

## SUSCEPTIBILITY OF METALS TO HYDROGEN-ASSISTED FRACTURE

S A N D I A N A T I O N A L L A B O R A T O R I E S

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The automotive and energy sectors are heavily investing in hydrogen fuel cell technology to power a clean, efficient future fleet. Hydrogen embrittlement of structural steels, however, is a significant concern, thus the scientific and engineering communities are studying the effects of long-term hydrogen exposure on structural materials for the storage and distribution of hydrogen.

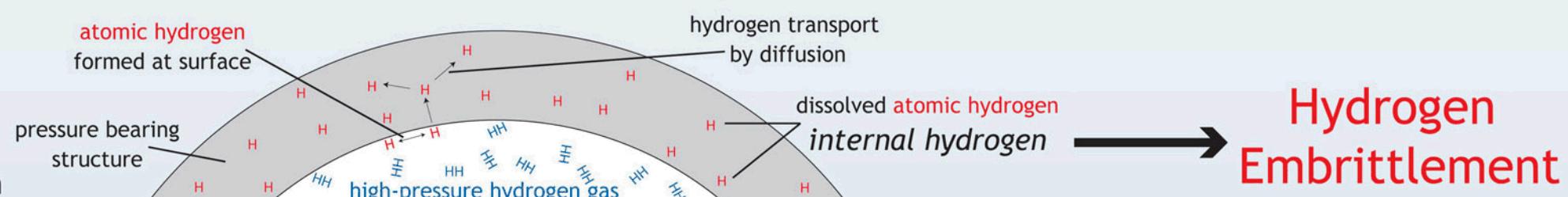
Hydrogen transport is a key component of hydrogen-assisted fracture and consists of important kinetic and thermodynamic elements

## Kinetics

- surface processes
- diffusion

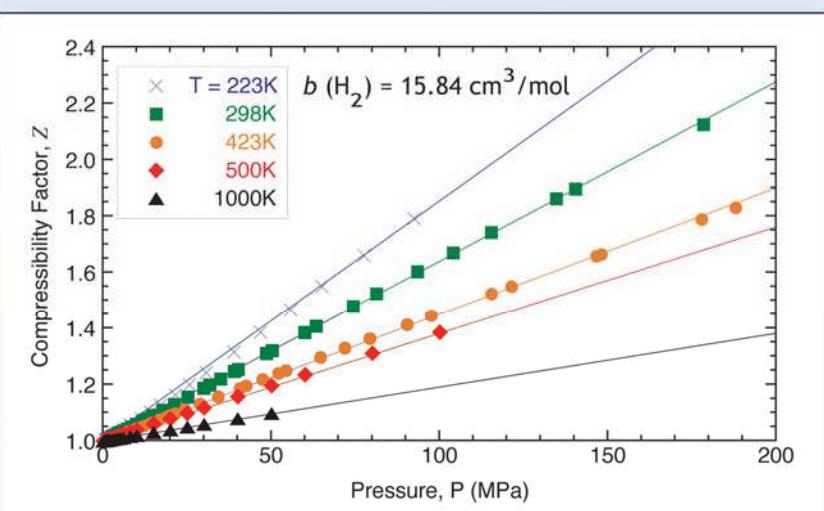
## Thermodynamics

- physics of hydrogen gas
- solubility of atomic hydrogen



## Physics of Hydrogen Gas

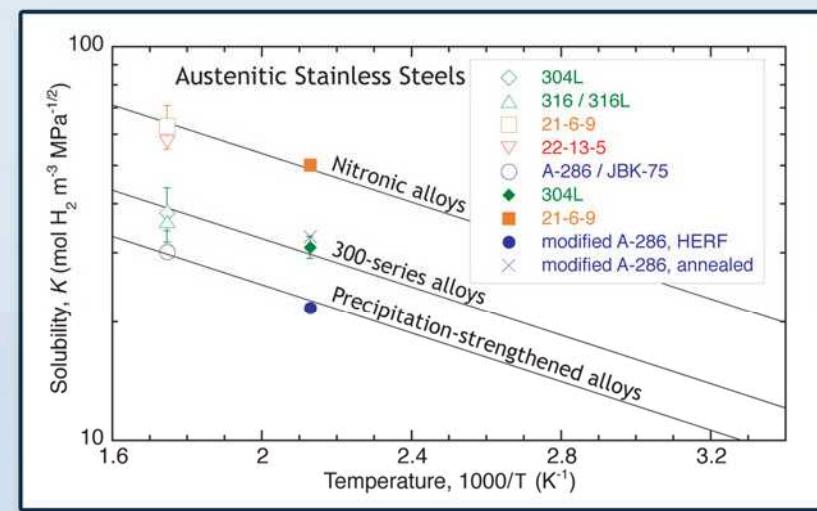
- Abel-Noble Equation of State predicts the behavior of high-pressure hydrogen gas well  
 $Z = 1 + bP/RT$
- Fugacity ( $f$ ) of high-pressure hydrogen is necessary for thermodynamic calculations  
 $f = P \exp(Pb/RT)$



## Thermodynamics of Dissolved Hydrogen

- Solubility has classic temperature dependence:  
 $K = K_O \exp(-E/RT)$
- Hydrogen dissolved in steels depends on the fugacity of the hydrogen gas

$$c_H = K f^{1/2}$$



## Diffusivity of Hydrogen in Metals

- Diffusion is extremely slow in austenitic stainless compared to other materials
- Diffusion distances for austenitic stainless steels are  $10^4$  times smaller than low-alloy steels

Materials	$D_o$ (m <sup>2</sup> /s)	$H_D$ (kJ/mol)	$D = D_o \exp(-H_D/RT)$ (m <sup>2</sup> /s)	$x = 2\sqrt{Dt}$ (mm)
Austenitic stainless steels	$5.76 \times 10^{-7}$	53.62	$2.3 \times 10^{-16}$	0.17
4130 Q&T low-alloy steel	$3.5 \times 10^{-7}$	7.95	$1.4 \times 10^{-8}$	1300
Pure Aluminum	$1.75 \times 10^{-8}$	16.2	$2.5 \times 10^{-11}$	56
OFHC copper	$1.06 \times 10^{-6}$	38.5	$1.9 \times 10^{-13}$	4.9

T = 298 K      t = 1 year

Different testing methodologies for evaluating effects of hydrogen on structural metals are used depending on the material characteristics and the desired engineering data

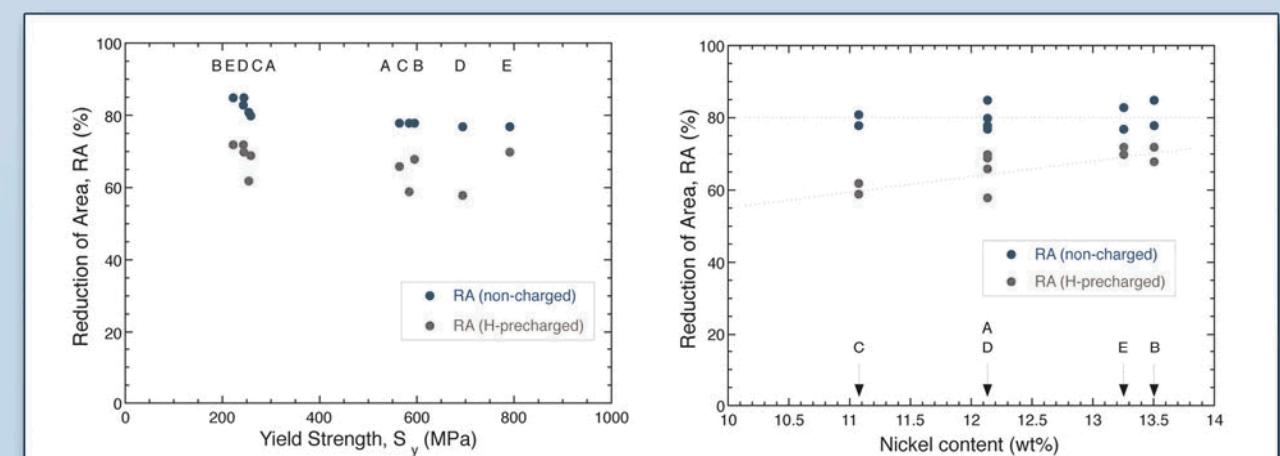
## Type 316/316L austenitic stainless steels with high concentrations of internal hydrogen (~140 wppm)

Gas phase thermal precharging with internal hydrogen prior to tensile testing in air

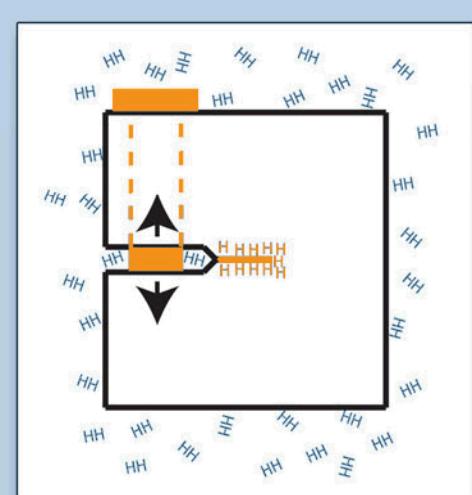
- for metals with low diffusivity (e.g., austenitic stainless steels)
- necessary for uniform supersaturation of H
- simulates long-term H<sub>2</sub> exposure



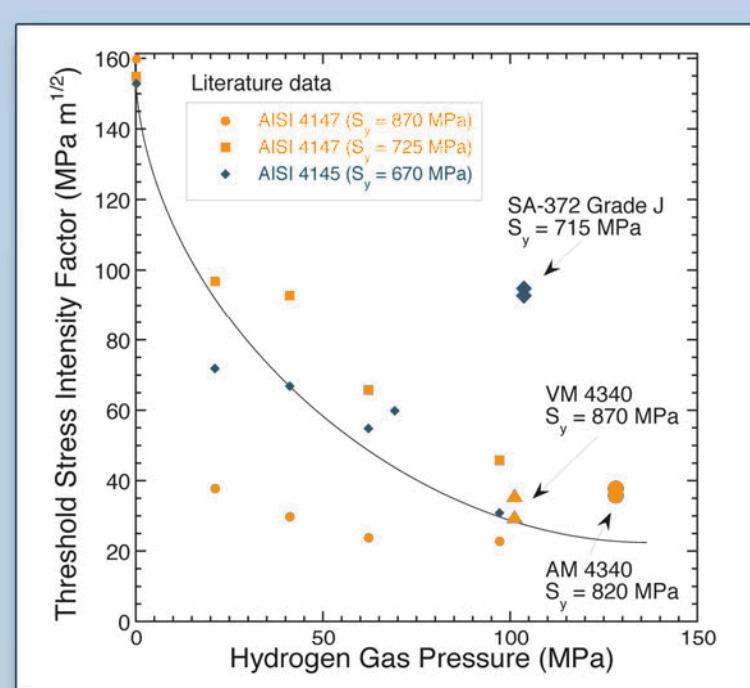
- Strain-hardening has little influence on ductility of H-precharged 316
- High nickel improves resistance to hydrogen-assisted fracture
- Other compositional variables, such as carbon, have less influence on deformation and fracture with high internal hydrogen content

Subcritical crack growth of low-alloy steels for thick-walled pressure vessels in high-pressure H<sub>2</sub>Static crack growth in high-pressure H<sub>2</sub> gas

- must allow time for hydrogen uptake to crack tip
- diffusive transport in austenitic stainless steels > 5000 hrs
- kinetics at surface can require >1000 hrs to initiate cracking in susceptible ferritic steels
- approximates service conditions of thick-walled vessels
- methodology adopted by ASME for hydrogen tanks



- Microstructural and processing effects are poorly understood
- Recent tests show that conventionally heat treated specimens have low threshold stress intensity factor ( $K_{TH}$ ) in high-pressure hydrogen gas, consistent with literature data
- Steel with proprietary heat treatment (SA-372 Grade J) shows substantial improvement in resistance to hydrogen compared to previous results



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