Hydrogen-Assisted Fracture: Materials Testing and Variables Governing Fracture

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SNL has 40+ years experience with effects of high-pressure hydrogen gas on materials

- Design and maintenance of welded stainless steel pressure vessels for containment of high-pressure H_2 isotopes
  - Extensive testing of stainless steels exposed to high-pressure H_2 gas
- Six-year program in 1970s focused on feasibility of using natural gas pipeline network for H_2 gas
  - Materials testing in high-pressure H_2 gas using laboratory specimens and model pipeline
  - Examined fusion zone and heat affected zones of welds
- Active SNL staff have authored 70+ papers and organized 6 conferences/symposia on H_2 effects in materials
  - Seventh conference on Hydrogen Effects on Material Behavior scheduled for Sept. 2008 at Jackson Lake Lodge, Wyoming

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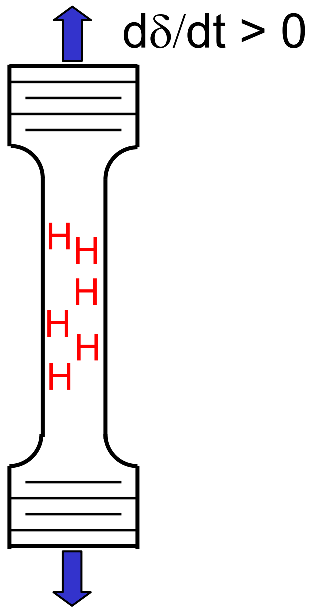
SNL/CA has capabilities for producing both strength of materials and fracture mechanics data

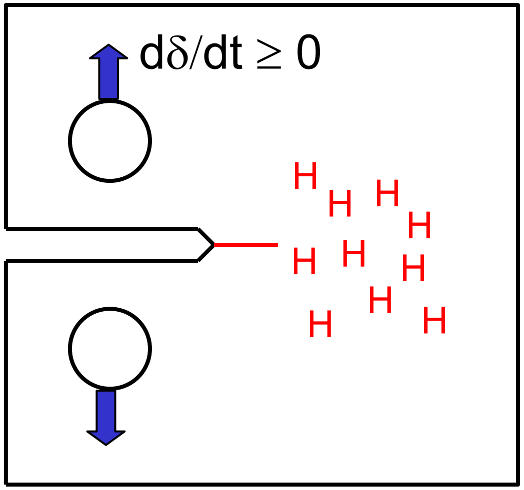
strength of materials:

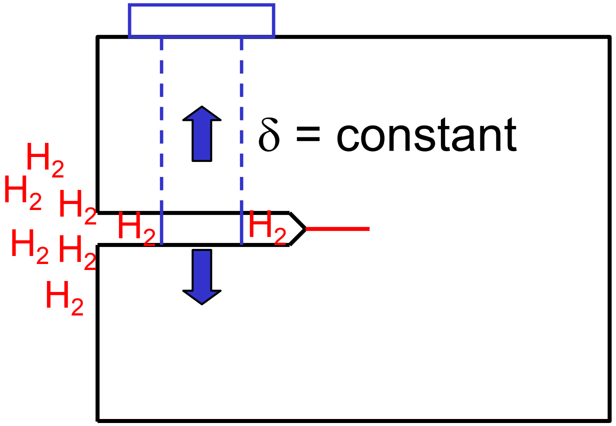
σ_{UTS}, σ_{YS}, ε_f, RA



fracture mechanics:

K_{IH}, K_{TH}





Thermal charging of specimens in H_2 gas

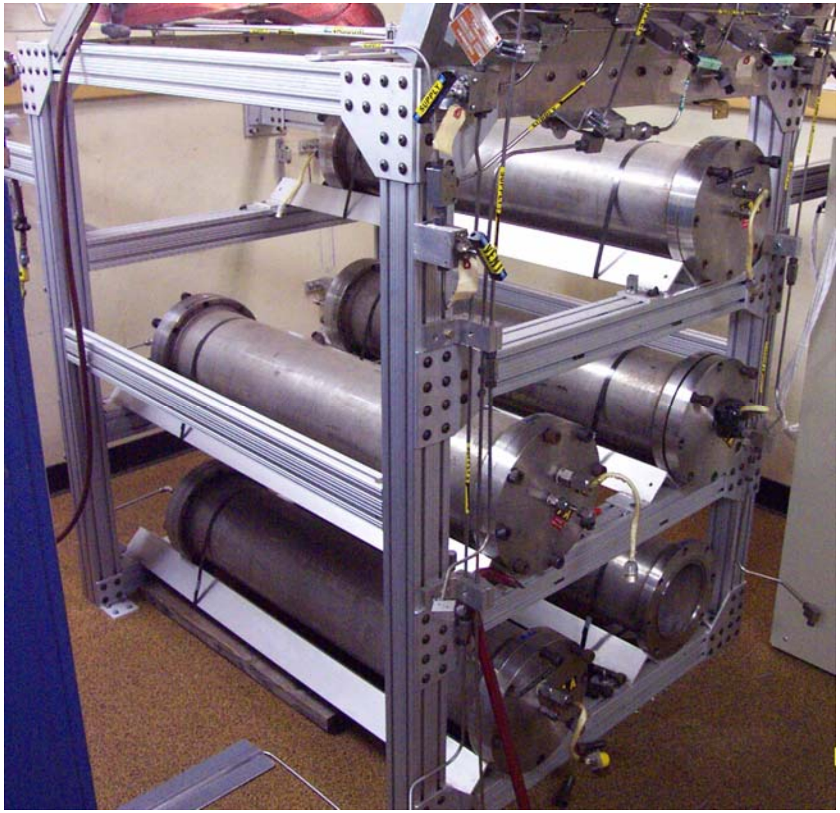
- Two high-temperature charging stations
  - temperatures up to 300 ºC (572 ºF)
  - pressures up to 138 MPa (20 ksi)
  - two to four A286 primary vessels in 304 secondary containment
  - H concentrations from 7,000 to 15,000 appm in stainless steels

- Specimens
  - compact tension and 3-pt bend fracture mechanics (K_{IH})
  - smooth and notched tensile (σ_{UTS}, σ_{YS}, ε_f, RA)

- Dedicated 90 kN (20 kip) servo-hydraulic load frame for rising displacement testing

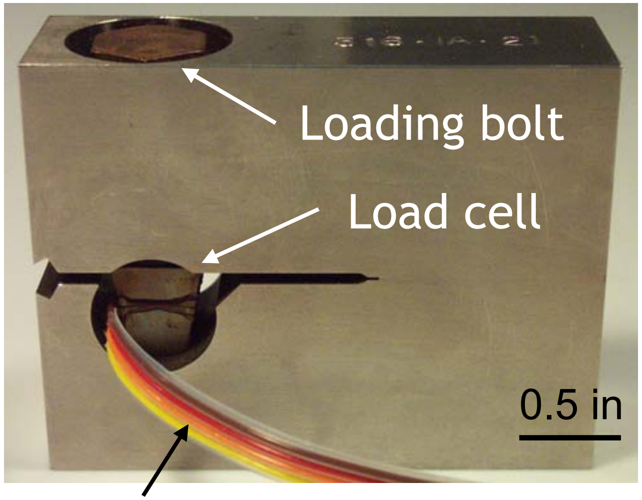
Measurement of K_{TH} in high-pressure H_2 gas

- Five stations for testing in high-pressure H_2 gas
  - pressures up to 200 MPa (29 ksi)
  - room temperature
  - A286 primary vessels in 304/321 containment

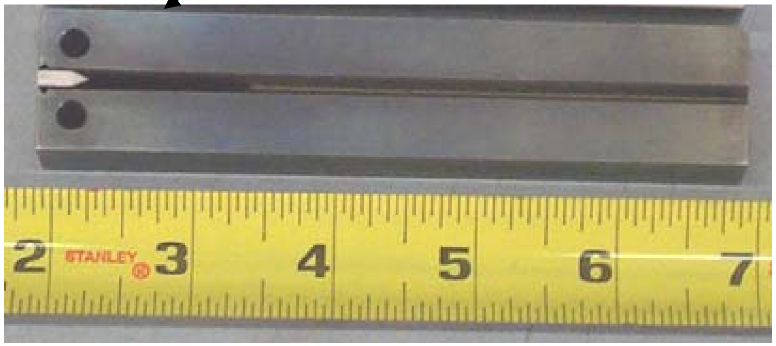


Measurement of K_{TH} in high-pressure H_2 gas: instrumented WOL and DCB specimens

- WOL specimens
  - procedures follow ASTM E1681-99
  - constant displacement with instrumented load cell
  - strain gages yield load vs. time: crack advance $\rightarrow$ load drop $\rightarrow$ K drop
  - crack arrests when $K = K_{TH}$ (load constant with time)



- DCB specimens
  - procedures follow NACE TM0177-96
  - constant displacement from wedge
  - strain gage signals crack initiation and arrest
  - crack arrests when $K = K_{TH}$ (strain gage signal constant)



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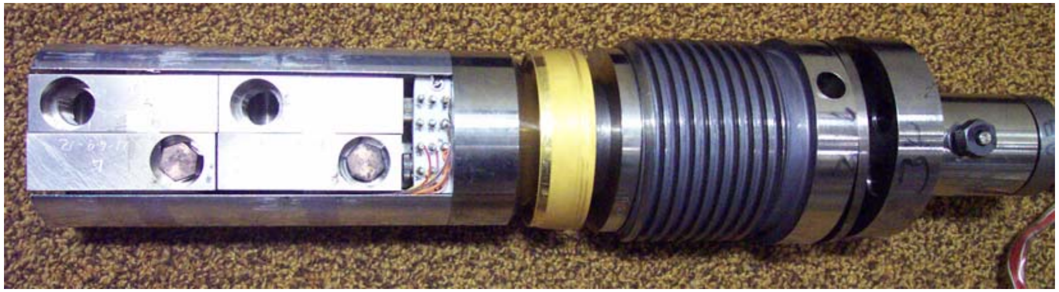
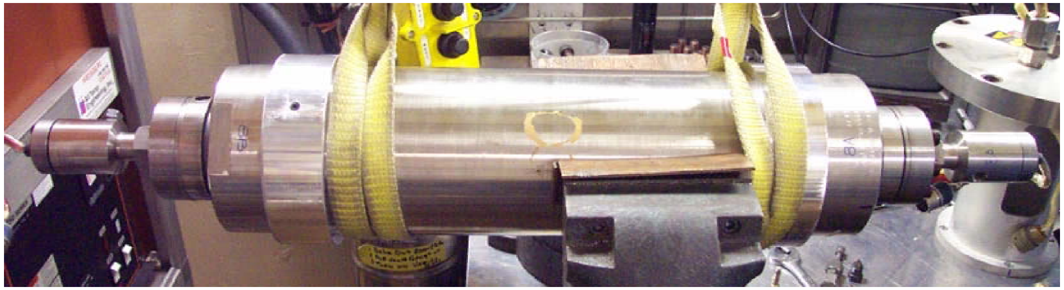
Measurement of K_{TH} in high-pressure H_2 gas: test assembly

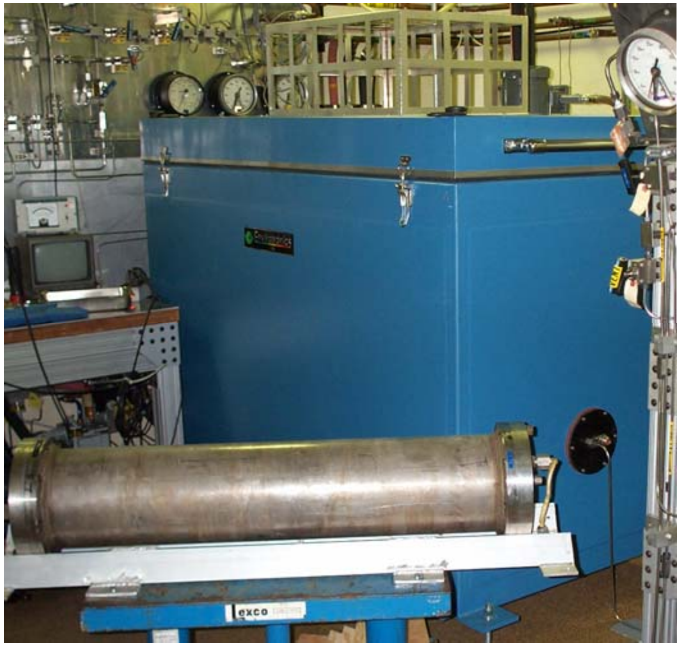
- Up to 4 WOLs in each cradle
  - 2 cradles/vessel
- Up to 8 DCBs in each modified cradle
  - 1 cradle/vessel
- Displacement loading applied in air





Test durations can be 1000+ hours for both stainless steels and ferritic steels

Measurement of K_{TH} in high-pressure H_2 gas: environmental chamber



- Temperatures
  - +175 ºC to -75ºC (-347 ºF to -103 ºF)
- Pressures
  - 200 MPa (29 ksi) below room temperature
  - 138 MPa (20 ksi) above room temperature
- Capacity
  - one test vessel (8 WOLs or 8 DCBs)

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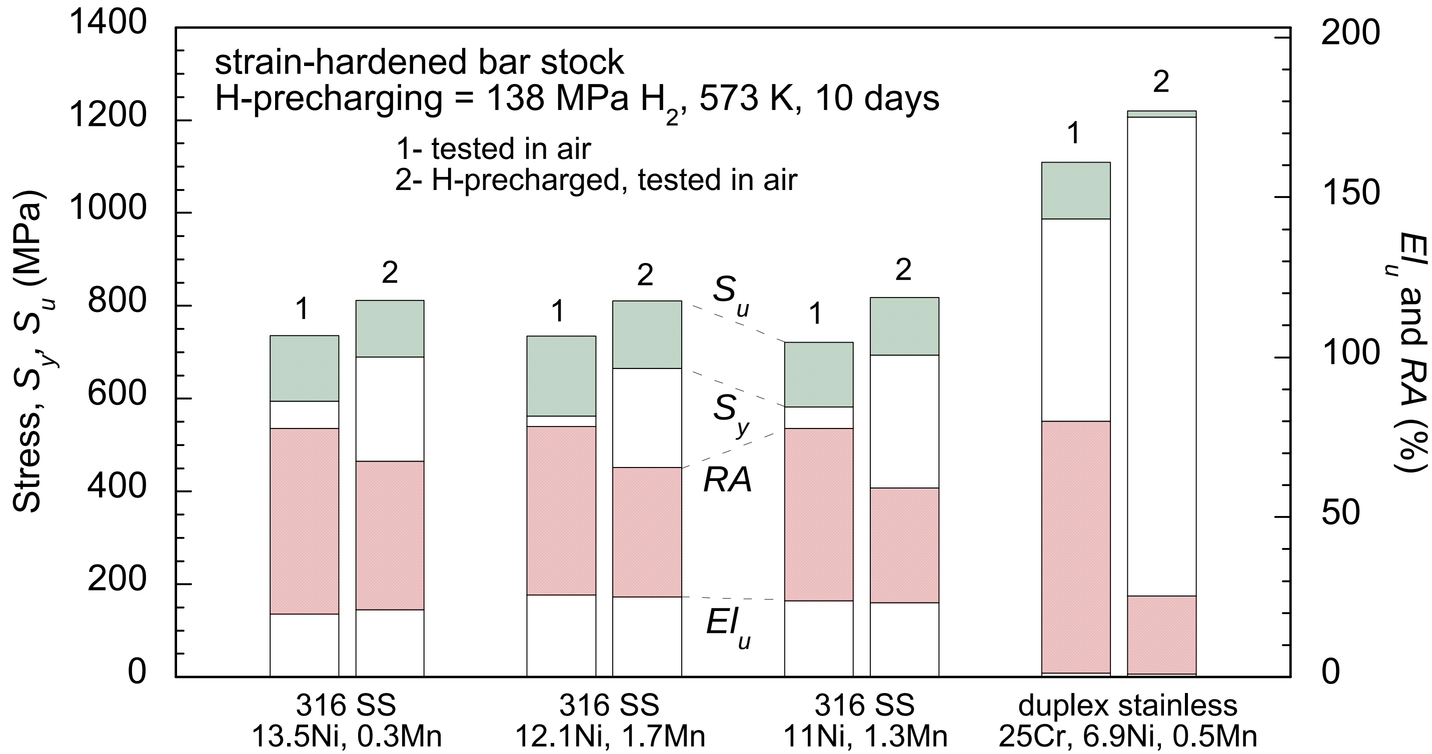
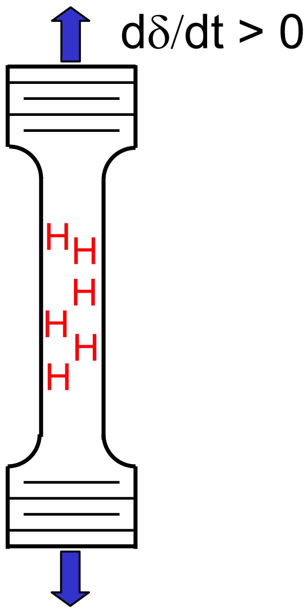
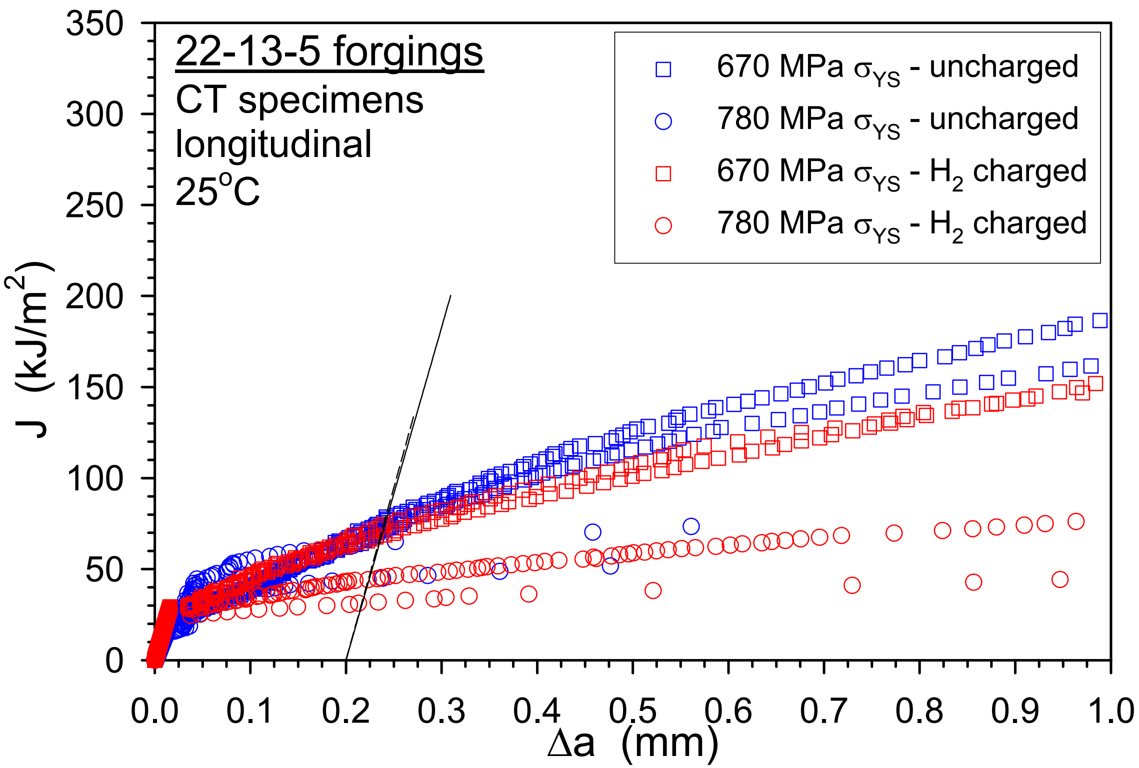
Tensile tests with internal hydrogen

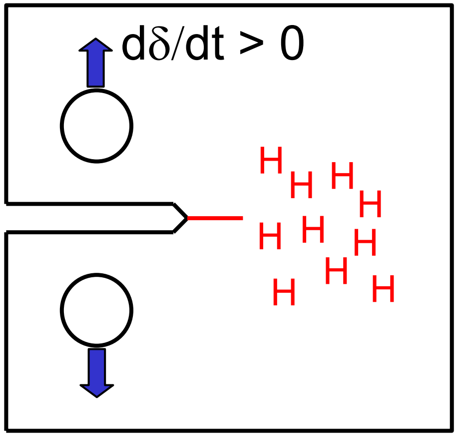




- Materials
  - Forged 22Cr-13Ni-5Mn and 21Cr-6Ni-9Mn stainless steels
  - Cold-worked and annealed 316 stainless steel
  - Cold-worked and annealed SAF 2507 duplex stainless steel
  - X-70 and X-80 pipeline steels

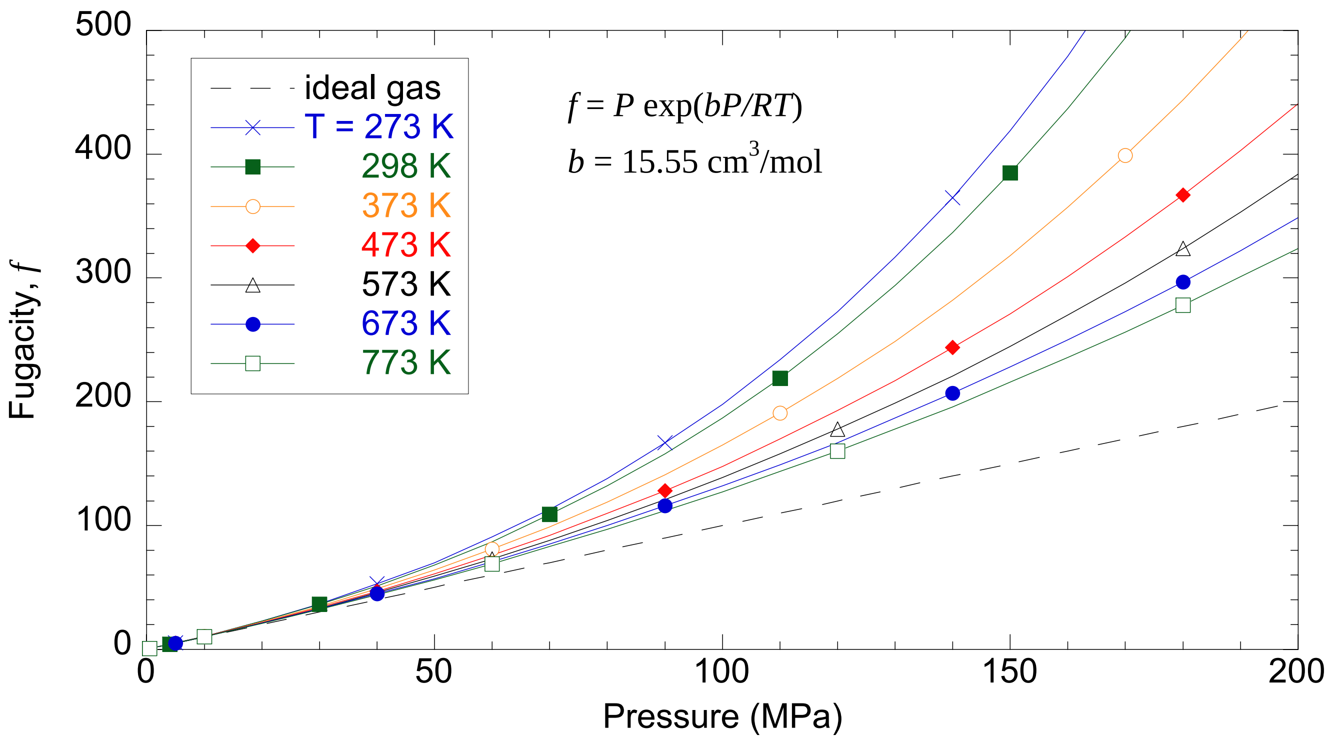
Fracture toughness tests with internal hydrogen





- Materials
  - Forged 22Cr-13Ni-5Mn and 21Cr-6Ni-9Mn stainless steels
  - Cold-worked 316 stainless steel
  - Cold-worked SAF 2507 duplex stainless steel
  - Stainless steel welds

Calculations involving high-pressure H_2 must consider fugacity



H concentration

$$\chi = K_o \exp\left(\frac{-\Delta H_s}{RT}\right) f^{1/2}$$

diffusional flux

$$J_\infty = \frac{\Phi_o \exp\left(\frac{-H_\Phi}{RT}\right)}{l} f^{1/2}$$

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Crack growth threshold tests in hydrogen gas

Quenched and tempered low-alloy steels

	Ni	Cr	Mo	C	Mn	Si	S	P
VM 4340	1.81	0.84	0.27	0.41	0.82	0.29	0.001	0.004
AM 4340	1.71	0.82	0.21	0.41	0.75	0.22	0.007	0.012
SA 372 Gr. J	-	0.96	0.18	0.48	0.92	0.30	0.002	0.010

Summary of tests

Material	σ_{YS} (MPa)	H_2 (MPa)	K_o (MPa$\sqrt{m}$)	K_{TH} (MPa$\sqrt{m}$)	Initiation time (hrs)
VM 4340	862	100	40-60	29-34	65
VM 4340	862	40	40-60	-	>500
VM 4340	600	100	50-75	-	>350
VM 4340	600	40	70-80	-	>500
AM 4340	828	100	40-60	-	>5000
AM 4340	828	130	40-60	35-37	1800
SA 372 Gr. J	718	80	35-105	-	>5000

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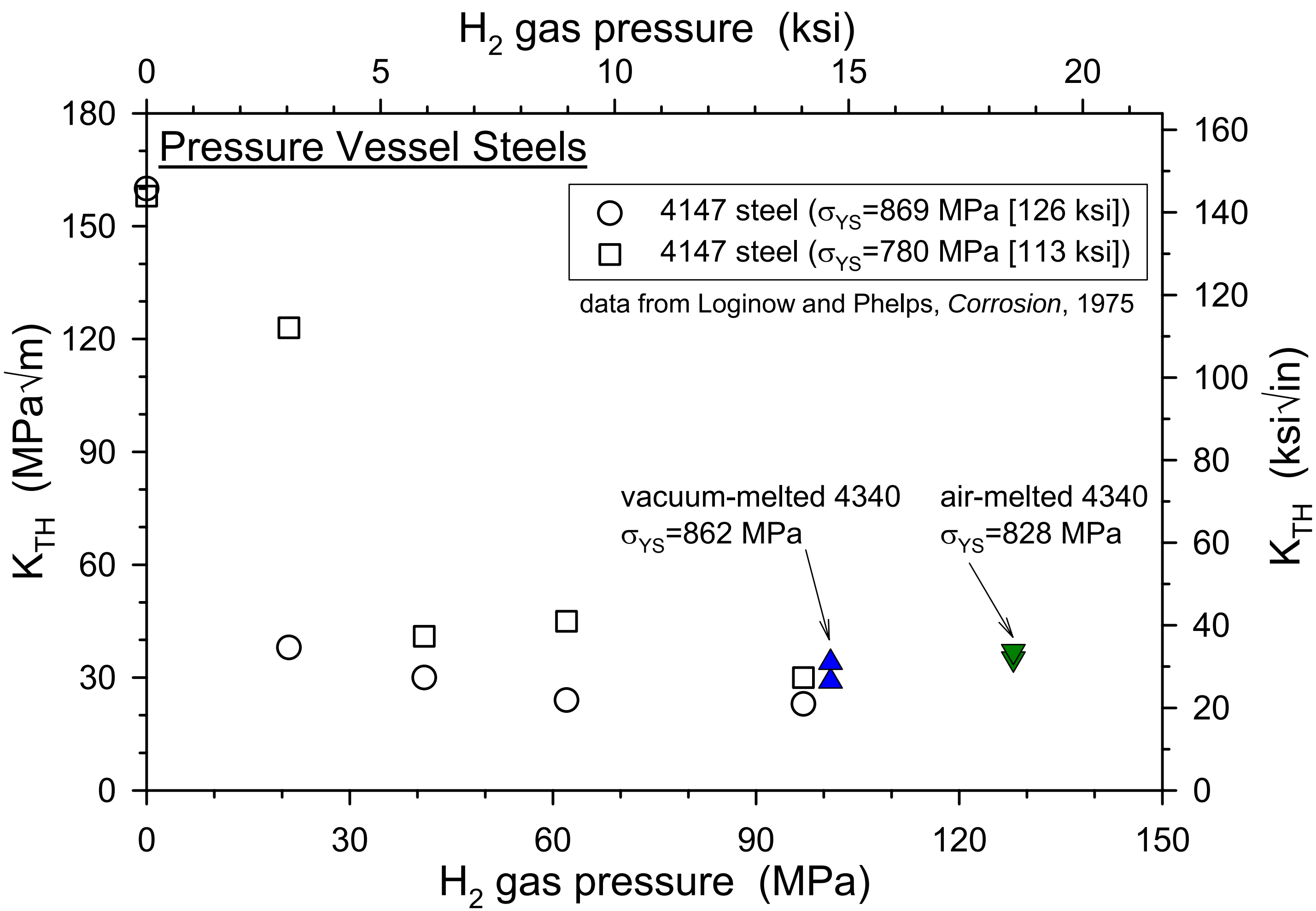
K_{TH} measurements for 4340 compared to literature data



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

Complications testing pressure vessel steels

- Time for initial crack extension in H_2 gas varies widely
  - 65 hrs for VM 4340 *vs* >5000 hrs for AM 4340 in same test vessel
  - H_2 gas purity important
    - W.T. Chandler and R.J. Walter, *ASTM STP 543*, 1974
  - surface oxides important
    - WOL and DCB specimens displacement loaded in air
  - Nelson, *ASTM STP 543*, 1974 $\rightarrow$ H_2 dissociation may govern crack extension in 4130 steel

- Long cracks complicate K_{TH} measurement in constant-displacement tests
  - $a/W \geq 0.8$ in VM 4340 WOL specimens

H_2 gas analysis in crack growth system

Gas sampling after H_2 flow through manifold

	O_2 (ppm)	H_2O (ppm)	N_2 (ppm)	CO (ppm)	CO_2 (ppm)	THC (ppm)
99.9999% H_2 spec.	<0.05	<0.5	<0.2	<0.01	<0.02	<0.01
manifold	0.2	<0.5	2	<0.1	<0.1	<0.1
manifold + mol. sieve	0.5	<0.5	2	<0.1	<0.1	<0.1

Gas sampling after H_2 flow through manifold + pressure vessel

	O_2 (ppm)	H_2O (ppm)	N_2 (ppm)	CO (ppm)	CO_2 (ppm)	THC (ppm)
99.9999% H_2 spec.	0.1	0.16	0.32	<0.02	<0.02	<0.01
manifold + vessel	0.3	2	2	<0.1	<0.1	0.8

Gas compositions from other laboratories

	O_2 (ppm)	H_2O (ppm)	N_2 (ppm)	CO (ppm)	CO_2 (ppm)	THC (ppm)
Loginow & Phelps	<5	50	1000	n/a	<10	n/a
Walter & Chandler	<0.2	~1	0.6-0.9	<0.5	<0.5	<0.5

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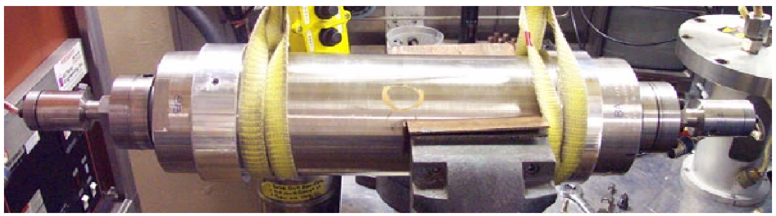
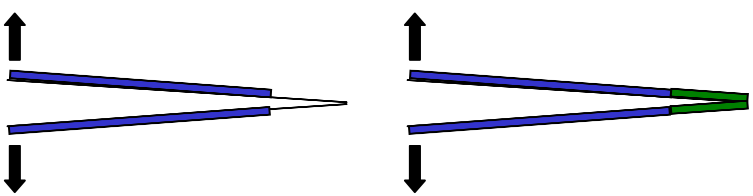
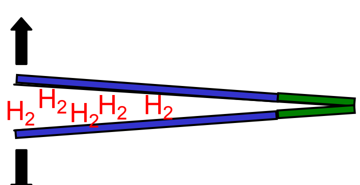
Preclude surface oxide effect with glovebox



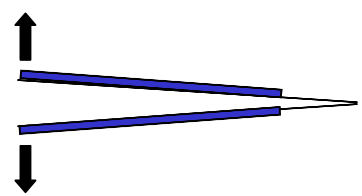
Loading crack in air



Exposure to hydrogen gas



Loading crack in glovebox



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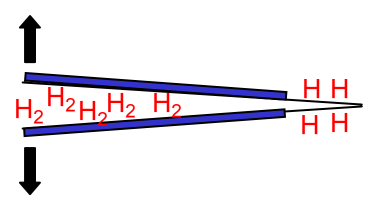
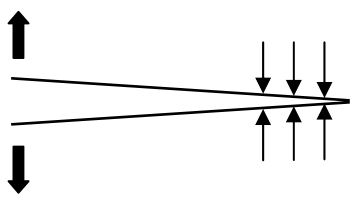


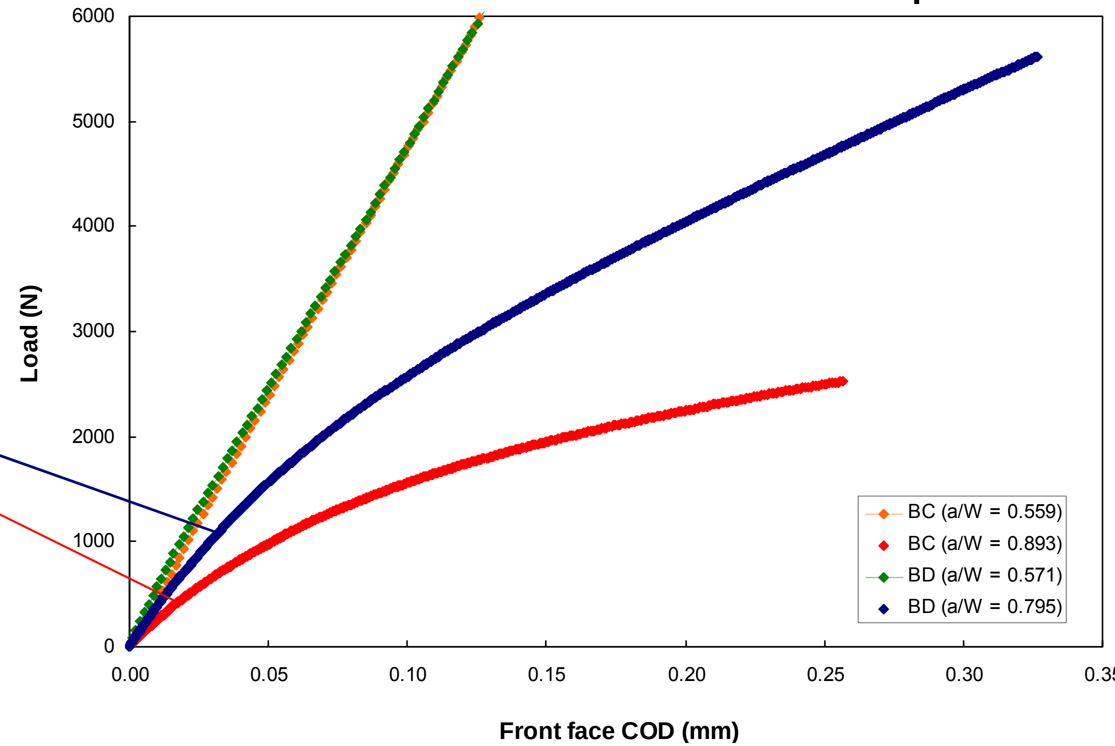
Long cracks result in elevated K_{TH} measurements

crack closure



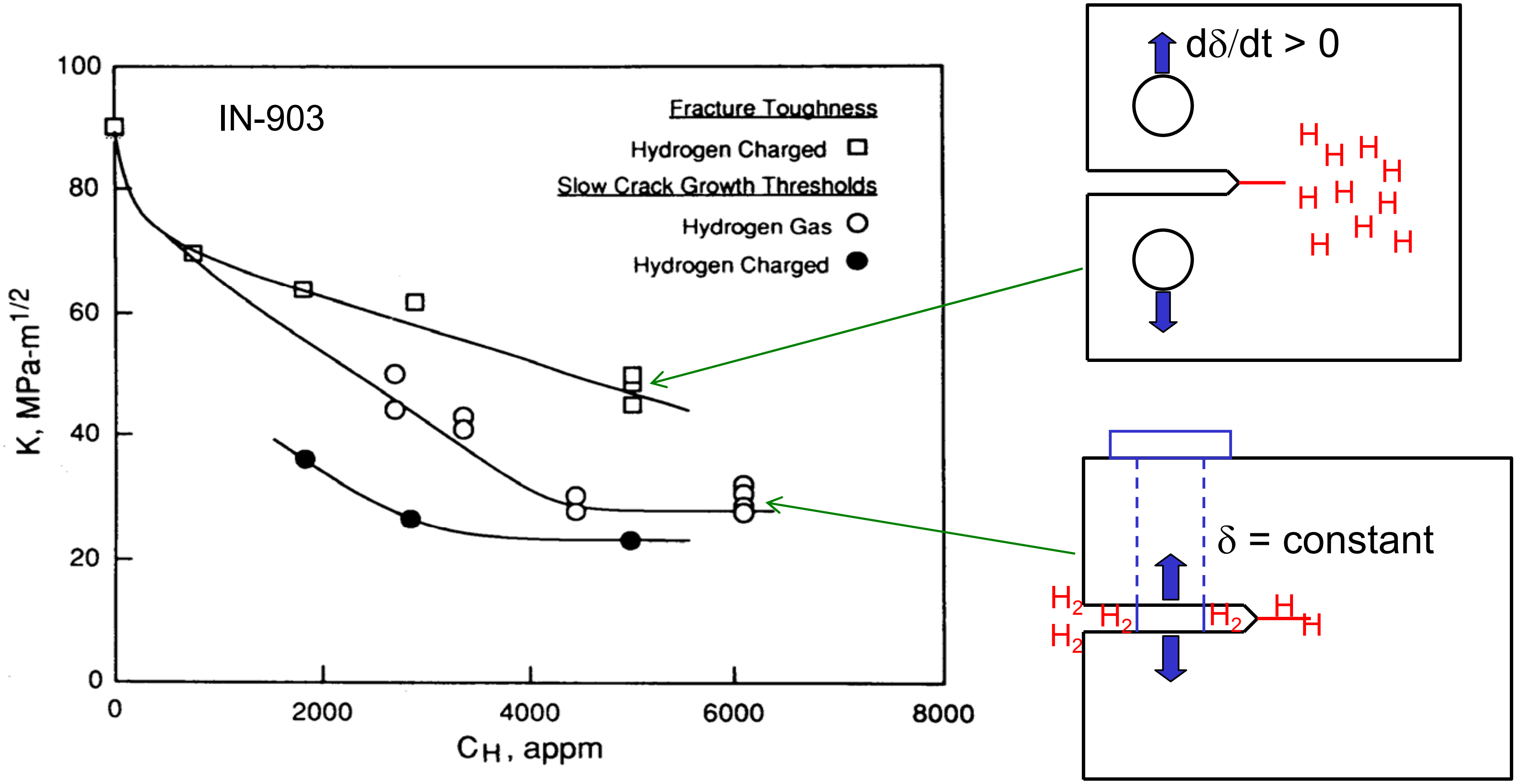
$$K_{TH} = K_{meas} + K_{cl}$$

Measured load vs. COD for WOL specimens



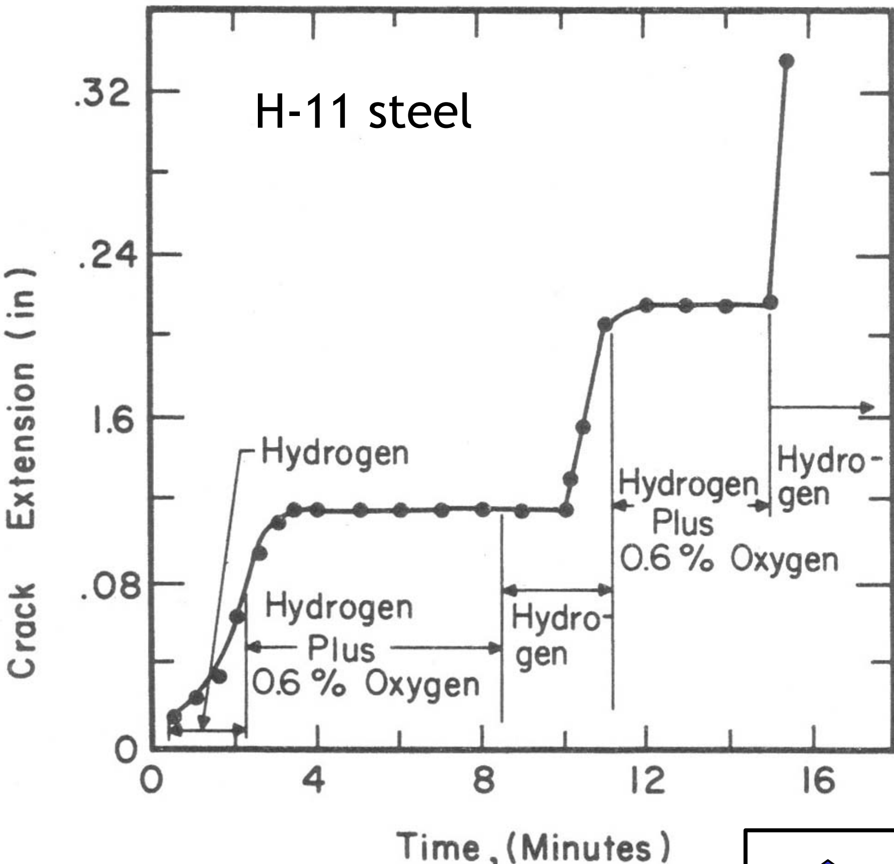
4340 specimen	Initial K (MPa√m)	K_{TH} (MPa√m) meas. load	K_{TH} (MPa√m) minus closure
VM (BC)	61	56	34
VM (BD)	43	46	29
AM (AC)	40	37	37
AM (AD)	62	47	35

H_2-assisted fracture depends on environment: hydrogen source

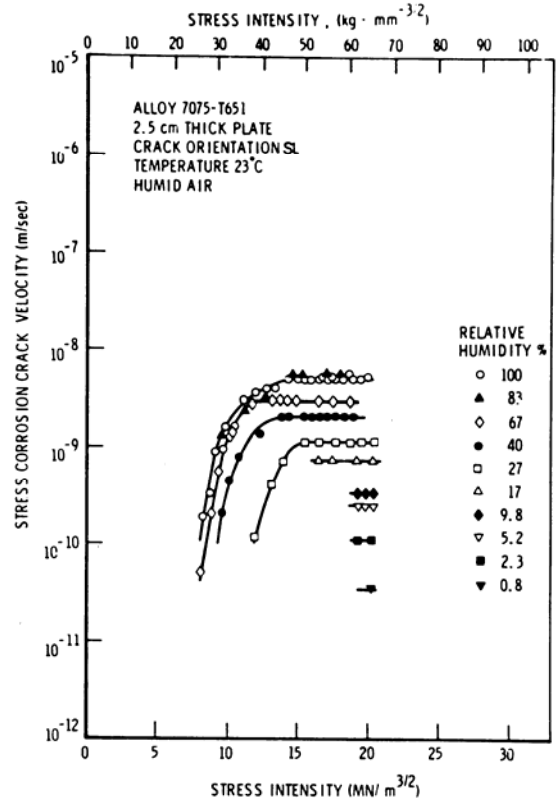


Data from: N.R. Moody et al., *Hydrogen Effects on Material Behavior*, 1990

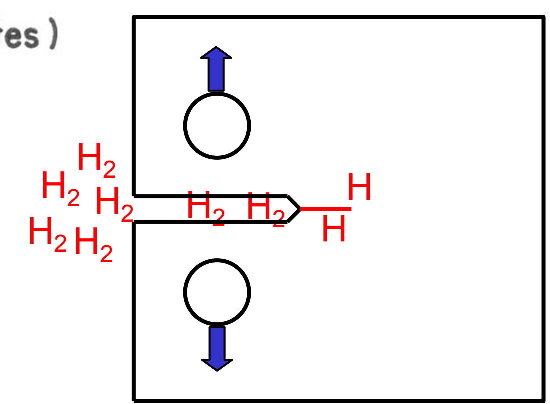
H_2-assisted fracture depends on environment: gas purity



Data from: H.H. Johnson, *Fundamental Aspects of Stress Corrosion Cracking*, 1967



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

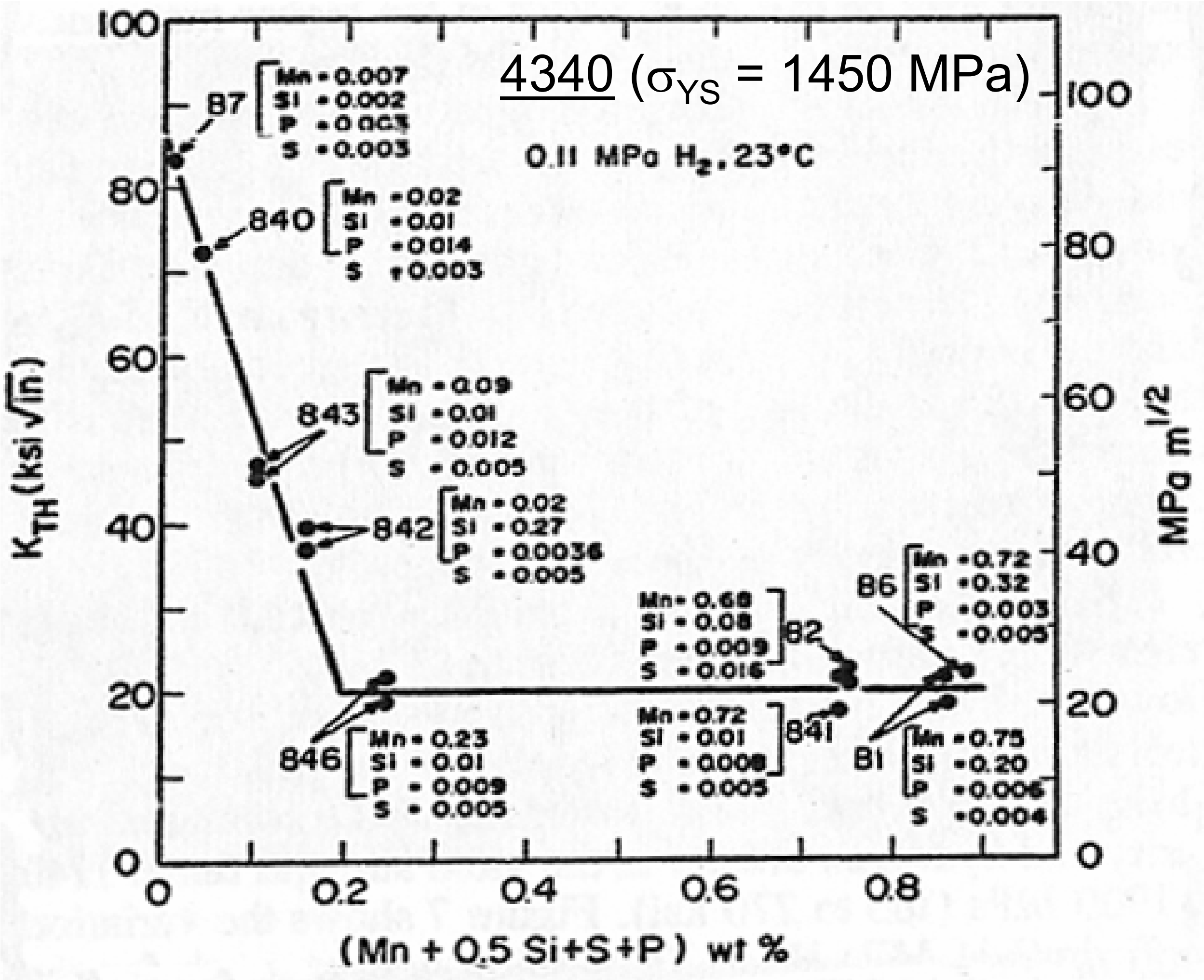


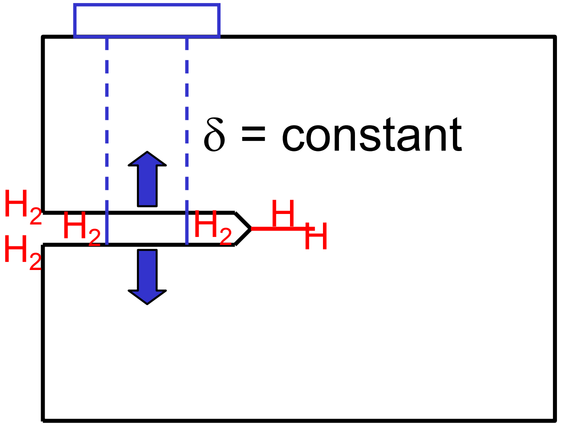
H_2-assisted fracture depends on environment: gas purity

- Impurities such as O_2 preferentially adsorb on clean metal surfaces → inhibits adsorption of H_2
  - limits H uptake at crack tip
- Effect of O_2 may depend on absolute partial pressure
  - effect of O_2 may be observed at lower concentrations for higher H_2 pressures
- Other impurities may have same effect as O_2
  - SO_2, CO, CS_2, CO_2

- Resource: *ASTM STP 543*, 1974

H_2-assisted fracture depends on material: composition





Data from: N. Bandyopadhyay et al., *Metallurgical Transactions A*, 1983

SUMMARY

- SNL can characterize hydrogen effects on materials using strength of materials and fracture mechanics approaches
  - thermal charging of test specimens using high-pressure H_2
  - static loading of test specimens in high-pressure H_2
- SNL has active programs testing materials in high-pressure H_2
  - pressure vessel steels and stainless steels
- Numerous variables impact hydrogen-assisted fracture of structural materials
  - environmental variables
  - material variables
  - mechanical variables