



# 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**

**Joint Hydrogen Delivery, Codes & Standards, Storage Tech Team**

**H-Mat Partner Kick-off**

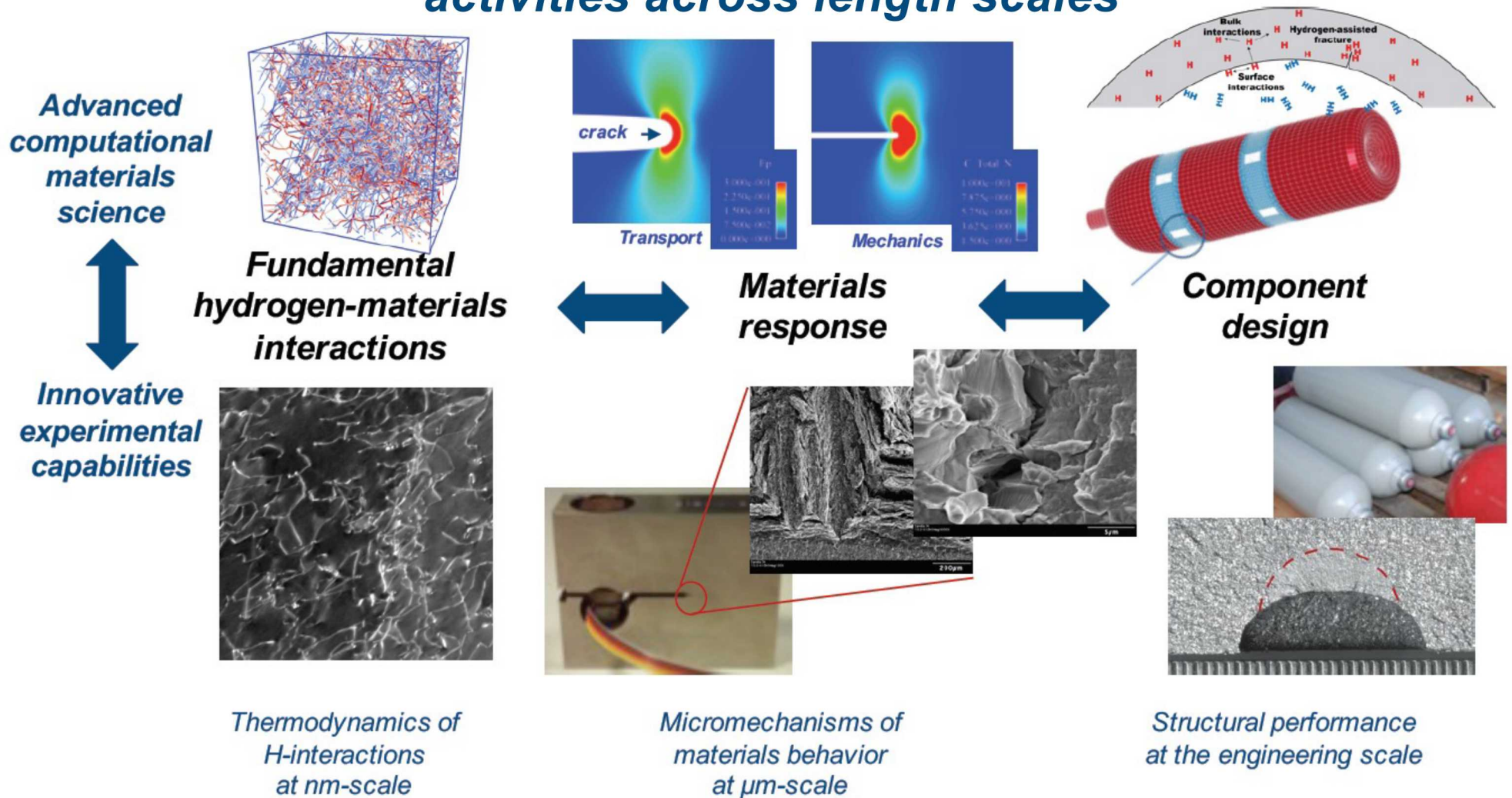
**March 25, 2020**

**Project ID# IN001**

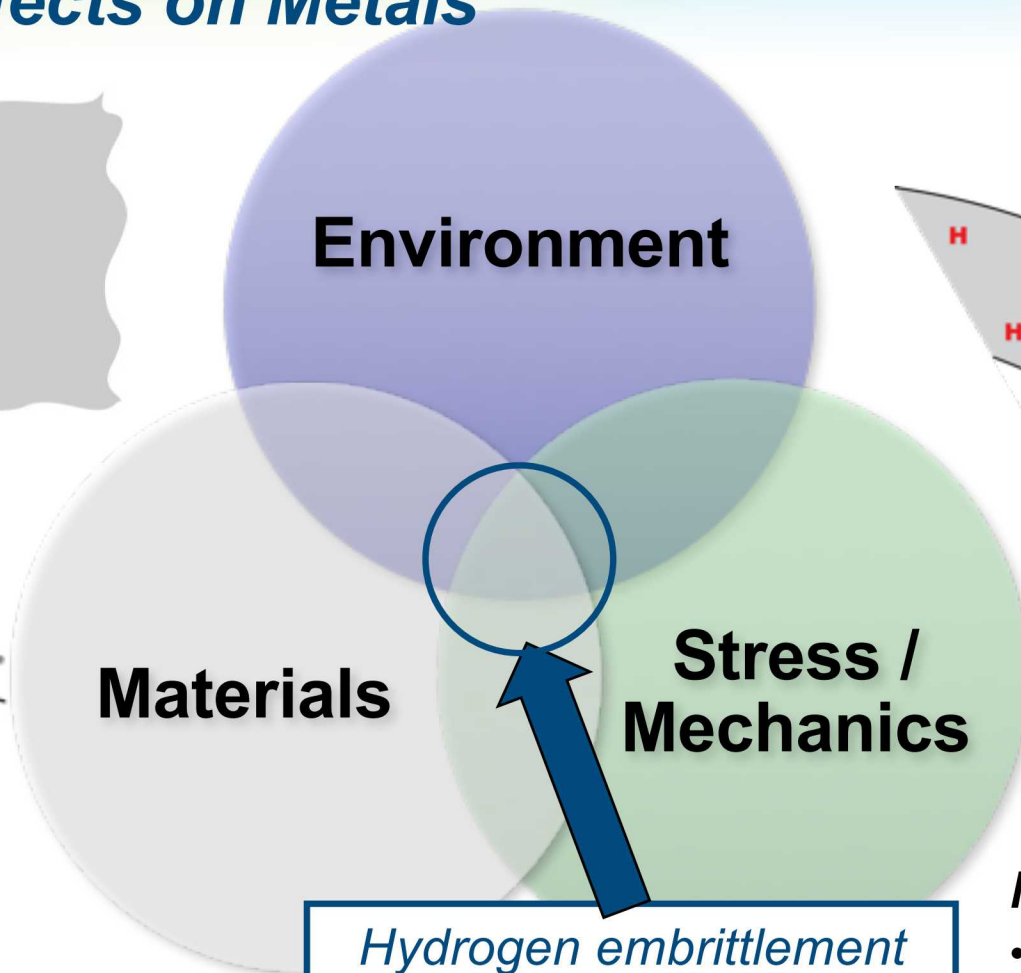
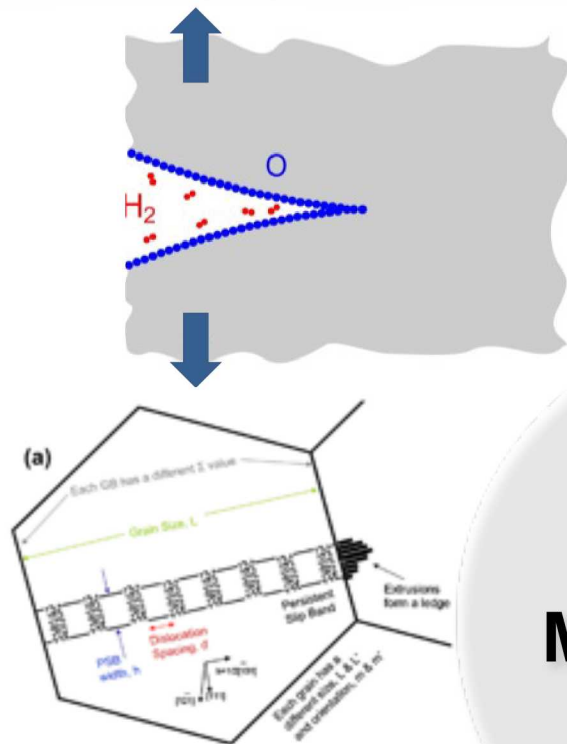
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# Engineering performance depends on mechanisms manifest at nanometer length scales

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

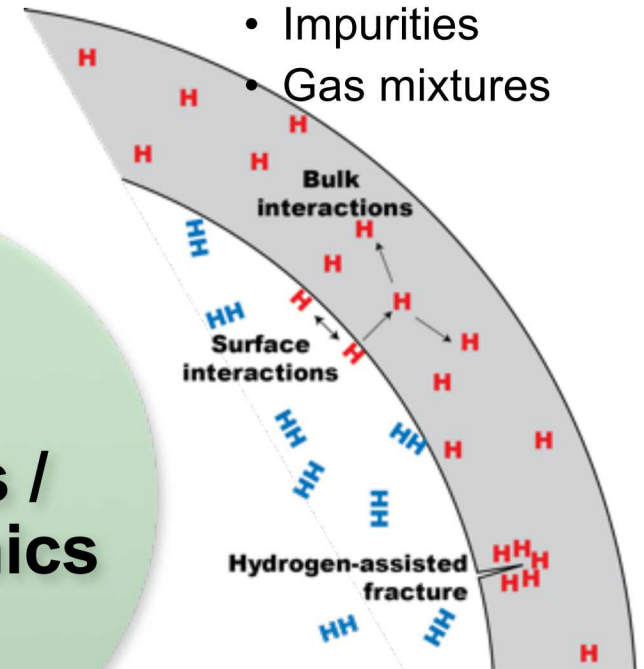


# Consider the intersection of *environmental*, *mechanics* and *materials* variables to understand *Hydrogen Effects on Metals*



## 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

# 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

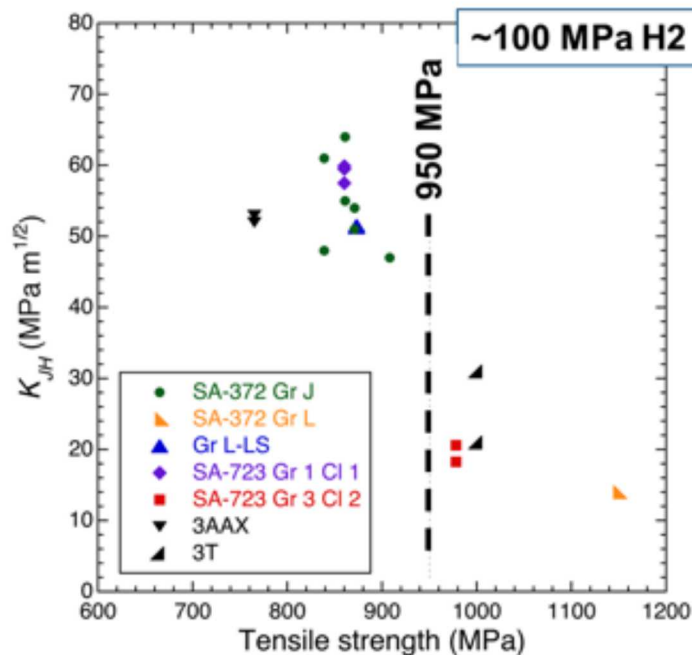
*Motivation:* elucidate the mechanisms of hydrogen-materials interactions to inform **science-based strategies to design the microstructure** of metals with improved resistance to hydrogen degradation

Task	Relevance and Objective
<b>High-strength ferritic steel microstructures</b>	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
<b>High-strength aluminum alloys</b>	Elucidate mechanisms of hydrogen embrittlement in high-strength aluminum alloys and the role of moisture in hydrogen surface interactions in this class of materials
<b>Transferability of damage and crack nucleation</b>	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
<b>Microstructure of austenitic stainless steels</b>	Identify governing physical processes of hydrogen embrittlement in austenitic stainless steels to design microstructures that mitigate the adverse effects of hydrogen environments
<b>Materials for cryogenic hydrogen service</b>	Identify materials for cryo-compressed hydrogen storage onboard vehicles, and develop key technical metrics for viable structural materials in this application

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

*Science question:*

**Are there high-strength steel microstructures that can be resistant to hydrogen effects?**



- Mechanical testing of steels in high pressure H<sub>2</sub>
- 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

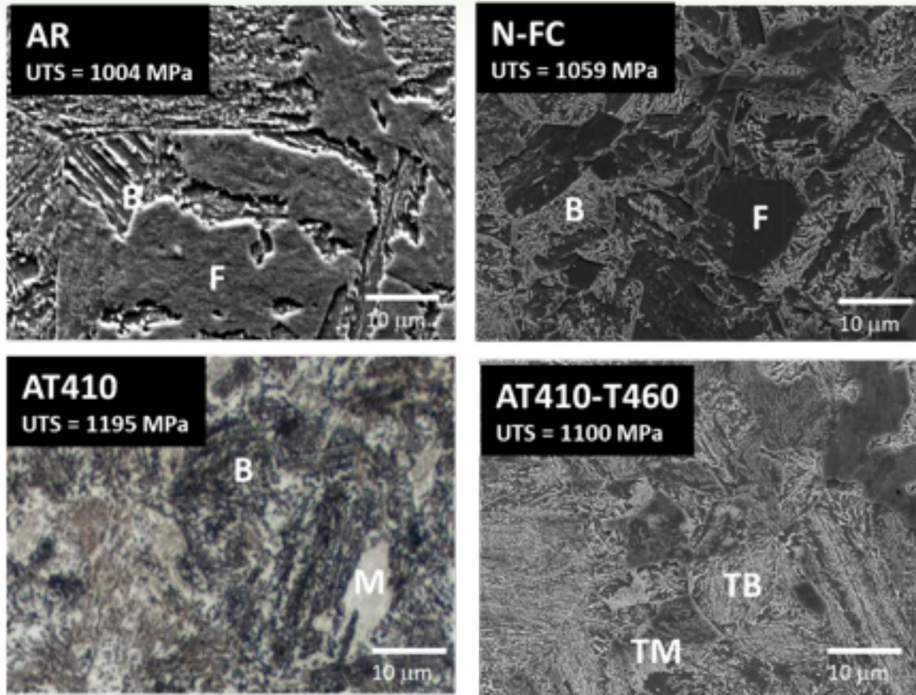


*Engineering goals:*

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

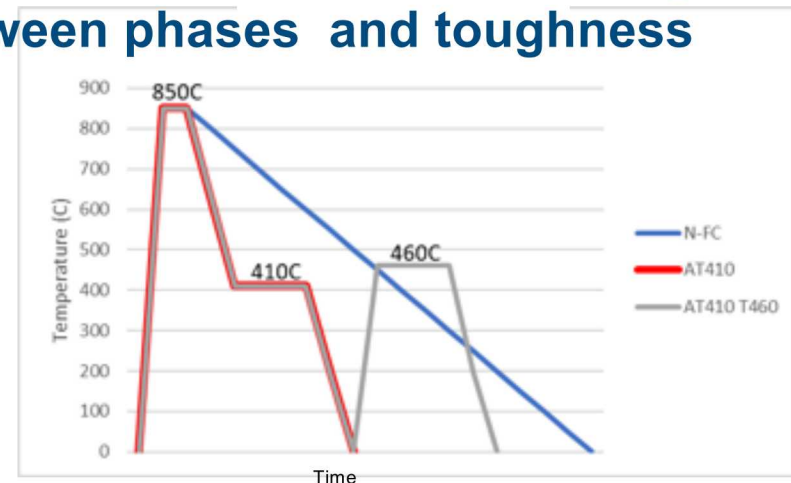
# High-strength ferritic steel microstructures (task M1)

## 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<sub>2</sub> ( $K_{IH} = 24 \text{ MPa m}^{1/2}$ )
- Measurements planned for additional 3 microstructures

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

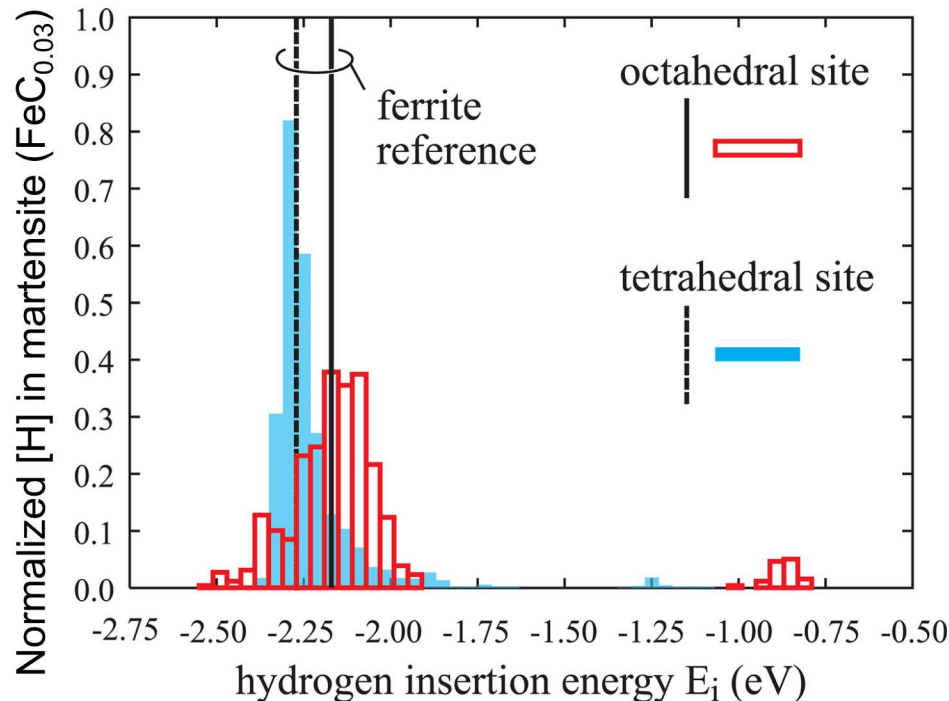
- 1) Examining role of grain boundaries in fracture resistance (impurities, prior austenite grain size). Can we reduce intergranular fracture?
- 2) Alter plasticity through incorporating more crack resistant phases (F,  $\gamma$ )

# High-strength ferritic steel microstructures (M1)

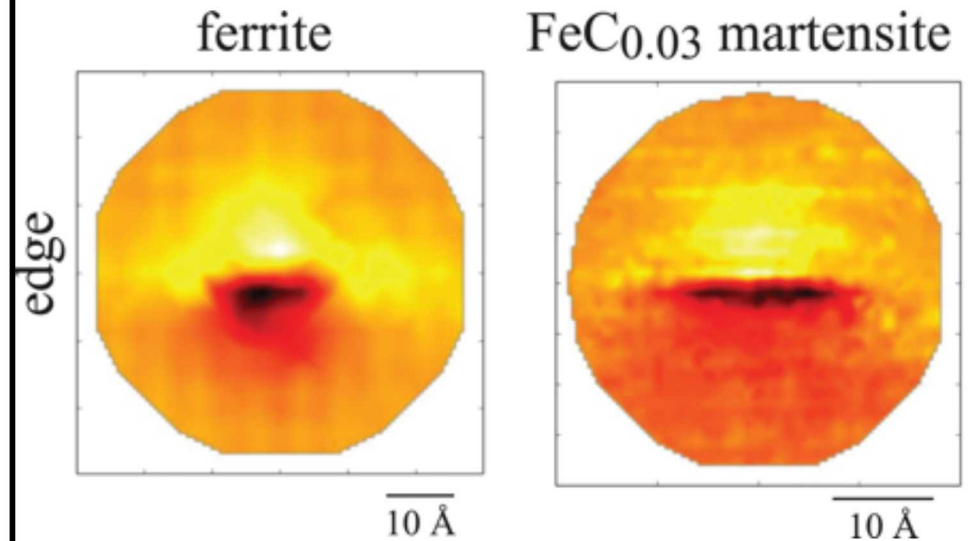
## Our Fe-C-H interatomic potential has revealed preferences of hydrogen in high strength steel microstructures

### 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:

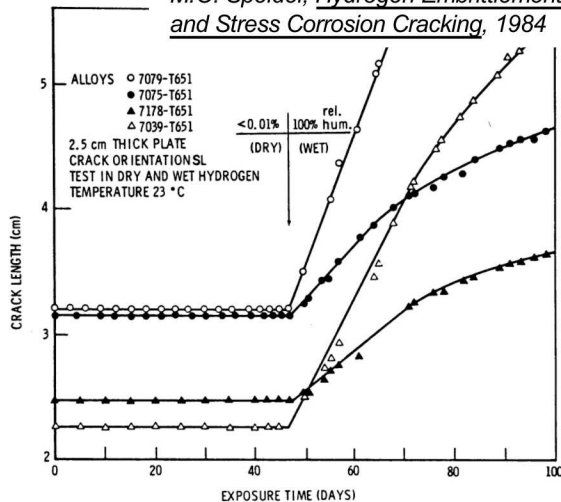
- H interactions with interfaces (martensite/cementite, prior  $\gamma$  GBs)
- Strain fields effects at interfaces
- Developing KPFM methods (SRNL) to visualize location of H

# 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<sub>2</sub> + H<sub>2</sub>O) 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:*

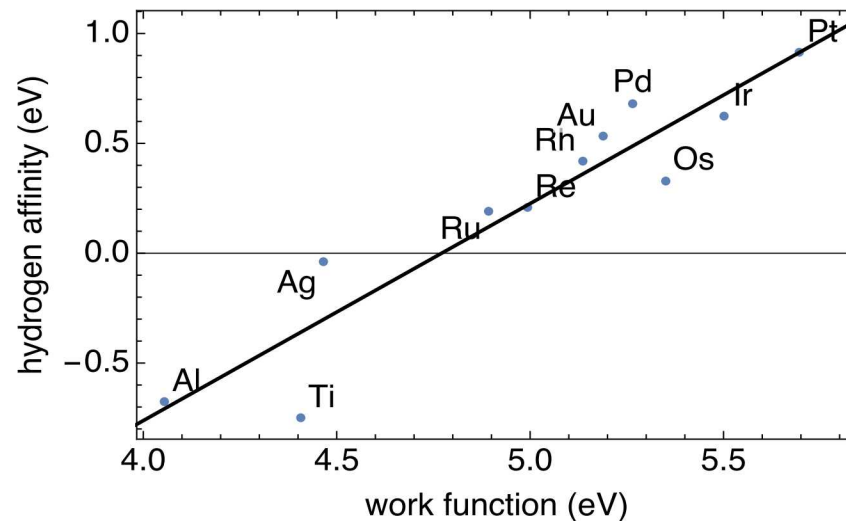
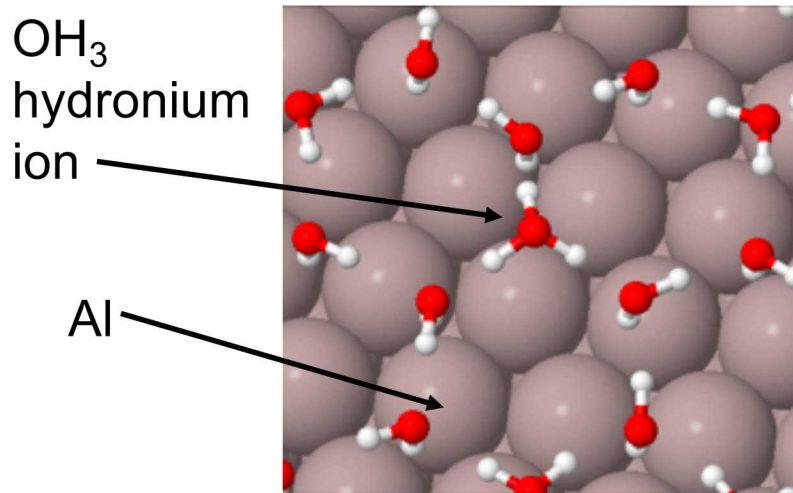
- **Hydrogen-compatible microstructures of aluminum alloys with yield strength >350 MPa that are insensitive to standardized moisture limits for fuel-grade hydrogen (5ppm H<sub>2</sub>O)**
- **Specification of environmental conditions under which aluminum is not degraded in gaseous (and liquid) hydrogen environments**

## High-strength aluminum alloys (task M2)

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

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  $\text{OH}_3$  ions on water layers: High electronic work function favors these ions:



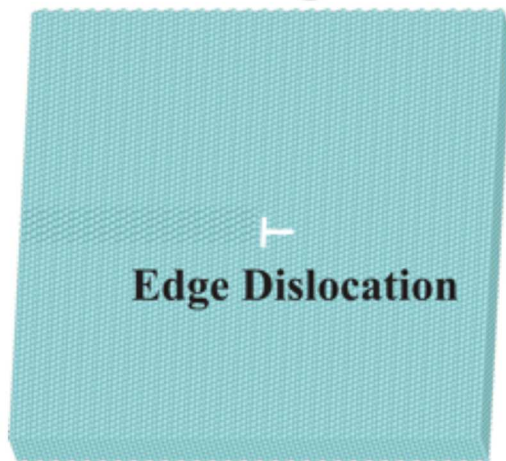
Clean, unalloyed and unoxidized Al has a low work function and adsorbed water does not enhance H uptake.

*In progress:*  $\text{H}_2\text{O}-\text{H}_2$  interactions on oxidized Al surfaces are being explored.

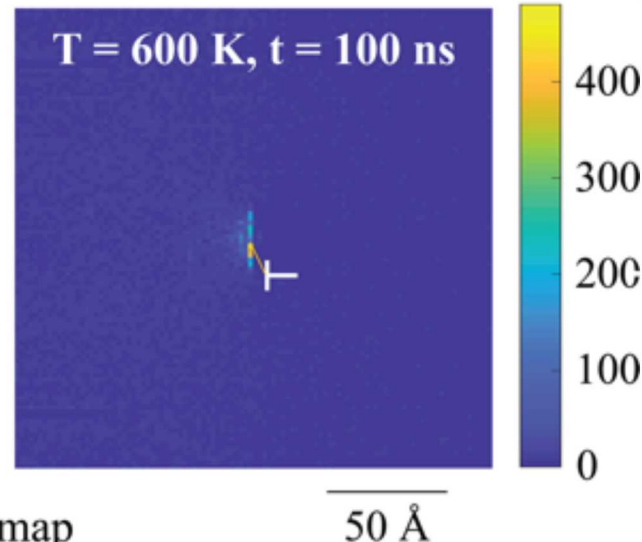
## High-strength aluminum alloys (task M2)

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

### MS Progress



### relative H concentration



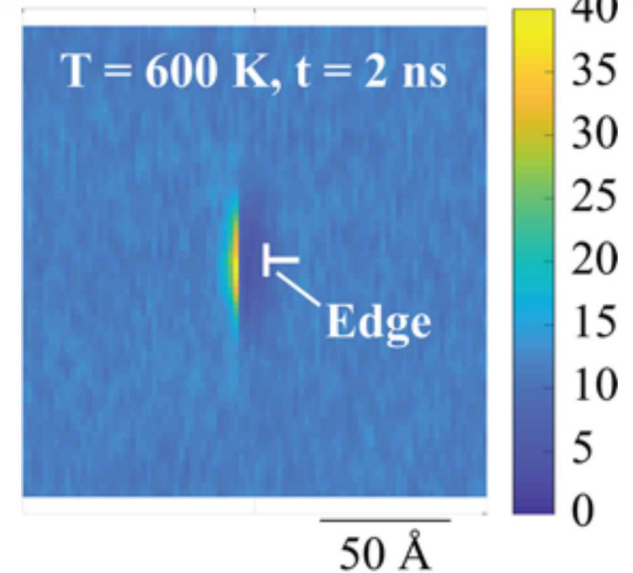
MS simulations => H energy map

Continuum + energy map => H concentration map at T and t

Energy + concentration maps => friction stress

### MD Progress

### relative H concentration



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

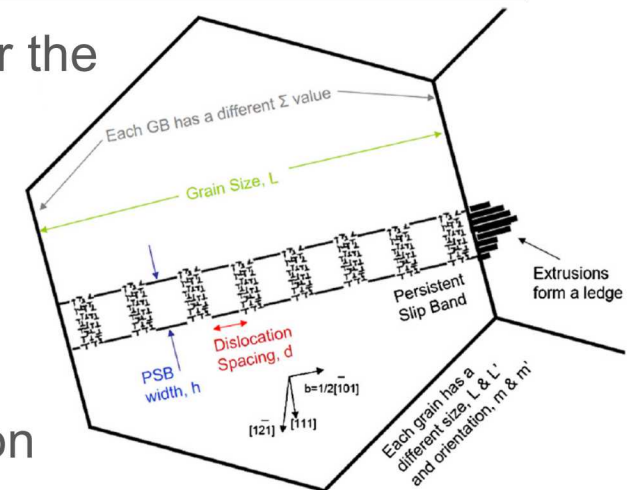
*In progress:* Time-averaged MD is being used to study kinetics of H atmosphere formation with preliminary success

# 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



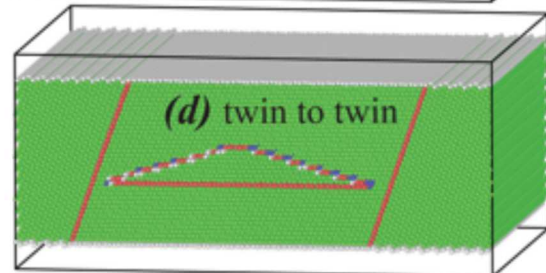
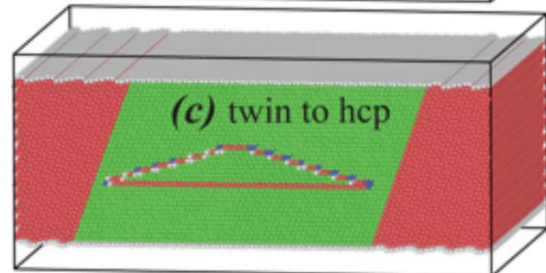
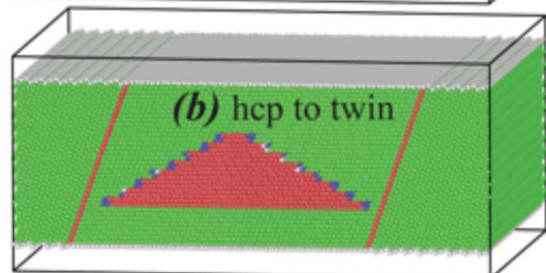
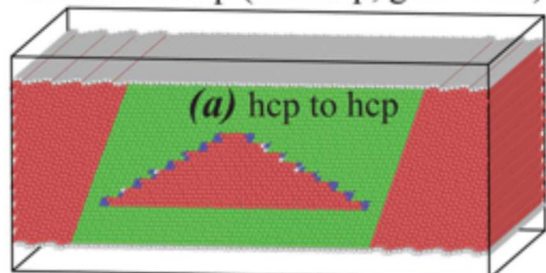
## Engineering goals:

- 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

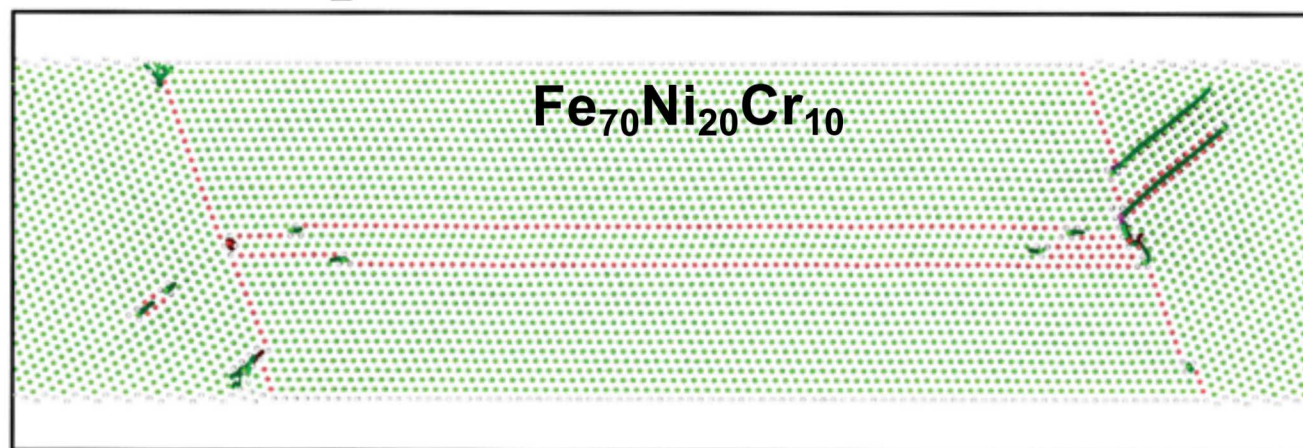
## Crack nucleation in stainless steels (task M3)

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

Structure map (red: hcp, green: fcc)



- 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

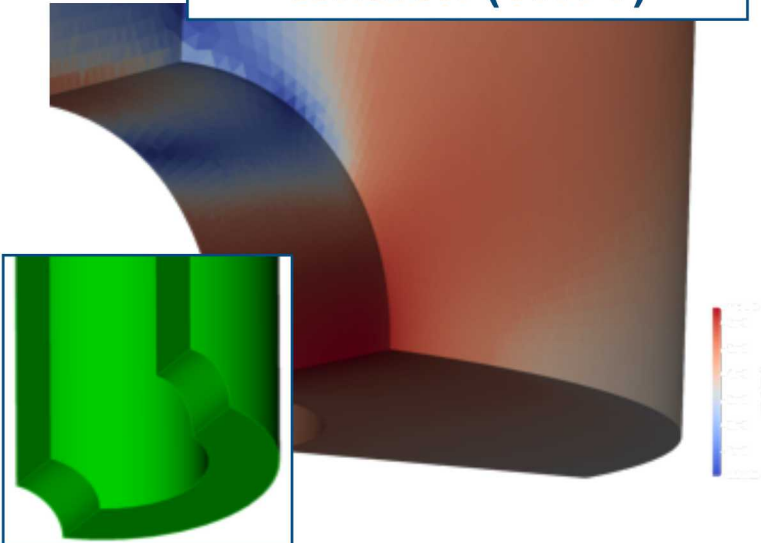
## Crack nucleation and role of geometry (task M3)

# 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:*

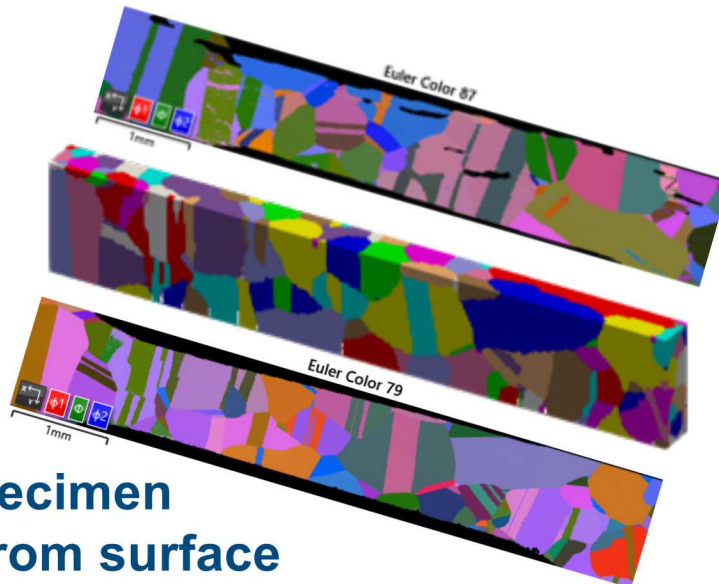
- **Results are being analyzed to identify field quantities and characteristic length scales that quantify crack initiation**



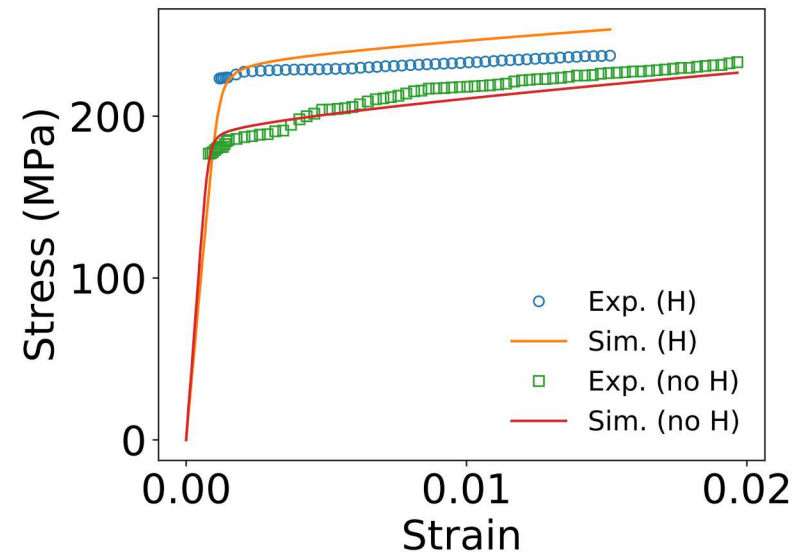
# Hydrogen-deformation interactions in stainless steels (task M4)

## 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



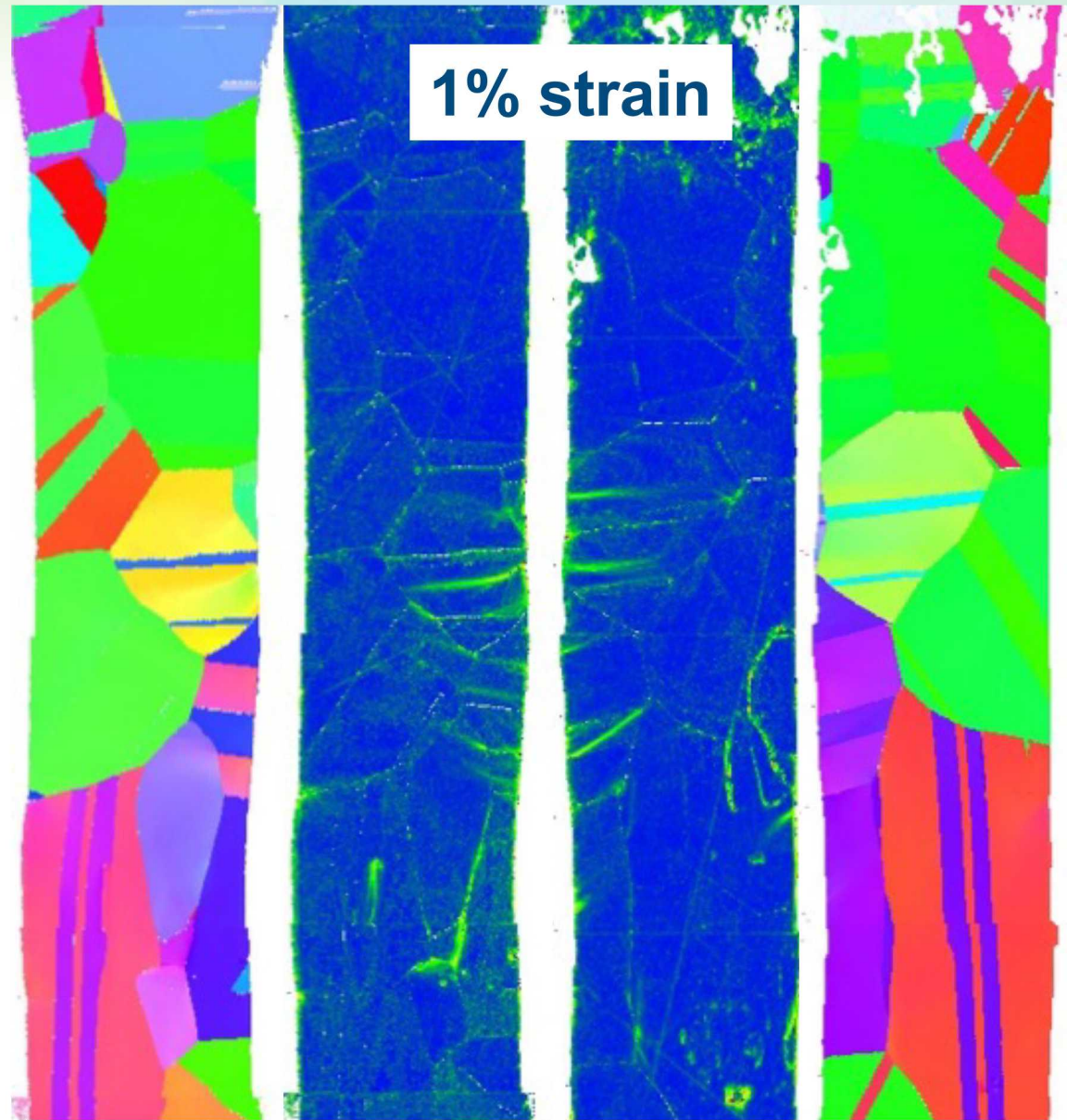
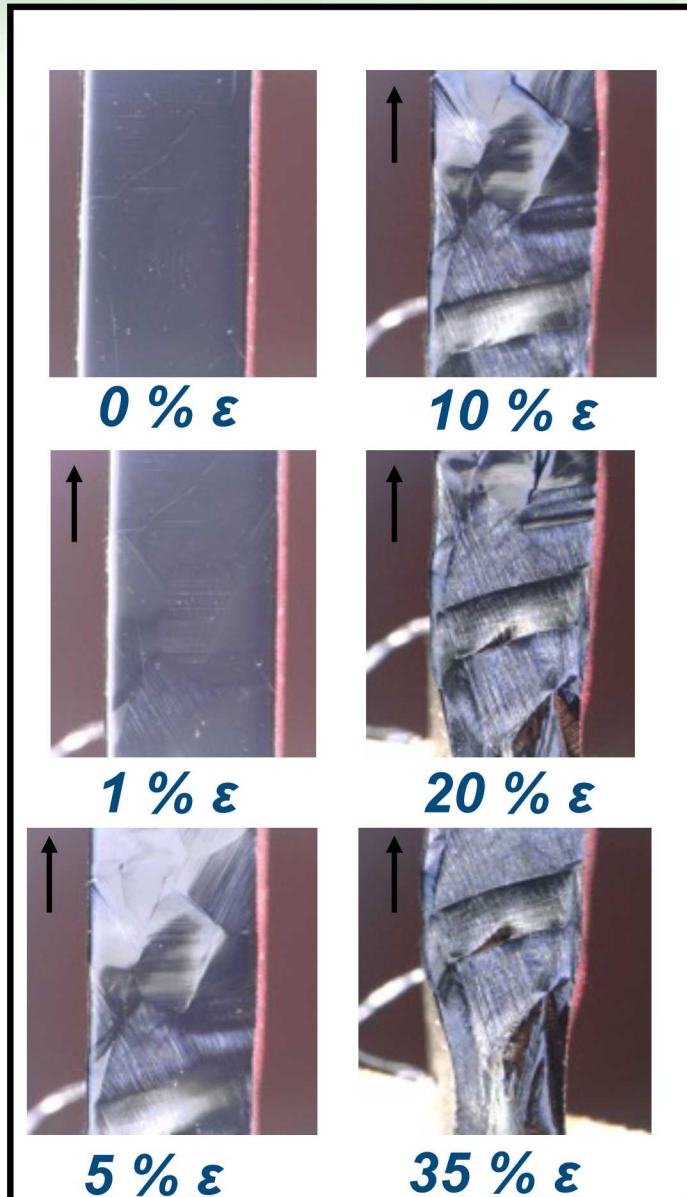
**Model specimen created from surface EBSD measurements**



**Results of experiment and simulation compare well in global measures**

# Hydrogen-deformation interactions in stainless steels (task M4)

## Tracking hydrogen-induced deformation changes





# Project Milestones

Task	FY20 Objective	Status
<b>High-strength ferritic steels</b>	Measure fracture resistance of ferrite-bainite microstructure with strength level ~ 1000 MPa in 106 MPa H <sub>2</sub>	One alloy tested (ferrite + bainite): fracture resistance = 24 MPa m <sup>1/2</sup> , 3 additional alloys to be tested in FY20
<b>High-strength aluminum alloys</b>	Generate evidence that hydrogen/water mixtures negatively affect the structural integrity of high-strength aluminum alloys	DFT calculations indicate that H <sub>2</sub> O on low work function metal surfaces (like clean Al) does not enhance H uptake
<b>Damage and crack nucleation</b>	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
<b>Austenitic stainless steels</b>	Compare experiment & simulation of oligocrystal, both with and without internal hydrogen	Comparison reveals potential hydrogen effects: decreased rate sensitivity, dislocation multiplication



# 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
  - *Univ Illinois, Colorado School of Mines, MIT-Harvard, Univ Alabama, Hy-Performance Materials Testing*
- 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 may 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  $\geq 50 \text{ MPa m}^{1/2}$  for specified minimum tensile strength of 1050 MPa and experimentally verify (represents 50% improvement in fracture resistance of PV steels with tensile strength  $> 950 \text{ MPa}$ )
- ***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

Task	Lead	Principal Contributors
<b>High-strength ferritic steels</b>	Joe Ronevich	<ul style="list-style-type: none"> <li>• Xiaowang Zhou, Catalin Spataru, Chris Nowak (computational)</li> <li>• Zhili Feng, Yanli Wang, Jason Wang (material/microstructure)</li> <li>• Joy McNamara, Will James (KPFM)</li> <li>• Brian Kagay, Chris San Marchi (experimental)</li> </ul>
<b>High-strength aluminum alloys</b>	Chris San Marchi	<ul style="list-style-type: none"> <li>• Norm Bartelt, Xiaowang Zhou, Chris Nowak (computational)</li> <li>• Joy McNamara, Will James (KPFM)</li> <li>• Joe Ronevich (experimental)</li> </ul>
<b>Damage and crack nucleation</b>	Jay Foulk	<ul style="list-style-type: none"> <li>• Ryan Sills, Vincente Pericoli, Xiaowang Zhou, Chris Nowak (computational)</li> <li>• Brian Kagay, Joe Ronevich, Chris San Marchi (experimental)</li> </ul>
<b>Austenitic stainless steels</b>	Coleman Alleman	<ul style="list-style-type: none"> <li>• Jay Foulk (computational)</li> <li>• Brian Kagay(characterization/experimental)</li> <li>• Chris San Marchi, Joe Ronevich (experimental)</li> </ul>