Materials for Safe Containment, Transport, Delivery, and Use of Hydrogen Fuel: Hydrogen Pipeline Safety

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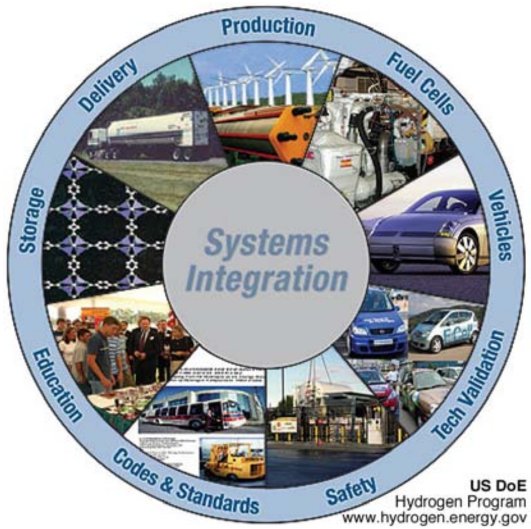
Motivation
Hydrogen is a promising medium for energy transfer

1. Advantages:
    - Plentiful
    - Inexpensive
    - Flexible
    - Renewable
    - Sustainable
    - Safe
2. Drawbacks:
    - Conversion efficiencies
        - Generators
        - Fuel cells
        - Compressors
    - Energy content per unit volume
        - Electrons v. Gas
        - Tube trucks
        - Pipelines
    - Safety (infrastructure)
        - Flammability Range (≈ 4-75 v% in air)
        - Hydrogen alters properties (embrittlement)
        - Codes and standards for safe high pressure containers
        - Reliable, evaluated, data on properties in hydrogen
        - Standardized test methods for measuring properties in hydrogen




Carlsbad, NM
August 19, 2000

Technical Issues
(1) Materials

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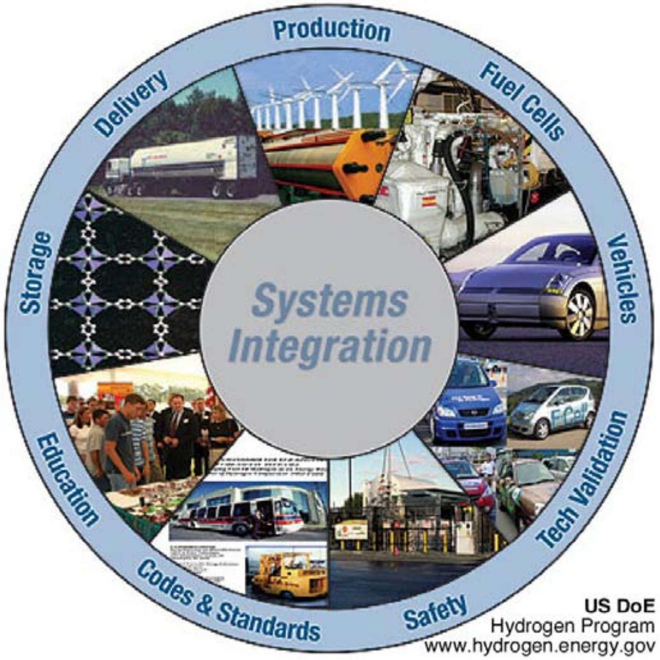
A hydrogen fuel infrastructure will require a variety of structural materials to operate in or contain hydrogen.



All types of structural materials will be exposed to hydrogen at elevated pressures and expected to perform their function. For example:

Steels - transmission pipelines, compressors, storage containers, dispensers

Al Alloys - containers, tube trucks, on-board storage

Polymers and PMCs - distribution pipelines, storage containers

Stainless Steels - fuel cell containers and components, on-board tubing and storage

Ni Based Alloys - compressors, valves, bearing surfaces

Others - Cu alloys, Ti Alloys, …

Will existing alloys will be able to meet our needs?

Current Programs (DOE PWG) - existing alloys and test methods

Future - alloy development and test methods that enable alloy optimization

Technical Issues
(2) Hydrogen effects properties (embrittlement)

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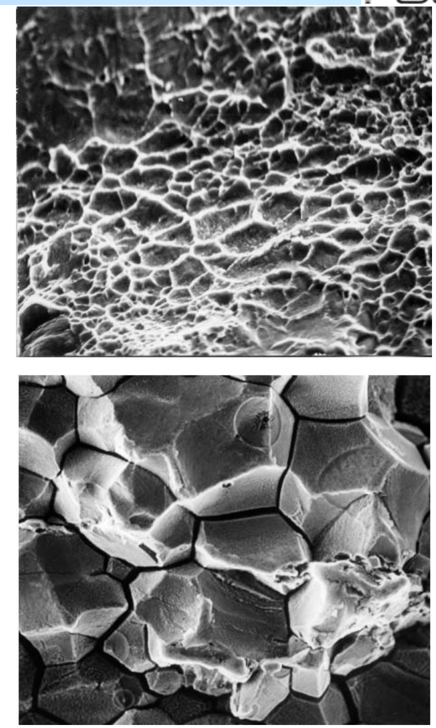
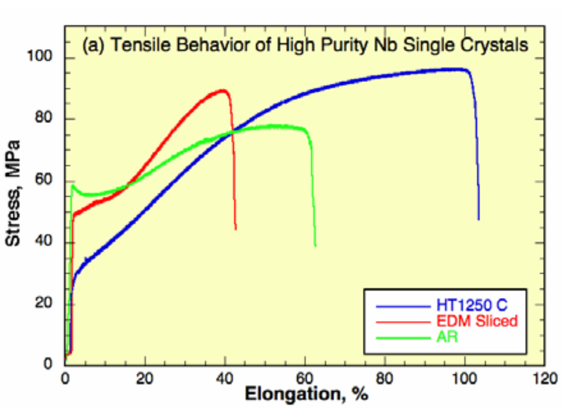
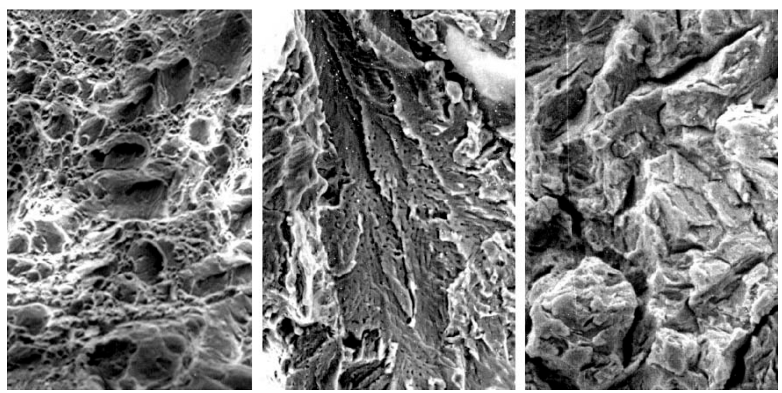
1. Hydrogen is one of the most influential alloying elements
2. Many metals and alloys readily absorb hydrogen from H_2(g) or other hydrogen bearing environments
3. Hydrogen dissolves as an interstitial and diffuses rapidly
4. Hydrogen alters physical properties
5. Hydrogen can dramatically alter the deformation and fracture behavior of metals and alloys by
    a) Modifying normal modes of deformation and fracture
    b) Precipitating as brittle metal hydrides or H_2(g) blisters
    c) Induce new brittle "cleavage-like" fracture modes
    d) Lowering the cohesive strength of interfaces



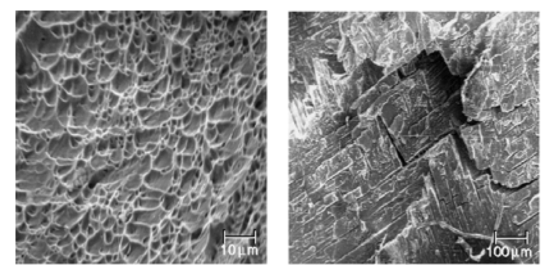
d) MVC-IG Transition in a Ni alloy



a) Effect of H on the ductility of ultra high purity Nb



c) Effect of increasing H fugacity on the fracture mode of a steel



b) Effect of H on the fracture mode of a titanium alloy

Technical Issues

(3) Hydrogen embrittlement and fracture testing

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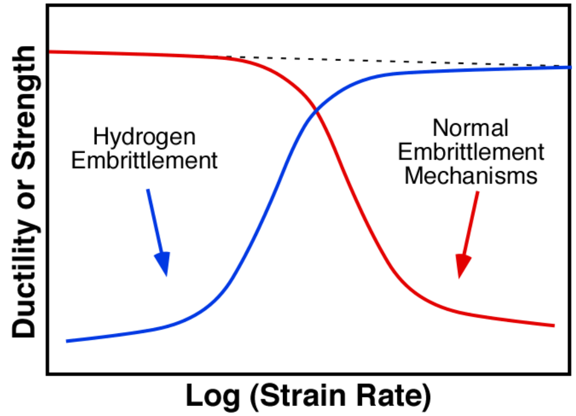
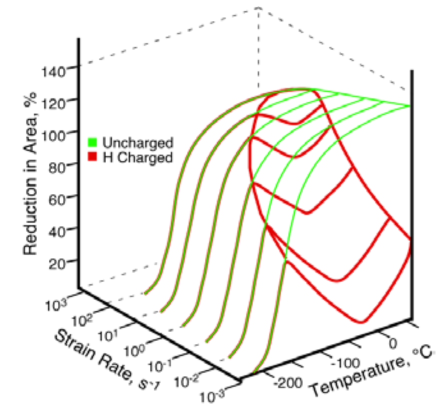
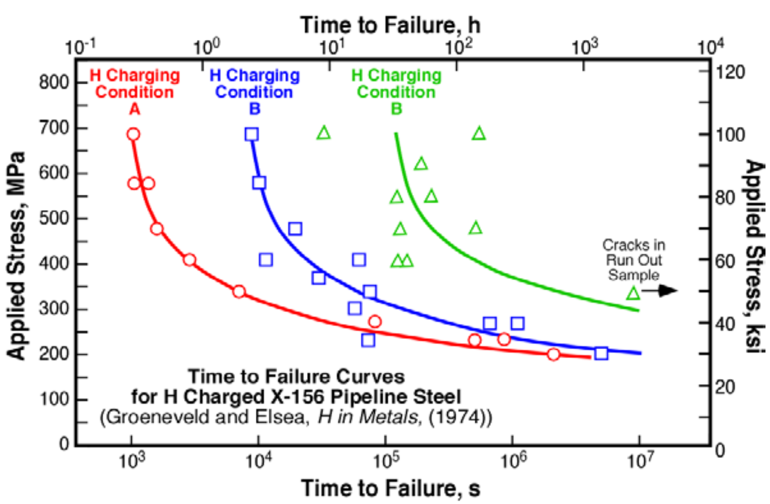
1. Embrittlement (?)
   - Reverse strain rate sensitivity from normal embrittlement mechanisms
   - Hydrogen must be present during loading (exception blistering)
   - Effect fully reversed on removal of H unless damage occurred
   - Temperature minimum
   - Slow, sub-critical, crack propagation





T. Toh and W. M. Baldwin, *SCC and Embrittlement*, W. D. Robertson edt. 176, (1956).



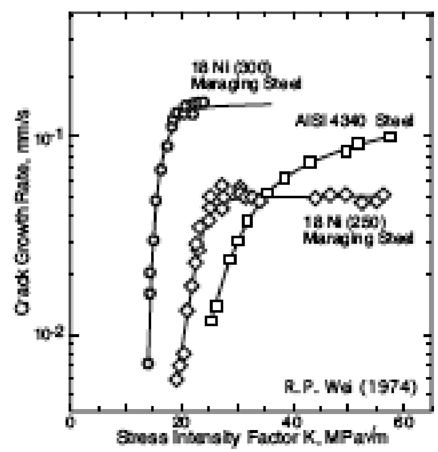
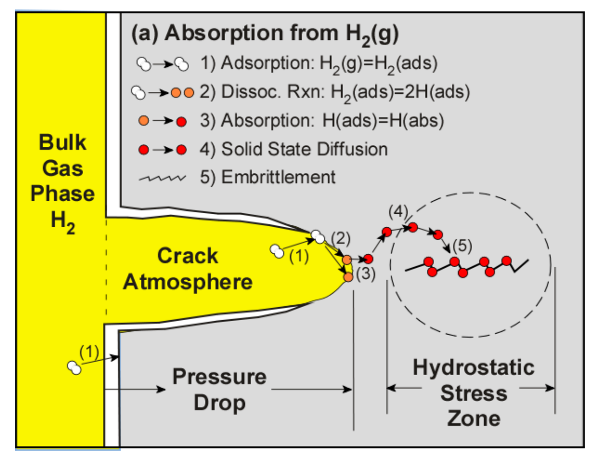


Figure 3 Crack growth in three steels exposed to hydrogen gas (14).



Technical Issues

(3) Hydrogen embrittlement and fracture testing (cont.)

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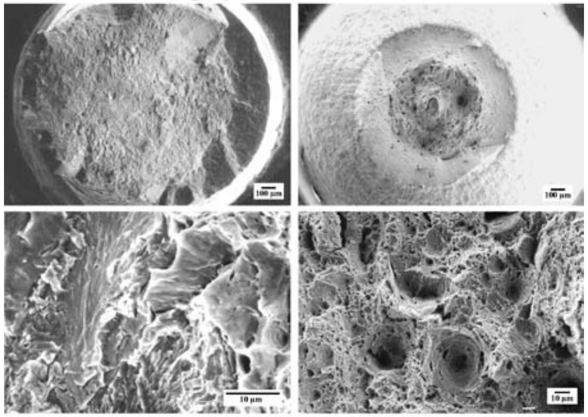
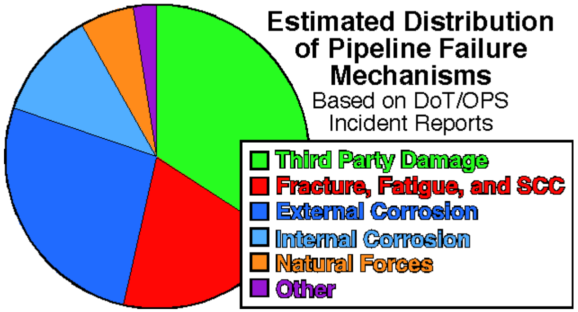
2. In-situ charging is required
   - Hydrogen must be present in the microstructure at the concentrations expected in service for an experiment to accurately represent the effects
   - Solubility varies with cold work
   - Cold work varies in the plastic zone at the crack tip (K, x,y,z)
   - Rapid diffusion in and out (pre-charging)
3. Susceptibility tends to increase with increasing strength
   - High strength steels are very susceptible, but not the only alloys susceptible
     - Lit. show H effects pure Fe and other elements
     - Other alloy classes are influenced (Ni, Ti, Al)
   - Existing H pipelines use low yield strength steels (<60ksi)
   - Existing H pipelines require special practices to keep yield strengths low
   - Existing natural gas and oil pipelines regularly fail by hydrogen embrittlement typically at "hard spots" at welds, bends, gouges, dings, and dents

SEM Fractographs of HSLA Simulated HAZ



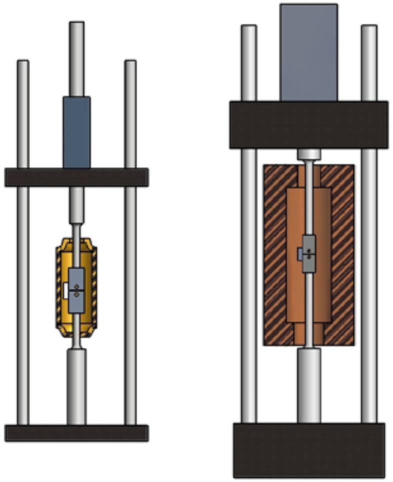
Region (3): High [$P(H_2)$] Region (1): Low [$P(H_2)$]



Technical Issues

(3) Hydrogen embrittlement and fracture testing (cont.)

4. Existing susceptibility measures tend to vary with the testing conditions
    - Strain rate dependence
    - Surface treatment and finish dependent
    - Gas purity dependent
    - Solubility dependence
    - Diffusivity (rate) dependence
5. Fracture (and deformation) properties do not scale well with sample size
    - Sample thickness constraint (plane strain v. plane stress)
    - Diffusion and sample size effects
6. Fatigue (cyclic) loading is relatively unexplored and provides bare surface and time for solid state diffusion during each load cycle
7. **The high pressure hydrogen gas "in-situ" testing chamber and the time required for hydrogen saturation of large samples becomes a "bottle-neck" limiting high throughput testing**



NIST is designing and assembling a 1 liter and 100 liter pressurized hydrogen test chambers for its hydrogen testing facility in Boulder

Outline of NIST Program

NIST Mission

- Measurements, standards, and data
- Unique testing facilities
- Data and information for codes and standards

Program Objectives

- Develop standard test methods for in-situ H_2(g) testing (with DOE PWG)
- Apply test methods and unique facility to generate critical evaluated data needed by SDOs for setting codes and standards that protect public safety (round robin testing with DOE PWG)
- Develop laboratory research and NDE methods that enable industry to develop better alloys and avoid catastrophic failures.

Hydrogen Pipelines

- Enabling - critical to economic viability of H as a fuel,
- Steels - construction costs limit materials,
- Safety - public safety and the perception of H as a safe fuel

Program Structure

- High-pressure H_2(g) testing facility
- Electrochemical methods for measuring solubility, diffusivity, cathodic charging, and embrittlement
- NDE methods for studying hydrogen effects
- Fundamental mechanistic studies

NIST High-Pressure Hydrogen Testing Facility
Construction Underway in Boulder, CO

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NIST is constructing a 75 square meter state-of-the-art research facility for the evaluation of the mechanical properties of materials in hydrogen gas.

Plans include evaluating hydrogen effects on ….

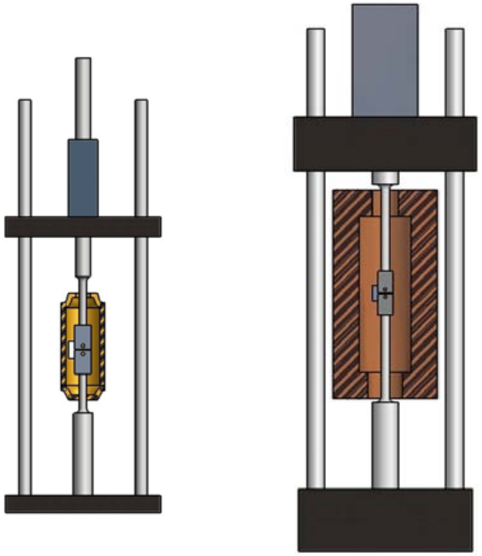
-- Fatigue rate sensitivity
-- Flow stress sensitivity
-- Surface finish (pipeline wall)
-- Microstructure (including weld joints)
-- Strengthening mechanisms (X65 and above)

Proposed Hydrogen Testing Capabilities

Testing up to 35 MPa, -80 to 100°C in various purities of hydrogen up to full pipe-wall thickness

- **Tensile:** smooth and notched tensile (1MN)
- **Fatigue:** initiation, high-cycle, low-cycle, (tensile-type, MT, CT) (100 kN, 1MN)
- **Fracture toughness:** K_{Ic} , CTOD, CTOA (1MN)
- **Creep:** rounds, flats (100kN)

Workshop/DOE PWG Meeting next summer in Boulder, CO with tours of new facility

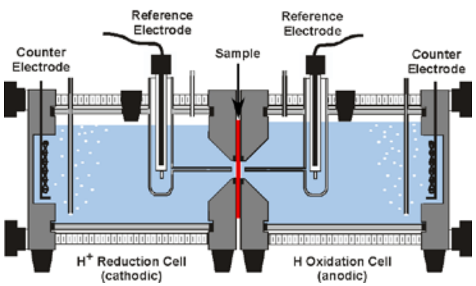


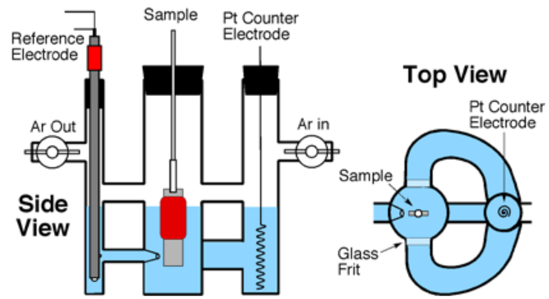
1 kN and 1 MN fatigue test machines with 1 liter and 100 liter pressurized hydrogen test chambers

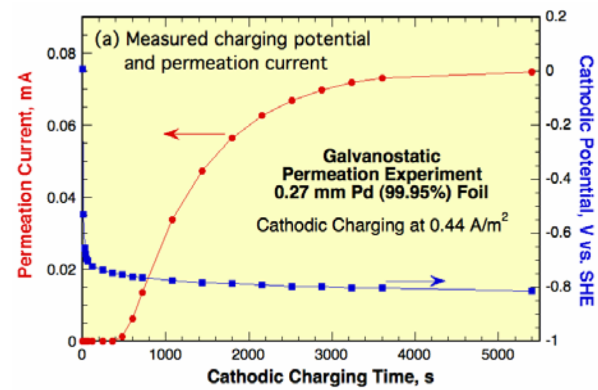
Electrochemical Methods

Inexpensive, convenient, accurate, and relevant

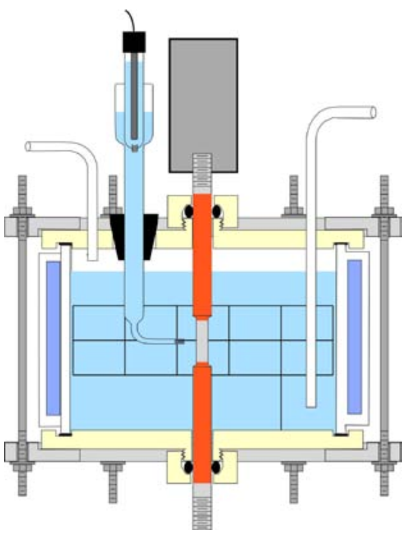
Diffusion and solubility measurements at ambient temperatures

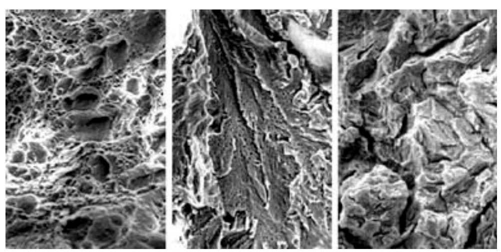






Cathodic charging methods for mechanical tests and evaluation of relevance to service in High Pressure H_2 Gas





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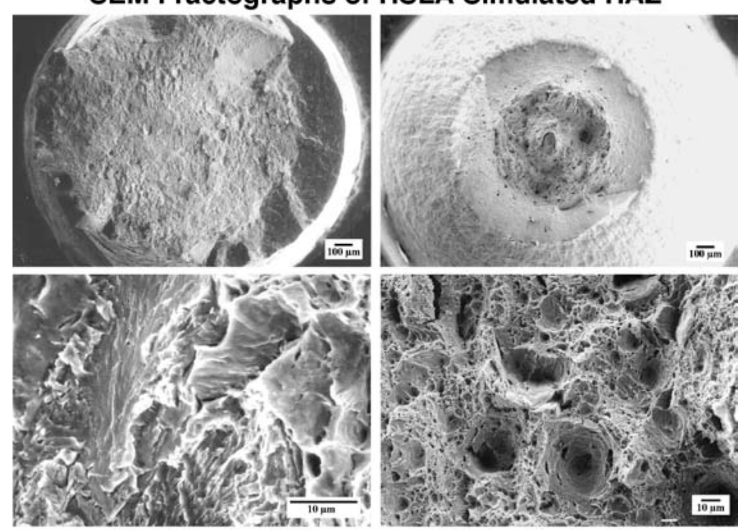

Region (3): High [P(H_2)] Region (1): Low [P(H_2)]

Nondestructive Methods for Studying Hydrogen Effects

Research Underway in Boulder, CO

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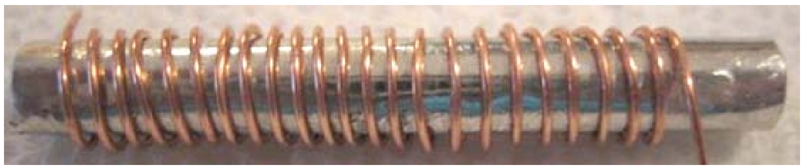
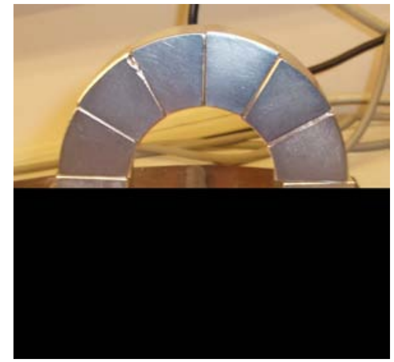
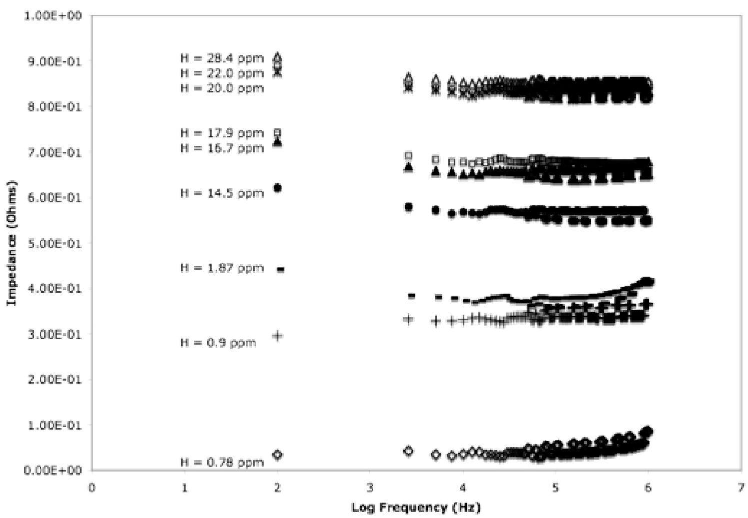
Low Frequency Impedance Laboratory Encircling Coil



Low Frequency Impedance Field Sensor

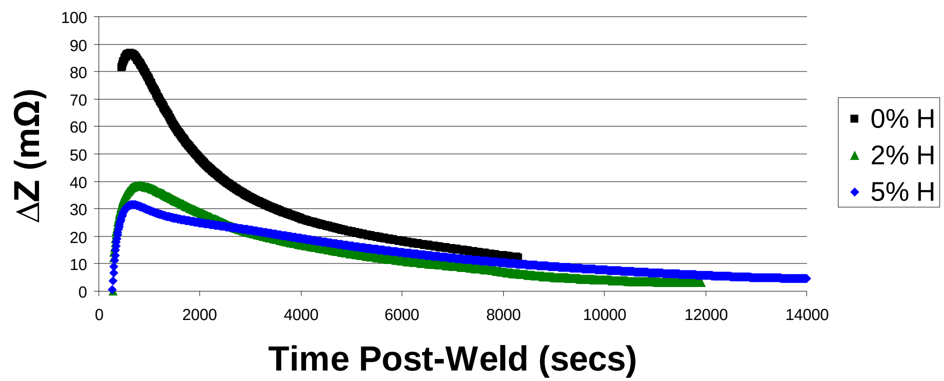


Impedance as a Function of Hydrogen Content in X80 Pipeline Steel Specimens



Low Frequency Impedance as a Function of Time as Hydrogen Diffuses out of Weld Metal

X100A @ f = 20 Hz



Fundamental Mechanistic Studies

Hydrogen influences the mechanical response of microstructures

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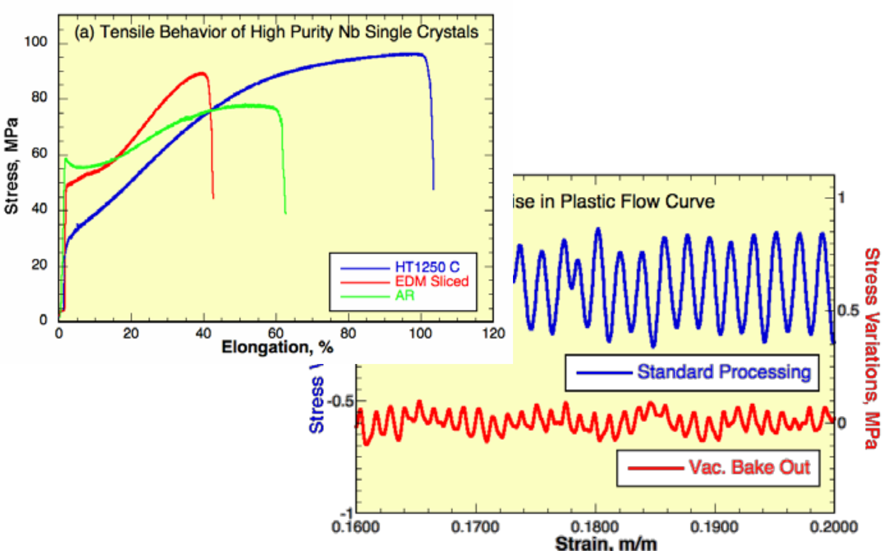
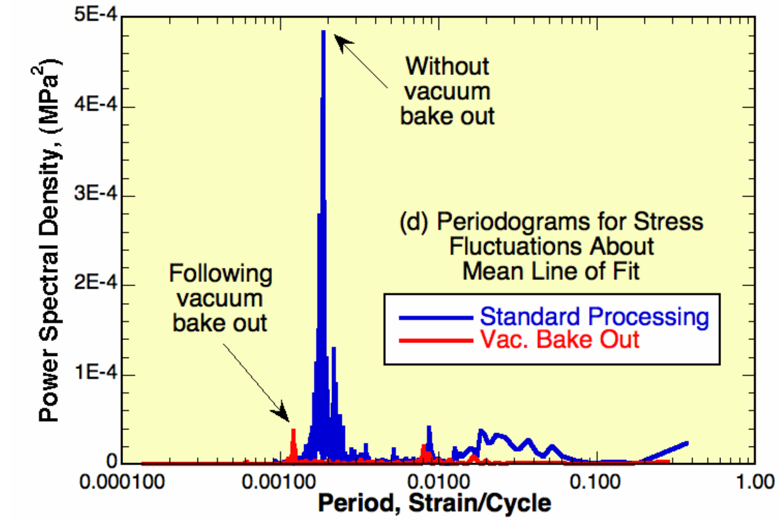
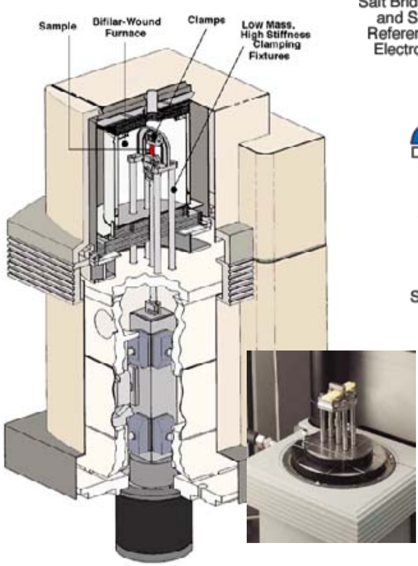
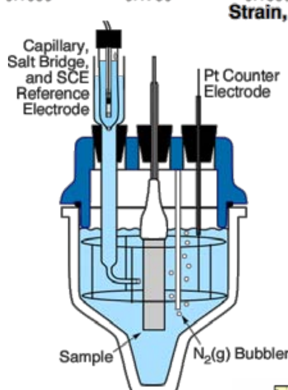


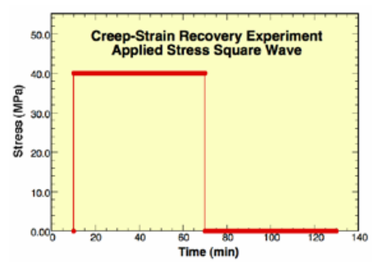


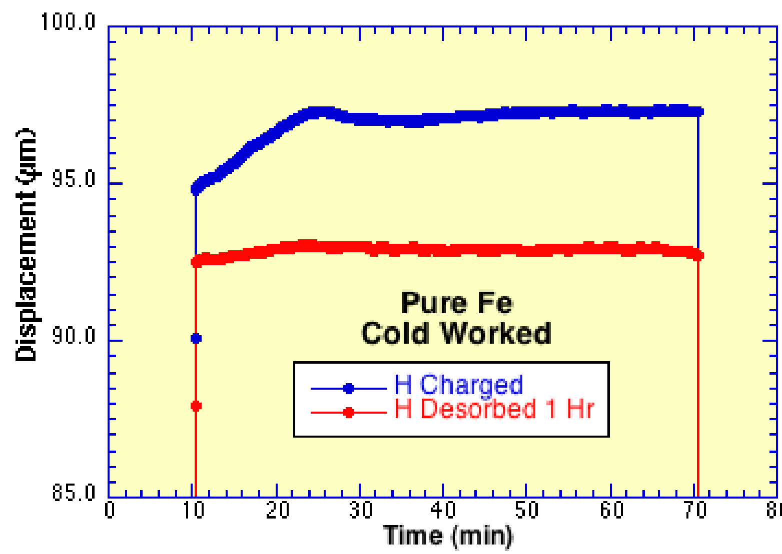




Samples cathodically charged with hydrogen

Samples tested in 3-point bending





Conclusions

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At NIST we are working hard to improve pipeline safety and to overcome the technical barriers that could inhibit the development and growth of hydrogen fuels

We are constructing a high pressure hydrogen gas testing facility in Boulder that will be capable of *in-situ* testing full pipeline wall thickness samples in hydrogen gas.

We are conducting research into electrochemical methods for rapid laboratory assessment of hydrogen absorption, solubility, diffusion, and embrittlement.

We are conducting research into non-destructive and analytical methods for detecting hydrogen and evaluating its effects on a microstructure.

Through this work and collaboration with industry, standards organizations, and other government agencies, NIST expects that an infrastructure of measurements, standards, and data for the safe transport, distribution, and use of hydrogen as a fuel will emerge enabling the growth of the hydrogen economy.