and interest in high-strength microstructure
  - *Luna Innovations:* SBIR on NDE to identify damage prior to cracking
- **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; visiting graduate student from U. Stuttgart

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 FY20

- ***Effect of geometry on crack nucleation and initiation***
  - Compare the evolution of plasticity subjected to varying constraint (notches in bars, holes in cylinders, notches in plates) with a focus on crack initiation
- ***Hydrogen-induced changes in deformation of austenitic stainless steel***
  - Assess phenomenology of hydrogen effects on deformation with crystal plasticity model and add new physical phenomena to capture these effects

FY21 (project continuation and direction determined by DOE annually)

- ***Identify ferritic steel***
  - Identify key components of microstructural design of steel to achieve equivalent fracture resistance of ≥50 MPa $m^{1/2}$ for specified minimum tensile strength of 1050 MPa and experimentally verify (represents 50% improvement in fracture resistance of PV steels with tensile strength > 950 MPa)
- ***Role of gaseous mixtures containing hydrogen and water on fracture resistance of high-strength aluminum alloys***
  - Using atomistic modeling framework, predict hydrogen uptake energetics and mechanisms as a function of hydrogen pressure and moisture content for model Al-O-H system

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**: Microstructural variations of typical low-alloy steel are being evaluated in H_2; MD simulations are clarifying hydrogen-microstructure interactions
  - **High-strength aluminum alloys**: Surface electronic work function of metals strongly affects H uptake in the presence of H_2O
  - **Crack nucleation**: Methodology developed to probe defect interactions on atomistic scale; FEA reveals vast differences in strain fields for same initiation
  - **Austenitic stainless steels**: Complementary methods to track deformation are being refined to inform and compare with crystal plasticity modeling

Acknowledgments – team members

Task	Lead	Principal Contributors
High-strength ferritic steels	Joe Ronevich	• Xiaowang Zhou, Catalin Spataru, Chris Nowak (computational) • Zhili Feng, Yanli Wang, Jason Wang (material/microstructure) • Joy McNamara, Will James (KPFM) • Brian Kagay, Chris San Marchi (experimental)
High-strength aluminum alloys	Chris San Marchi	• Norm Bartelt, Xiaowang Zhou, Chris Nowak (computational) • Joy McNamara, Will James (KPFM) • Joe Ronevich (experimental)
Damage and crack nucleation	Jay Foulk	• Ryan Sills, Vincente Pericoli, Xiaowang Zhou, Chris Nowak (computational) • Brian Kagay, Joe Ronevich, Chris San Marchi (experimental)
Austenitic stainless steels	Coleman Alleman	• Jay Foulk (computational) • Brian Kagay (characterization/experimental) • Chris San Marchi, Joe Ronevich (experimental)

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
- DIC = Digital image correlation
  - measures local (in situ) strain based on displacement of surface features
- EBSD = Electron backscattered diffraction
  - measures local crystallography at submicron length scales, which can be used to characterize deformation and dislocation density
- KPFM = Kelvin probe force microscopy
  - measures local surface potential at submicron length scales, which can be used to characterize hydrogen distribution on surfaces

Technical reviewer comments and response

- "Further elaboration on the Fe-C-H (density functional theory [DFT] and molecular dynamics [MD]) models is requested. If this is for ferritic stainless steels, then it is unclear how relevant these models are if Cr is not incorporated."
  - **The Fe-C-H interatomic potential enables MD simulations of fundamental microstructural elements characteristic of pressure vessel and pipeline steels (i.e., ferritic steels). For info is available in https://doi.org/10.1002/jcc.26176**
- "The details surrounding the DFT modeling and MD modeling are unclear. It is also unclear if there are any plans to look at the uptake behavior independent of cracking in the hydrogen and H2O environment; this would facilitate seeing the extent to which hydrogen uptake will occur. Additionally, it would be beneficial to couple some of the MD simulations at the crack tip to the focused ion beam milling (FIB) of **transmission electron microscopy (**TEM**)** results by Gangloff and Ro that quantified the structure."
  - **The reviewer mentions two different modeling activities.**
    - **The DFT studies are aimed at the thermodynamics of hydrogen interactions with the surface. Here the energetics of this interaction has been quantified for the first time and explains anomalous experimental results (previously unpublished because they could not be explained). A journal publication is in preparation.**
    - **The MD simulations are focused on hydrogen dislocation interactions. The reference to Ro, Agnew and Gangloff is an interesting one that we should consider. However, it's important to note that The length scale of the TEM observations are much too large for MD simulations.**
  - **Measuring hydrogen uptake in aluminum alloys is extremely difficult. We hope that the KPFM work will illuminate this aspect.**

Technical reviewer comments and response

- It is unclear if the team has a means of quantifying the initiation lives or if there is strong evidence that the hydrogen will actually affect the initiation life. This is of particular importance if the project team wants to move toward engineering applications. Oftentimes, large-scale defects (much larger than the atomistic or dislocation processes) will lead to initiation on engineering components
  - **The team has developed methods for quantifying crack initiation using DCPD (refer to work within the SCS program, for example). These results suggest that fatigue is not controlled by "large-scale defects" in the materials being studied (austenitic stainless steels) – in contrast to commodity steels.**
  - **The modeling work is targeted at deformation induced damage that may contribute in fatigue and fracture. Fracture surfaces clearly show evidence of a plasticity-mediated processes that are modified by the presence of hydrogen and this is the target of these studies. The transition from MD to engineering scale is a huge step, but we are working at the ends trying to push toward the middle.**
- It is unclear how the team is incorporating the hydrogen into the crystal plasticity model. It is also unclear what parameters the team is modifying, as well as how the boundaries are being handled. It is unknown whether the project team is tuning this via constitutive laws gathered from polycrystals that have been hydrogen-charged or from single crystals.
  - **Initial CP work has focused on accounting for hydrogen through modification of constitutive relationships from standard formulations. This process can use either oligocrystal specimens where the simulation strongly reflects the microstructure of the specimen, or single crystals. We are pursuing both. The details had been planned for presentation and publication at the International Hydrogen Conference. We are happy to share more details and engage in collaboration, but in this format it is not possible to communicate all the details.**