

SUSCEPTIBILITY OF METALS TO HYDROGEN-ASSISTED FRACTURE

SAND2007-1791P

CHRIS SAN MARCHI, BRIAN SOMERDAY, DORIAN BALCH,
KEVIN NIBUR, JEFF CAMPBELL AND KEN LEE

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.

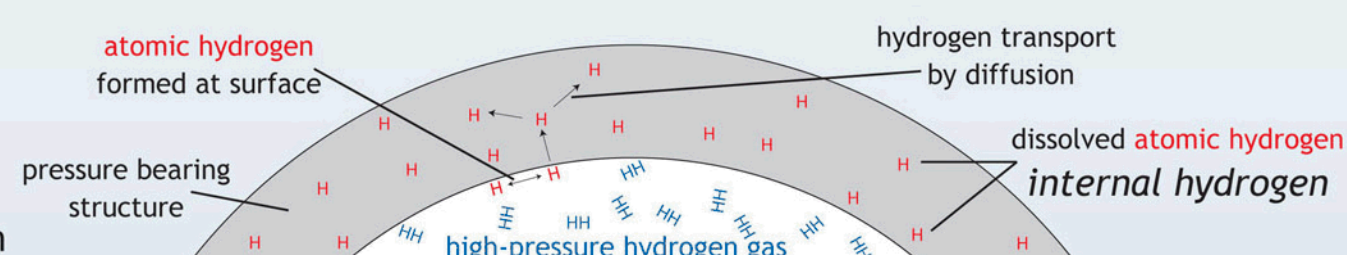
Hydrogen transport is a key component of hydrogen-assisted fracture and consists of important kinetic and thermodynamic elements

Kinetics

- surface processes
- diffusion

Thermodynamics

- physics of hydrogen gas
- solubility of atomic hydrogen

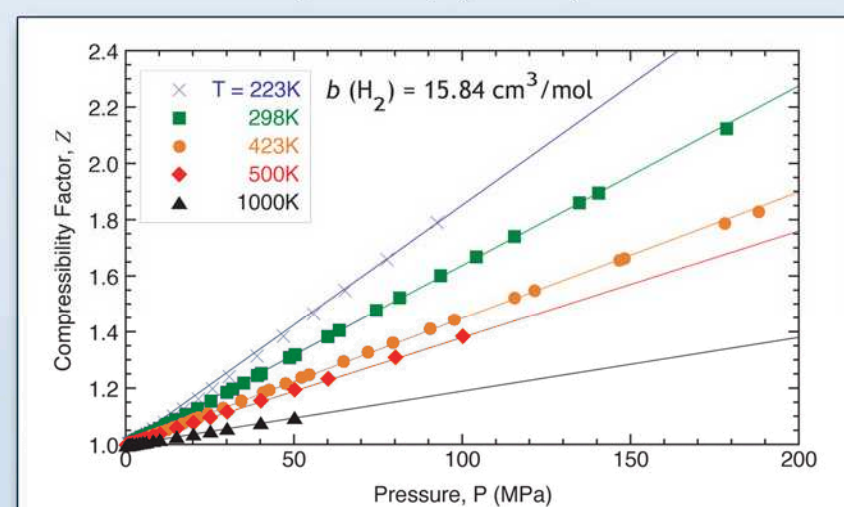


Hydrogen Embrittlement

Physics of Hydrogen Gas

- Abel-Noble Equation of State predicts the behavior of high-pressure hydrogen gas well
- Fugacity (f) of high-pressure hydrogen is necessary for thermodynamic calculations

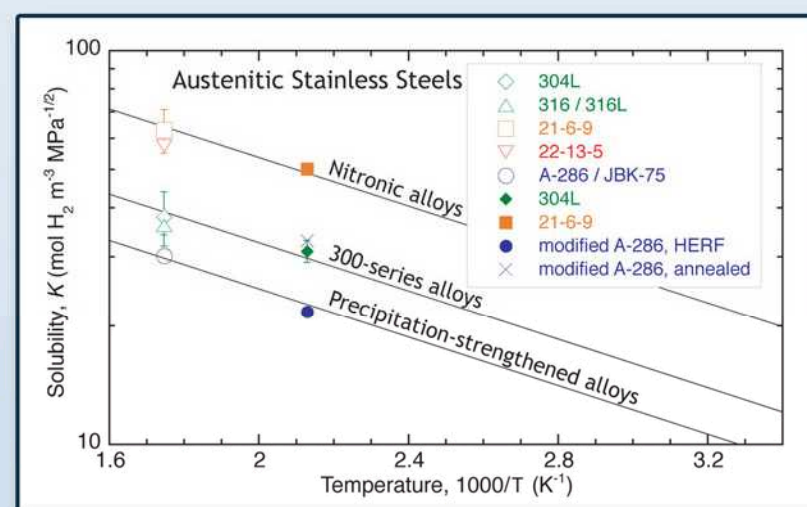
$$f = P \exp(Pb/RT)$$



Thermodynamics of Dissolved Hydrogen

- Solubility has classic temperature dependence:
- 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_0 (m ² /s)	H_D (kJ/mol)	$D = D_0 \exp(-H_D/RT)$ (m ² /s)	$x = 2\sqrt{Dt}$ (mm)
Austenitic stainless steels	5.76×10^{-7}	53.62	2.3×10^{-16}	0.17
4130 Q&T low-alloy steel	3.5×10^{-7}	7.95	1.4×10^{-8}	1300
Pure Aluminum	1.75×10^{-8}	16.2	2.5×10^{-11}	56
OFHC copper	1.06×10^{-8}	38.5	1.9×10^{-13}	4.9

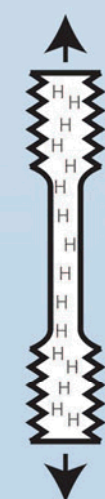
$T = 298 \text{ K}$ $t = 1 \text{ year}$

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

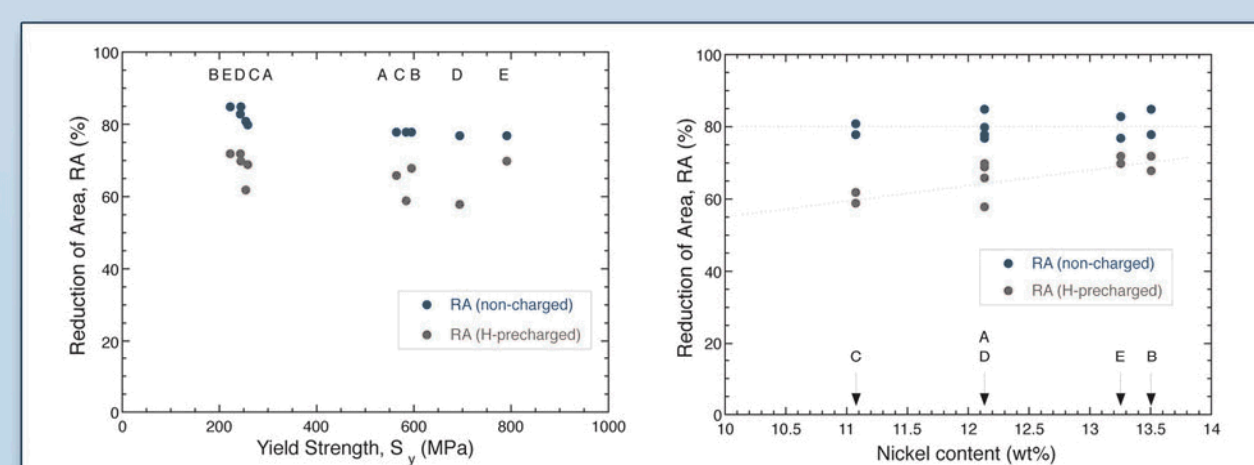
Type 316/316L austenitic stainless steels with high concentrations of internal hydrogen (~140 wppm)

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_2 exposure



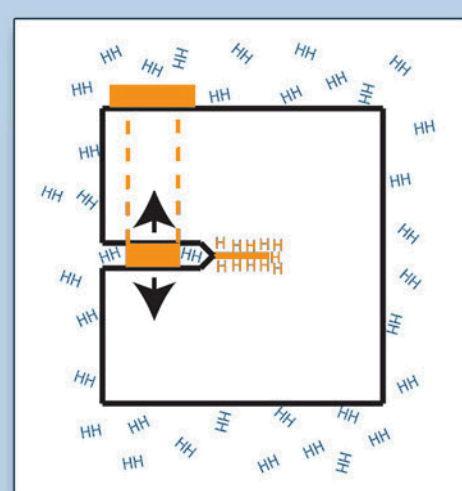
- Strain-hardening has little influence on ductility of H-precharged 316
- High nickel improves resistance to hydrogen-assisted fracture
- Other compositional variables, such as carbon, have less influence on deformation and fracture with high internal hydrogen content



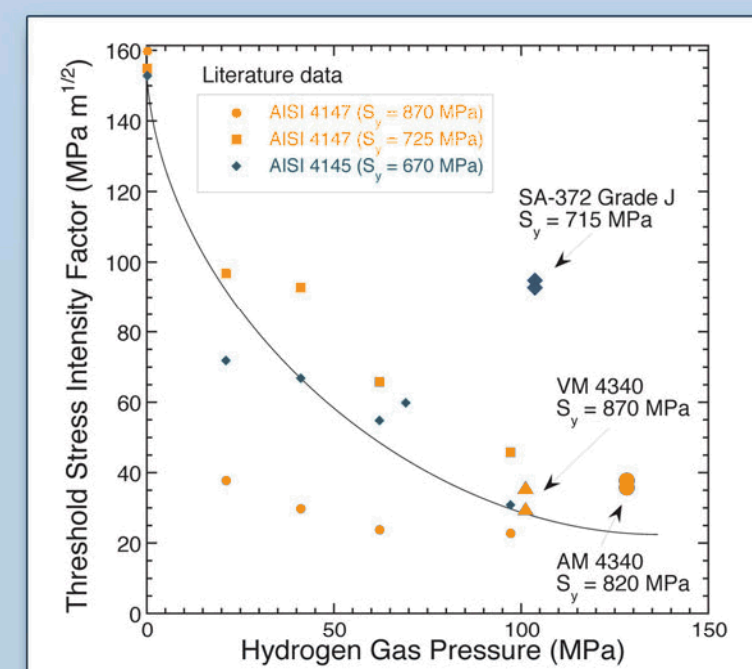
Subcritical crack growth of low-alloy steels for thick-walled pressure vessels in high-pressure H_2

Static crack growth in high-pressure H_2 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



The support of the Department of Energy is acknowledged through the Safety, Codes and Standards program element managed by Pat Davis of the Hydrogen, Fuel Cells and Infrastructure program, Office of Energy Efficiency and Renewable Energy.