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Hydrogen Effects in Engineering Materials

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Livermore, CA

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Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Motivation and Goals:
Hydrogen Compatibility of Engineering Materials

- Department of Energy (DOE) program on Codes and Standards
  - **Technical Reference on Materials Compatibility** for hydrogen storage and distribution
    - Hydrogen gas pressure to 150 MPa
    - Temperature: -50˚C to 150˚C
  - Identify guidelines for materials of construction
  - Recommend suitable testing procedures
  - Clarify phenomenology of hydrogen-assisted fracture (dispel myths)

• Piping, tubing, and devices	austenitic stainless steels
• Pressure vessel steels	quench and tempered steels aluminum composites
• Pipeline steels	low alloy steels microalloyed steels

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Outline

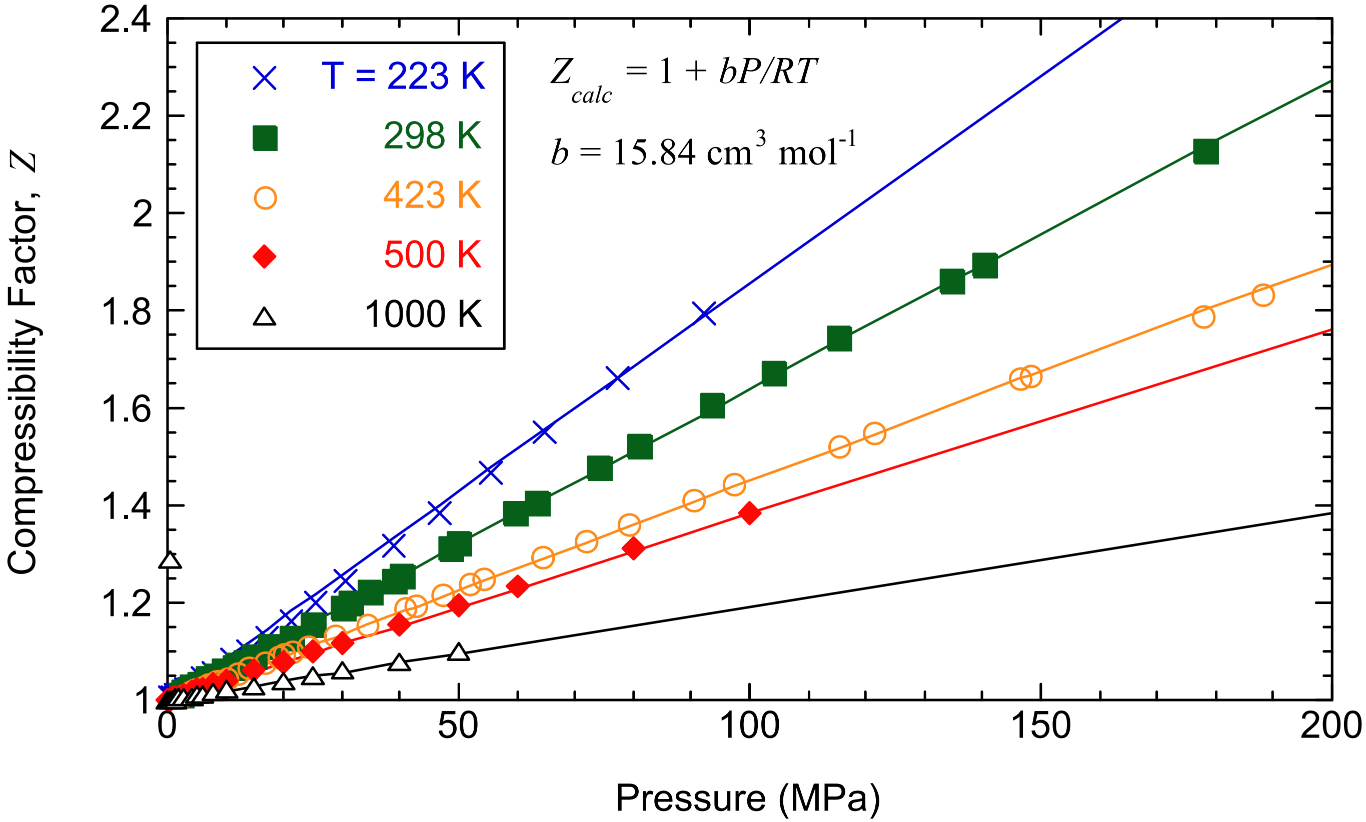
- Thermodynamics of high-pressure hydrogen
  - Equation of state for hydrogen
  - Permeation, diffusion and dissolution of hydrogen in stainless steel
- Mechanisms of hydrogen-assisted fracture
  - Important variables: materials, mechanical, environmental
- Current activities in hydrogen effects in materials: studies at Sandia National Laboratories

Perspective of authors:

–Metallurgists interested in design of hydrogen compatible structures; a challenging task since

few generalizations are meaningful in the study of hydrogen effects

Non-Ideal Behavior of High-Pressure Hydrogen



Fitting data of Michels et al (1955) for
$223 < T < 473$ K
$P < 200$ MPa

$b = 15.84\ cm^3\ mol^{-1}$

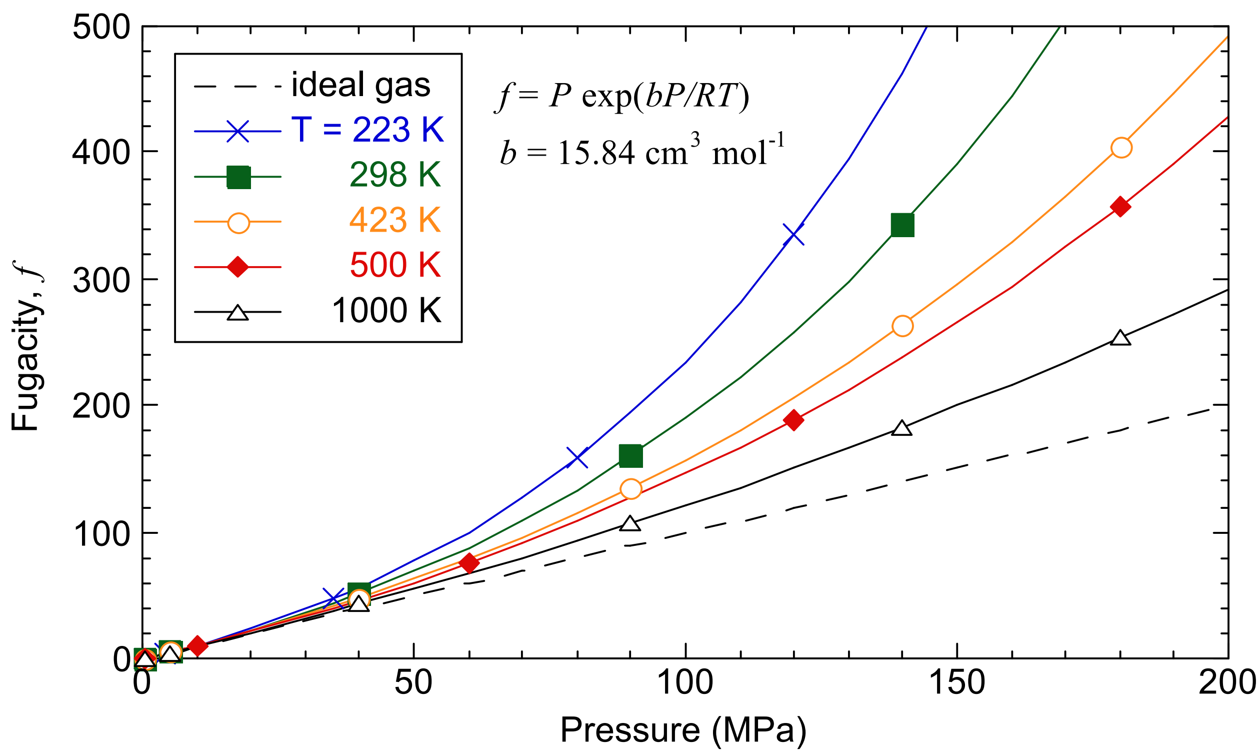
- Compressibility factor $Z = PV_m/RT$
  - for ideal gas $Z = 1$ Ideal gas EOS
  - at high pressure $Z > 1$ Abel-Noble EOS

$$V_m^{o} = RT/P$$

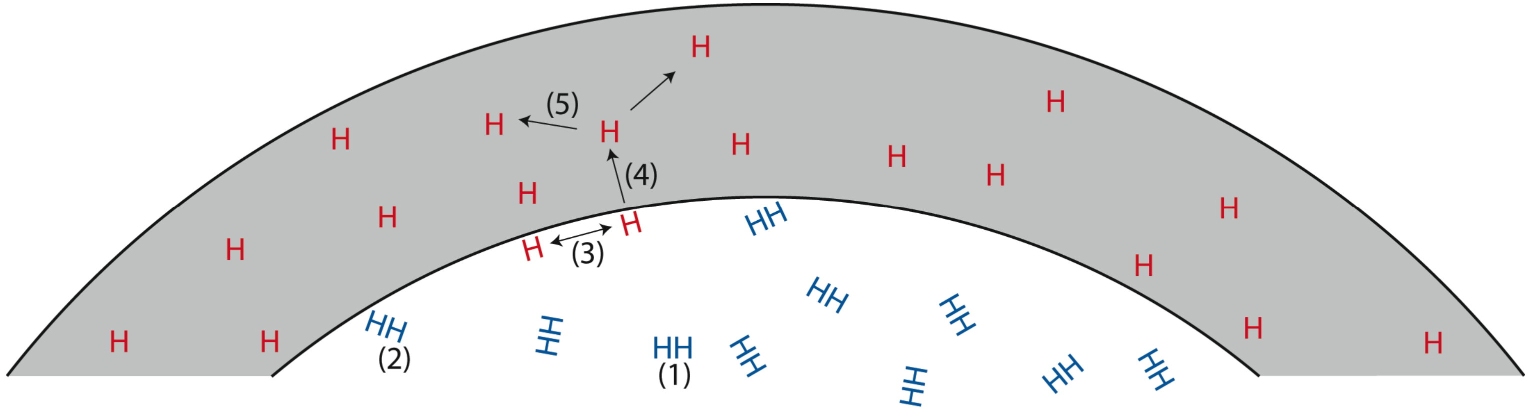
$$V_m = V_m^{o} + b$$

Thermodynamic functions use fugacity

- Definition of fugacity: $\ln\left(\frac{f}{P}\right) = \int_0^P \left(\frac{V_m}{RT} - \frac{1}{P}\right) dP$
- Abel-Noble equation of state —> $f = P \exp\left(\frac{Pb}{RT}\right)$



Diffusion, Dissolution and Permeation



Chemical Equilibrium: $\frac{1}{2}H_2 \leftrightarrow \underline{H}$

(1) Hydrogen gas
(2) Physisorption
(3) Dissociation
(4) Dissolution
(5) Diffusion

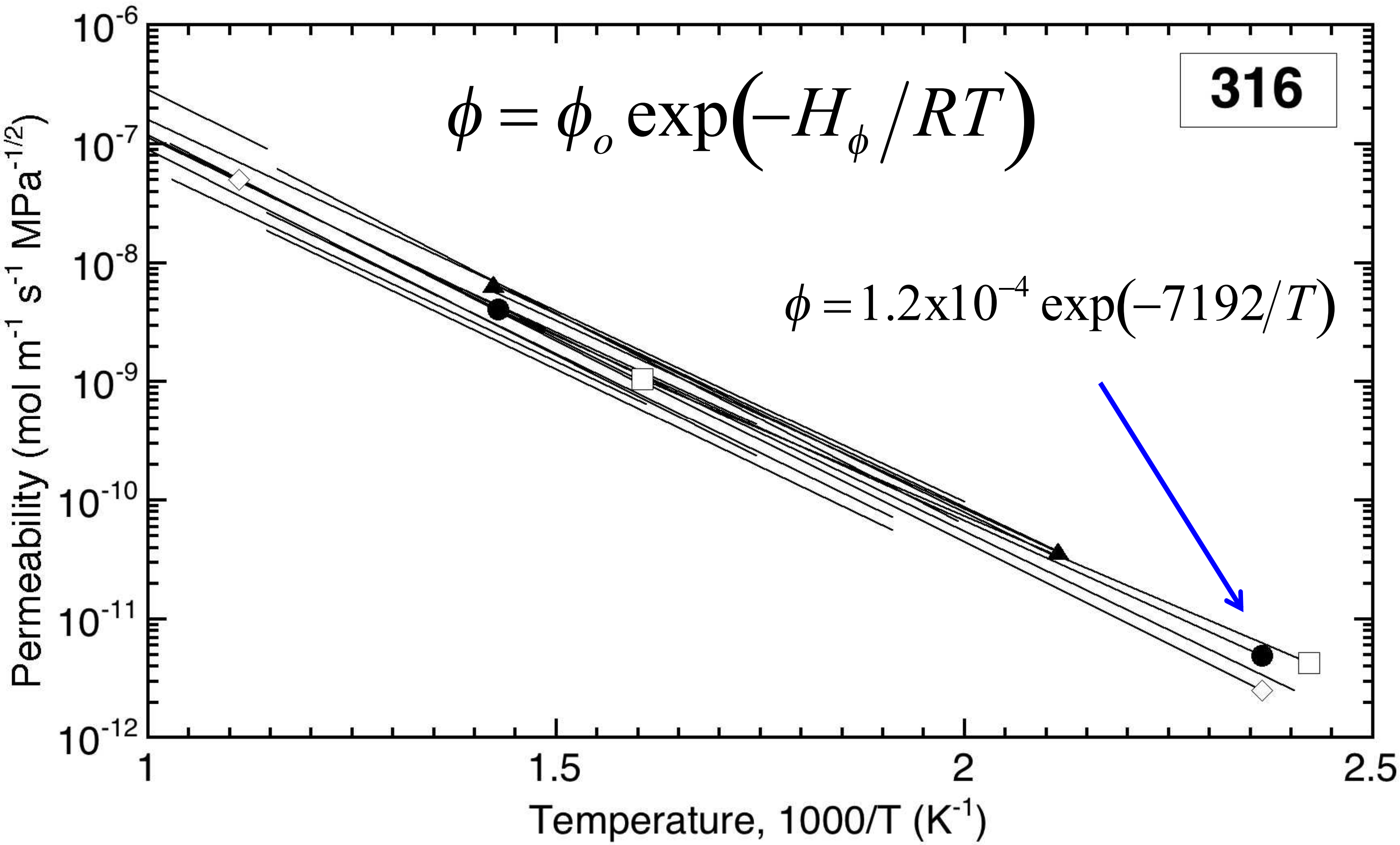
Solubility $K = \frac{c_L}{\sqrt{f}}$

Diffusivity $J_\infty = D\frac{c_L}{t} = \frac{DK}{t}\sqrt{f}$

Permeability $\phi \equiv DK$

Permeation of Hydrogen

• single-phase austenitic stainless steels: independent of alloy and microstructure



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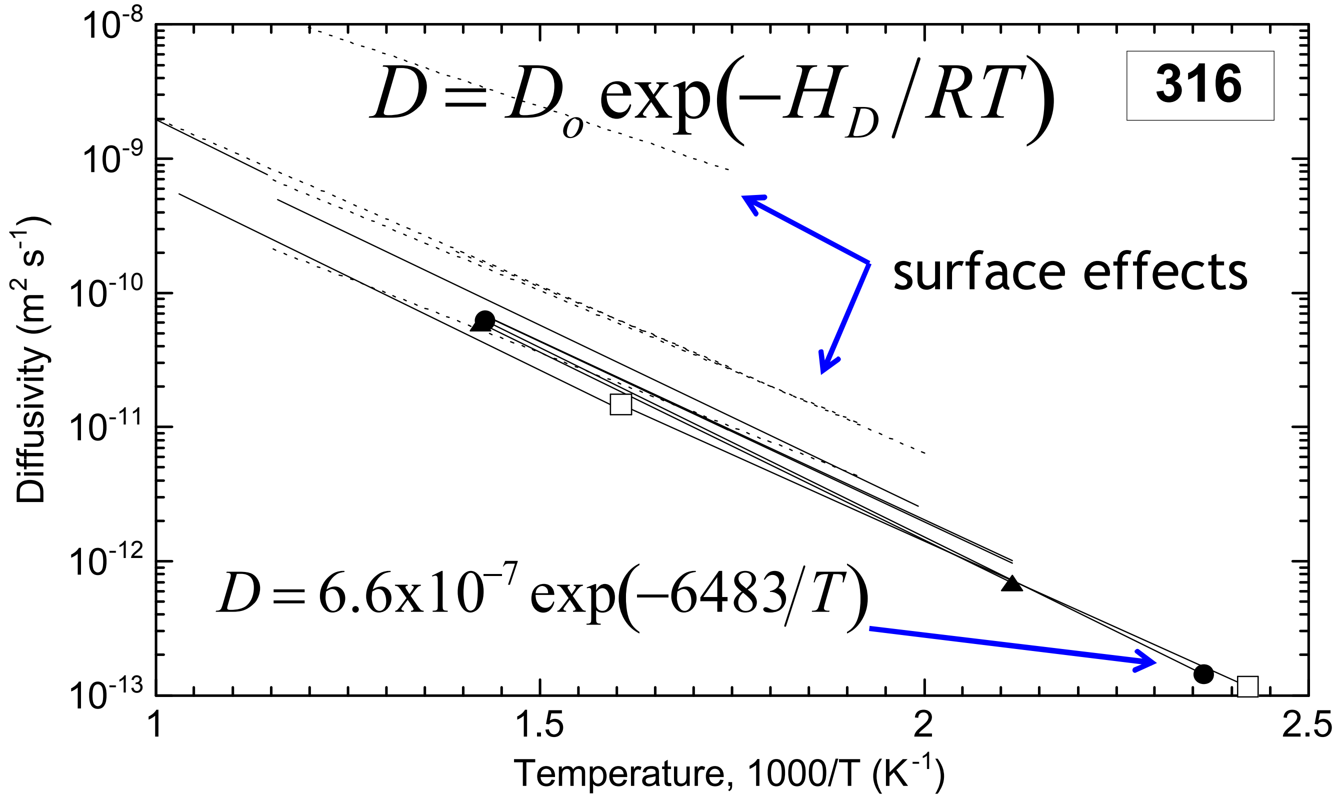
Diffusion of Hydrogen

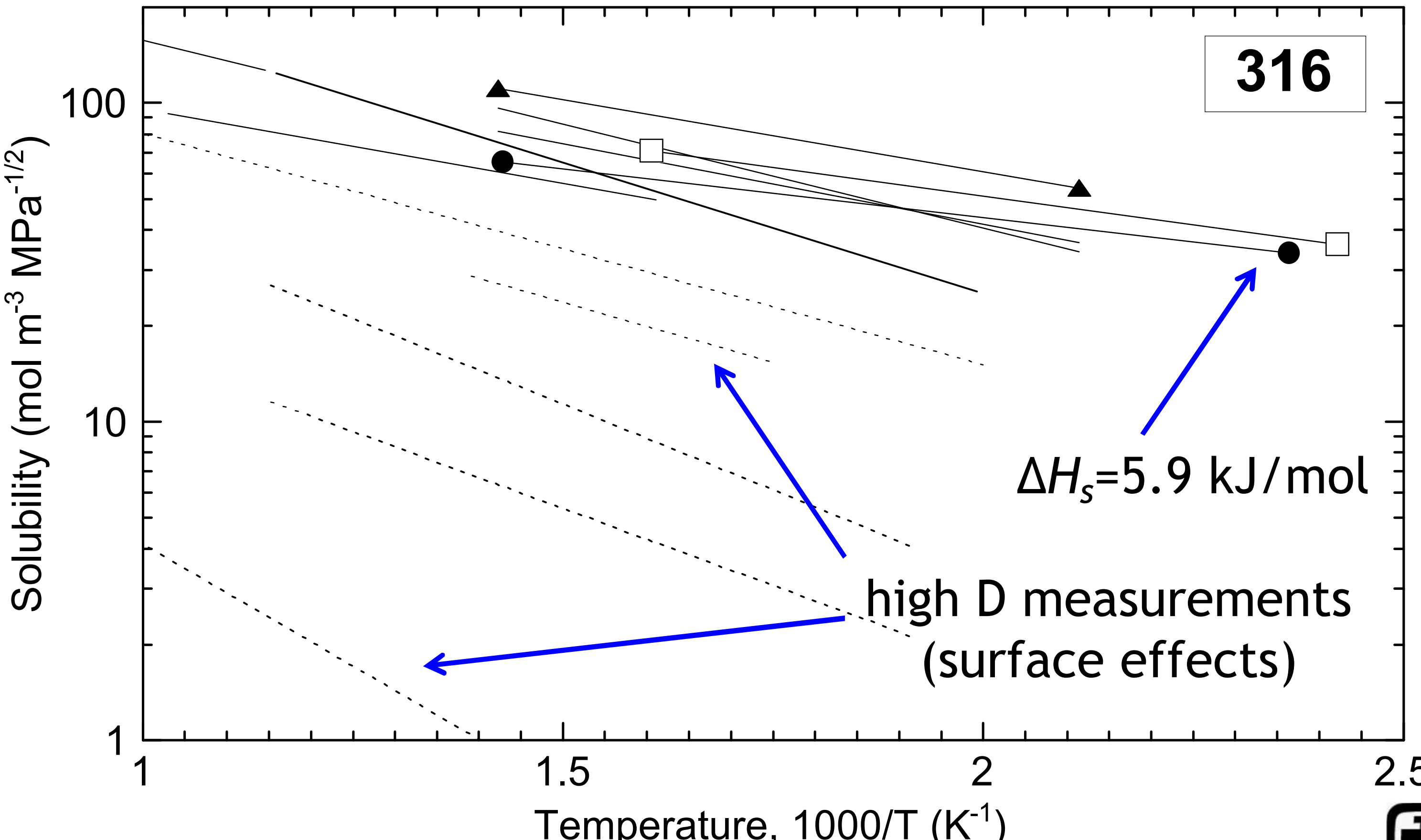
- Diffusivity determination from permeation experiments requires analysis of transient data
  - transient data are more sensitive to surface condition
  - studies reporting high diffusivity did not take precautions to remove surface oxides or films



Solubility of Hydrogen

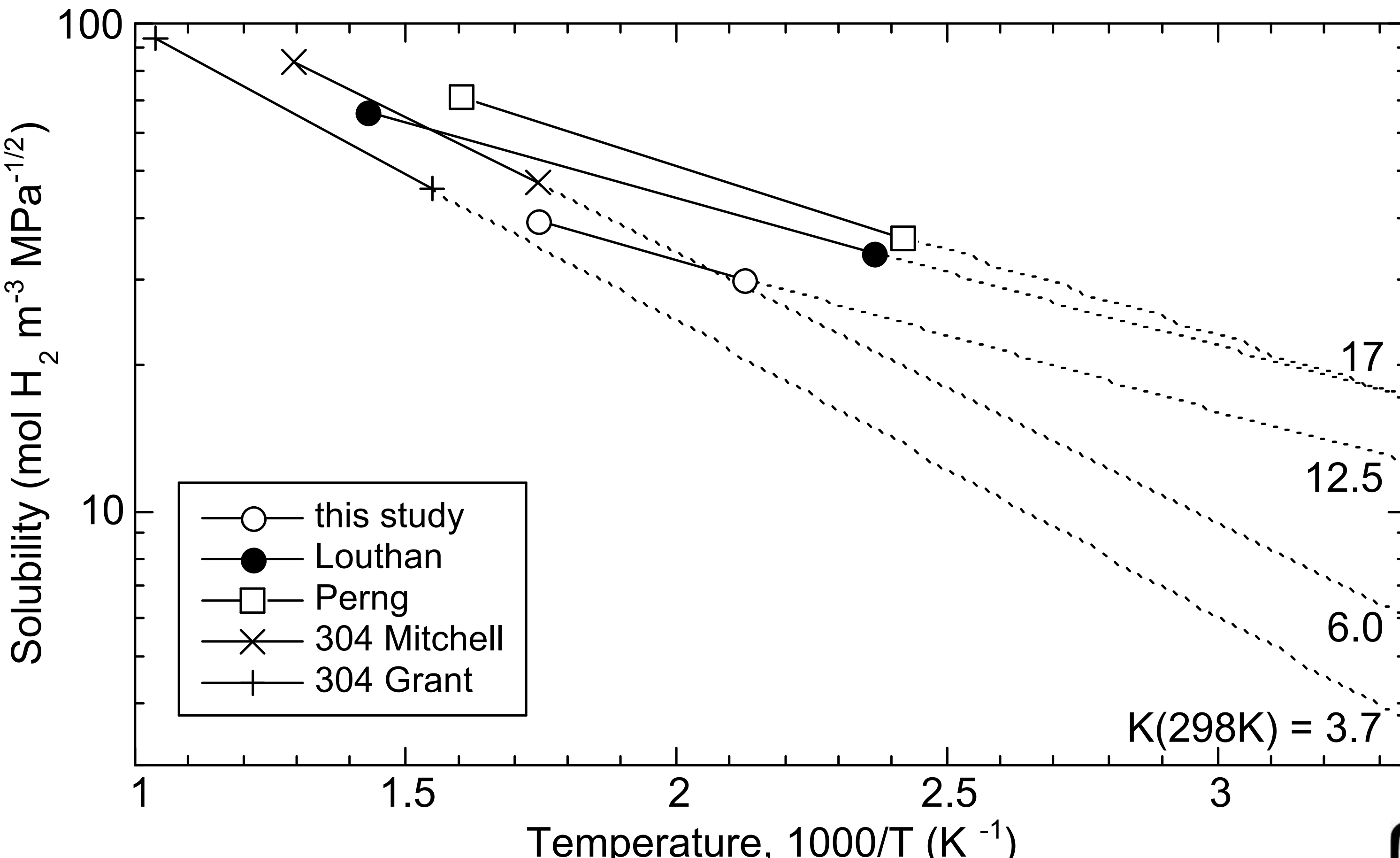
Solubility: $$K = \phi / D = K_o \exp(-\Delta H_s / RT)$$

- depends on quality of diffusivity relationships



Extrapolation of Solubility Relationships

- Lowest values of ΔHs provide conservative values of solubility when extrapolated to room temperature



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Solubility Established by H Extraction

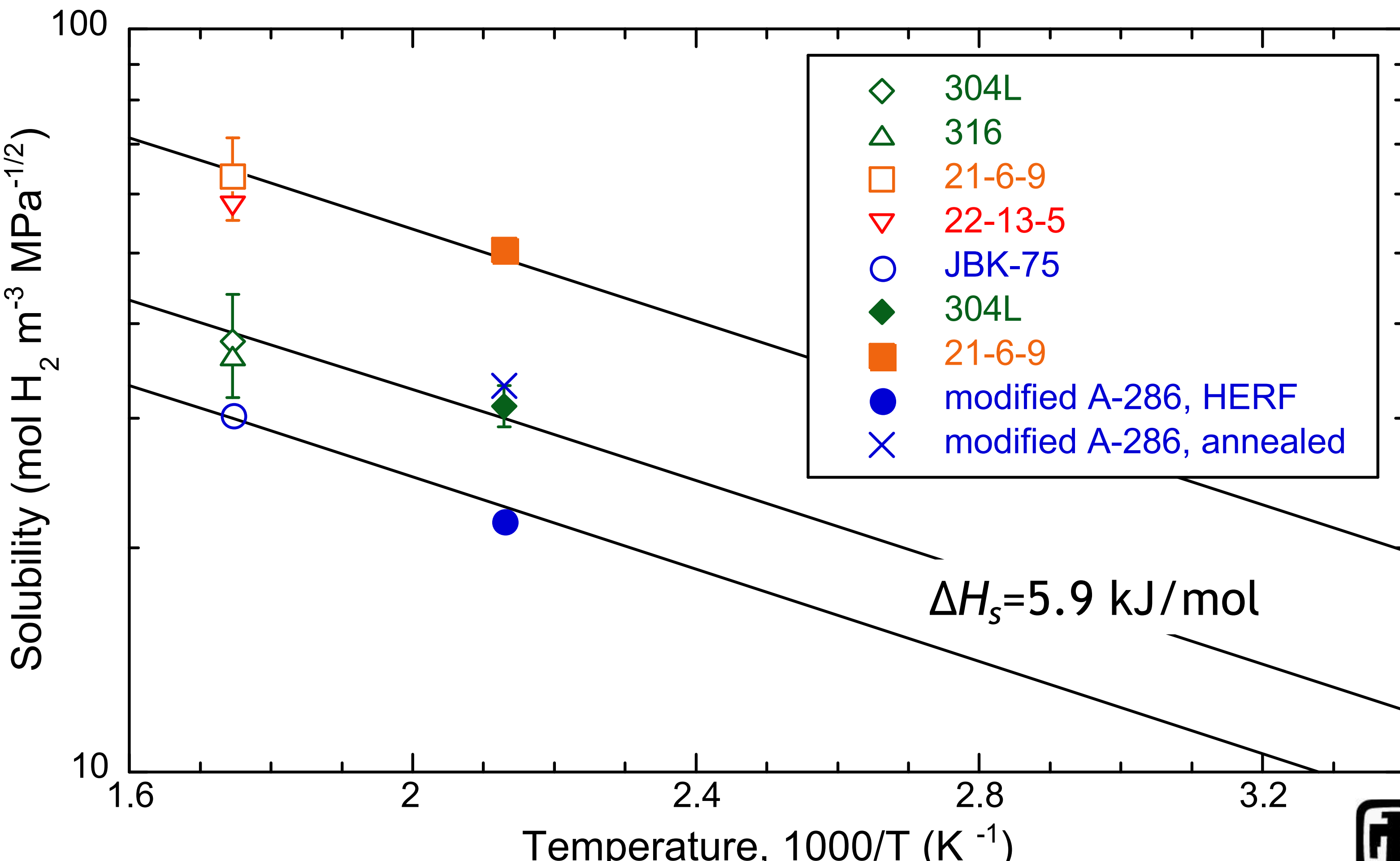
- Thermal precharging of material with hydrogen
  - typical exposure conditions: 138 MPa H_2 at 300 ºC
  - uniform H concentration developed in test specimens
- Hydrogen concentration measured using H extraction
- low H trap binding energy in stainless steels
  - Extraction measurements yield approximate lattice concentration
- Solubility calculated from

$$K = c_L \big/ \sqrt{f}$$

- Measurements for
  - 300-series stainless steels: *304L* & *316*
  - Cr-Ni-Mn stainless steels: *21Cr-6Ni-9Mn* & *22Cr-13Ni-5Mn*
  - Precipitation-strengthened stainless steels: *A-286* & *JBK-75*

Recommended Solubility Relationships

- Solubility determined from H extraction measurements
  - Solubility (& diffusion) is a function of alloy



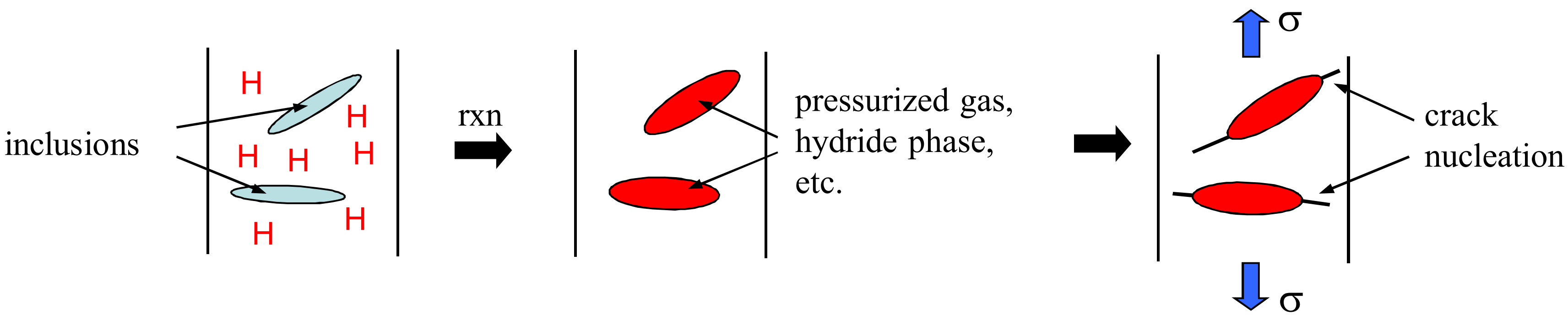
Conclusions and Recommendations

- Abel-Noble equation of state $$V_m = RT/P + b$$
- Fugacity $$f = P\exp\left(\frac{Pb}{RT}\right)$$ $$b = 15.84\ \ \mathrm{cm^3 \cdot mol^{-1}}$$
- Permeation measurements consistent for all austenitic stainless
  - use Louthan and Derrick: $$\phi = 1.2\text{x}10^{-4}\exp(-7192/T)\ \left[\mathrm{mol\ H_2 \cdot m^{-1} \cdot s^{-1} \cdot MPa^{-1/2}}\right]$$
- Solubility relationships
  - for 300-series stainless steel: $$K = 136\exp(-710/T)\ \left[\mathrm{mol\ H_2 \cdot m^{-3} \cdot MPa^{-1/2}}\right]$$
  - for Cr-Ni-Mn stainless steel: $$K = 224\exp(-710/T)\ \left[\mathrm{mol\ H_2 \cdot m^{-3} \cdot MPa^{-1/2}}\right]$$
- Diffusivity relationships calculated from $D = \phi/K$
  - for 300-series stainless steel: $$D = 8.8\text{x}10^{-7}\exp(-6483/T)\ \left[\mathrm{m^2 \cdot s^{-1}}\right]$$
  - for Cr-Ni-Mn stainless steel: $$D = 5.4\text{x}10^{-7}\exp(-6483/T)\ \left[\mathrm{m^2 \cdot s^{-1}}\right]$$

Hydrogen-Assisted Fracture Mechanisms in Metals

Hydrogen attack:

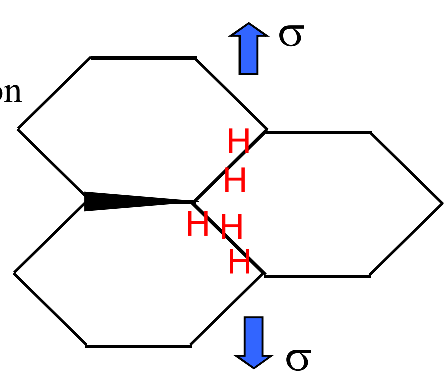
chemical reaction of atomic hydrogen with microstructural features

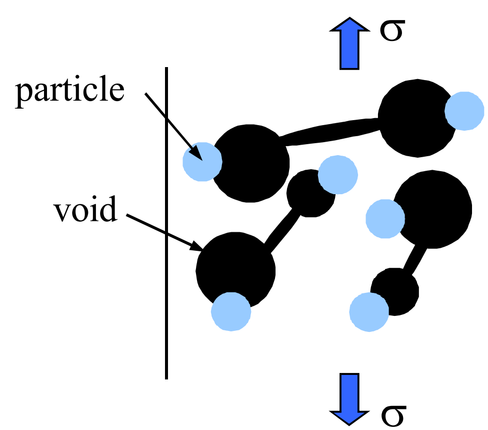


Hydrogen solute effects:

solute hydrogen enhanced failure of interfaces and deformation mechanisms

Hydrogen accumulation at interfaces affects strength of interface (grain boundaries, second phases, inclusions)





Hydrogen enhanced shear localization

All Conceivable Variables Can Influence Hydrogen Effects

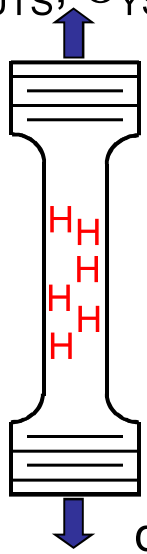
- Material Variables
  - Yield strength
  - Composition
  - Microstructure (welds)
- Mechanical Variables / Test Method
  - Frequency (Fatigue)
  - Presence of preexisting flaws (i.e., tension vs. fracture toughness)
  - Strain rate effects (i.e., static load versus rising load)
  - Mixed mode loading
- Environmental Variables
  - Gas pressure and purity
  - Temperature
  - Hydrogen source: internal versus environmental

How should laboratory scale tests be translated into meaningful design data for hydrogen compatibility?

Testing Methodologies

Strength of Materials:

σ_{UTS}, σ_{YS}, ε_f, RA



$d\delta/dt > 0$

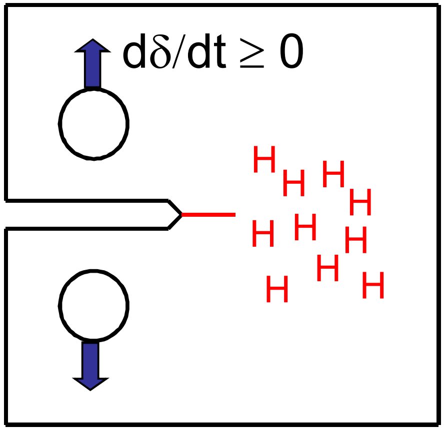
Testing in air after precharging with atomic hydrogen

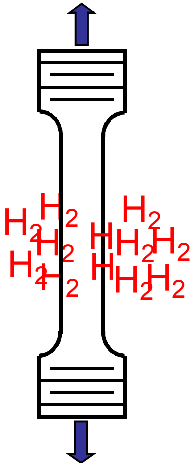
IHAC

Internal Hydrogen Assisted Cracking

Fracture Mechanics:

K_{IH}, K_{TH}

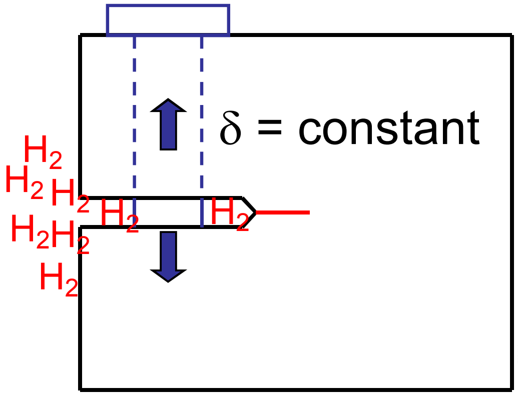




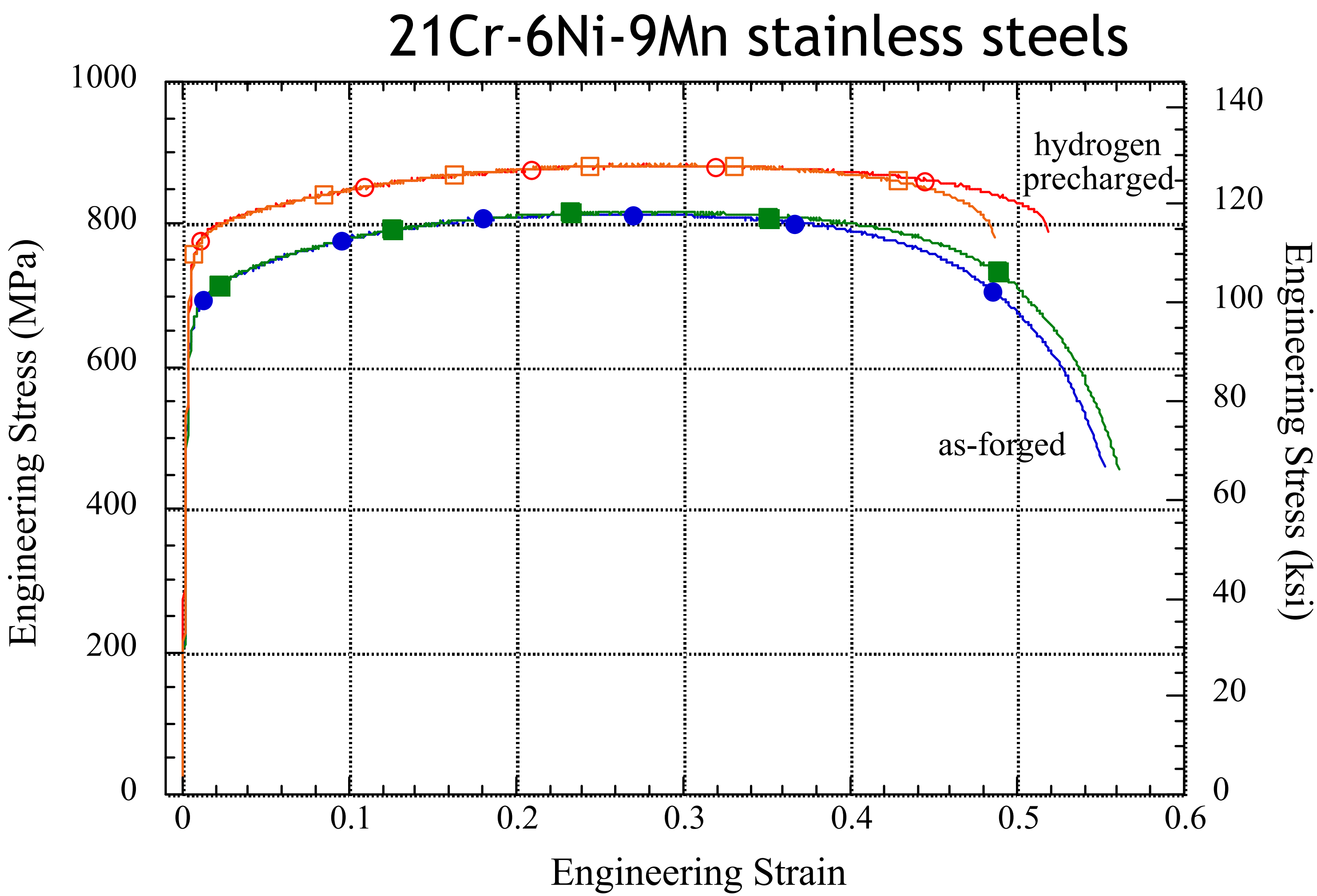
Testing in hydrogen gas

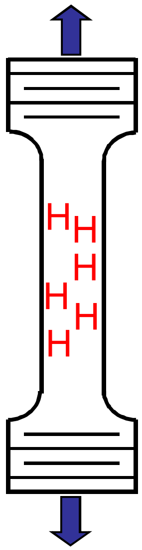
HEAC

Hydrogen Environment Assisted Cracking

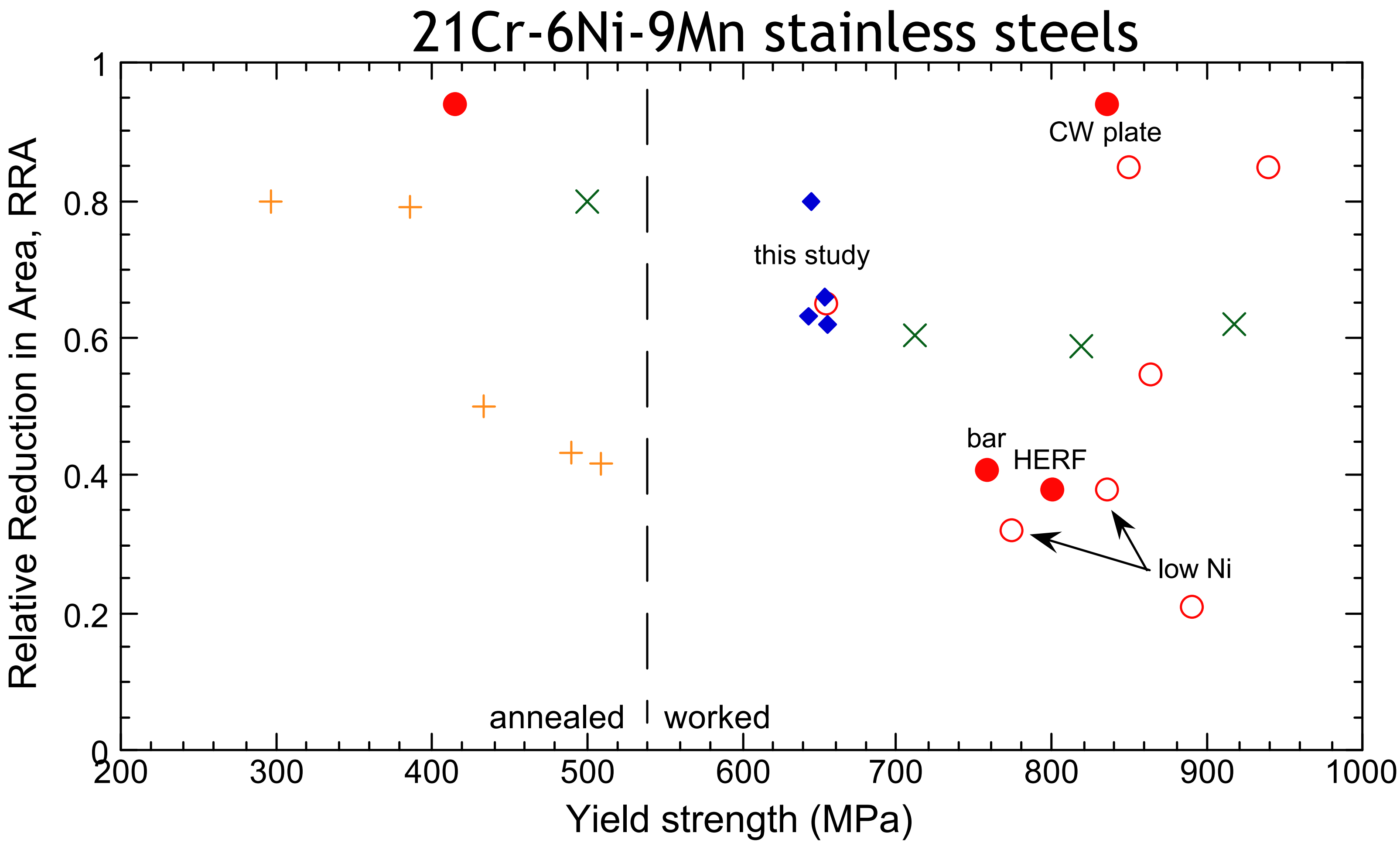


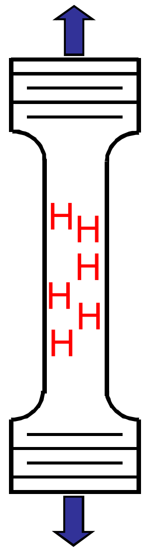
Tensile flow curves are affected by internal hydrogen





Hydrogen-assisted fracture generally NOT well understood





Data: from several sources and different environment conditions

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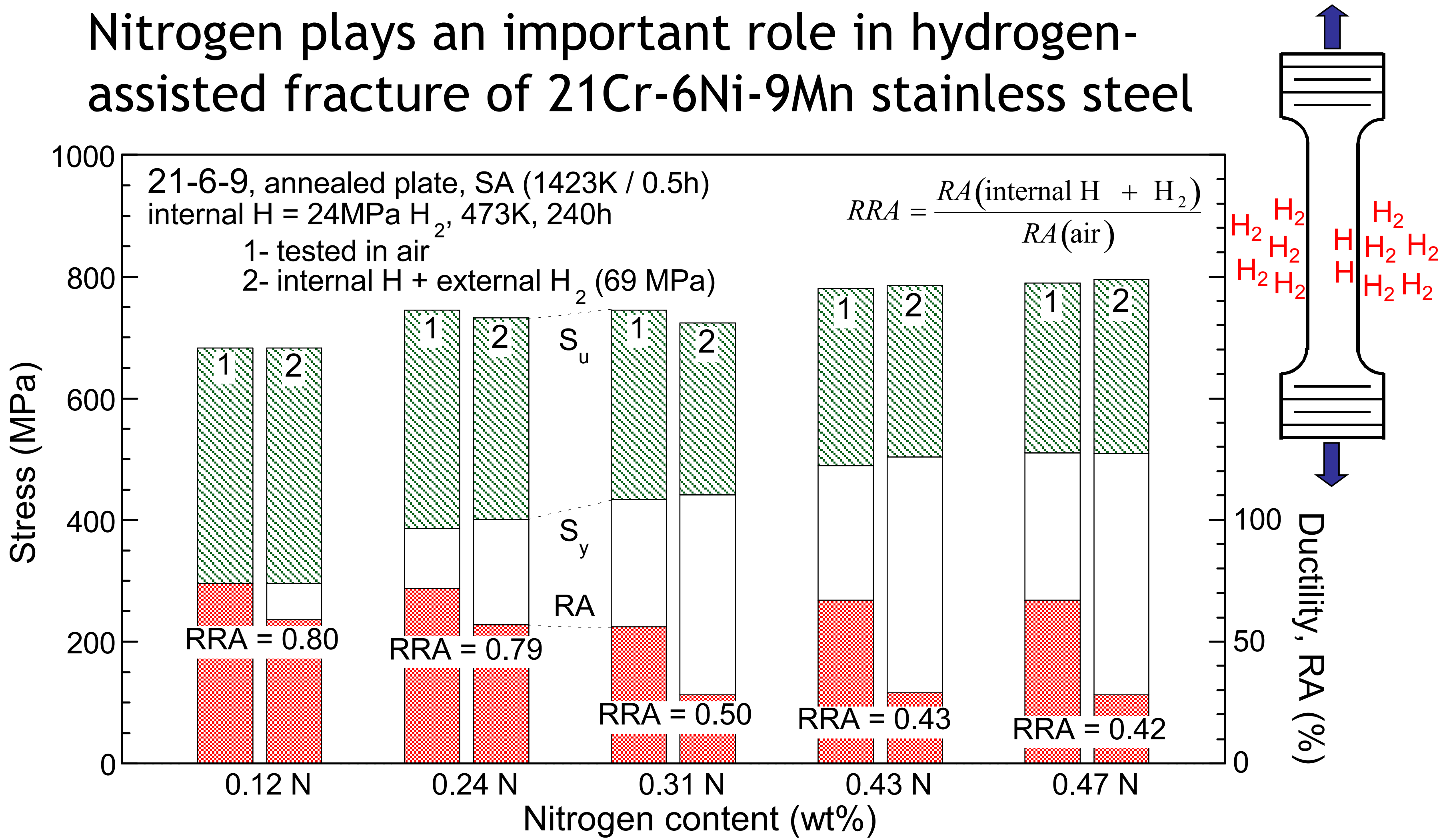
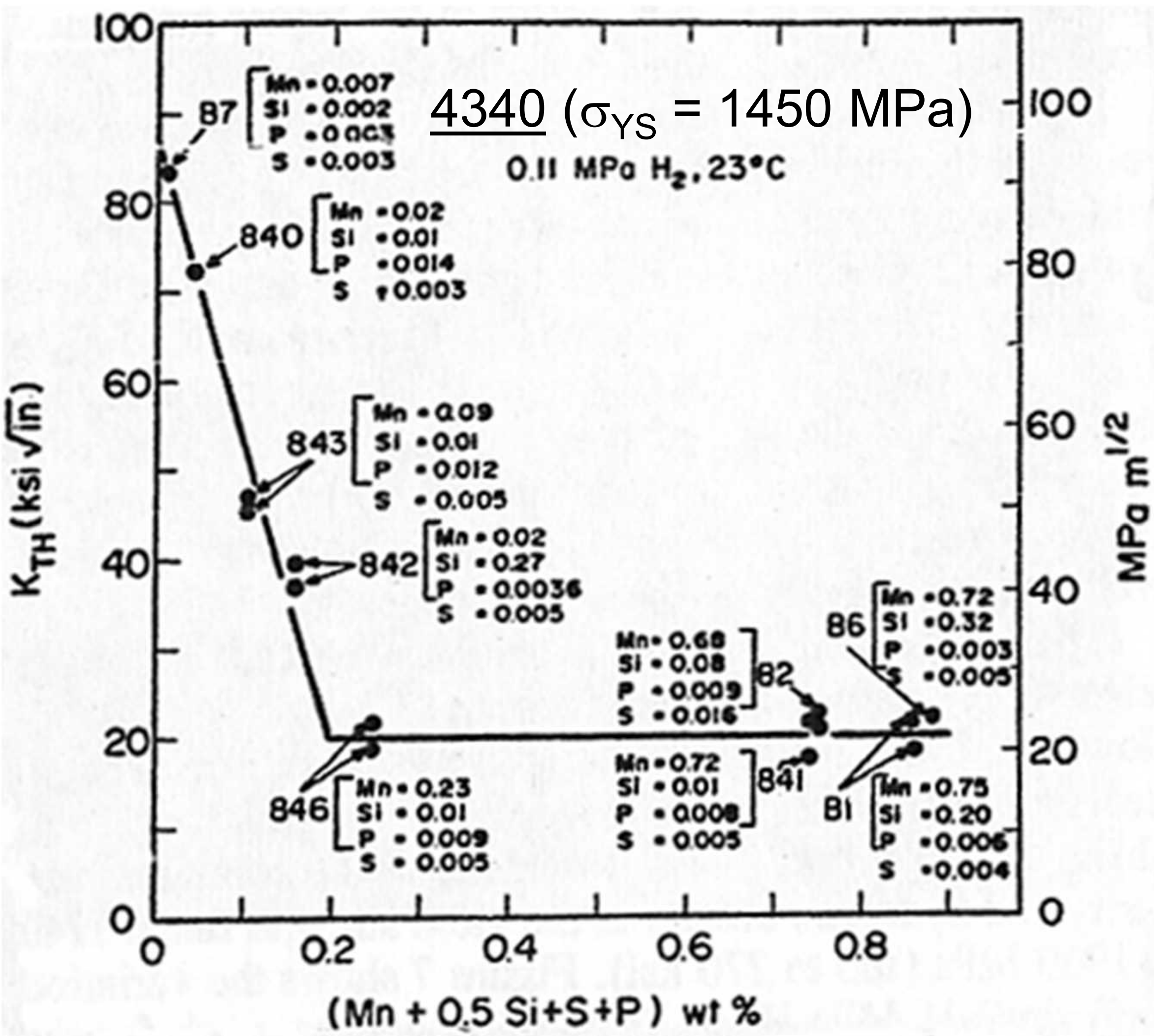
Material Variables: *Composition*

Nitrogen plays an important role in hydrogen-assisted fracture of 21Cr-6Ni-9Mn stainless steel

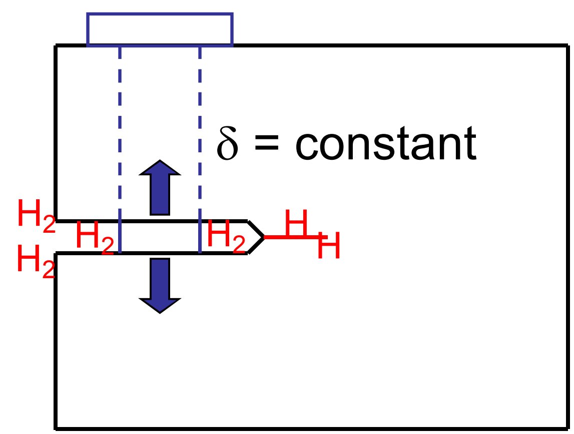


Data: from Odegard 1980.

Material Variables: *Composition*



K_{TH} can be strongly dependent on alloying element: Mn and Si are detrimental to K_{TH} of 4340



N. Bandyopadhyay et al., Metallurgical Transactions A, 1983

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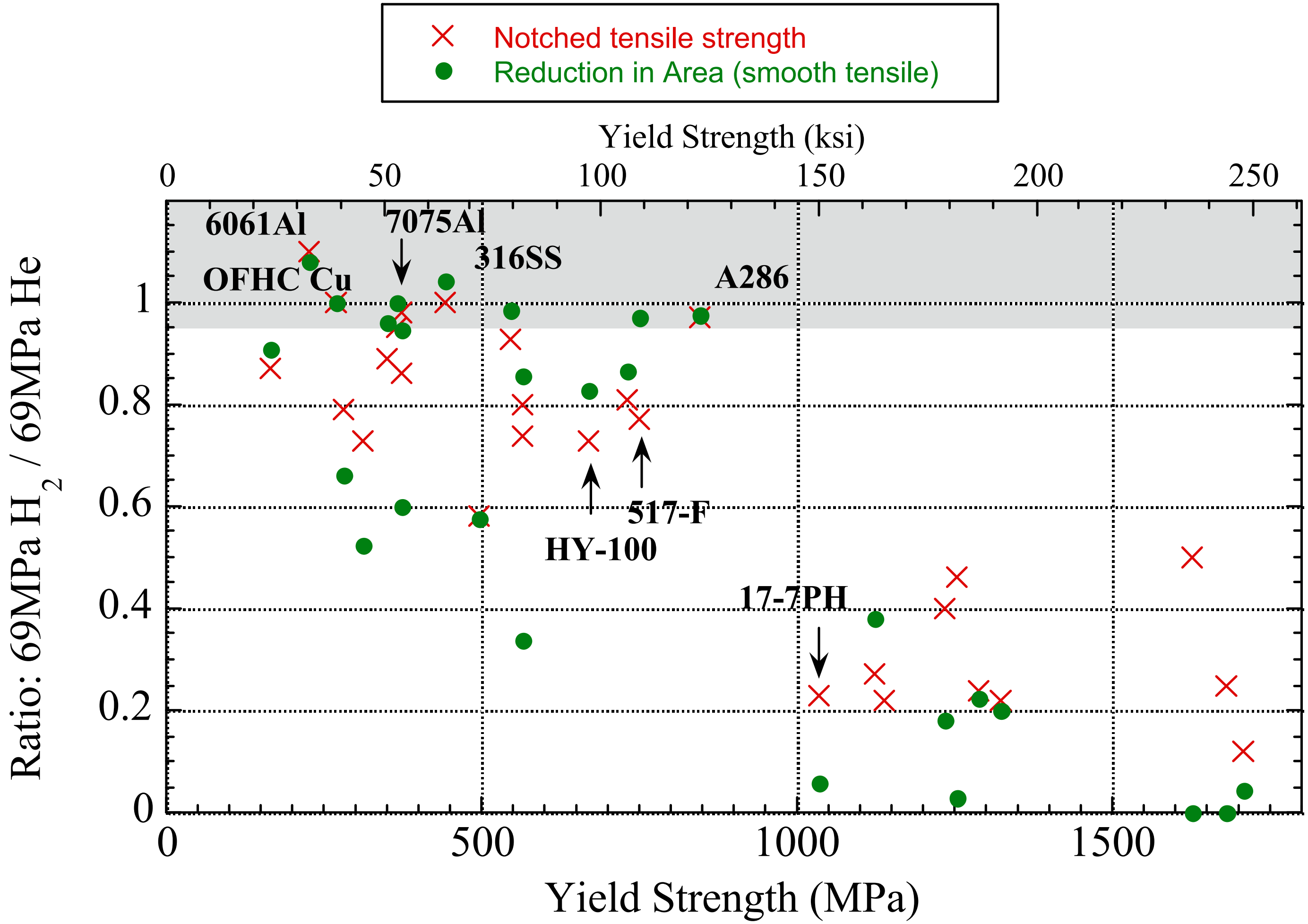
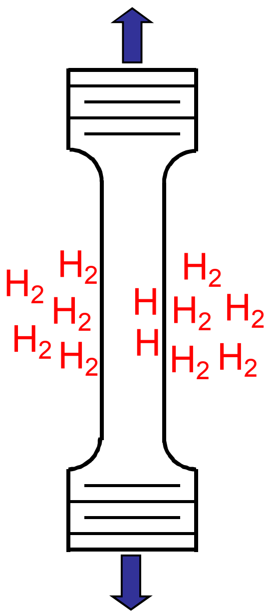
Material Variables: *Yield Strength*

Low yield strength materials tend to have greater resistance to hydrogen-assisted fracture





Jewitt et al, Hydrogen Environment Embrittlement of Metals, NASA-CR-2163, 1973

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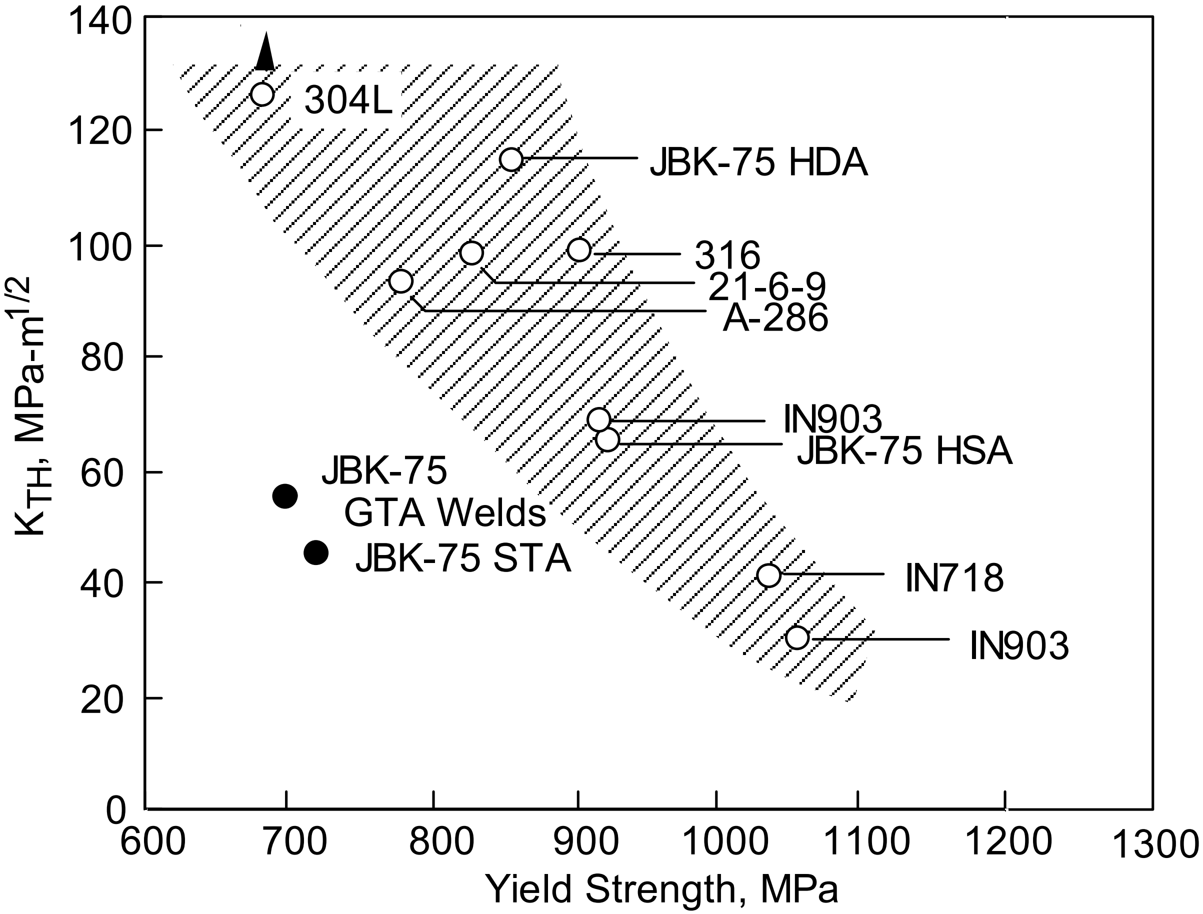
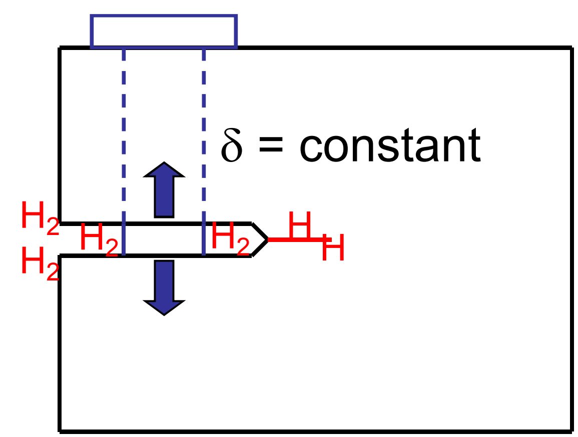
Material Variables: *Yield Strength*



K_{TH} of stainless steels depends on yield strength and microstructure



Data from: M.W. Perra, *Environmental Degradation of Engineering Materials in Hydrogen*, 1981

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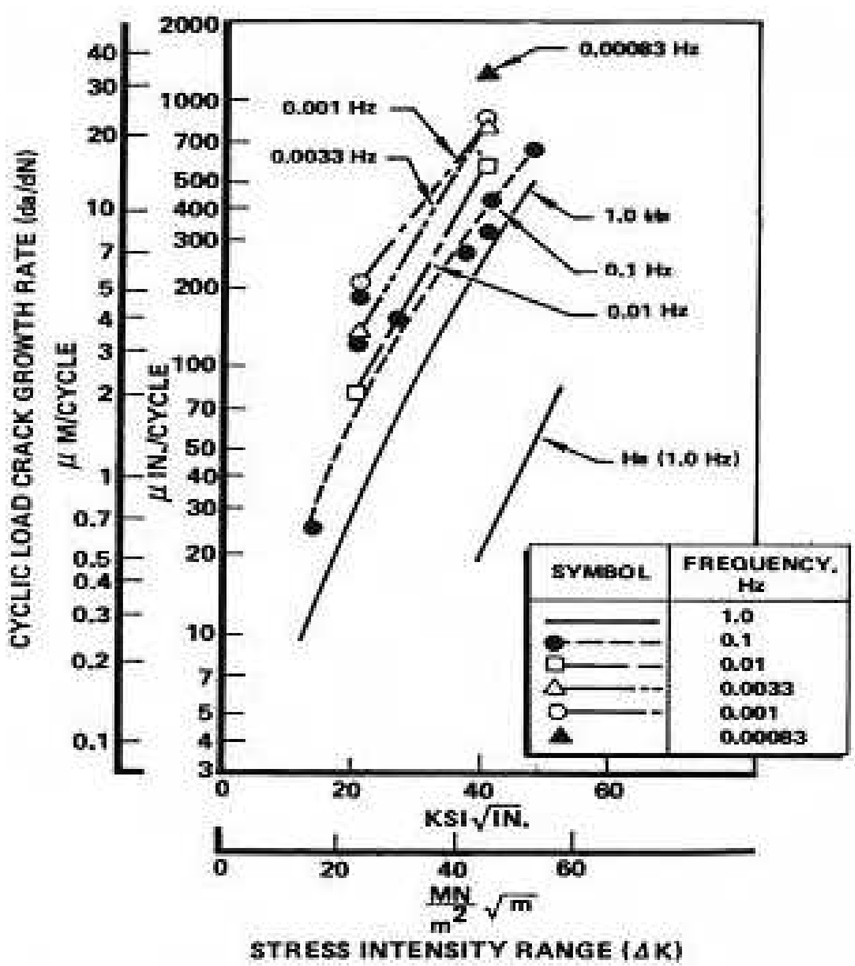
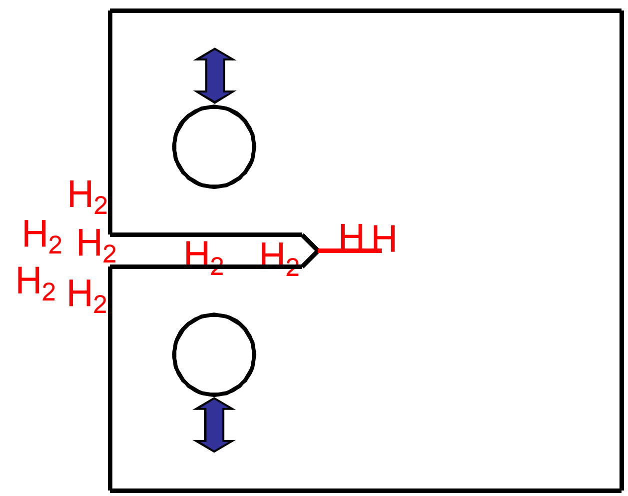
Mechanical Variables: *Fatigue/Frequency*

SA-105 Grade II steel (P_{H2} = 103 MPa)

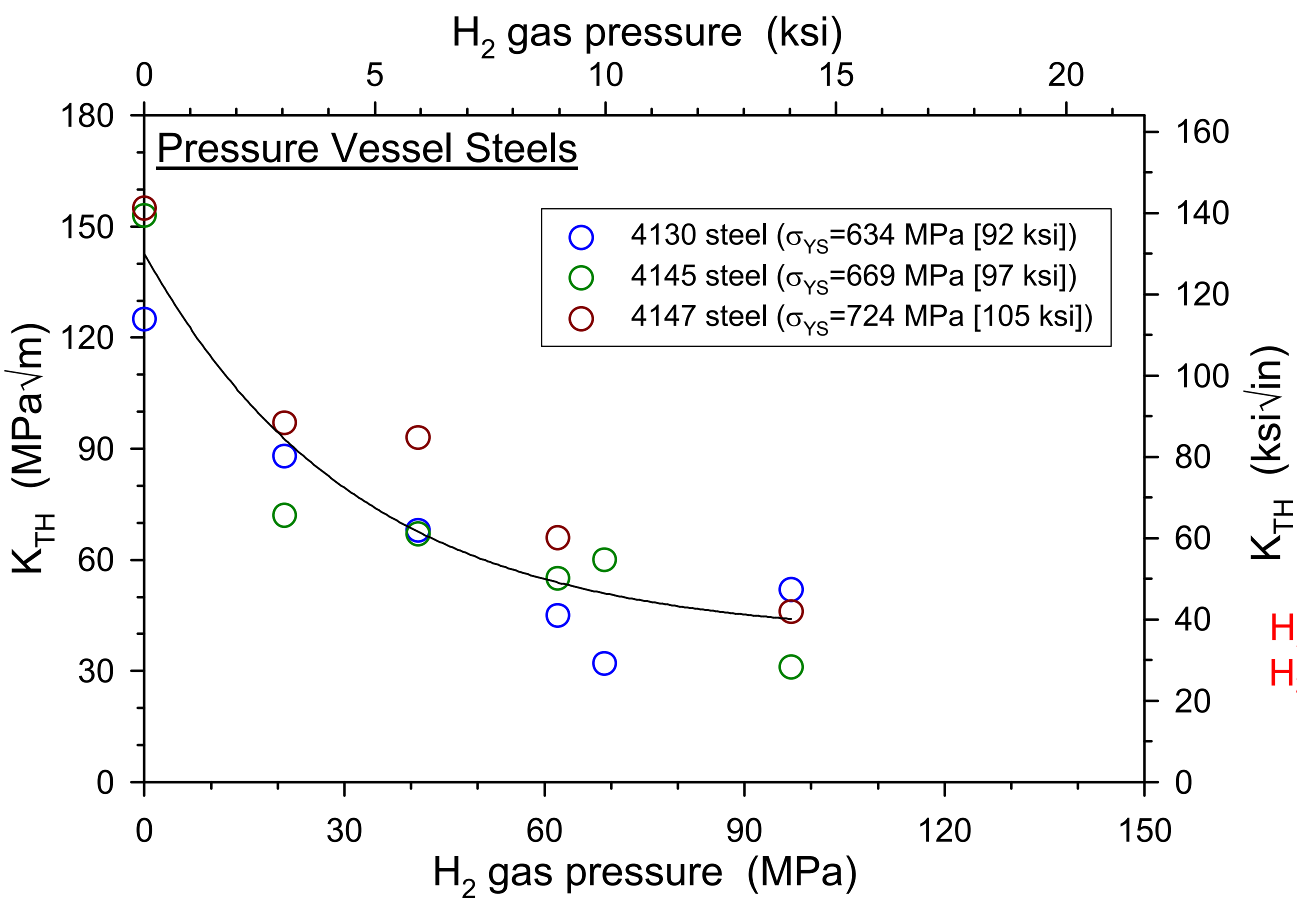


Materials are more susceptible to low-frequency loading

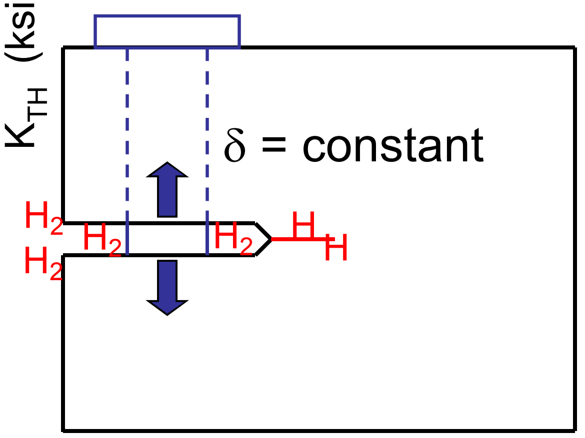


Walter and Chandler, Effect of Hydrogen on Behavior of Materials, 1975

Environmental Variables: *Gas Pressure*

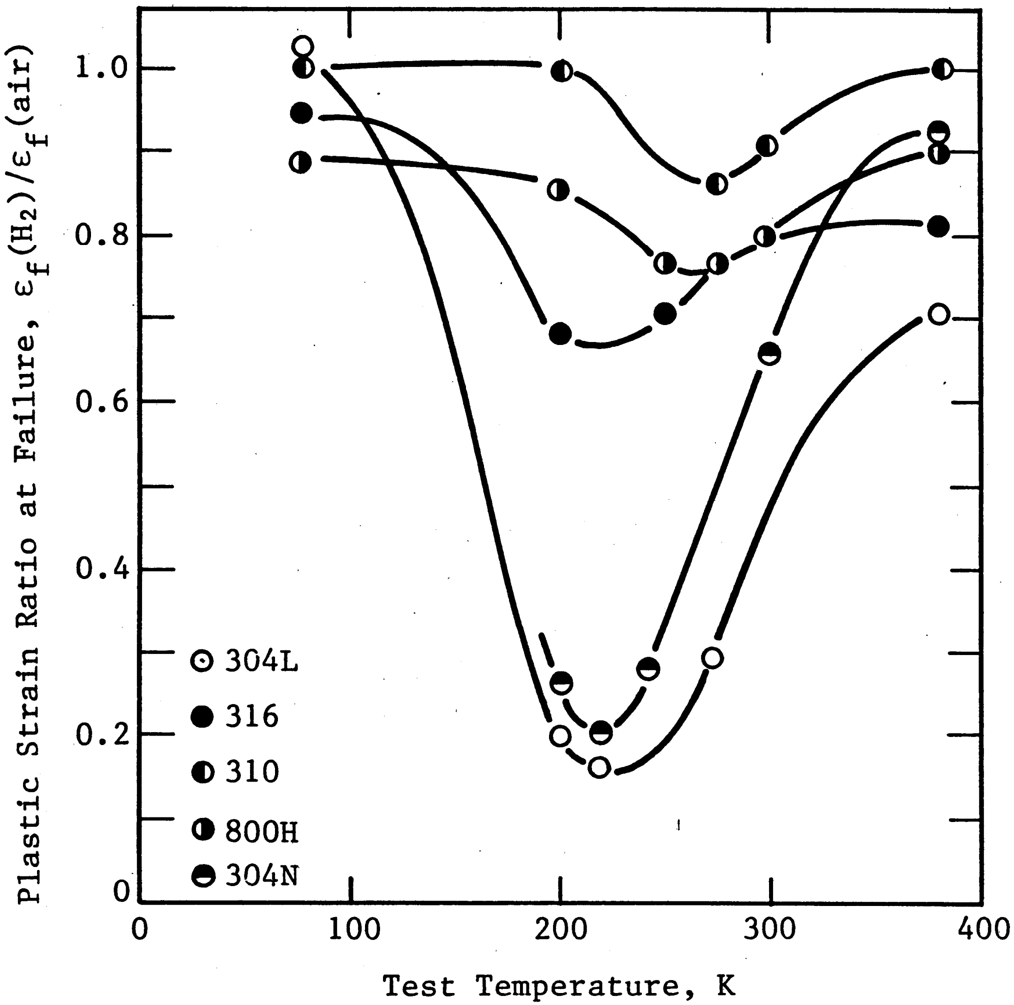


Hydrogen susceptibility increases with hydrogen gas pressure



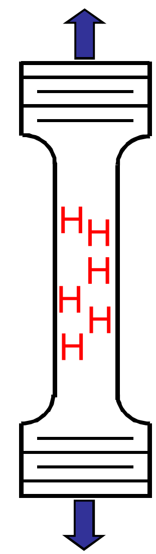
Loginow and Phelps, <u>Corrosion</u>, 1975

Environmental Variables: *Temperature*



G.R. Caskey, "Hydrogen Compatibility Handbook for Stainless Steels", 1983

Austenitic stainless steels are most susceptible to hydrogen-assisted fracture near 200K



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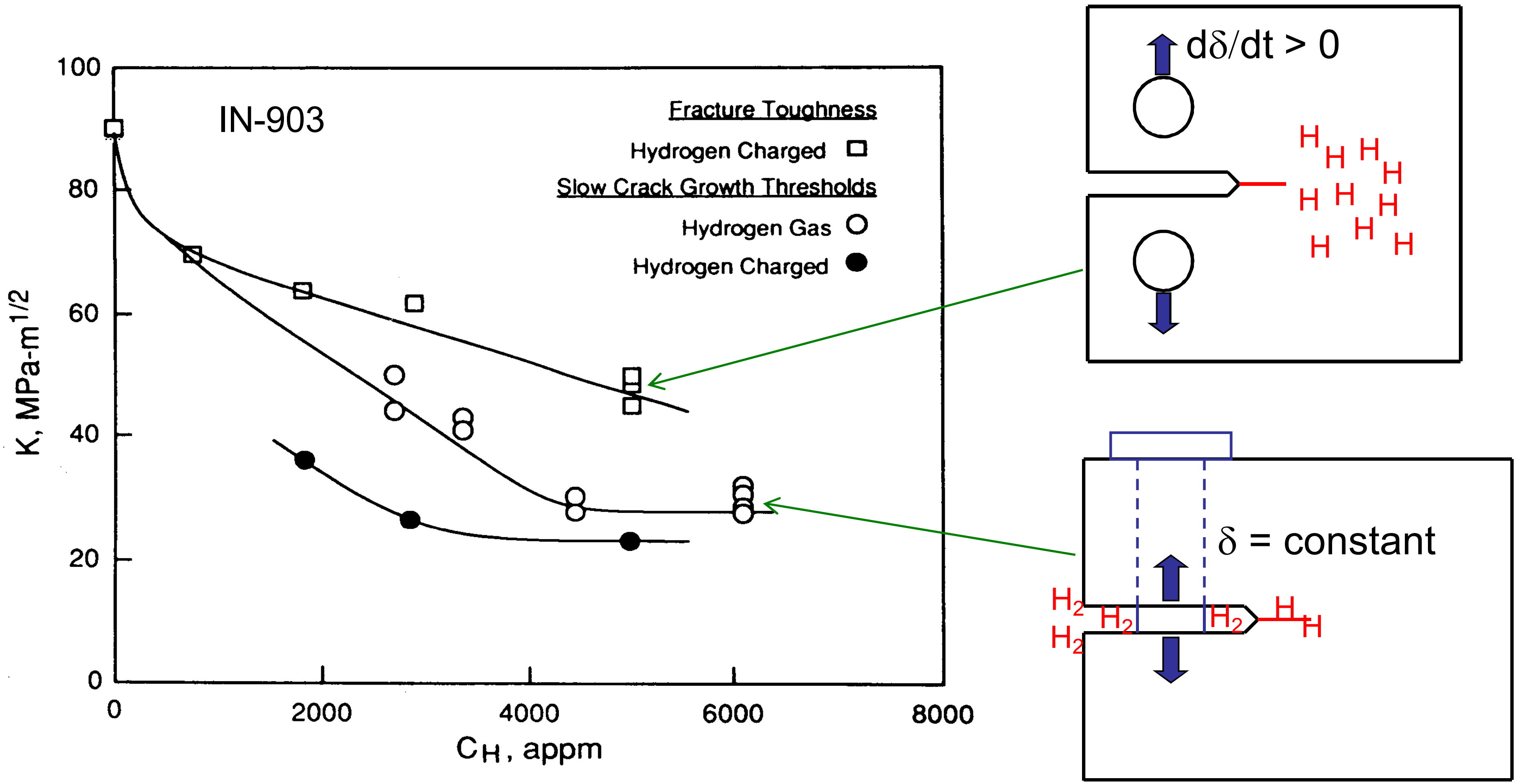
Environmental Variables: *Hydrogen Source*



Data from: N.R. Moody et al., *Hydrogen Effects on Material Behavior*, 1990

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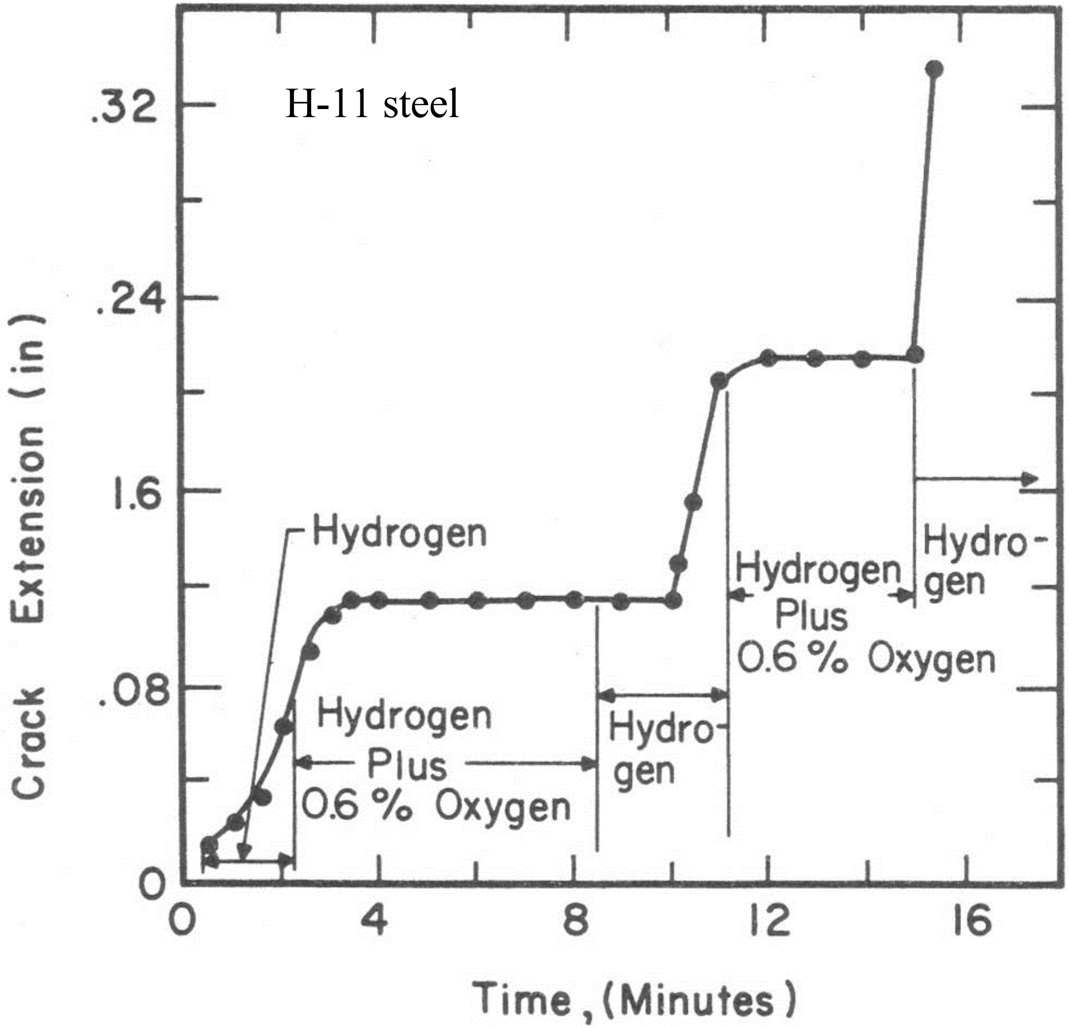
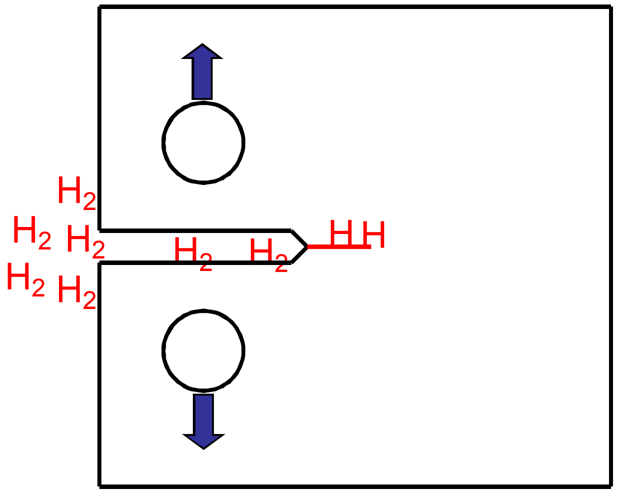
Environmental Variables: *Gas Purity*

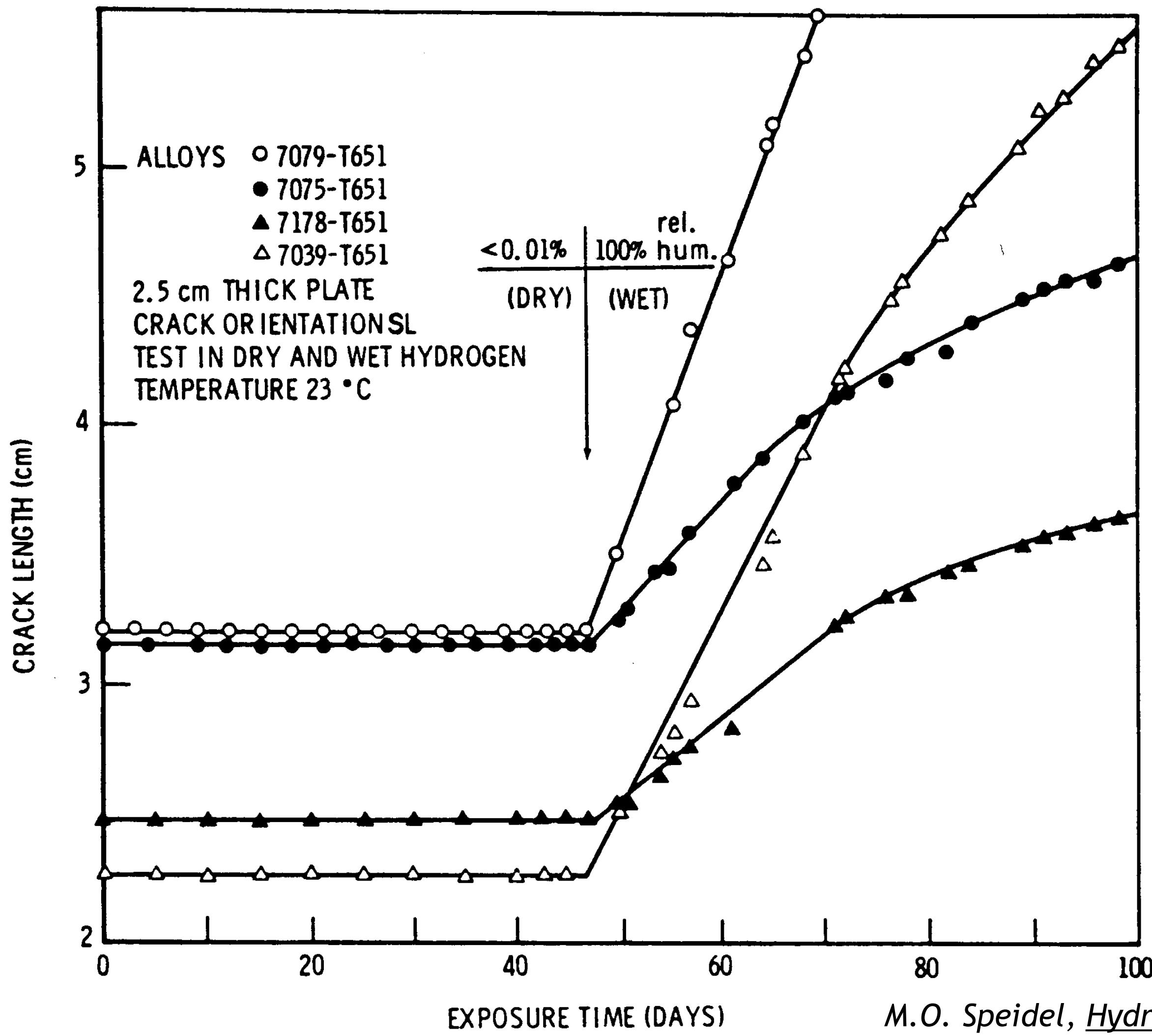


Adsorbed species can change kinetics of hydrogen uptake

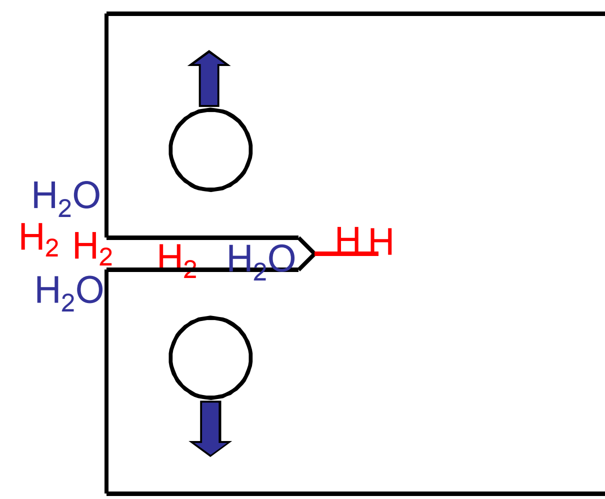


H.H. Johnson, Fundamental Aspects of Stress Corrosion Cracking, 1967

Environmental Variables:
Gas Purity



Aluminum alloys become susceptible to hydrogen-assisted fracture in presence of water



M.O. Speidel, Hydrogen Embrittlement and Stress Corrosion Cracking, 1984

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- Multiprogram national laboratory with breadth of responsibilities primarily to Department of Energy (DOE)
  - 40+ years of original research in hydrogen effects, design and maintenance of hydrogen pressure vessels.
  - Built and maintained a small hydrogen pipeline in the late ‘70s for research purposes, sponsored by DOE.
  - Co-organizer of topical conferences on Hydrogen Effects on Materials Behavior (7th conf.: September 2008, Jackson Lake Lodge WY)
  - **Support development of Codes and Standards for Hydrogen**
  - Center of Excellence for the development of metal hydride storage materials

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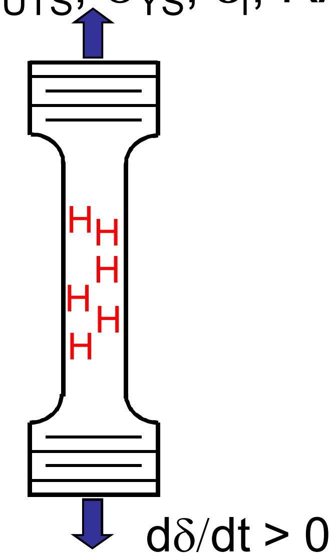
Current Activities on Hydrogen Compatibility at SNL

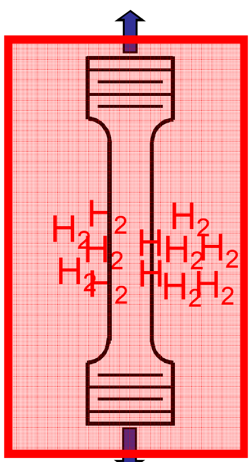
- Codes and Standards for the Hydrogen Economy
  - Analysis of unintended hydrogen release scenarios
  - Risk assessment
  - **Technical Reference on Hydrogen Compatibility of Materials**
    - Critical review and compilation of data on the effects of gaseous hydrogen on material performance
    - Materials testing focused on generating fracture mechanics data for relevant engineering materials in gaseous hydrogen environments
    - To be released incrementally via SNL website http://www.ca.sandia.gov/matlsTechRef/
- Applicability of Failure Assessment Diagrams for gaseous hydrogen environments (R6 methodology)
- Hydrogen compatibility of welds in stainless steel

Testing Methodologies

Strength of Materials:

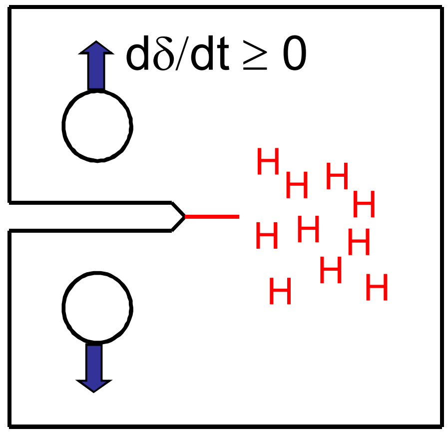
σ_{UTS}, σ_{YS}, ε_f, RA

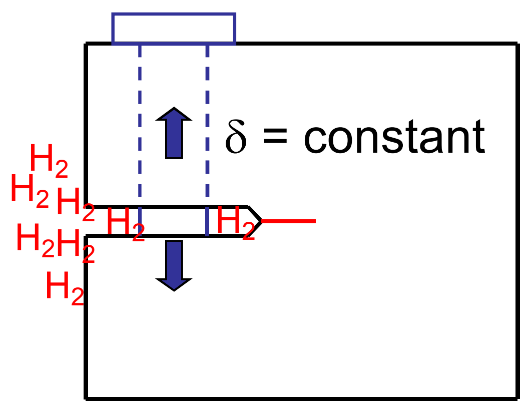




Fracture Mechanics:

K_{IH}, K_{TH}





Current capabilities at Sandia

Thermal precharging in high-pressure H_2 gas, testing in air

- pressure up to 138 MPa
- temperature up to 300˚C

Static testing in high-pressure H_2 gas

- pressure up to 200 MPa
- temperature: -75˚C to +175˚C

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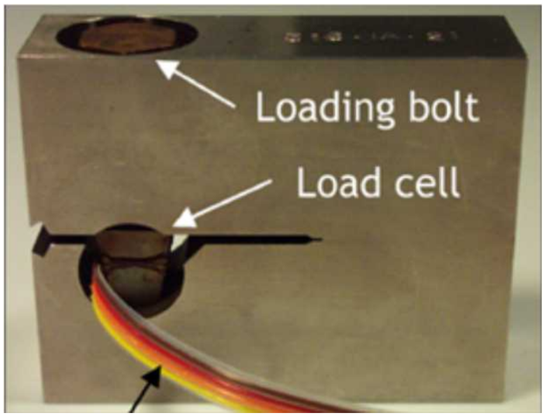
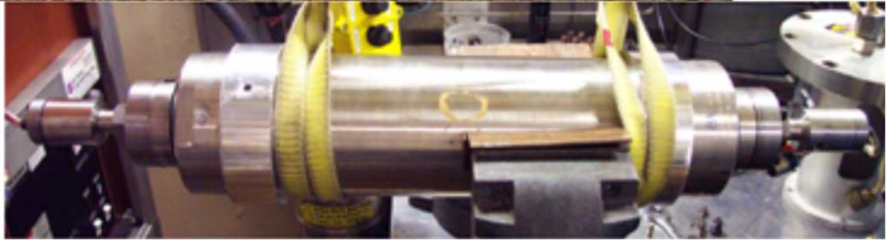
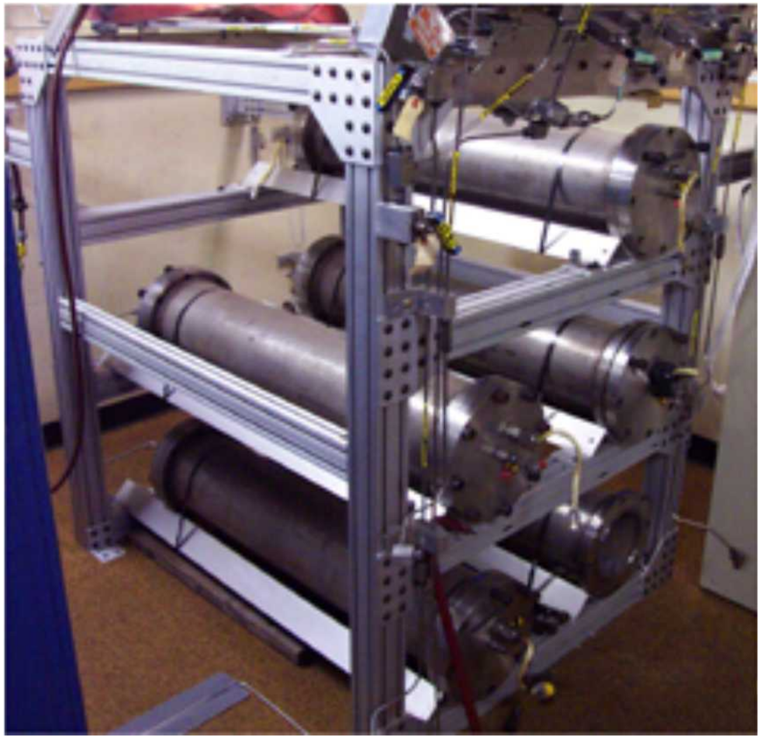
Slow Crack Growth Facility



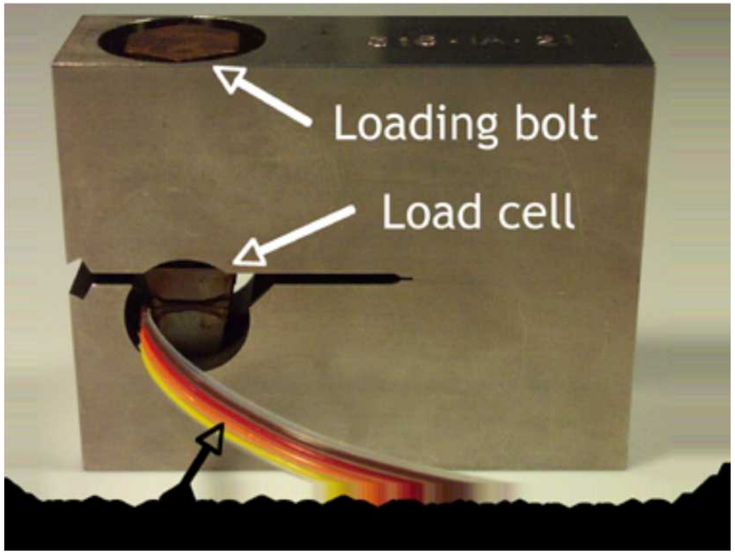


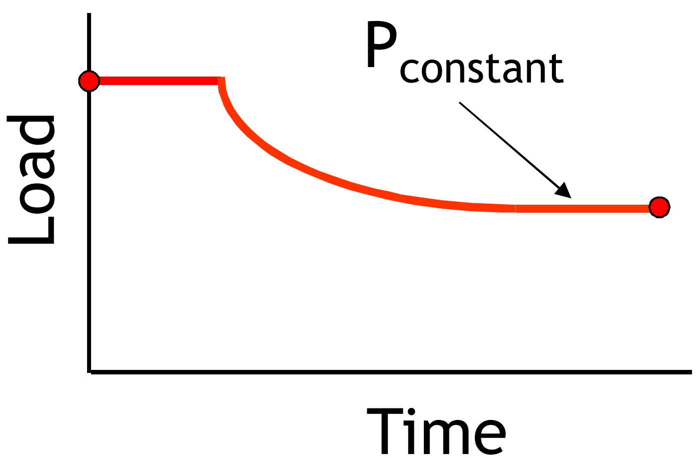
- Closely mimics service conditions of static structures
- High-pressure hydrogen environment (up to 200 MPa)
- Environmental chamber for temperature studies (-75˚C to 175˚C)
- Test duration: up to 5000 hours
- Practical limit on crack advance: 10^{-11} m/s

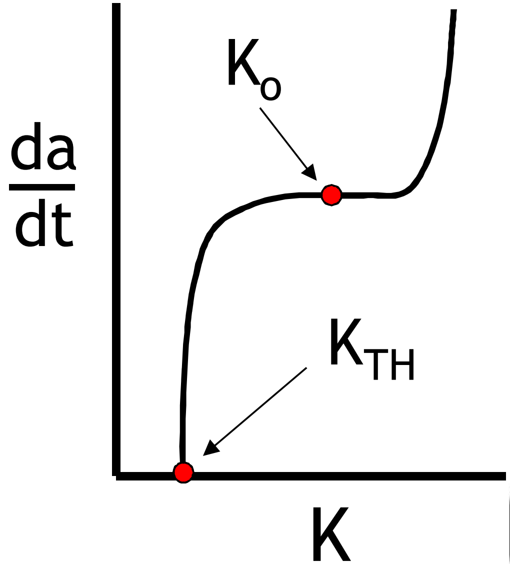


Instrumented WOL specimens

- Constant displacement using instrumented load cell
- Samples bolted to $K_{Ic} > K_o > K_{TH}$
- Strain gages supply load vs. time: crack advance → load drop
- Crack arrests when $K = K_{TH}$







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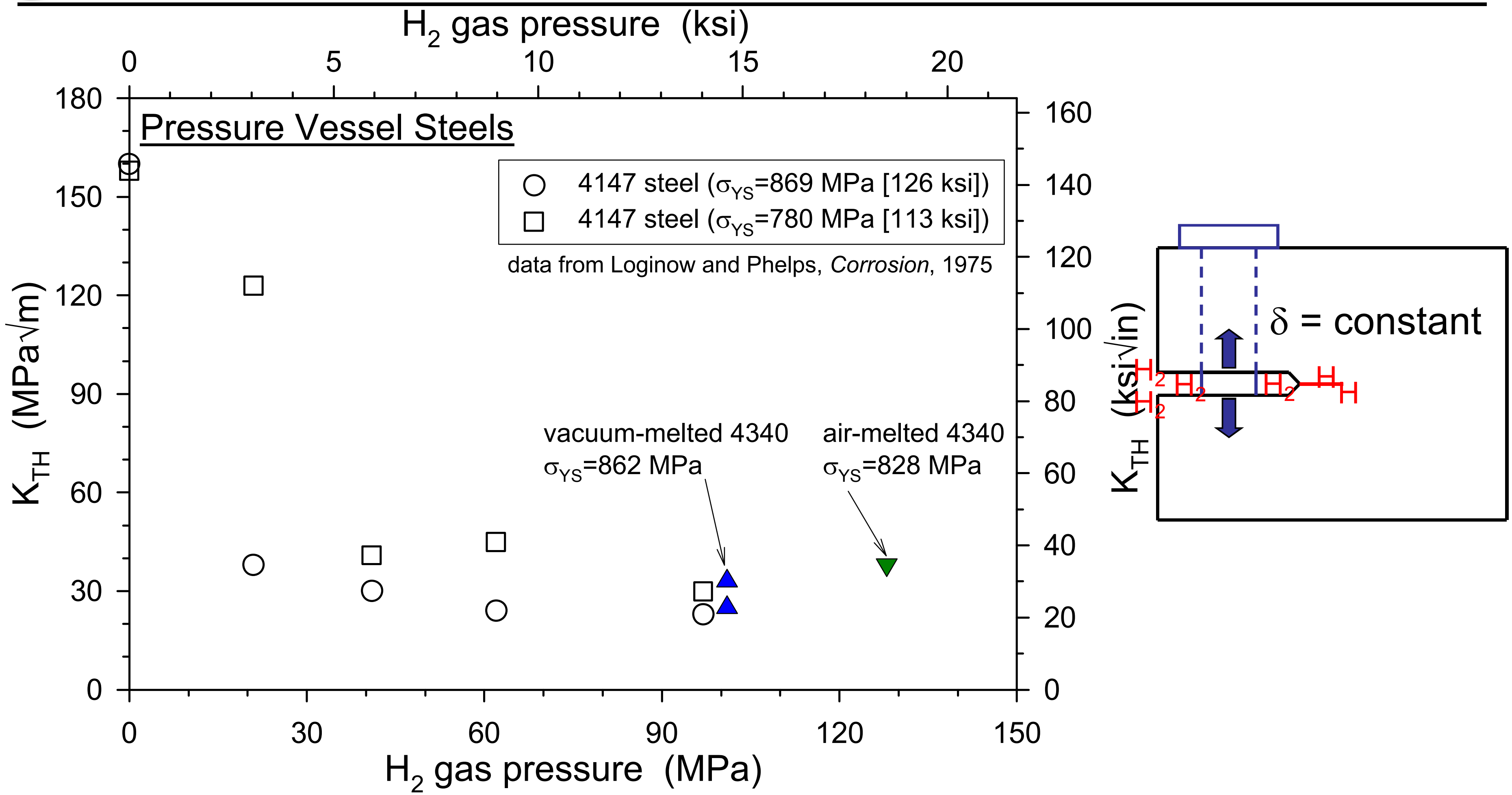
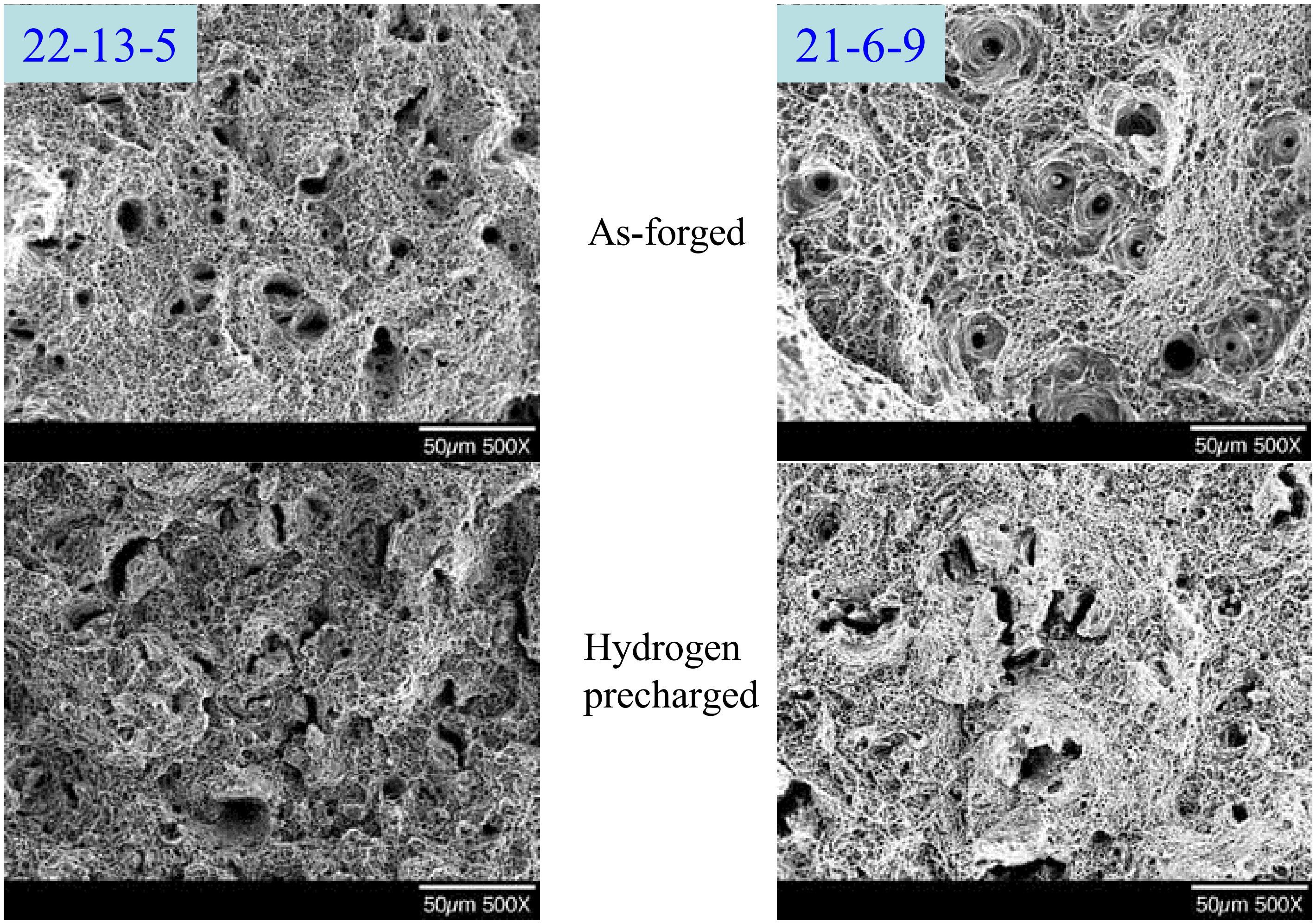
K_{TH} measurements for 4340 steel



Initial K_{TH} measurements for modern "clean" steels are similar to data for older steels

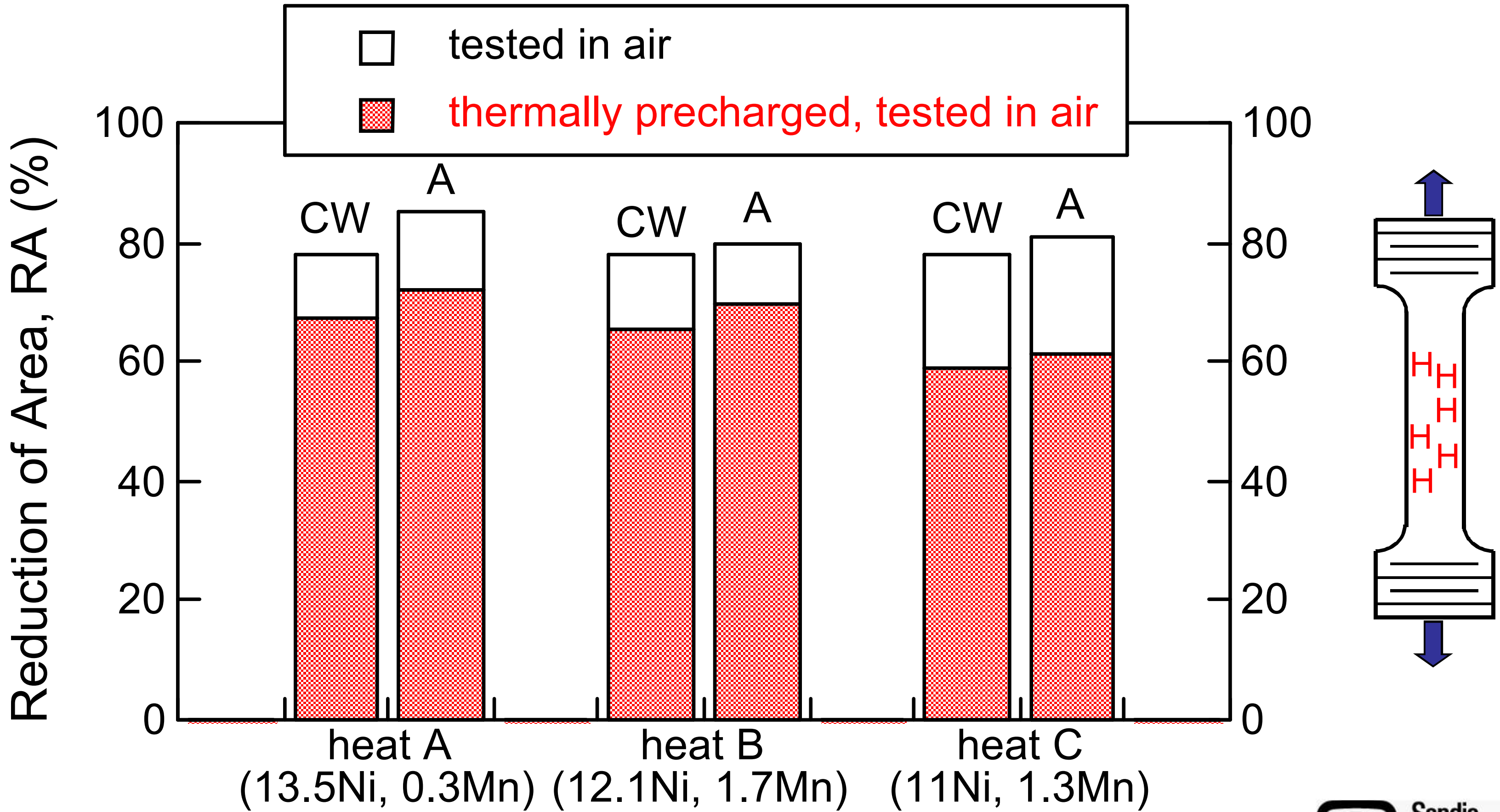
Ductile fracture mechanisms: microvoid coalescence



Material Variables:
Composition & Deformation

316/316L Stainless Steel

High Ni improves resistance to H-assisted fracture



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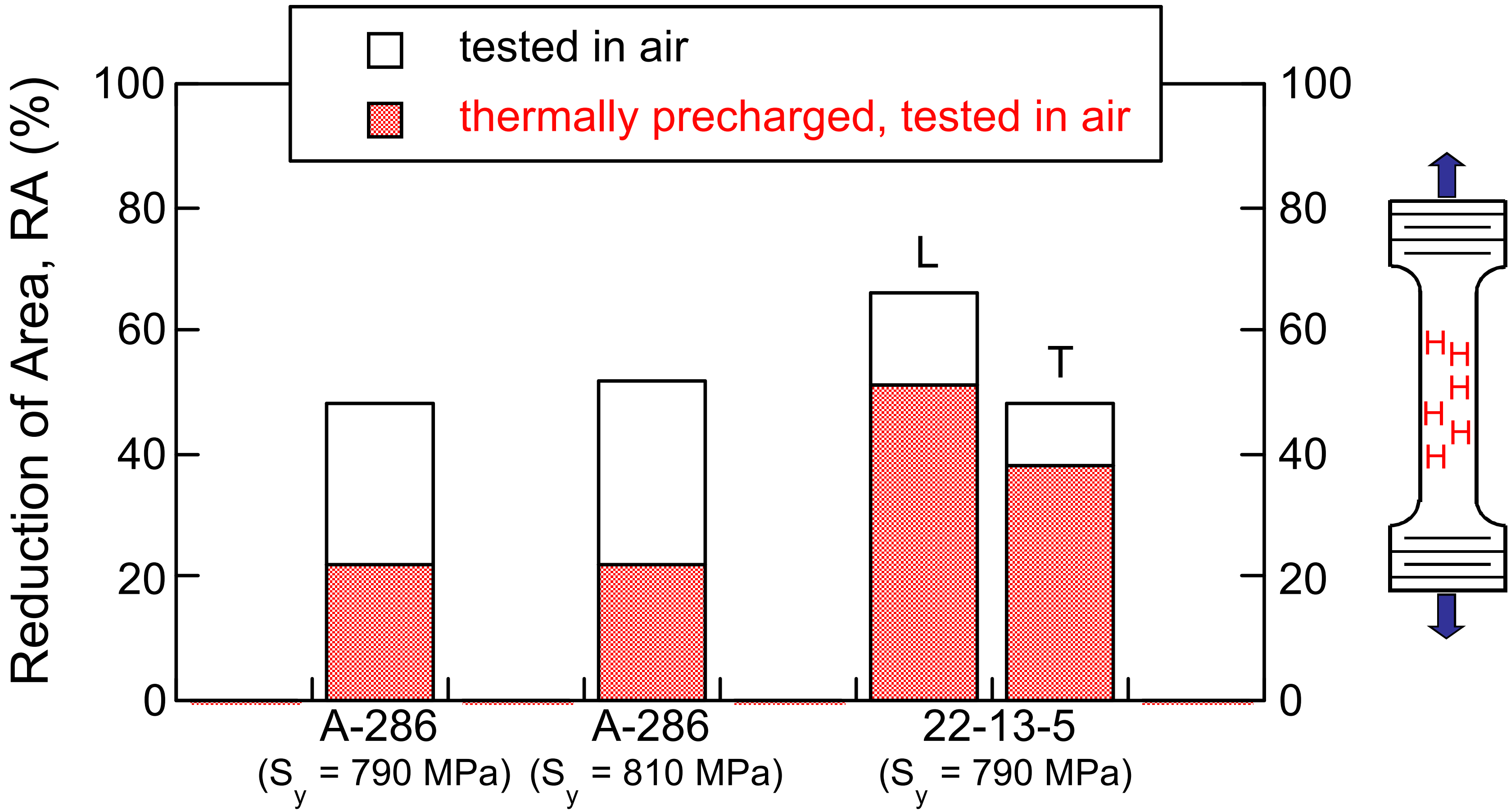
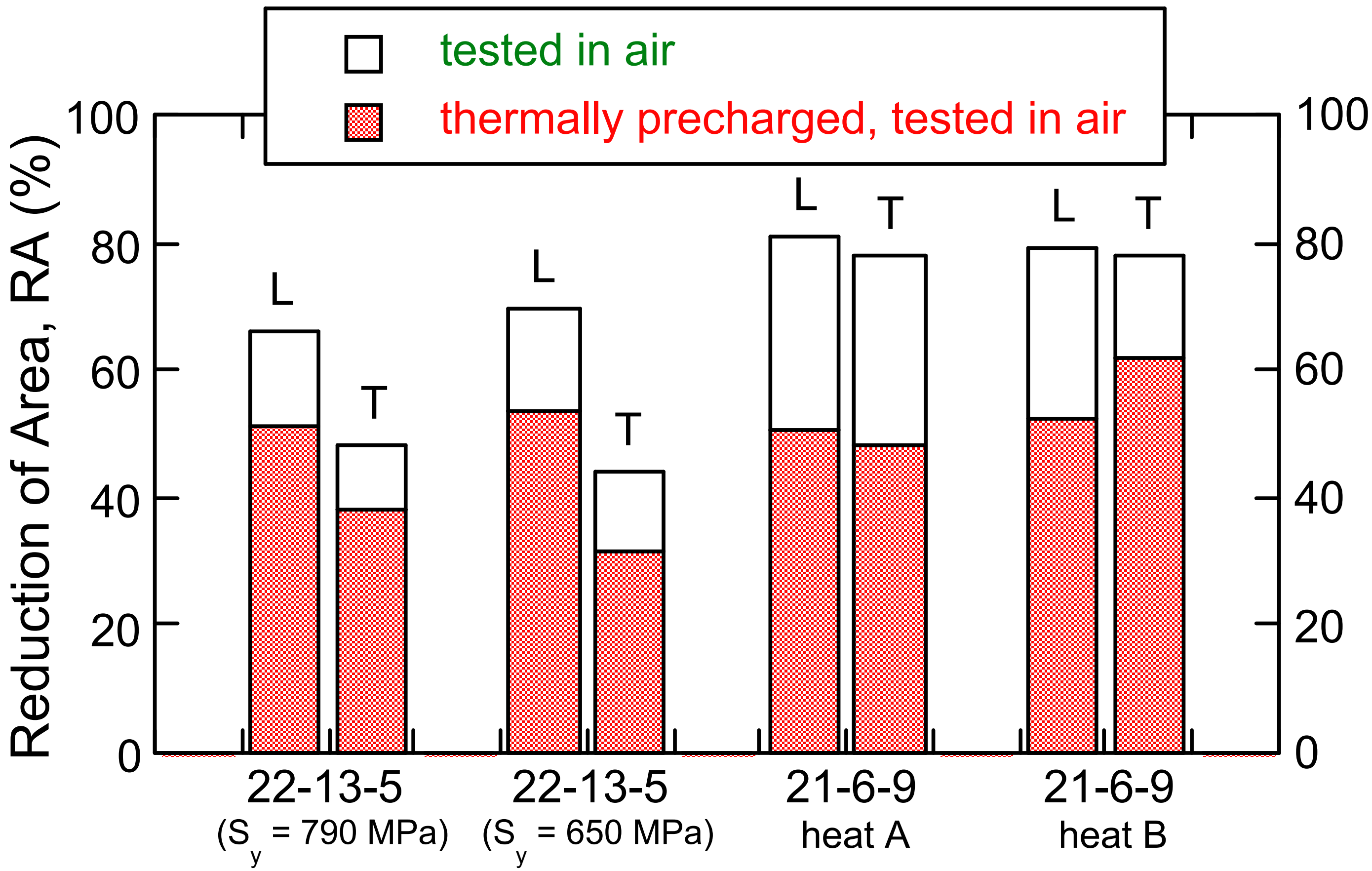
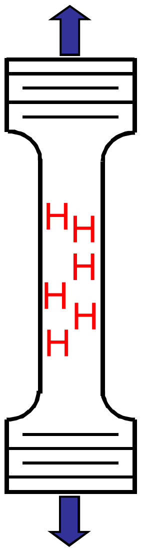
Material Variables:
Microstructure & Phases



Material Variables:
Composition & Orientation





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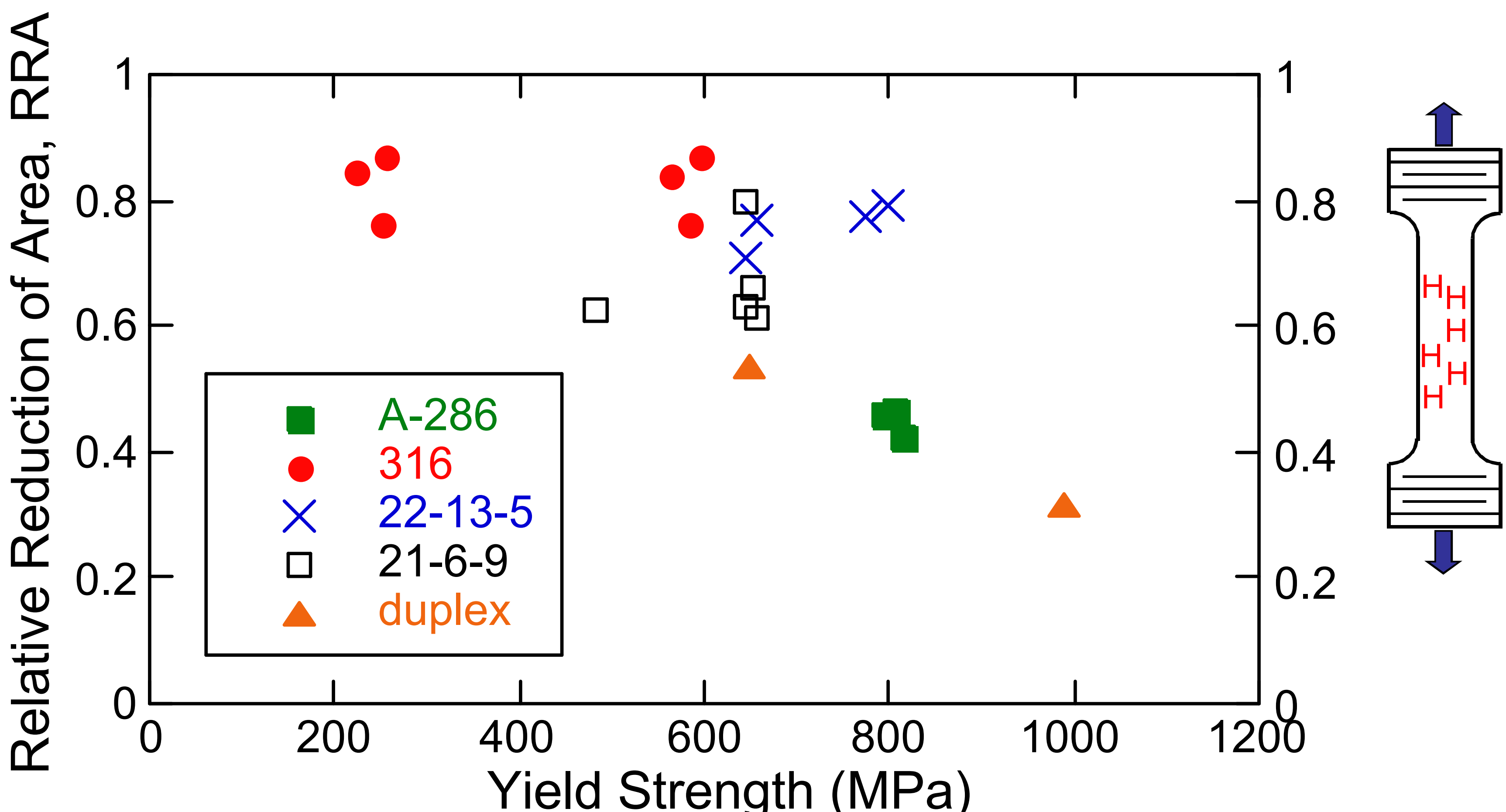
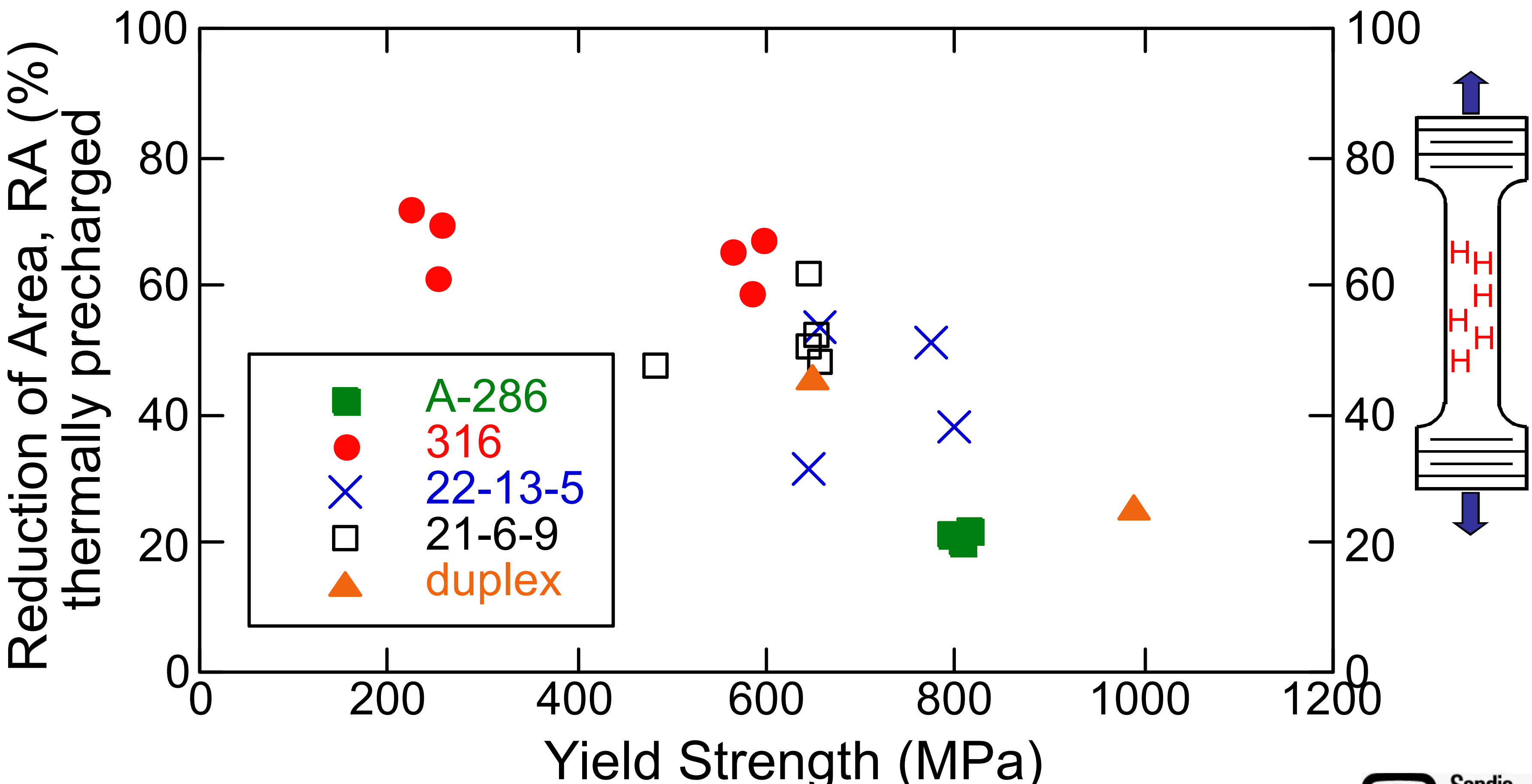
Material Variables:
Composition & Yield Strength



Material Variables:
Composition & Yield Strength



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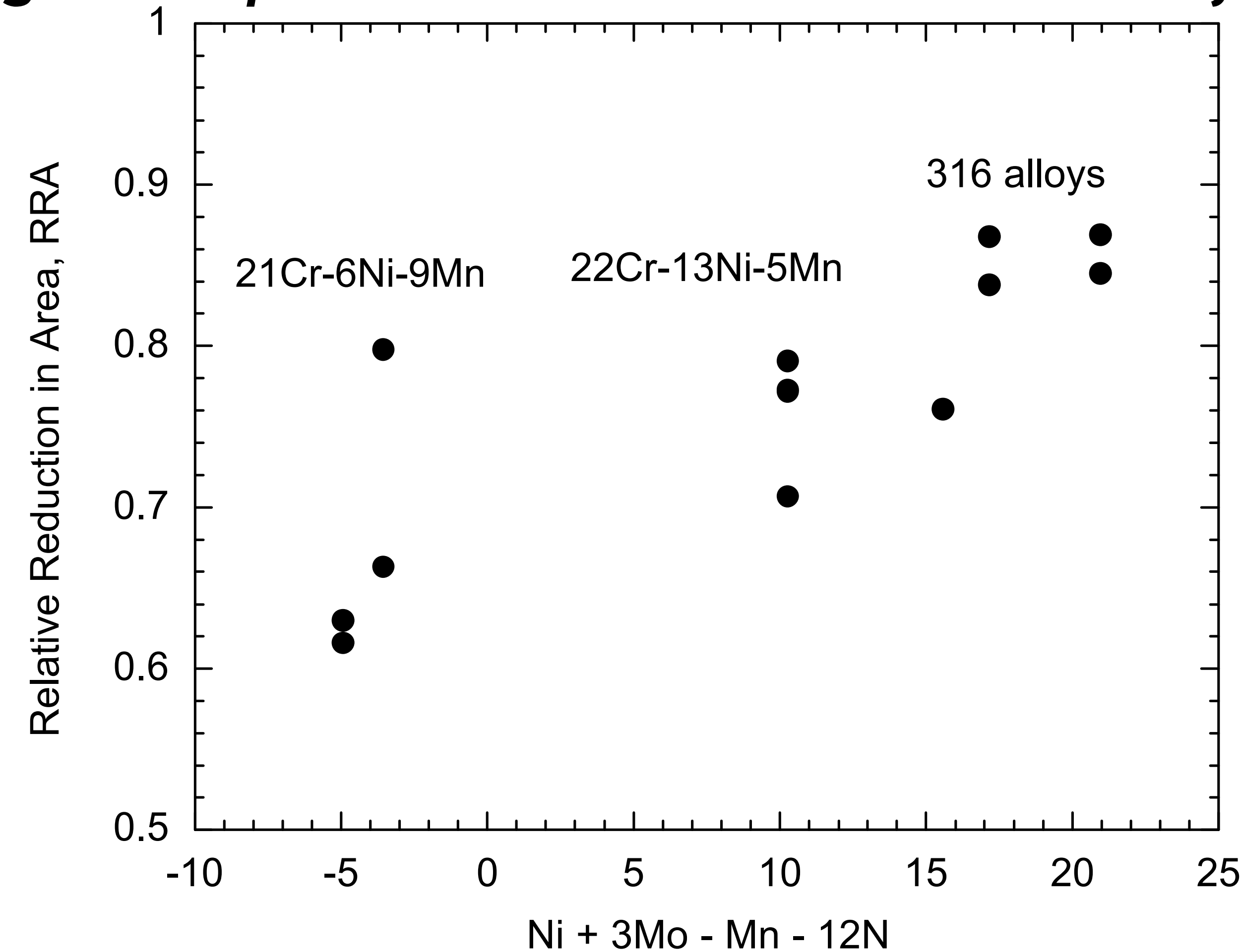
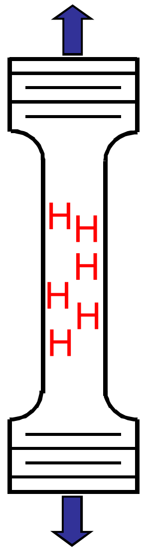
Material Variables: *Composition*

IHAC of Stainless Steels
High Ni improves resistance to H-assisted fracture





Summary

- Simple Abel-Noble EOS for hydrogen
- Permeation and diffusion nominally independent of compositional and microstructural variables for stainless steels
- Solubility depends on composition

- Hydrogen embrittlement in hydrogen gas is a bulk effect
- Many variables contribute to resistance/susceptibility to hydrogen-assisted fracture

- Fracture mechanics testing in gaseous hydrogen environment reveals low resistance to HEAC in pressure vessel steels
- High nickel content in SS improves resistance to IHAC
  - e.g. not all 316 alloys are equivalent