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Recent Advances in Codes and Standards for Materials Compatibility in High-Pressure Hydrogen Service

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Sandia National Laboratories

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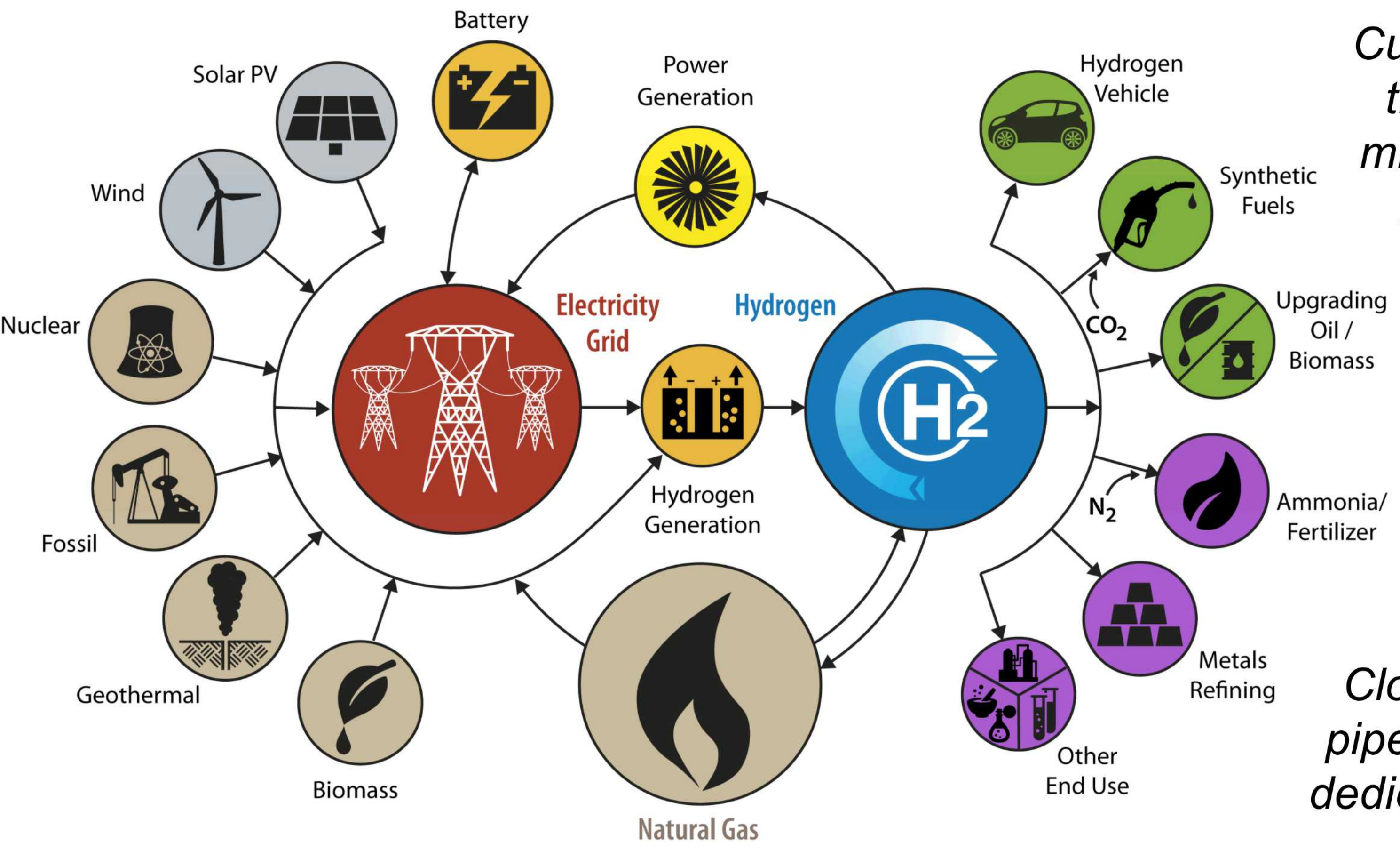
Outline

- Motivation: Hydrogen as an energy carrier
- Hydrogen embrittlement: what it is and why it's important
- SNL capabilities for hydrogen effects on materials
- Hydrogen-materials compatibility research and impact on codes and standards
  - Materials qualification for FCEVs – SAE J2579 Appendix B and GTR No. 13 Phase 2
  - Fatigue crack growth in pressure vessels – ASME BPVC VIII.3 KD-10
  - Fatigue crack growth in pipeline steels – ASME B31.12

Hydrogen can be used as an energy carrier to store and convey energy as well as to serve a wide range of industrial and transportation applications

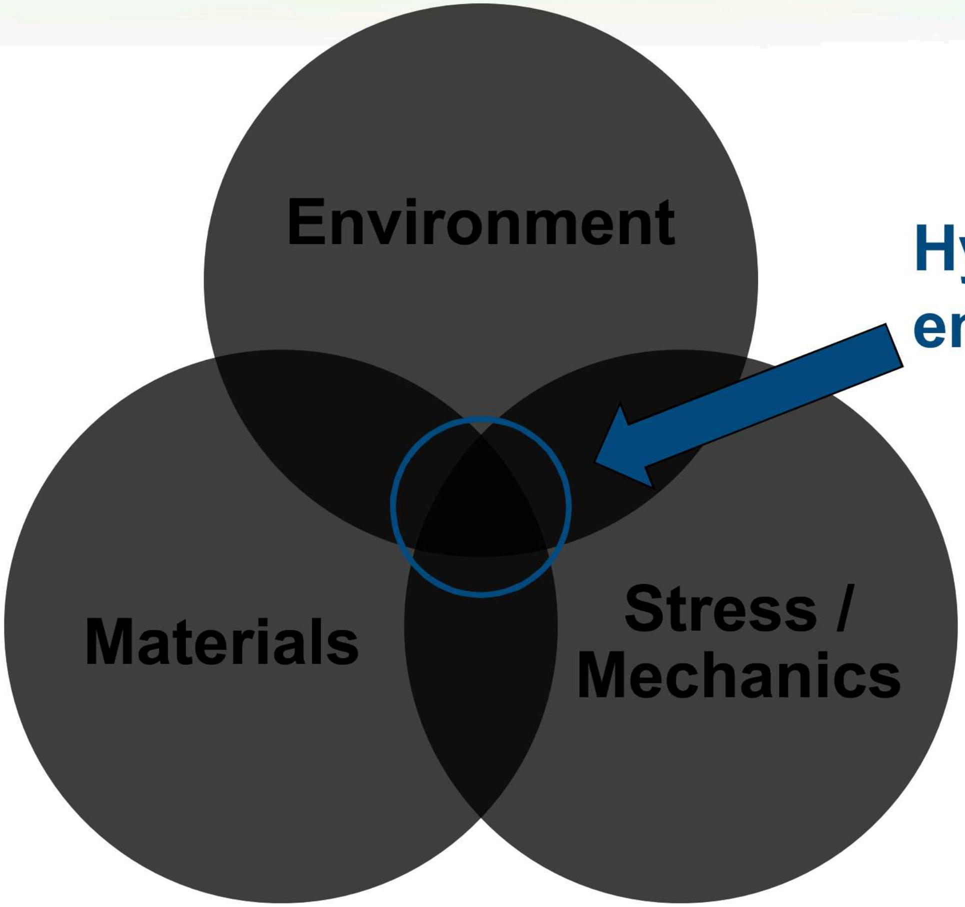


Current H2 usage in the US is about 10 million MT annually, mostly for refining and fertilizer production

Close to 1,000 km of pipeline in the US are dedicated to hydrogen conveyance

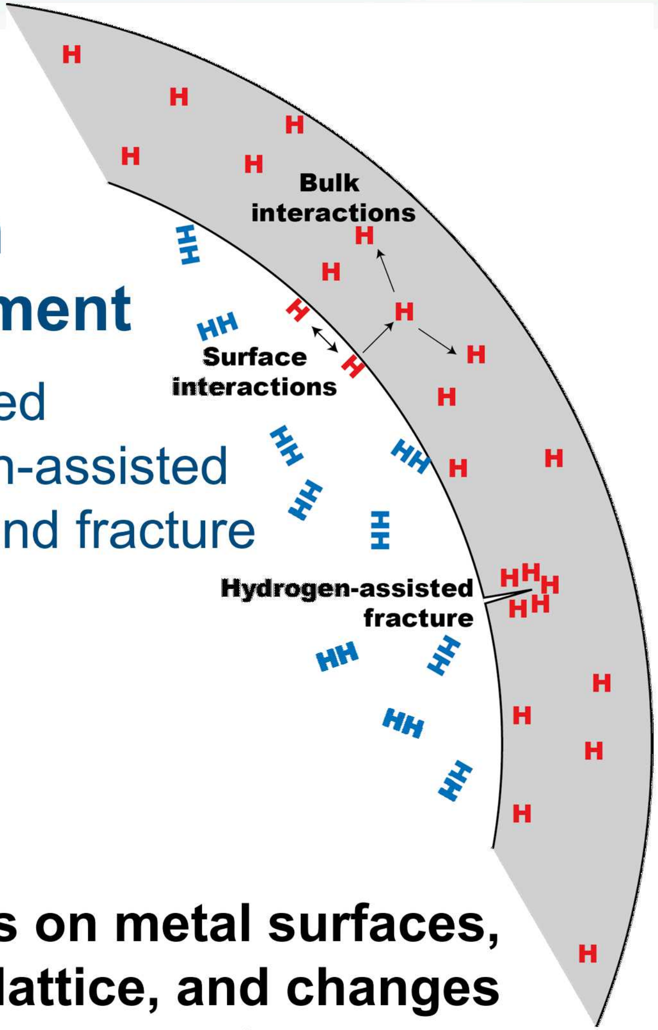
Illustrative example, not comprehensive; from H2@Scale Concept, developed by FCTO/DOE

Hydrogen embrittlement occurs in materials under the influence of stress in hydrogen environments



Hydrogen embrittlement

also called hydrogen-assisted fatigue and fracture

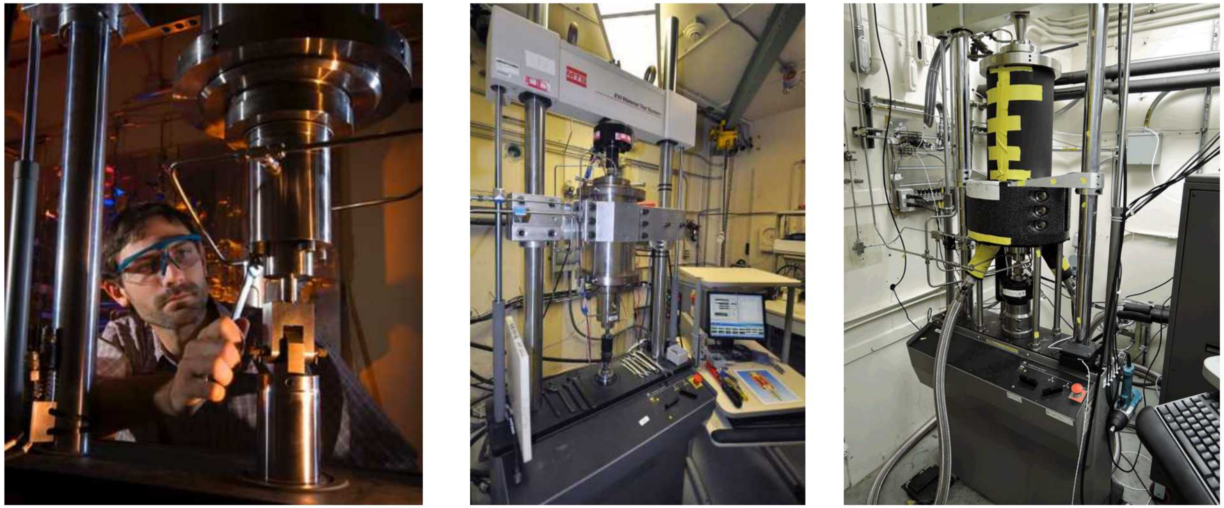


Hydrogen dissociates on metal surfaces, dissolves into the metal lattice, and changes the mechanical response of the metal

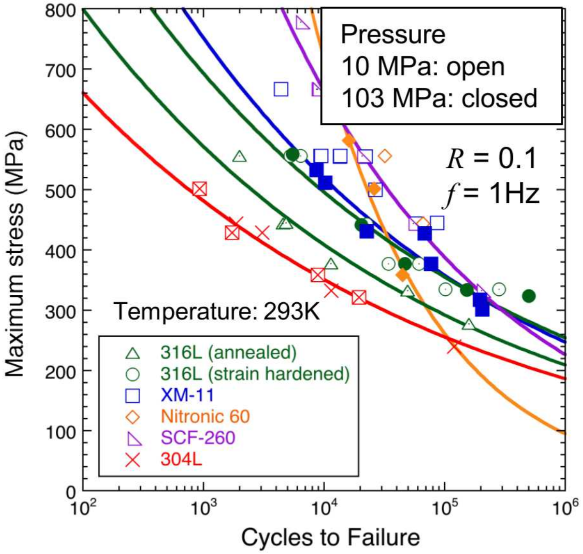
Hydrogen Effects on Materials Laboratory

This laboratory is a core capability for the U.S. Department of Energy and houses specialized equipment for evaluating materials performance in high-pressure gaseous hydrogen.

- **Fracture and fatigue testing in high-pressure gaseous hydrogen** – Tensile, fracture and fatigue test configurations with concurrent gaseous hydrogen exposure at pressure up to 140 MPa (20 ksi).
- **High-pressure fracture and fatigue testing at temperature** – Tensile, fracture and fatigue configurations loaded at controlled (constant) temperature in the range of 220K to 450K concurrent with gaseous hydrogen exposure at pressure up to 140 MPa (20 ksi).



Fatigue life



B.P. Somerday *et al*, *International Journal of Hydrogen Energy* (2017)

Hydrogen Effects on Materials Laboratory

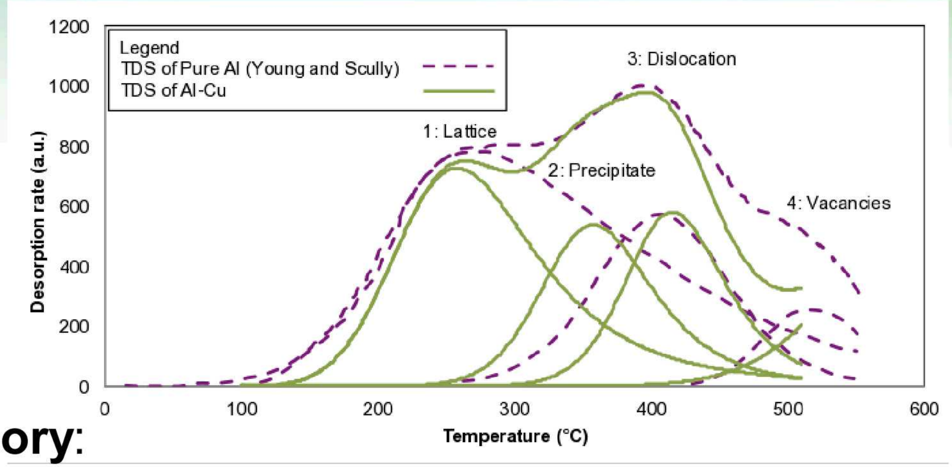
- **Constant-displacement, environmentally-assisted crack growth testing** – Instrumented fracture mechanics specimens are loaded to constant displacement and exposed to gaseous hydrogen at pressure up to 200 MPa (29 ksi). The temperature can be independently controlled (usually constant) in the range of 200K to 440K. Subcritical cracking threshold and crack velocity can be measured.

- **Thermal precharging** – Test specimens are exposed to high-pressure gaseous hydrogen or deuterium (up to 140 MPa) at elevated temperature (up to 573K) to produce controlled hydrogen content within the specimens prior to evaluation.

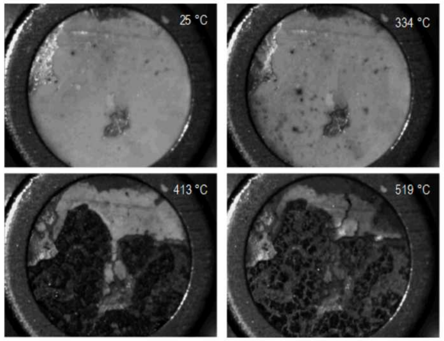
- **Pressure cycling in controlled temperature** – Exposure of metals and non-metals (polymers) to pressure cycles up to 100 MPa (14.5 ksi) at controlled (constant) temperature within the range 220K and 400K.

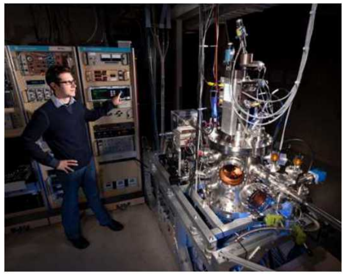
Other capabilities for hydrogen & materials research

Hydrogen Transport and Trapping Laboratory: Capabilities for measuring transport (or diffusion) of hydrogen in materials, including: gas-phase permeation, thermal desorption spectroscopy (TDS) and local-electrode atom probe (LEAP) tomography.

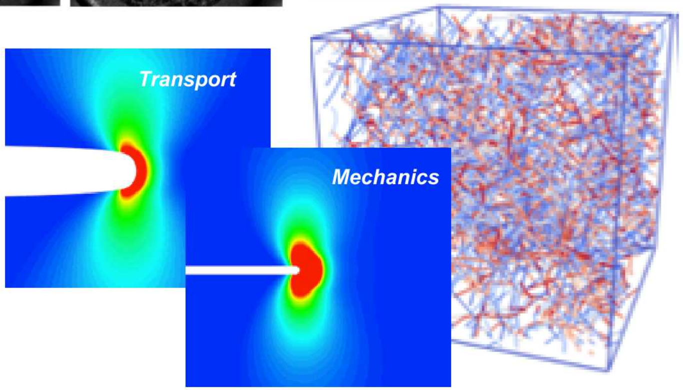


Hydrogen Surface-Interactions Laboratory: Capabilities for measuring adsorption and desorption of hydrogen at a material's surface, including: angle-resolved ion energy spectrometry (ARIES), ambient pressure x-ray photoelectron spectroscopy (AP-XPS), low-energy electron microscopy (LEEM) and scanning transmission x-ray microscopy (STXM).





Computational Materials Science: Atomic-through-continuum models used to identify the mechanisms that govern hydrogen-assisted fatigue and fracture, diffusion and transport of hydrogen within materials, and the evolution of microstructural features that can trap hydrogen (e.g. dislocations, grain boundaries).



Materials qualification for fuel cell electric vehicles

Establish materials compatibility for high-pressure hydrogen service in context of hydrogen fuel cell electric vehicles

- SAE Fuel Cell Safety Task Force
  - Tasked with developing standards for fuel cell vehicles in context of safety, including J2579 – *Standard for Fuel Systems in Fuel Cell and Other Hydrogen Vehicles*, which includes requirements for materials in contact with high-pressure gaseous hydrogen
  - Meets quarterly with broad representation from automotive OEMs
- SAE H2 Compatibility Expert Team
  - Representation from nationally funded research programs: MPA Stuttgart (Germany), Kyushu University (Japan), AIST (Japan) and Sandia National Laboratories (USA)
  - Collective learning through “round robin” testing campaign – Development and demonstration of test methodologies to execute fatigue tests in high-pressure hydrogen at low temperature

Collective learning activity (”round robin”)

Test	Test conditions	Environment	Number of tests
Slow strain rate tension (SSRT)	≤5 x10^{-5} s^{-1}	Control -40˚C	3
		90 MPa H2 -40˚C	3
Notched tension-tension fatigue	Sa = 200 MPa R = 0.1 1 Hz	Control -40˚C	3
		90 MPa H2 -40˚C	3
Smooth tension-compression fatigue	Sa = 320 MPa R = -1 1 Hz	Control -40˚C	3
		90 MPa H2 -40˚C	3

Test method for hydrogen compatibility of materials

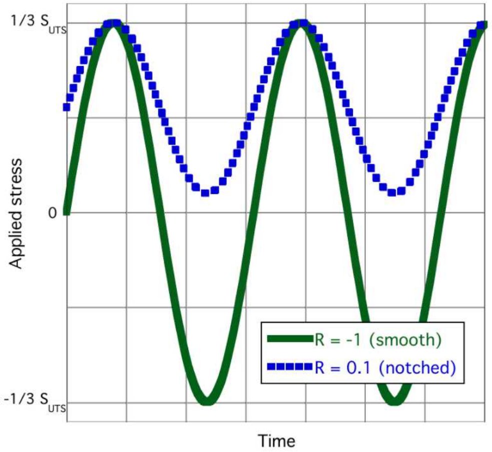
SAE J2579, Appendix B.3 is essentially a generic test method for evaluation of structural metals for service in high-pressure gaseous hydrogen

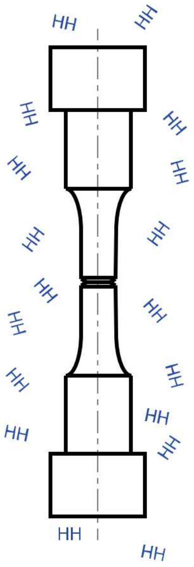
- Part 1: Definition of materials and environmental test conditions
  - Composition, Test properties: specified minimum Sy, Su, El
  - Pressure ≥ 1.25 NWP, Temperature = 228K
  - Gas purity according to CSA CHMC1 (2 ppm O_2, 10 ppm H_2O)
- Part 2: SSRT
  - Minimum of three (3) tests
  - Average property values > specified minimum Sy and Su values
  - Average elongation (El) > 12%
  - Additionally, Su/Sy > 1.07
- Part 3: Fatigue life test (next slide)
- Part 4: Welds
  - Same testing requirements as for non-welded materials

In general, CSA CHMC1 is referenced for the test methods (CHMC1 references ASTM standards)

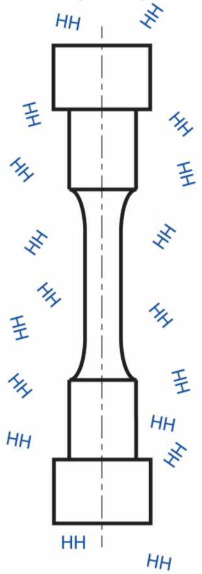
Fatigue life test

- Force-controlled (axially loaded cylindrical) fatigue test in the defined hydrogen environment
  - Frequency of 1 Hz, Maximum stress shall be 1/3 of measured Su (air)
- Minimum of three (3) tests
- Two test configuration options
  - Option 1: smooth test specimen with R = -1, or
  - Option 2: notched test specimen with R = 0.1





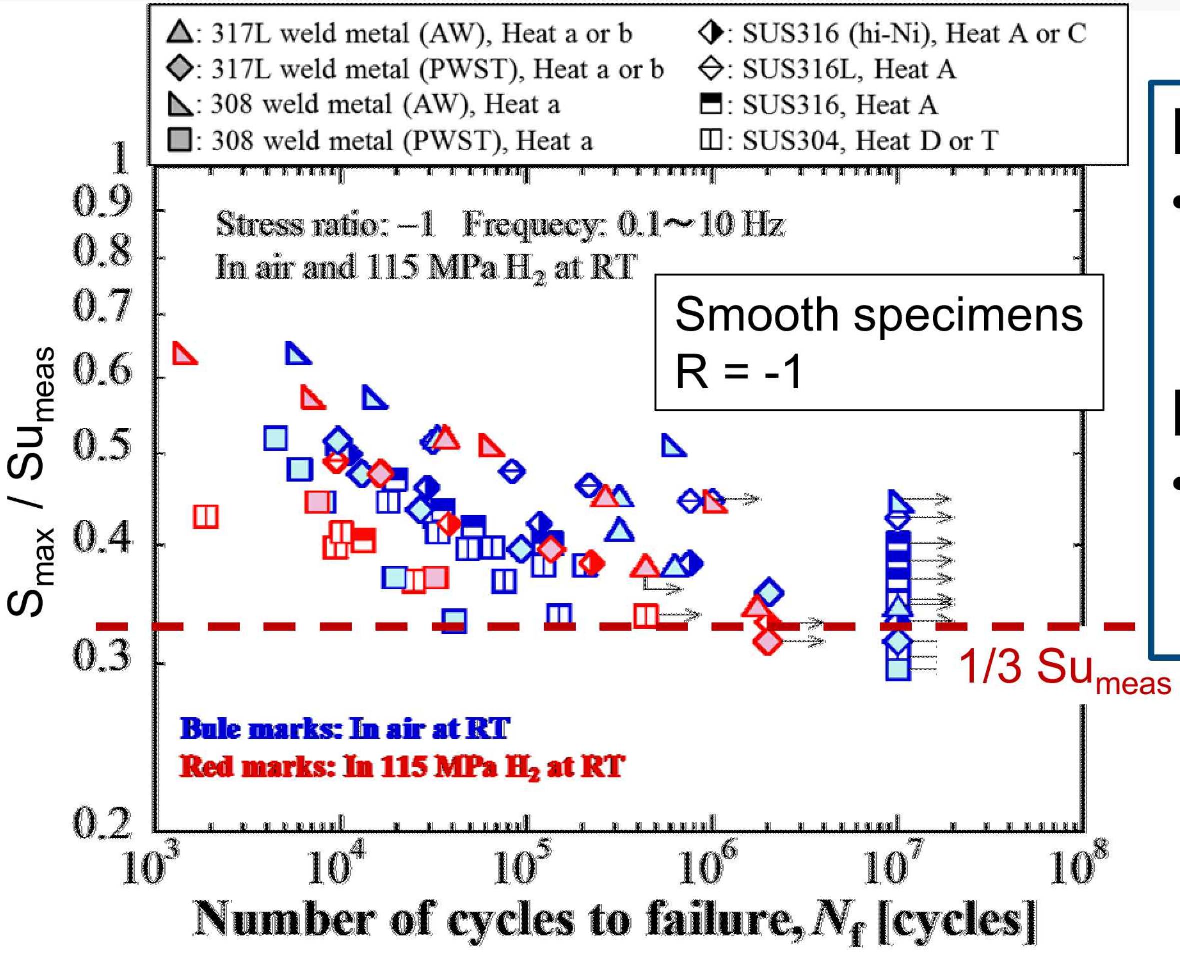
notched tension tension



smooth tension compression

- Cycles to failure >200,000 cycles for each test, or >100,000 cycles for each of 5 notched test specimens

Fatigue life of smooth specimens is typically infinite at stress of 1/3 Su_{meas}



Requirement:

- N_f > 200,000 cycles at S_{max} = 1/3 Su_{meas}

Rationale:

- Ensure fatigue life at high stress is >> than design life

Data from: M. Nakamura et al., M&M2017 conference, 7-9 October 2017, Hokkaido, Japan

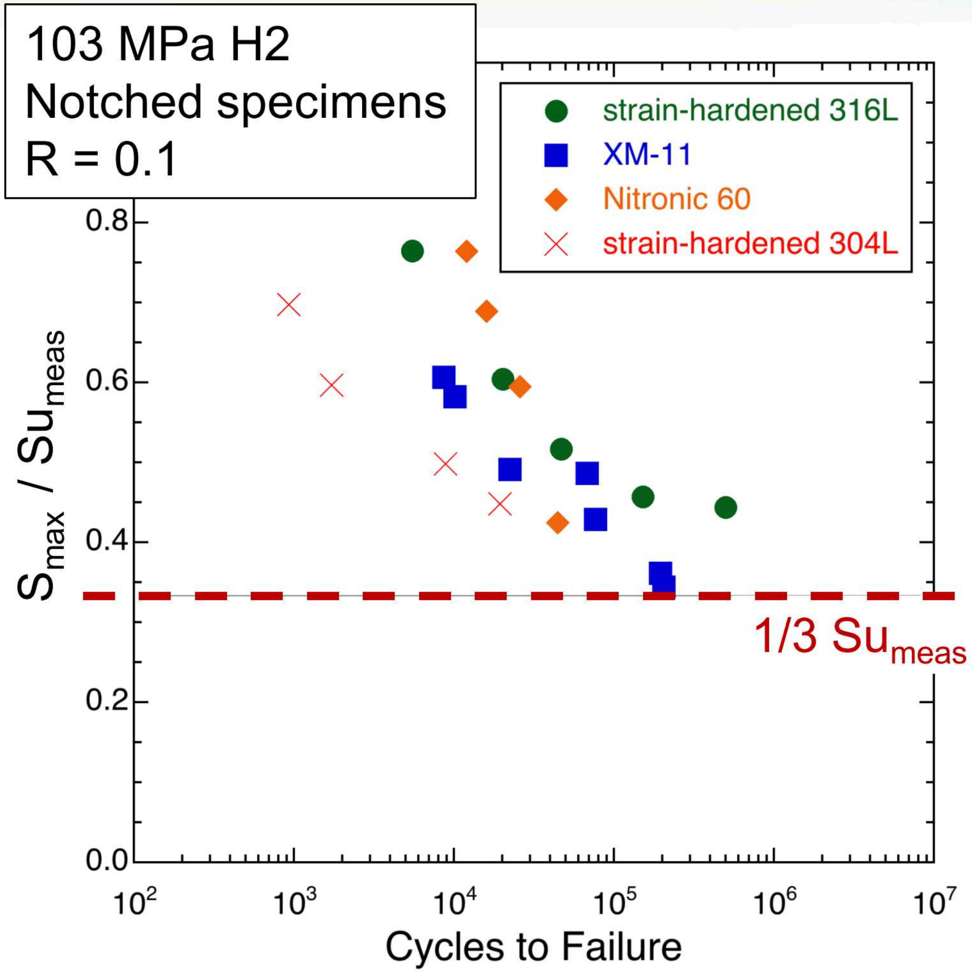
Diverse range of austenitic stainless steels have been evaluated, including high-strength alloys

material	Yield (MPa)	Tensile (MPa)	Cr	Ni	Mn	N	Typical allowable stress (MPa)
316L	280	562	17.5	12	1.2	0.04	115
CW 316L	573	731	17.5	12	1.2	0.04	218
304L	497	721	18.3	8.2	1.8	0.56	195
XM-11	539	881	20.4	6.2	9.6	0.26	207
Nitronic 60	880	1018	16.6	8.3	8.0	0.16	218
SCF-260	1083	1175	19.1	3.3	17.4	0.64	333

Wide range of strength

Wide range of Ni/Mn content

Notched specimens assess sensitivity to stress concentration for typical maximum stress (1/3Su)



Requirement:

- Nf > 100,000 cycles at S_{max} = 1/3 Su_{meas}

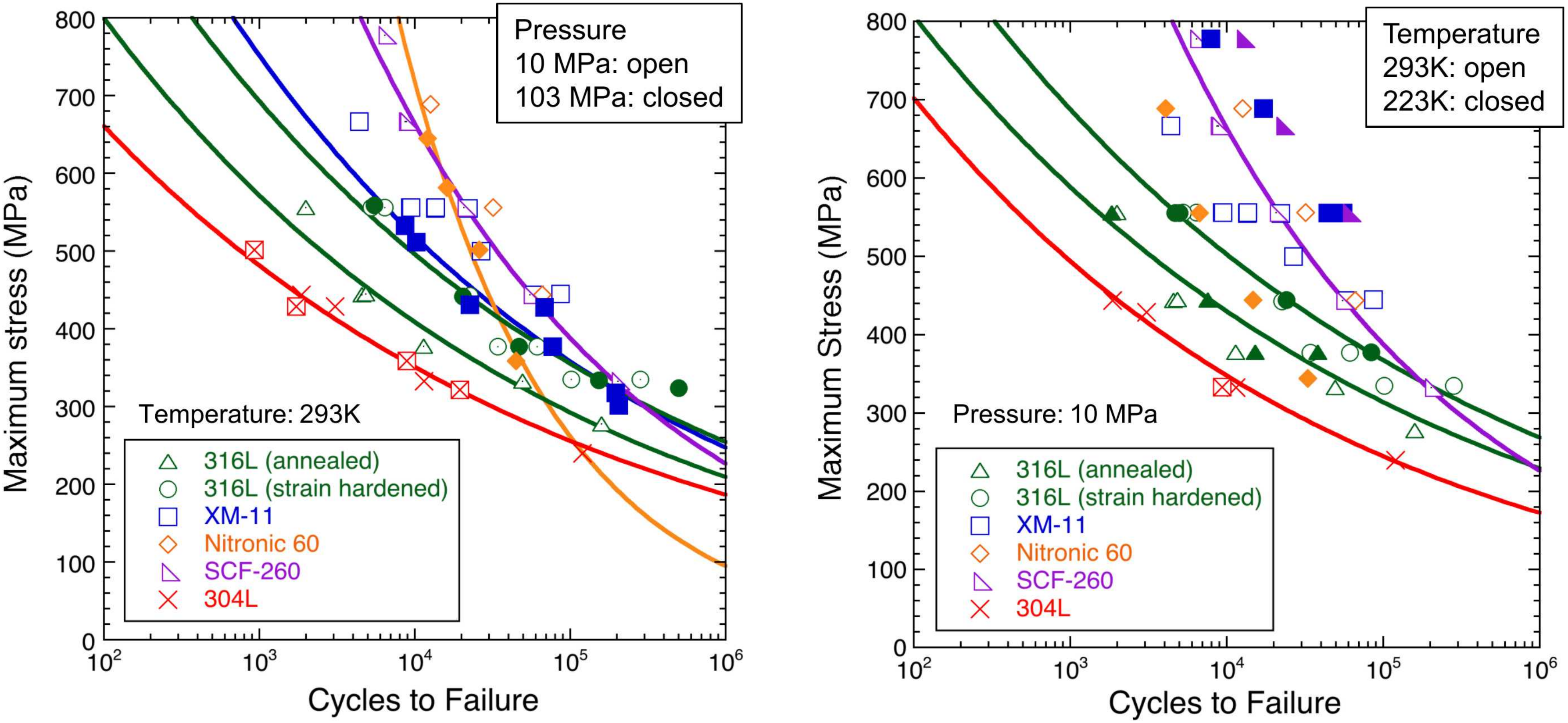
Rationale:

- Ensure fatigue life at high stress is >> than design life

Data from: C. San Marchi et al., 43rd MPA Seminar, 11-12 October 2017, Stuttgart, Germany

Fatigue life at low temperature appears to be greater than at room temperature

R = 0.1, *f* = 1Hz



- Pressure has modest effect, if any, on fatigue life
- Temperature has either no effect or increases fatigue life
- Nitronic 60 is an exception for both pressure and temperature

Resolved issues

- Proposal to have SSRT and fatigue testing at different test pressures
  - Pressure effect is small between 1.25 and 1.5 NWP, when NWP is large.
  - For simplicity and consistency, experts agreed to keep the same pressure for both test methods: test pressure = 1.25 NWP
- Verification of gas purity
  - Confirmation of purity of test gas is essential
  - Gas purity shall be verified at least every 12 months
- Multiple options for fatigue life testing
  - Accept both smooth and notched specimens for screening of hydrogen sensitivity

Open questions

- Use absolute properties or relative response for SSRT evaluation
  - Proposed compromise to include both relative and absolute requirements:
    - Yield strength > Sy ; Tensile strength > Su
    - Yield strength > 0.80 YS(T) – new relative requirement
    - Tensile/yield > 1.07 ; Elongation > 12%
- Temperature for fatigue life testing
  - Most data suggest that austenitic stainless steels show longer fatigue life at low temperature: Fatigue test at room temperature only?
- Welding
  - Additional requirements?
- Additional testing requirements for aluminum alloys
  - Stress corrosion cracking (SCC) threshold
  - Test method and evaluation criteria for SCC being formulated by High-Pressure Institute of Japan HPIS E 103:2018
    - Method seems equivalent to ISO 7539-6
    - Criteria should be incorporated in SAE J2579
- How to incorporate “new” materials into SAE J2579
  - Replace table B.2 and periodically update with tested materials?

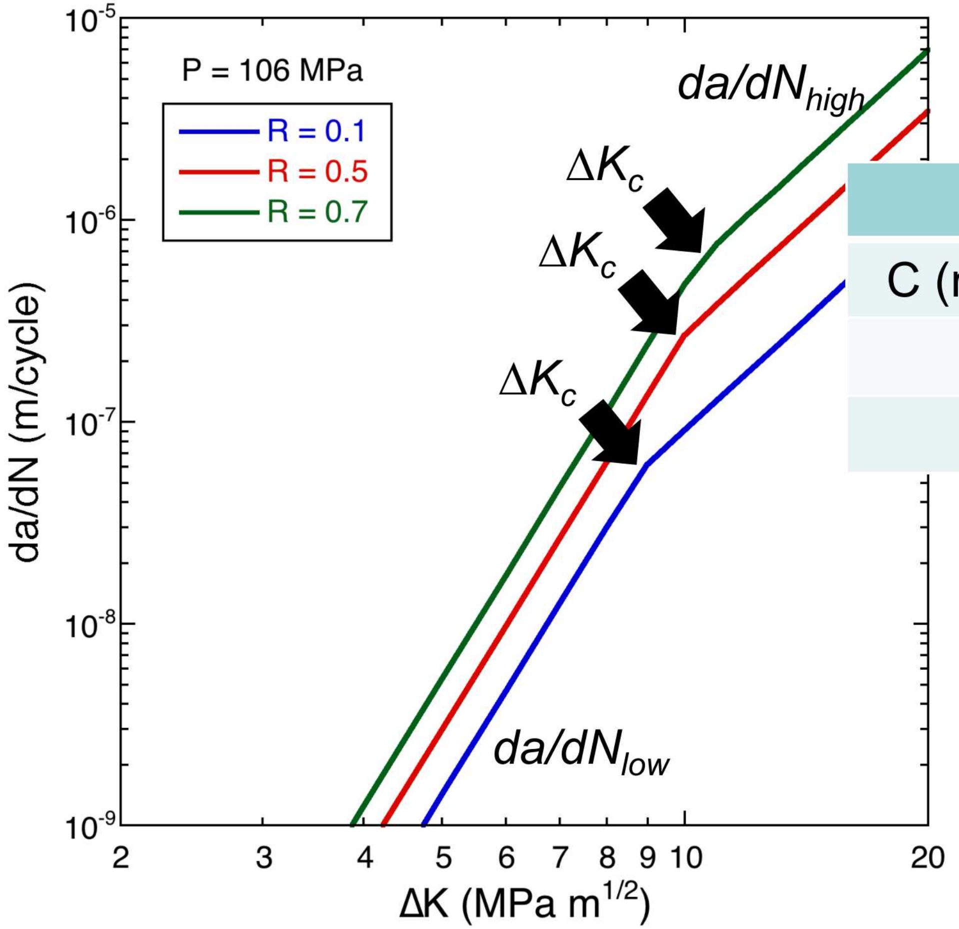
Fatigue crack growth in pressure vessel steels

(testing at SNL in gaseous hydrogen at pressure of ≥103 MPa (15 ksi))

Designation	Tensile strength (MPa)	Yield Strength (MPa)
Cr-Mo steels		
SA-372 Grade J (A71)	839	642
SA-372 Grade J (B50)	871	731
SA-372 Grade J (A72)	908	784
SA-372 Grade J (AV60Z)	890	760
34CrMo4	1045	850
Ni-Cr-Mo steels		
SA-372 Grade L	1149	1053
SA-372 Grade L-LS †	873 †	731 †
SA-723 Grade 1 – Class 1	860	715
SA-723 Grade 3 – Class 2	978	888

† Does not meet SA-372 (low strength)

Formulation of power law relationship for fatigue crack growth



$$\frac{da}{dN} = C\left[\frac{1 + C_H R}{1 - R}\right]\Delta K^m$$

	da/dN_{low}	da/dN_{high}
C (m/cycle)	3.5×10^{-14}	1.5×10^{-11}
m	6.5	3.66
C_H	0.4286	2.00

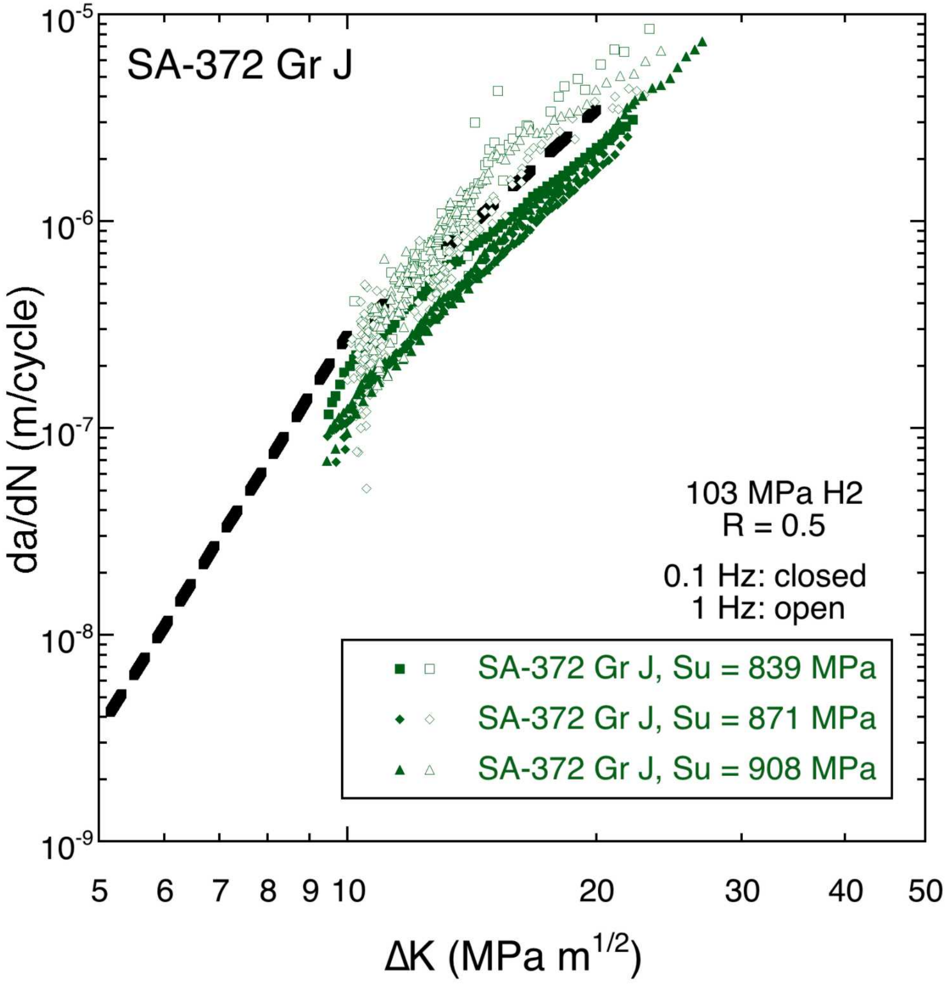
$$\Delta K < \Delta K_c: \quad da/dN = da/dN_{low}$$

$$\Delta K \geq \Delta K_c: \quad da/dN = da/dN_{high}$$

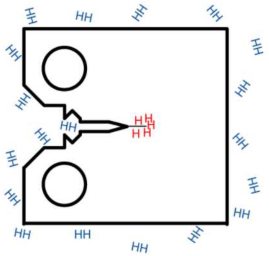
$$\Delta K_c = 8.475 + 4.062R - 1.696R^2$$

ΔK, ΔK_c units: MPa $m^{1/2}$

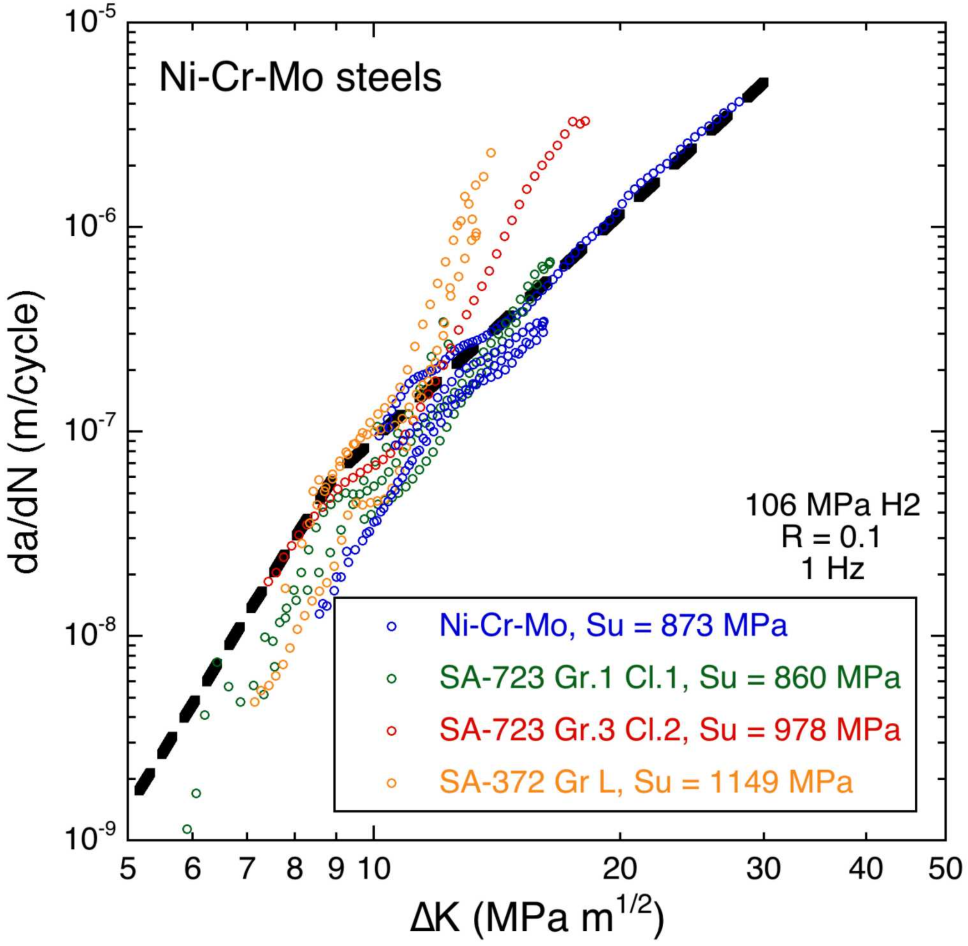
Fatigue crack growth rates of SA-372 Grade J R=0.5



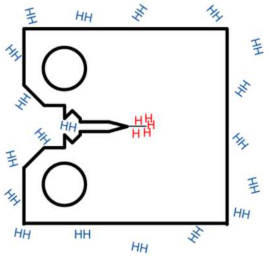
- Gaseous hydrogen at pressure of 103 MPa
- R = 0.5
- 0.1 Hz data from PVP2013-97455
- 1 Hz data from ICHS 2009



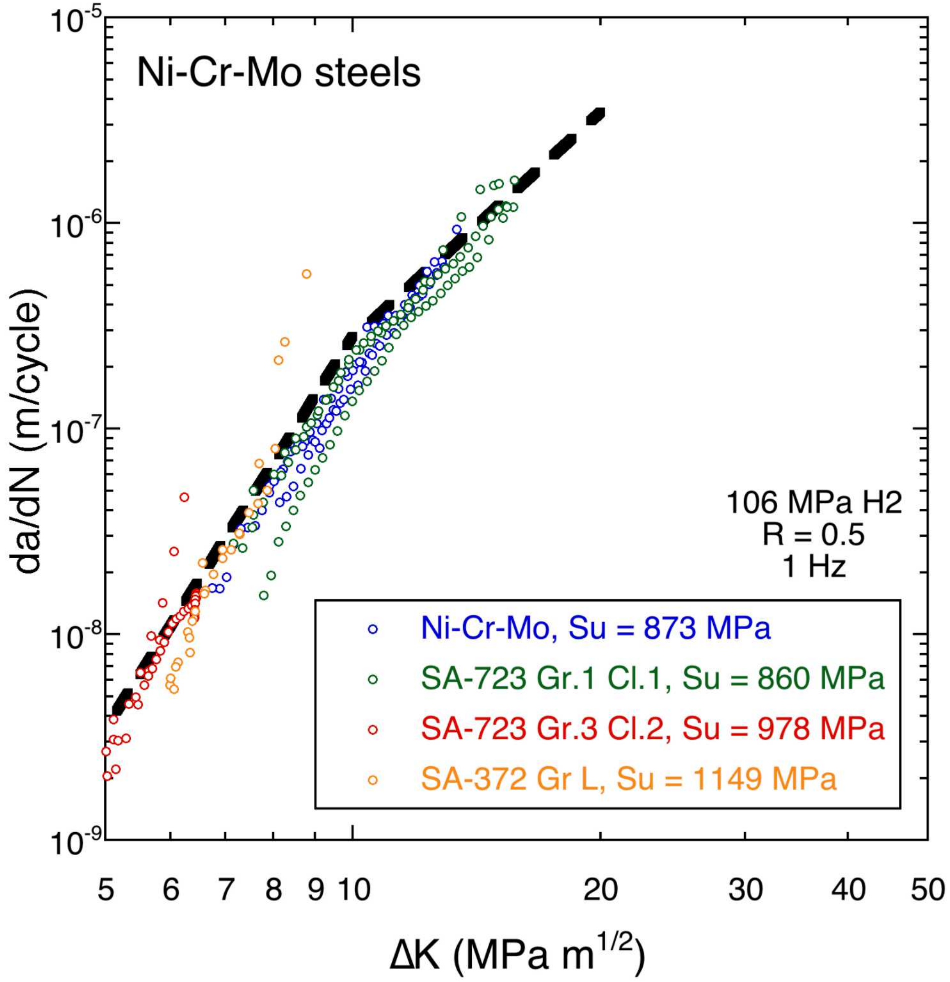
Fatigue crack growth rates of Ni-Cr-Mo steels R=0.1



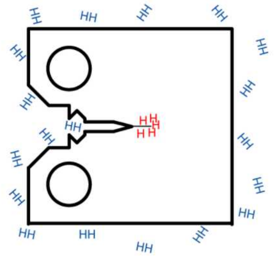
- Gaseous hydrogen at pressure of 106 MPa
- R = 0.1
- Frequency of 1 Hz
- Data from ICHS 2017



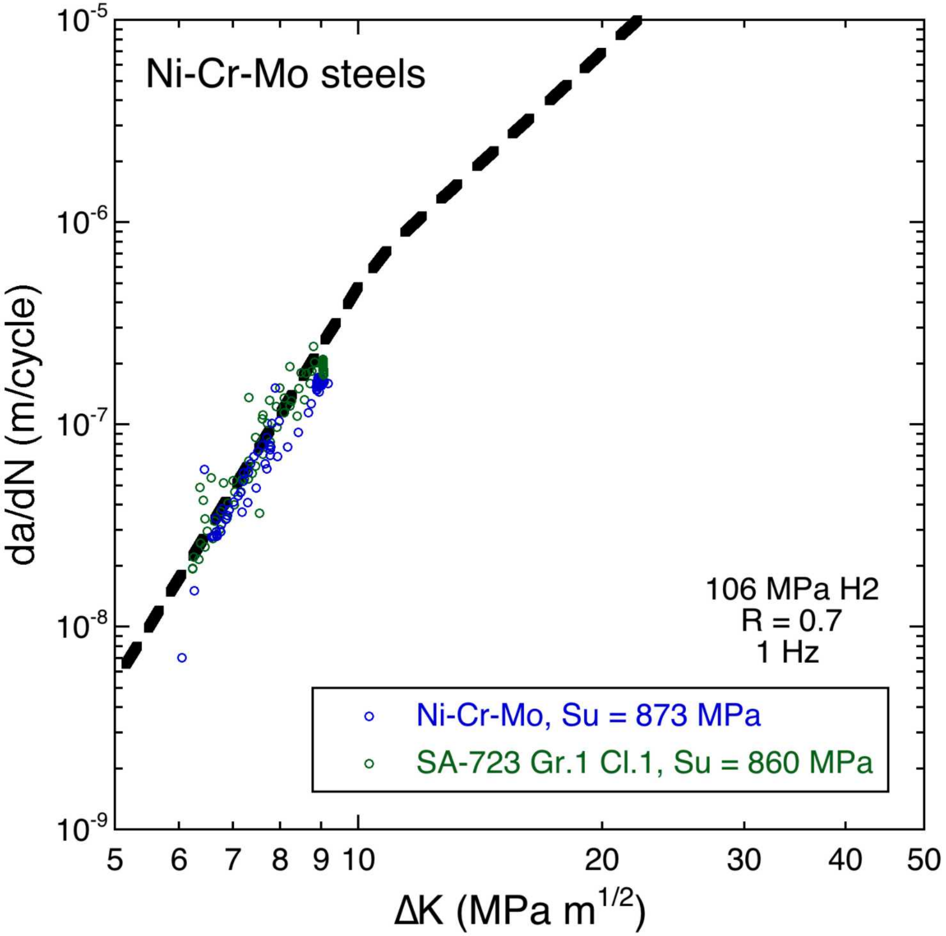
Fatigue crack growth rates of Ni-Cr-Mo steels R=0.5



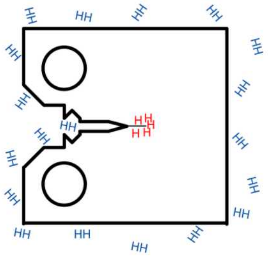
- Gaseous hydrogen at pressure of 106 MPa
- R = 0.5
- Frequency of 1 Hz
- Data from ICHS 2017



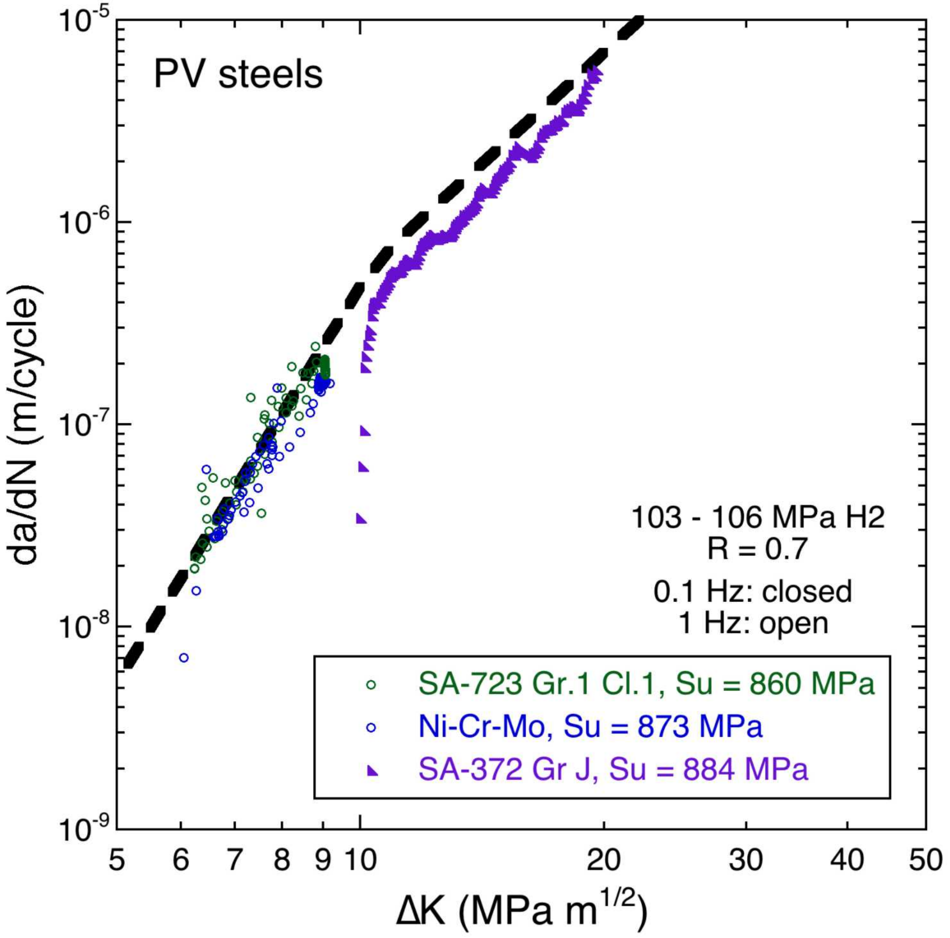
Fatigue crack growth rates of Ni-Cr-Mo steels R=0.7



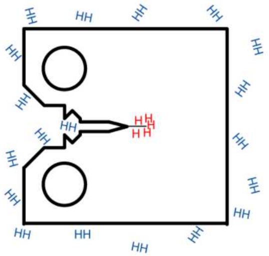
- Gaseous hydrogen at pressure of 106 MPa
- R = 0.7
- Frequency of 1 Hz
- Data from ICHS 2017



Fatigue crack growth rates at R = 0.7 both Cr-Mo and Ni-Cr-Mo PV steels

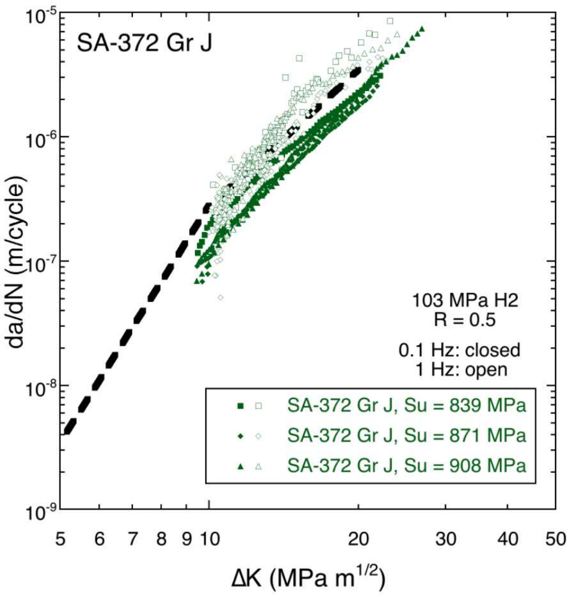


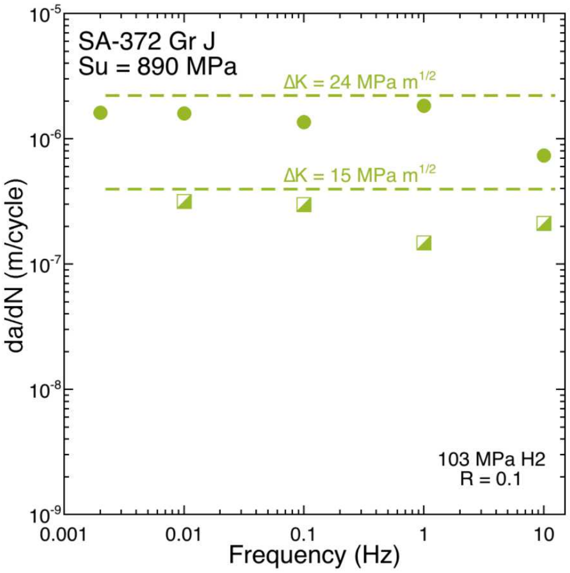
- Gaseous hydrogen
- R = 0.7
- Cr-Mo steel data (0.1 Hz) from NIST (unpublished?)
  - P = 103 MPa
- Ni-Cr-Mo steel data (1 Hz) from ICHS 2017
  - P = 106 MPa

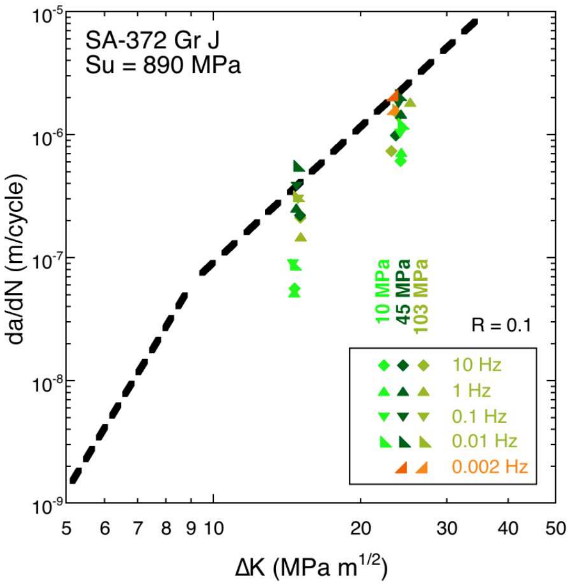


Test frequency

- Frequency in range of ≤ 1 Hz has little, if any, effect on measured fatigue crack growth rates
  - Difference in measured rates with frequency (≤ 1 Hz) is consistent with specimen to specimen variability
  - Dashed lines represent proposed power law relationship

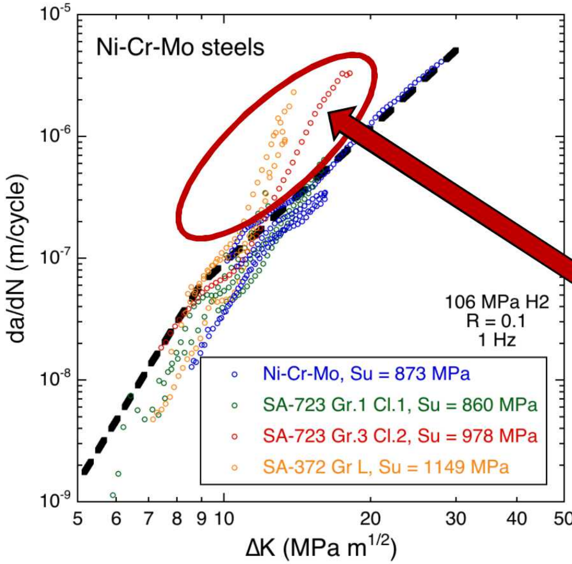






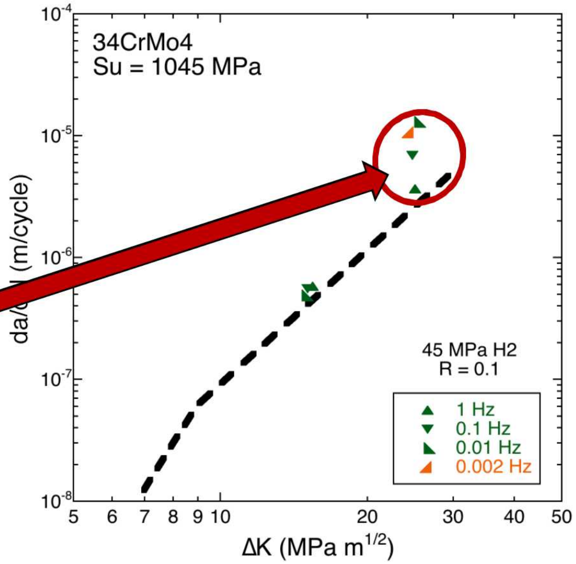
Basis for limiting strength

- High-strength steels show transition to accelerated crack growth related to baseline behavior (*eg*, stage III)
  - only observed in tests of high-strength steels: tensile strength > 950 MPa
  - Related to fracture resistance: as K_{max} approaches K_{JH} (where K_{JH} is measured as J_{IC} from ASTM E1820 in gaseous hydrogen)

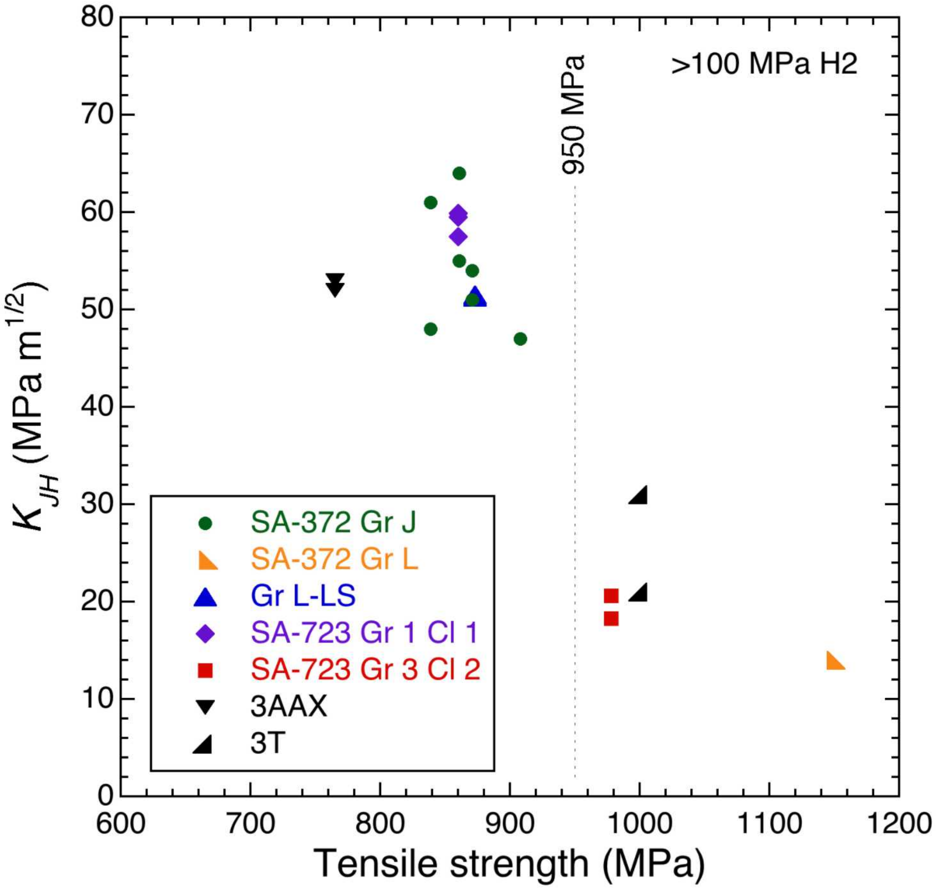


For PV steels with Su > 950 MPa

- Accelerated fatigue crack growth rate is observed
- K_{JH} < 30 MPa $m^{1/2}$



Basis for limiting strength
Fracture resistance – rising load (K_{JH})

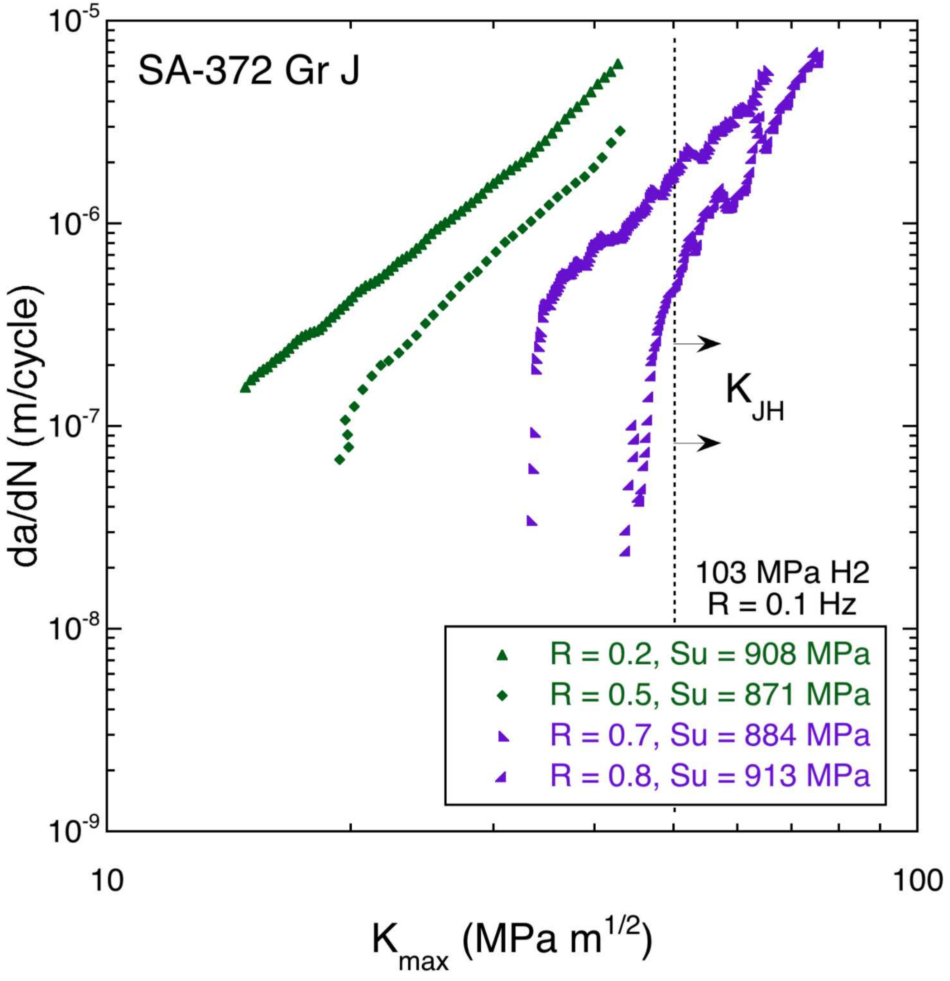


Pressure vessel steels display low fracture resistance in high strength condition

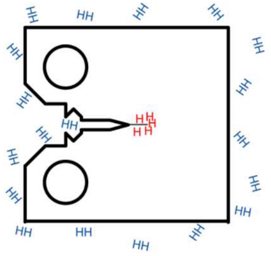
- **For tensile strength < 950 MPa**
  - **$K_{JH} > 45$ MPa $m^{1/2}$**
- **For tensile strength > 950 MPa**
  - **$K_{JH} < 30$ MPa $m^{1/2}$**

K_{JH} = elastic-plastic plane-strain fracture toughness in gaseous hydrogen (ASTM E1820)

Basis for limiting K_{max}



- "Stage III" fatigue crack growth begins at $K_{max} < K_{JH}$
  - The the proposed relationships do not capture stage III
- $K_{JH} \geq 45\text{-}50$ MPa $m^{1/2}$ for tensile strength < 950 MPa
- Therefore $K_{max} \leq 35$ MPa $m^{1/2}$ is a conservative bound on the proposed relationships for tensile strength < 950 MPa



Summary of pressure vessel steel findings

- Review of fatigue crack growth rate for PV steels generally shows consistency of fatigue response independent of alloy and strength
  - *Exception*: tensile strength > 950 MPa shows transition to stage III crack growth at low K_{max}
- Two-part power law was established to bound FCGR behavior as a function of load ratio, R
  - Transition between "two parts" also quantitatively established

$$\frac{da}{dN} = C\left[\frac{1 + C_H R}{1 - R}\right]\Delta K^m$$

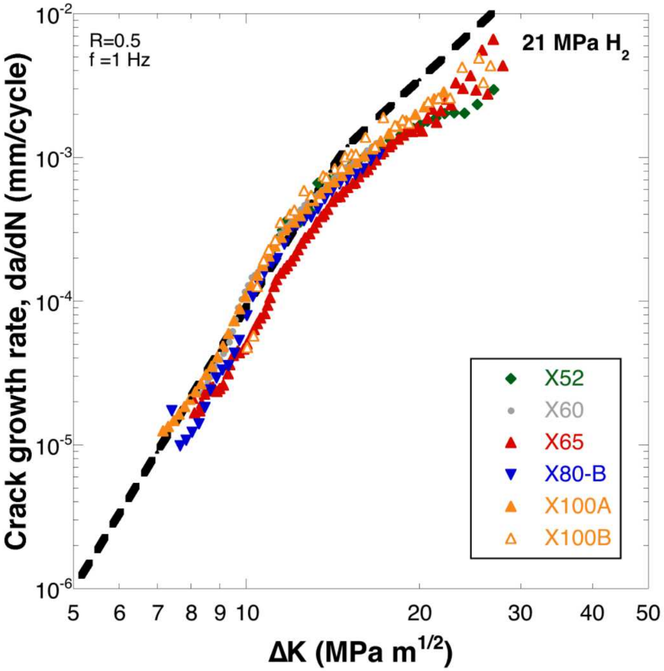
$$\Delta K_c = 8.475 + 4.062R - 1.696R^2$$

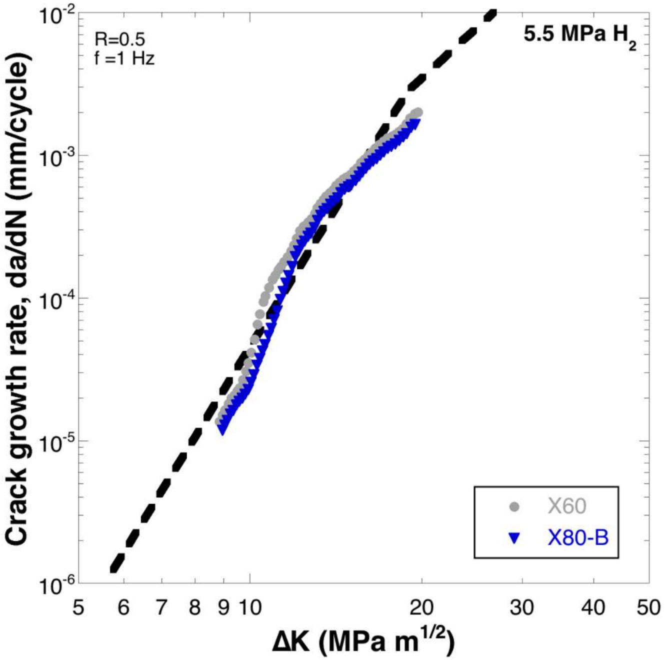
- Proposed constraints for use of established relationships
  - Tensile strength < 950 MPa
  - $K_{max} \leq 35$ MPa $m^{1/2}$

Next step: Pressure term can be added to extend applicability to lower pressure and other steels

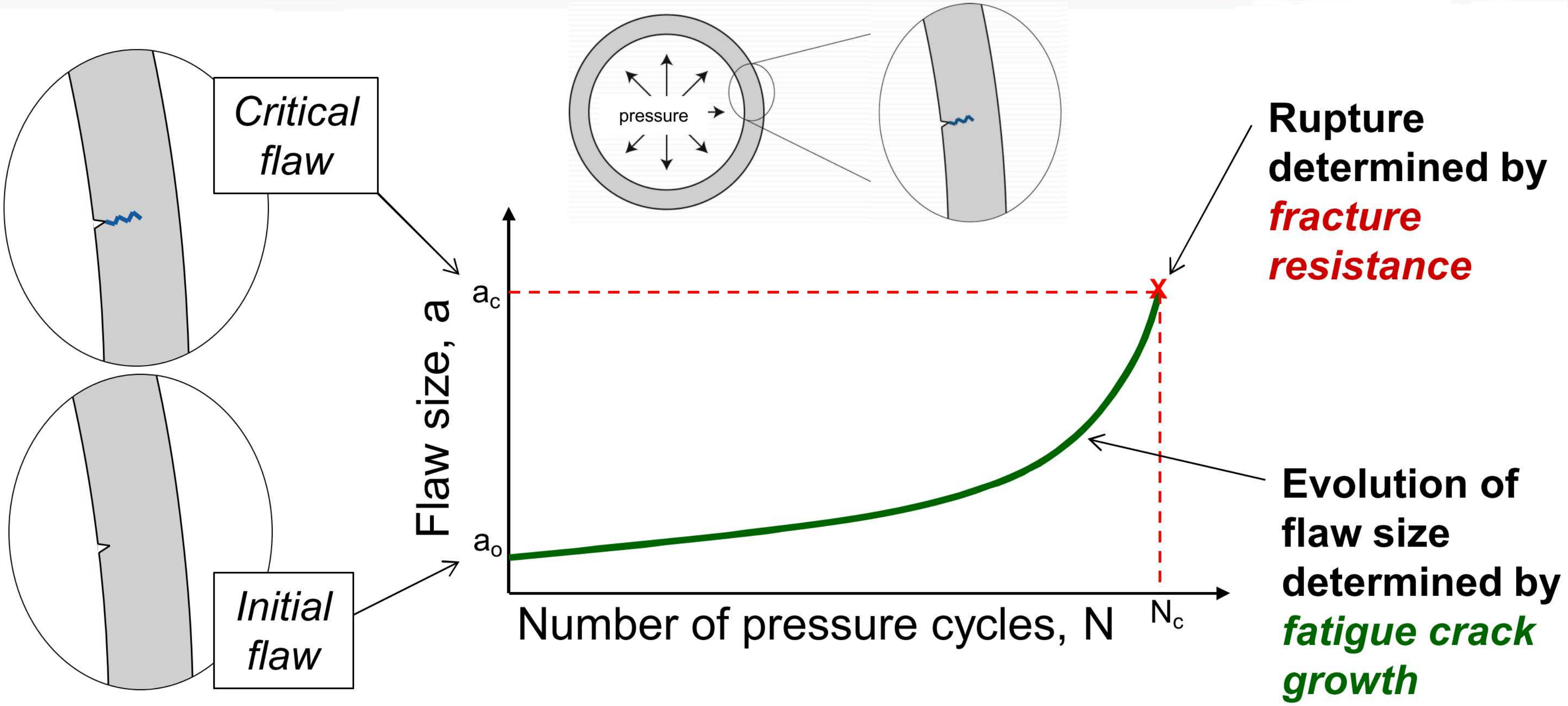
$$\frac{da}{dN} = C\left[\frac{1 + C_H R}{1 - R}\right]\Delta K^m \left(\frac{f}{f_{ref}}\right)^{1/2}$$

- f is fugacity (related to pressure) and f_{ref} is the reference fugacity for which other terms were developed





Fracture mechanics-based assessment of fatigue and fracture of pipelines

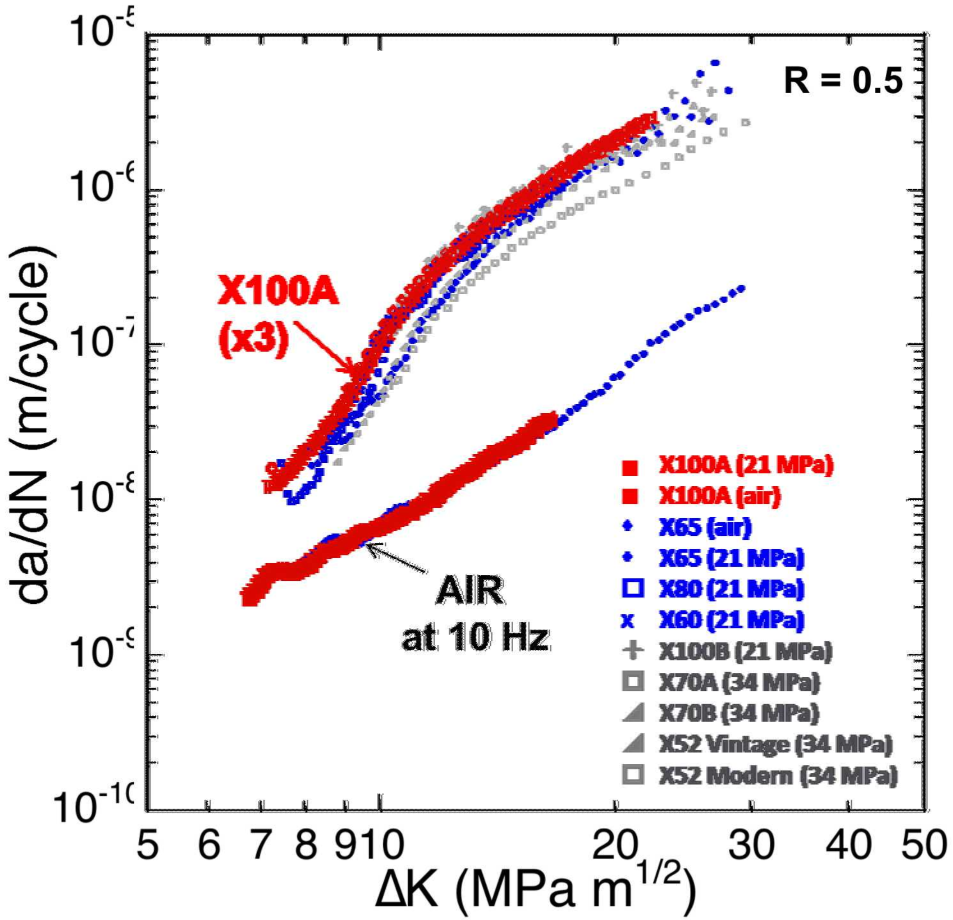


Rupture determined by *fracture resistance*

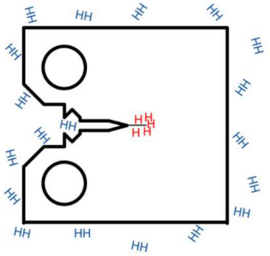
Evolution of flaw size determined by *fatigue crack growth*

ASME B31.12 describes rules for hydrogen pipelines with reference to ASME BPVC Section VIII, Division 3, Article KD-10

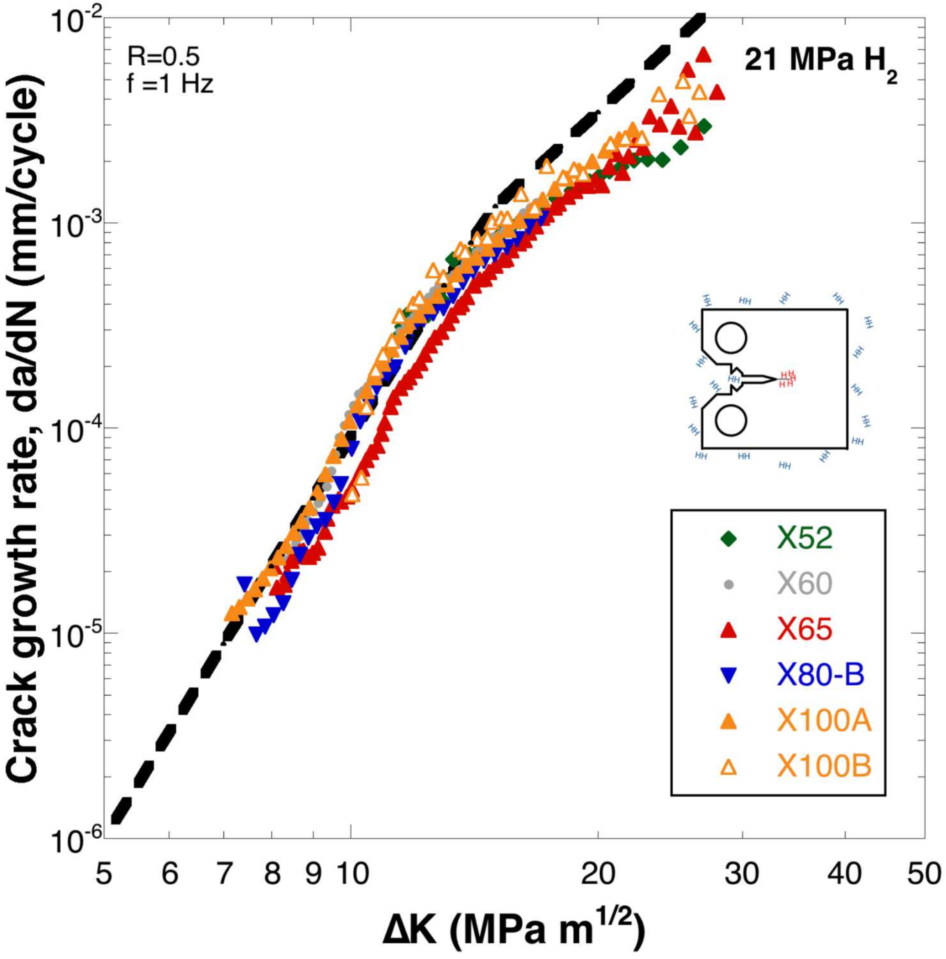
Various pipeline steels tend to show very similar fatigue crack growth rates in gaseous hydrogen



- A wide variety of pipeline steels display nominally the same fatigue response in high-pressure gaseous hydrogen
- The effect of pressure on fatigue crack growth rates is modest for high-pressure hydrogen



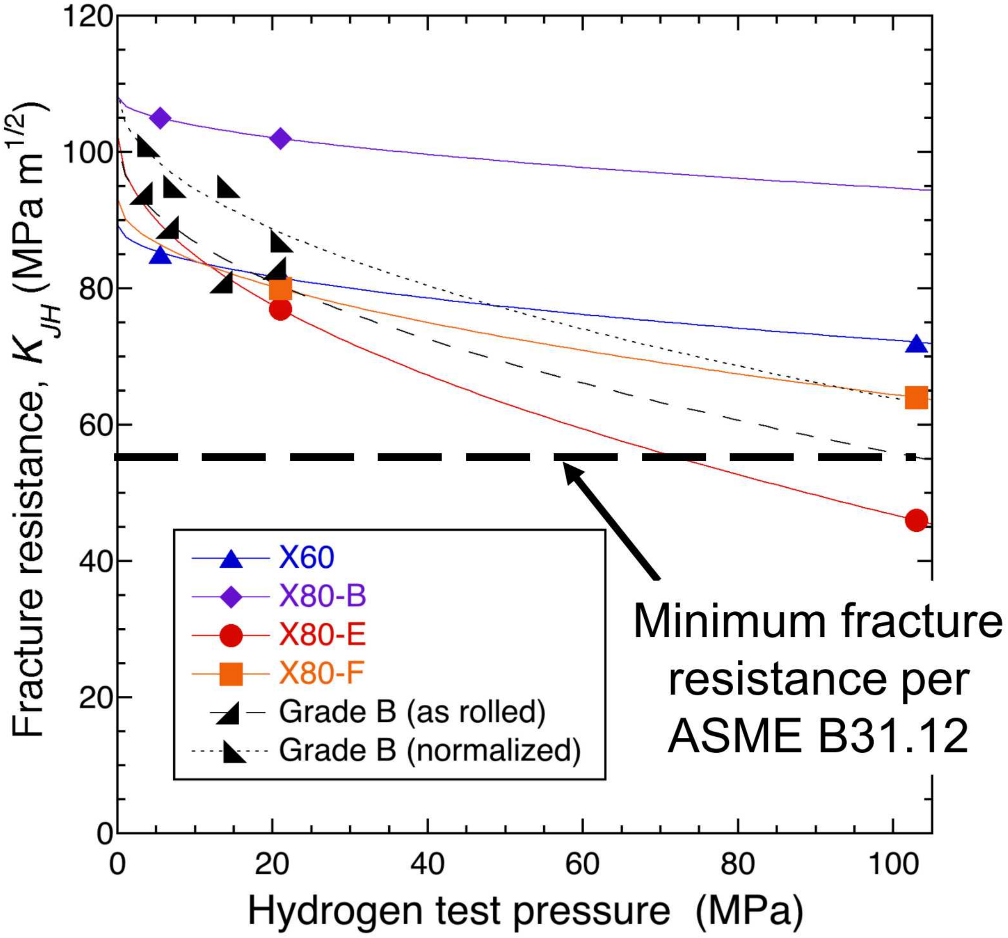
The effects of hydrogen on fatigue crack growth can be captured with "master" design curve



- Tested steels represent:
  - Wide range of strength
  - Wide range of microstructure
- A relatively simple master curve has been developed (dashed line) that bounds fatigue crack growth performance in gaseous hydrogen

$$\frac{da}{dN} = C_1 \left[\frac{1 + C_2 R}{1 - R}\right] \Delta K^m \left(\frac{f}{f_0}\right)^{1/2}$$

Pipeline steels have relatively high fracture resistance in gaseous hydrogen

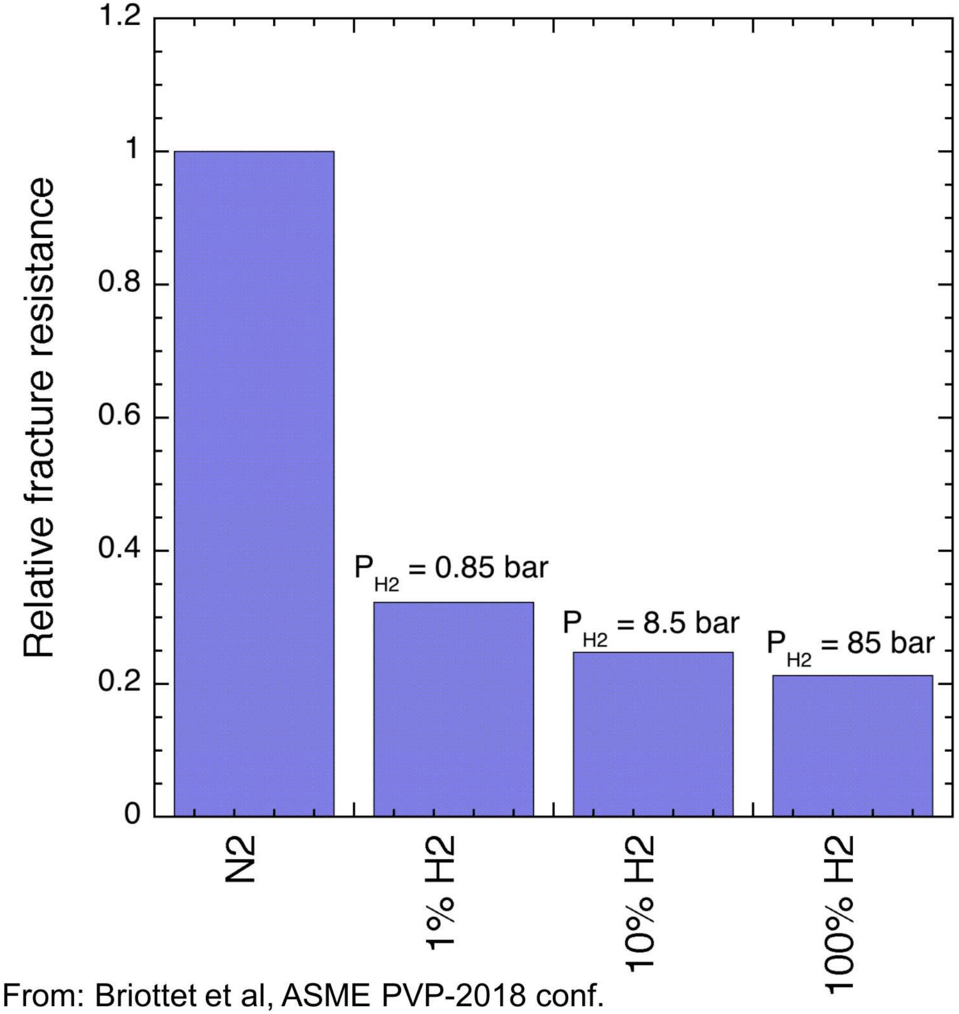


Minimum fracture resistance per ASME B31.12

- Data sets that evaluate effect of pressure on fracture are relatively limited
- Available data suggest fracture depends on pressure
- Fracture resistance (even at low pressure) is significantly lower than in air

From: San Marchi et al, ASME PVP-2011 conf.

Low pressure hydrogen has substantial effect on fracture resistance of pipeline steels

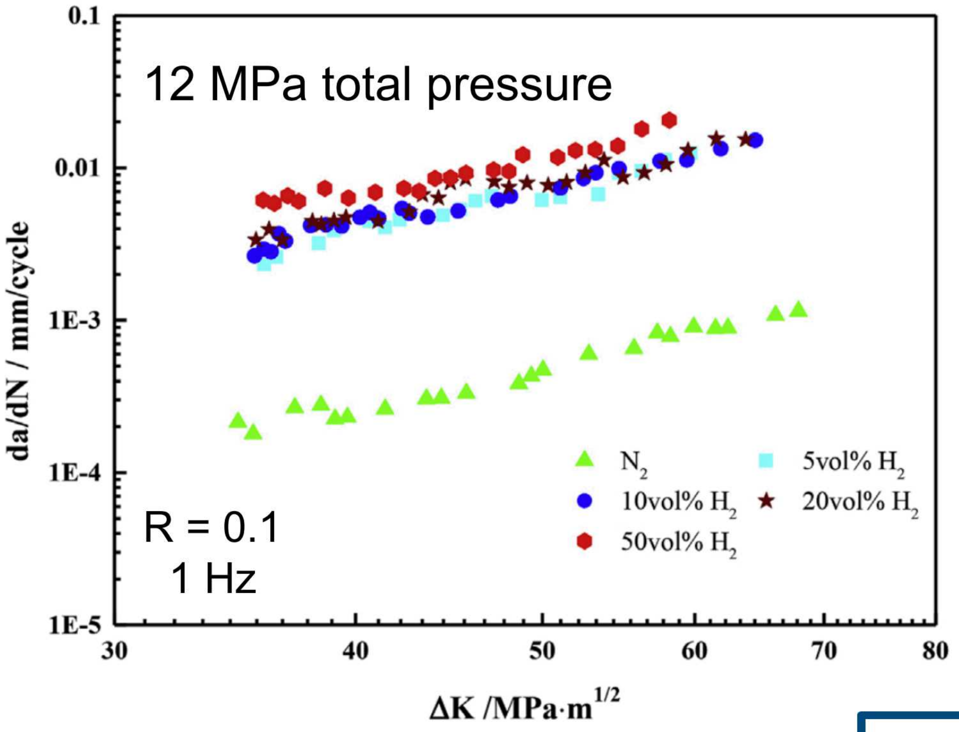


From: Briottet et al, ASME PVP-2018 conf.

- Measurements of fracture resistance in gaseous mixtures of H_2 and N_2 show substantial effects of H_2
- 1% H_2 is only modestly different than 100% H_2

<1 bar of H_2 reduces fracture resistance

Low pressure hydrogen has substantial effect on fatigue crack growth of pipeline steels

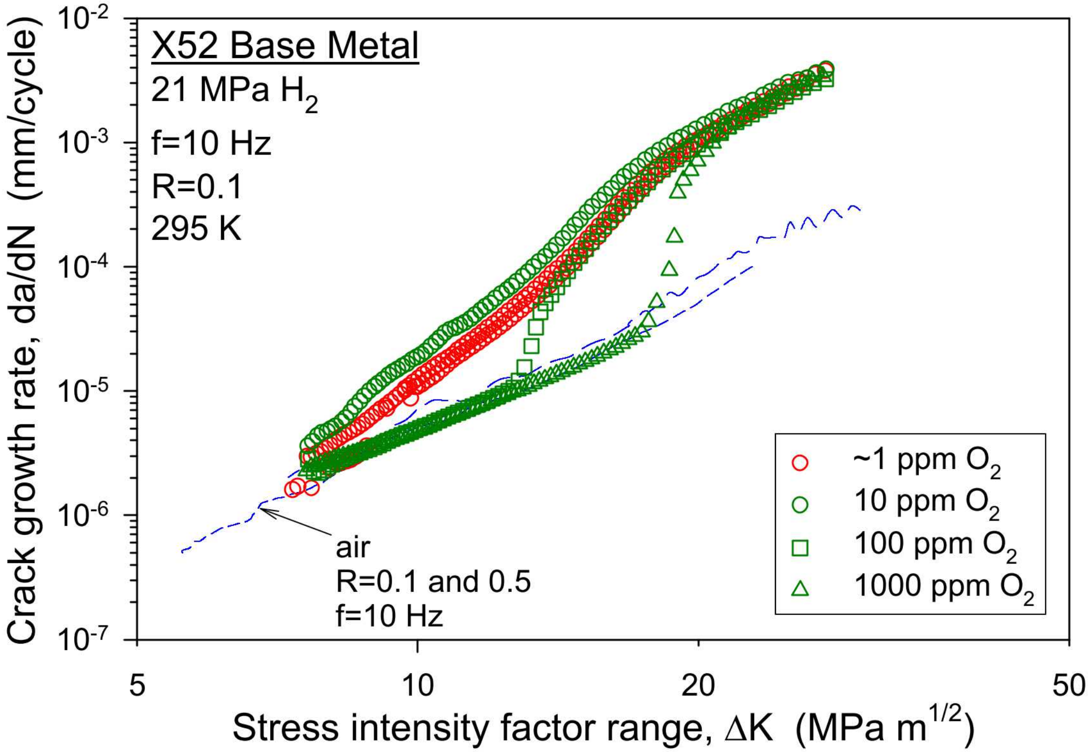


From: Meng et al, *IJ Hydrogen Energy* **42** (2017) 7404.

- Measurements in gaseous mixtures of H_2 and N_2 show acceleration of fatigue crack growth rate with 5% H_2
  - But little additional acceleration with higher H_2 content

Small amounts of hydrogen can have substantial effect on fatigue and fracture

Impurities can influence measurements, but can also provide pathways to mitigate the effects of hydrogen



- Oxygen mitigates H_2–accelerated fatigue crack growth rates at low ΔK
- Attributed to oxygen diffusion to new crack surfaces

From: Somerday et al, *Acta Mater* **61** (2013) 6153.

Impurity content in H_2 can have substantial effects on both measurements and in-service performance

The role of mixed hydrogen gas environments and impurities should be considered carefully

- Small partial pressure of gaseous H_2 can have substantial effects on fracture and fatigue of steels
- Oxygen can mitigate effects of H_2 in ferritic steels
  - Sensitive to mechanical and environmental variables
  - Other passivating species can have similar effects
- Structural integrity of pipelines carrying mixed gases will depend sensitively on the details
  - NG has many impurities, which can mitigate H_2 effects
  - Pure methane is inert and even small additions of H_2 can be significant

Materials compatibility for hydrogen containment structures depends on the application and the design

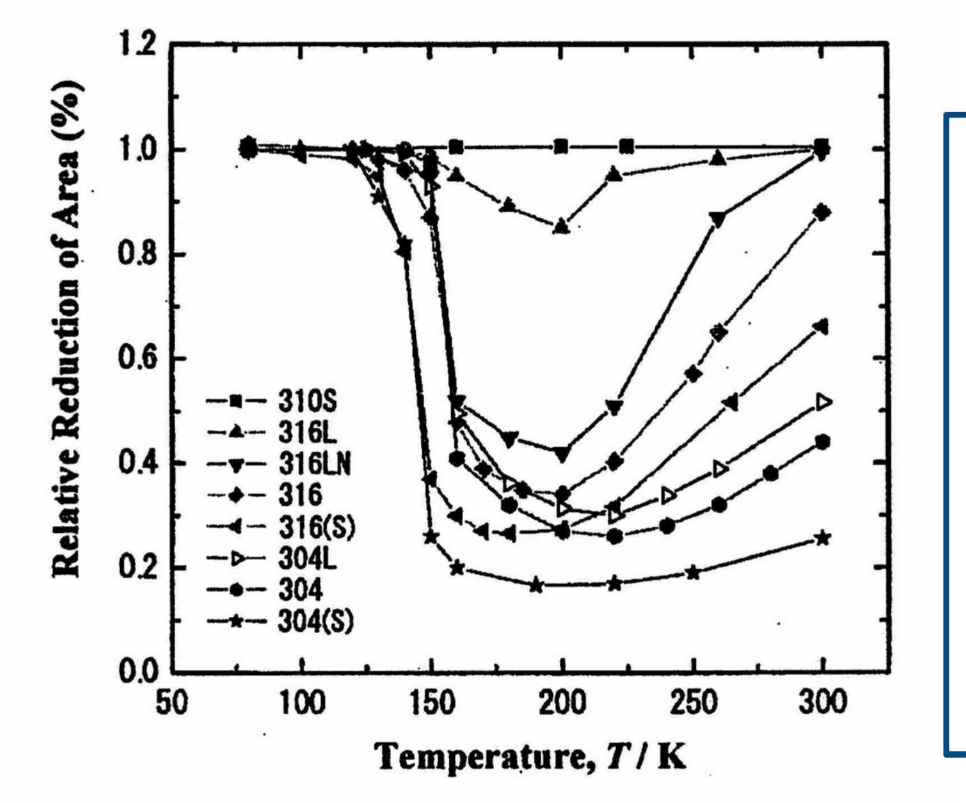
Summary of pipeline steel findings

- Why hydrogen in pipelines?
  - ***Hydrogen is a carbon-free energy carrier***
- What is hydrogen embrittlement and when is it important?
  - ***Hydrogen degrades mechanical properties of most metals***
- How does gaseous hydrogen affect fatigue and fracture of pipeline steels?
  - ***Fatigue is accelerated by >10x and fracture resistance is reduced by >50%***
- Is there a threshold below which hydrogen effects can be ignored?
  - ***NO, even small amounts of hydrogen have large effects***
- Can the effects of hydrogen be masked by other physics?
  - ***Oxygen can mitigate the effects of hydrogen in some cases, which perhaps can be exploited***

Backup slides

Materials qualification for FCEVs

Tensile properties are degraded in gaseous hydrogen especially at low temperature



Requirement:

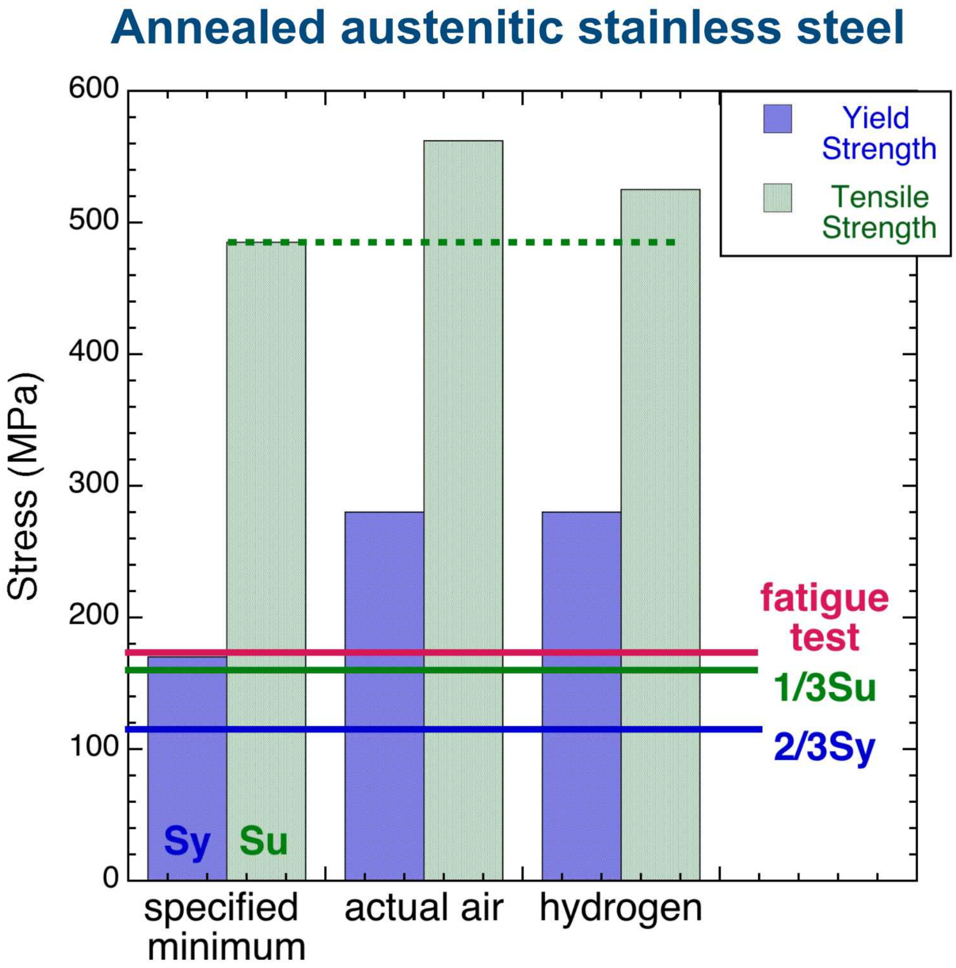
- Minimum specified strength properties are maintained
- Ductility is consistent with pressure applications

Rationale:

- Known and ductile tensile response

Data from: Fukuyama et al., *J Japan Inst Metals* 67 (2003) 456-459.

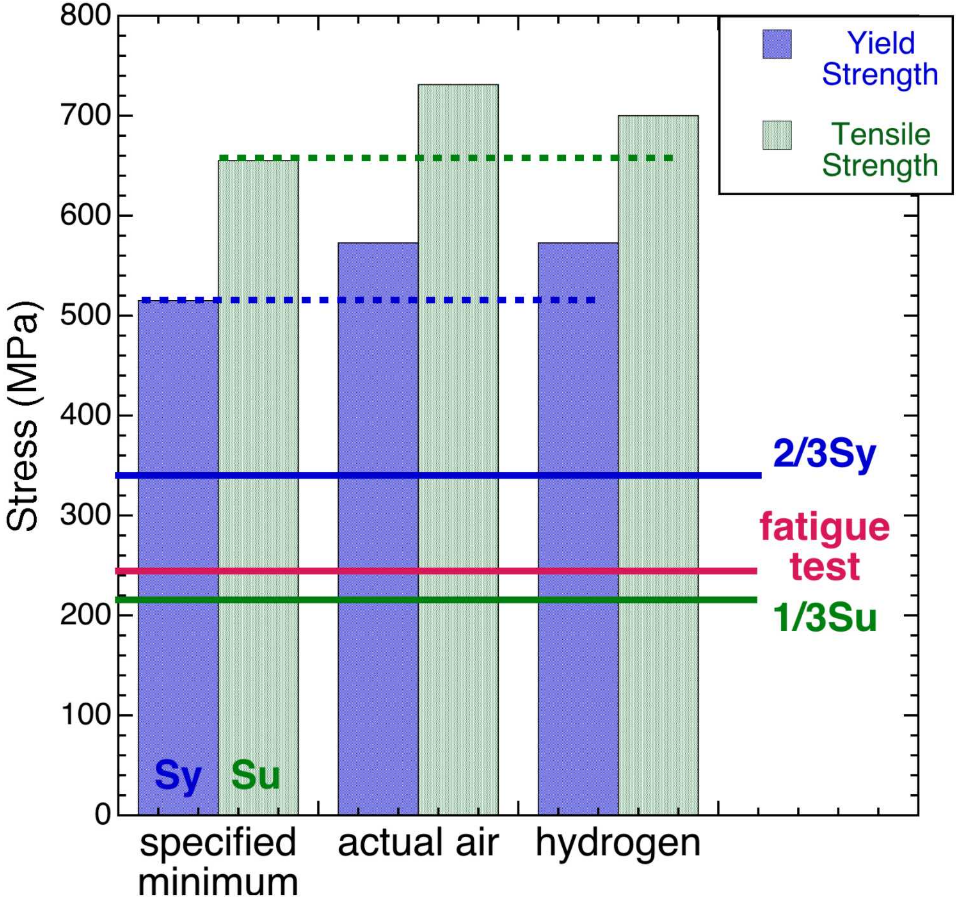
Tensile strength properties are not degraded in gaseous hydrogen for acceptable materials



- Common stress limitations for fatigue design: minimum of 2/3 Sy and 1/3 Su
- Yield and tensile strengths are typically not affected by hydrogen
- Maximum stress during fatigue testing (J2579) always greater than 1/3 Su

High-strength materials can be evaluated by method and enable higher stress designs

Strain-hardened austenitic stainless steel

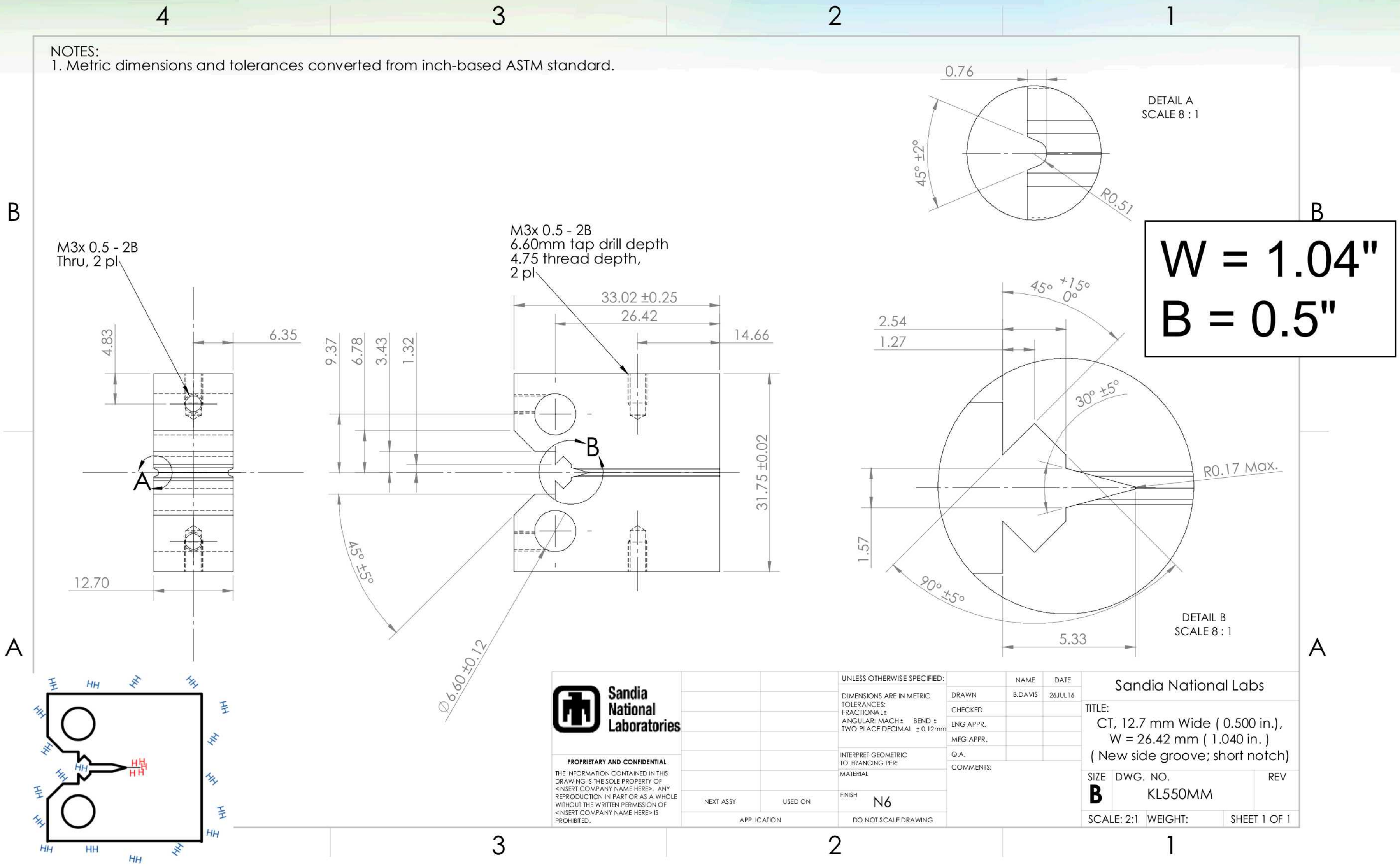


- **1/3 Su of high-strength materials can be more then twice that of annealed material**
- **Implicitly, increase of design stress enables lower weight and lower cost designs without compromising performance**
  - **Justified by fatigue performance**

Backup slides

Fatigue crack growth in pressure vessels

Testing geometry – Compact Tension (CT)



W = 1.04"
B = 0.5"

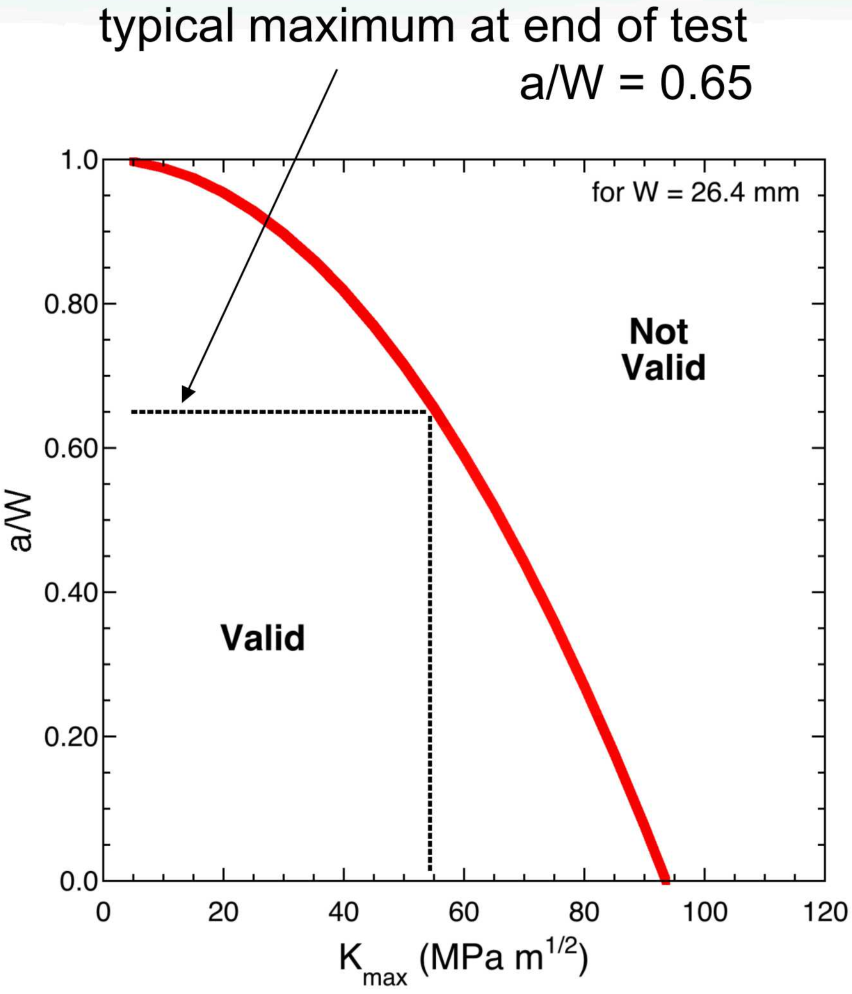
ASTM E647 testing validity

For testing at Sandia

- **Fatigue crack fronts are uniform unless stated otherwise**
- **Ligament requirements**

$$(W - a) \geq \left(\frac{4}{\pi}\right)\left(\frac{K_{max}}{S_y}\right)^2$$

  - **Satisfied in all cases for SNL data**
  - **May not be true of other data at high load ratio (R > 0.5)**



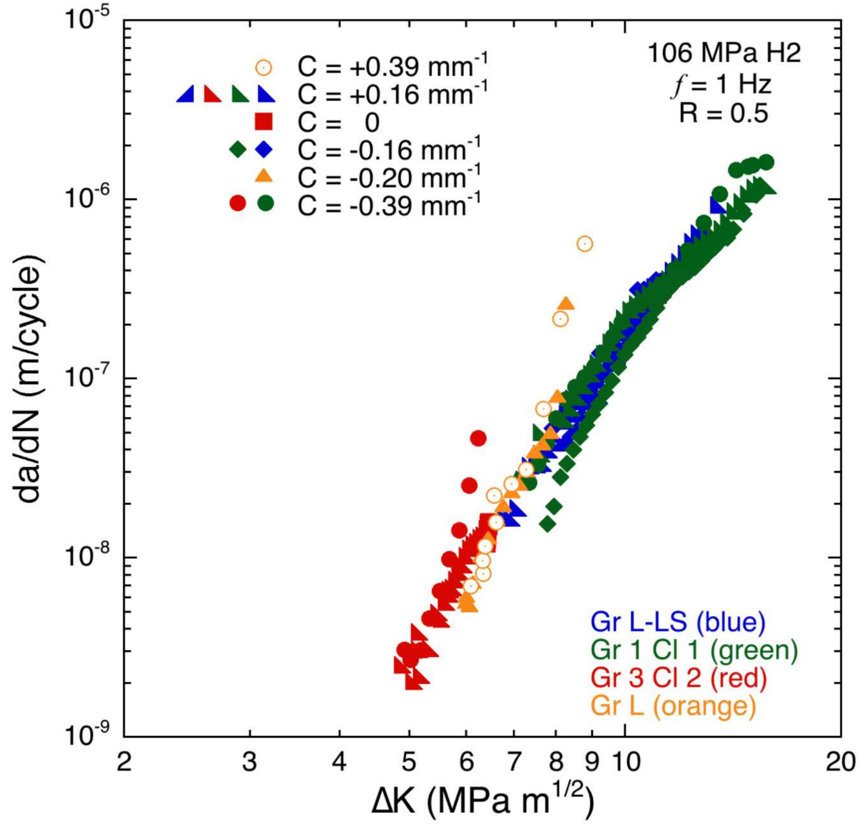
ASTM E647 testing validity

- **Variation of K-gradient was utilized to accelerate some tests**

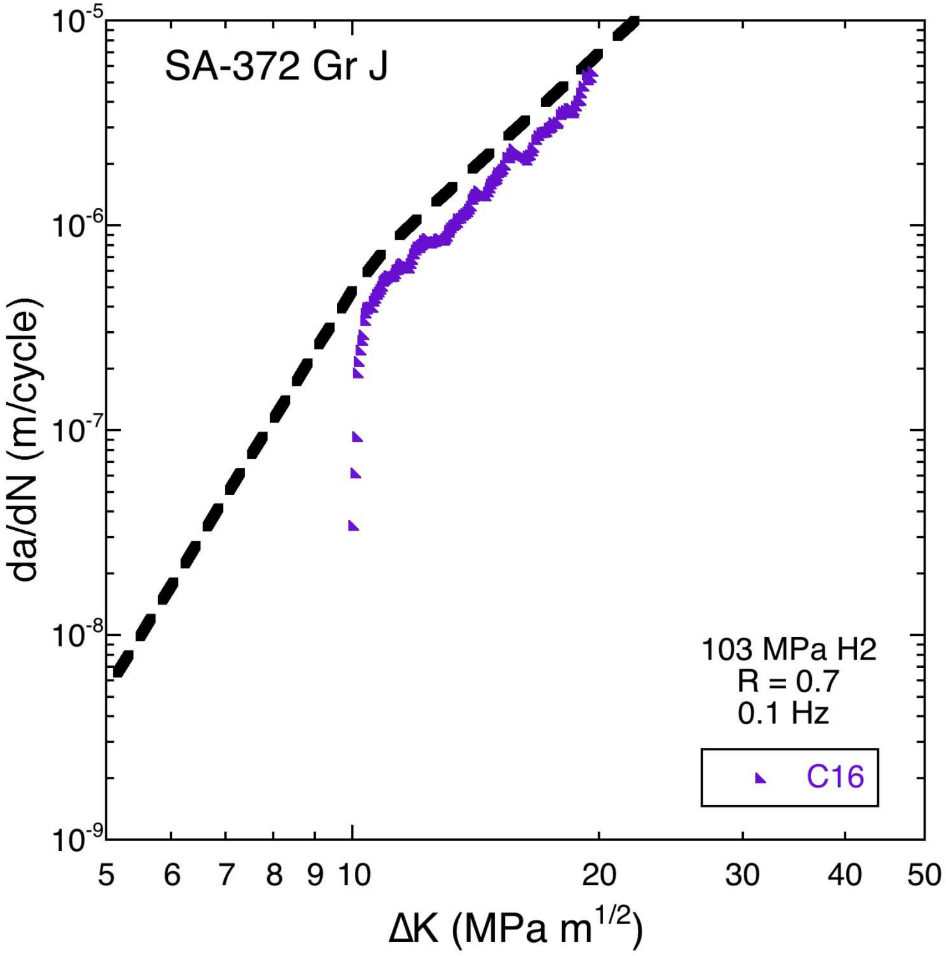
$$C = \left(\frac{1}{K}\right)\left(\frac{\mathrm{d}K}{\mathrm{d}a}\right)$$

- **No dependence on the K-gradient has been observed in any testing**
  - **K-gradient varied in the range of +/- 0.39 mm^{-1} for several values of R**
  - **Data generally acquired at Δa sufficient to obtain >5 data points per decade of da/dN**
  - **Consistent data for both K-increasing and K-decreasing**

For comparison: constant load test is C ~ +0.1 mm^{-1}



Fatigue crack growth rates of SA-372 Grade J R=0.7

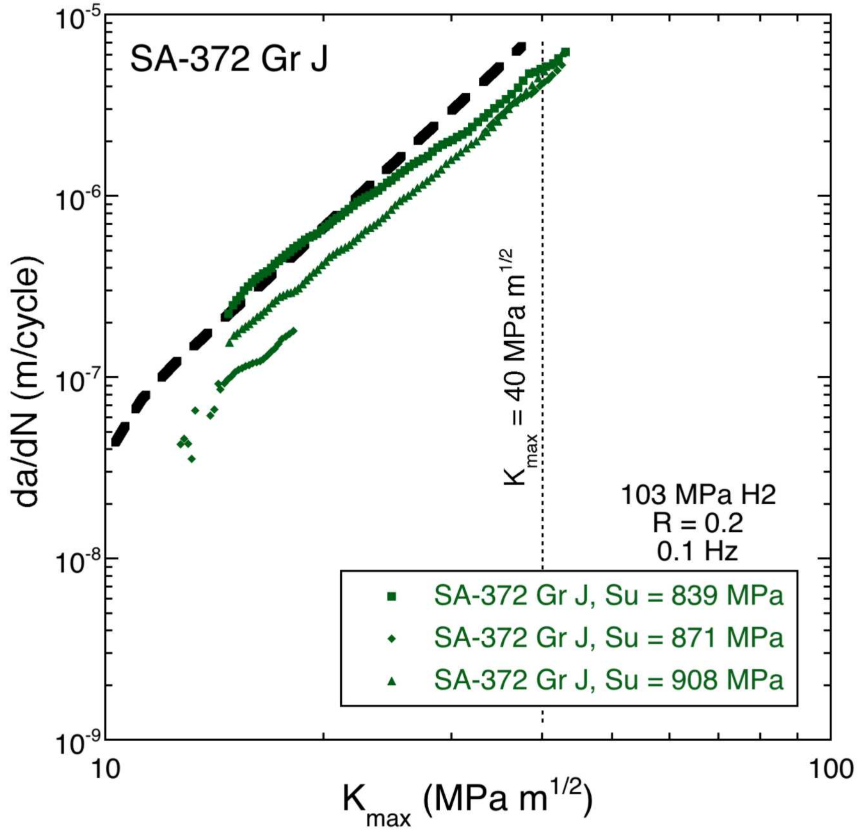


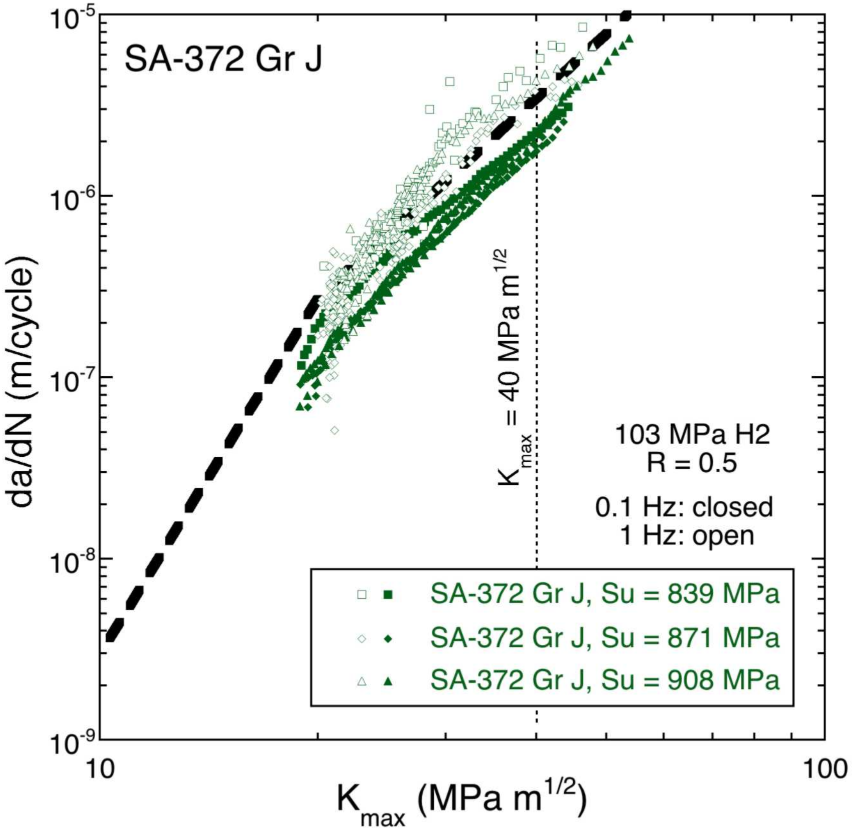
- Gaseous hydrogen at pressure of 103 MPa
- R = 0.7
- 0.1 Hz
- Data not published?
  - Not from SNL

Designation	Tensile strength (MPa)	Yield Strength (MPa)
SA-372 Gr J (C16)	884	711
SA-372 Gr J (C57)	904	787
SA-372 Gr J (C58)	913	764

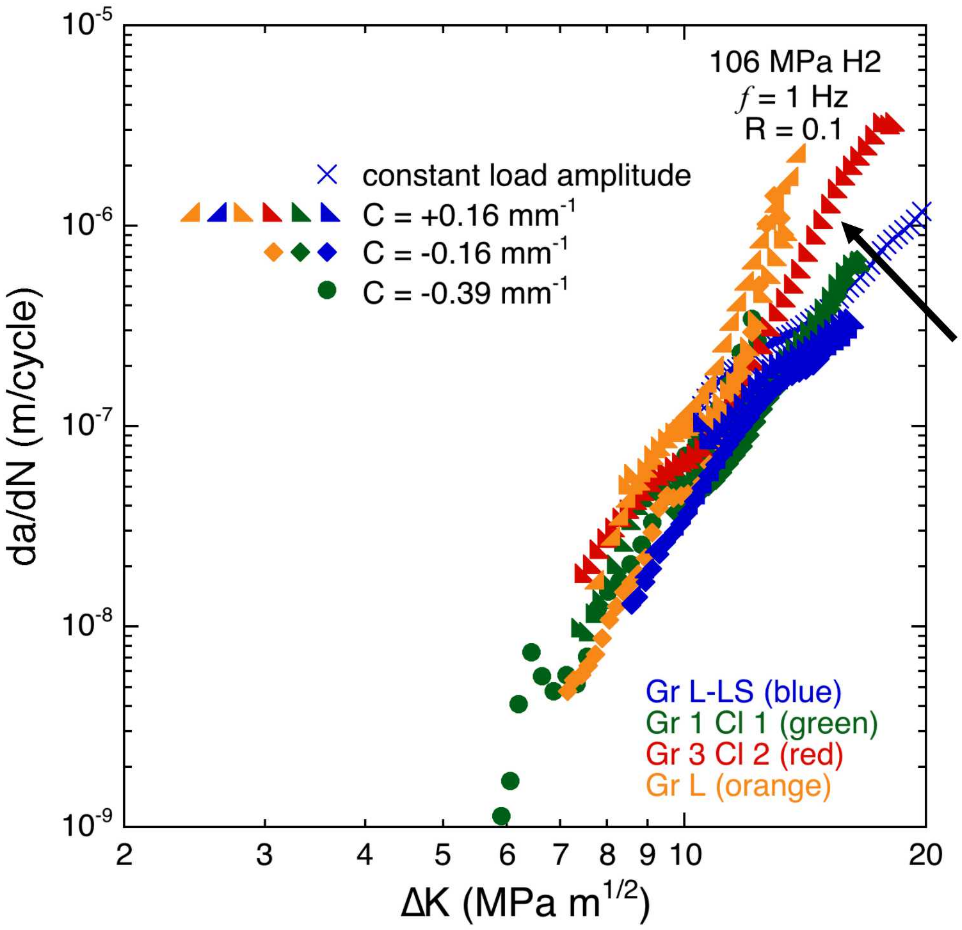
Basis for limiting K_{max}

- No evidence of transition to stage III for K_{max} up to 40 MPa $m^{1/2}$ in SA-372 Gr J steels
- For steels shown below:
  - Measured K_{JH} values in 103 MPa H2 are within the range of 47-61 MPa $m^{1/2}$ (5 measurements)

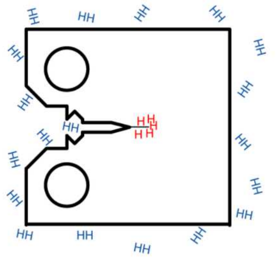




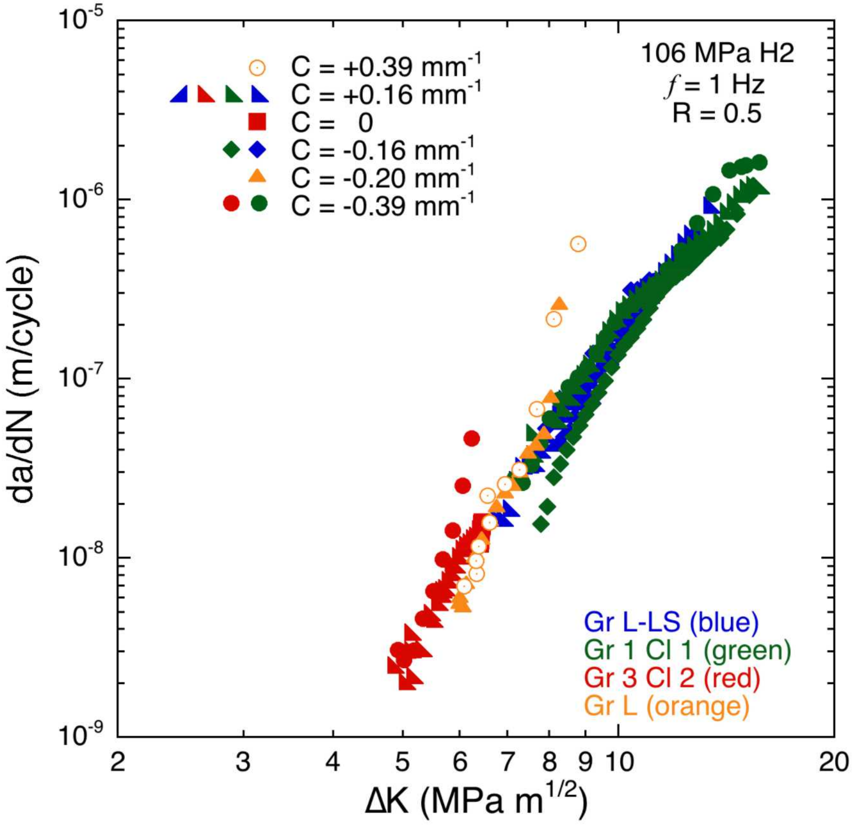
Appendix: FCGR data for variable K-gradient

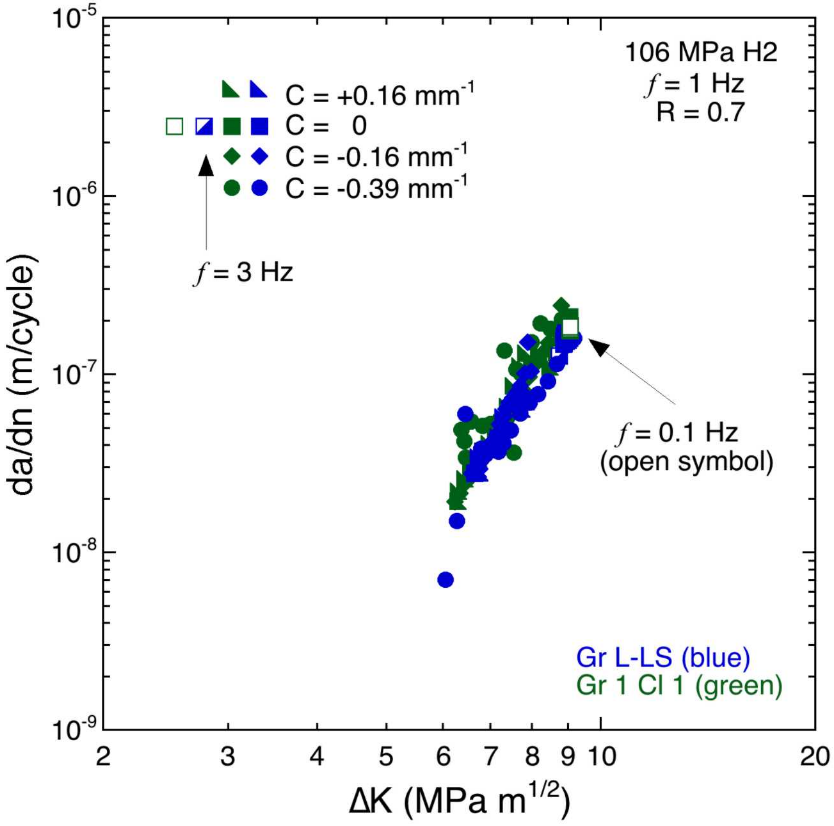


- These steels represent a wide range of strength and composition for Ni-Cr-Mo PV steels
- Deviation from from the basic trend represents K_{max} approaching the fracture resistance (stage III of fatigue crack growth)
  - Apparent only for the high-strength steels
    K_{max} ➡ K_{JH}

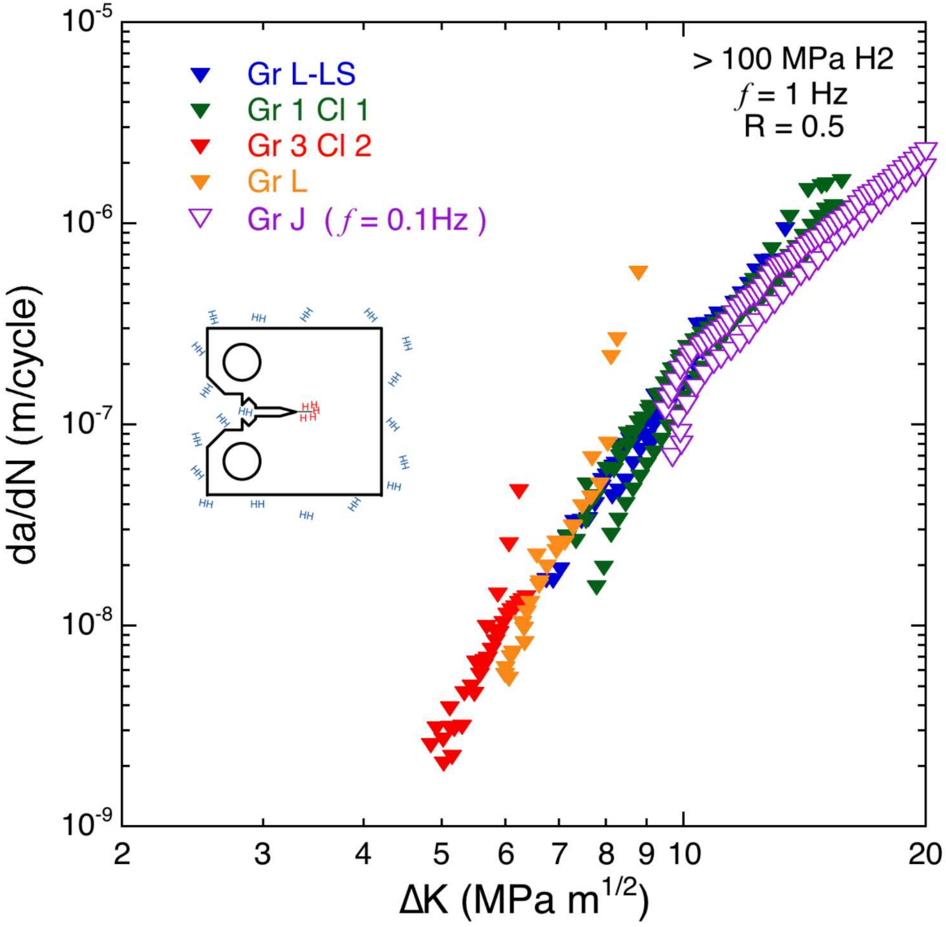


Appendix: FCGR data for variable K-gradient



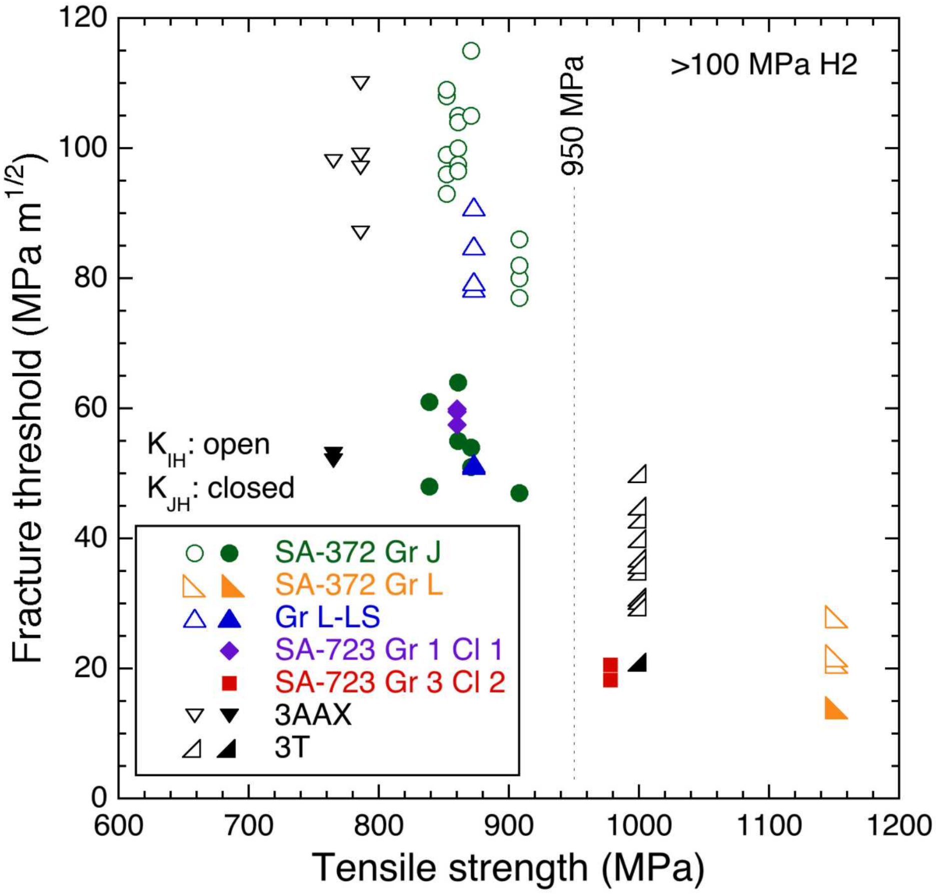


Appendix: comparison of Cr-Mo and Ni-Cr-Mo



- Cr-Mo and Ni-Cr-Mo steels show similar fatigue crack growth rates in gaseous hydrogen
  - Cr-Mo: SA-372 Grade J
  - Ni-Cr-Mo: SA-723 Grades (SA-372 Grade L also)
- Crack growth rates are not sensitive to frequency between 0.1 and 1 Hz (at least for ΔK > ~9 MPa $m^{1/2}$)
- Single master curve for fatigue crack growth of both Cr-Mo and Ni-Cr-Mo steels appears reasonable

Appendix: Fracture arrest threshold (K_{IH}) compared to fracture initial threshold (K_{JH} – rising load)

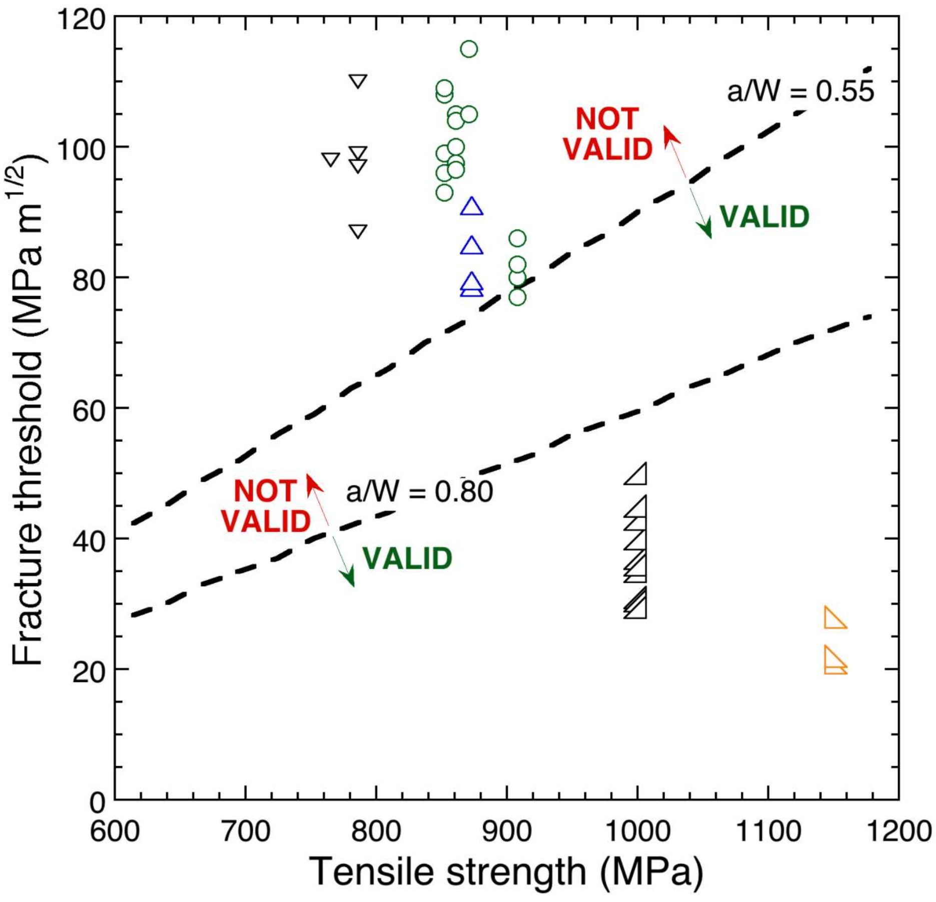


- For tensile strength < 950 MPa
  - $K_{JH} > 45$ MPa m$^{1/2}$
  - $K_{IH} >> K_{JH}$
- For tensile strength > 950 MPa
  - $K_{JH} < 30$ MPa m$^{1/2}$
  - K_{IH} approaches K_{JH}

K_{JH} = elastic-plastic plane-strain fracture toughness in gaseous hydrogen (ASTM E1820)

K_{IH} = threshold stress intensity factor in gaseous hydrogen (ASTM E1681) – arrest threshold

Appendix:
Validity of K_{IH} measurements



- Validity criterion from ASTM E1681

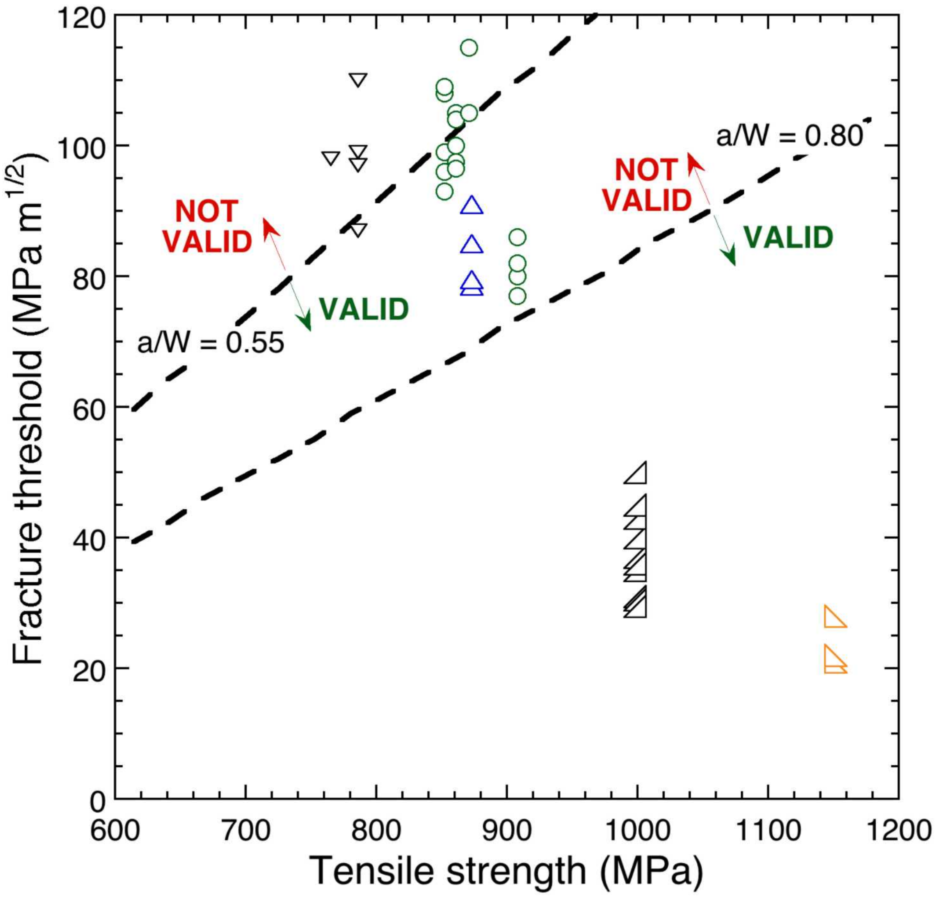
$$(W - a) \geq 2.5\left(\frac{K_{max}}{S_y}\right)^2$$

  - Calculated for different ligaments: *b/W* = (1- *a/W*)
  - K_{IH} is determined at arrest
  - Typically at arrest *a/W* > 0.8
  - Not valid if the ratio of K to Sy (or Su) is large relative to remaining ligament

K_{IH} = threshold stress intensity factor in gaseous hydrogen (ASTM E1681) – arrest threshold

Tensile strength is estimated from yield strength (linear relationship)

Appendix: Validity of K_{IH} measurements



- Validity criterion from ASTM E1681

$$(W-a) \geq \frac{4}{\pi}\left(\frac{K_{max}}{S_y}\right)^2$$

  - Calculated for different ligaments: *b/W* = (1- *a/W*)
  - K_{IH} is determined at arrest
  - Typically at arrest *a/W* > 0.8
  - Not valid if the ratio of K to Sy (or Su) is large relative to remaining ligament

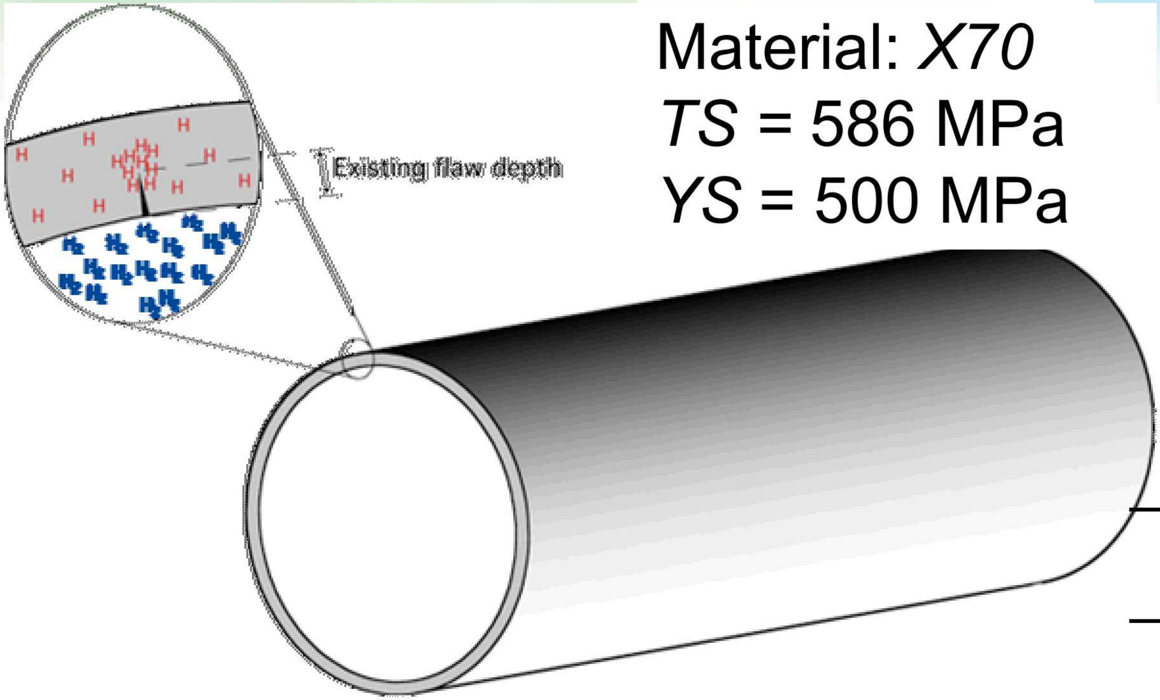
K_{IH} = threshold stress intensity factor in gaseous hydrogen (ASTM E1681) – arrest threshold

Tensile strength is estimated from yield strength (linear relationship)

Backup slides

Fatigue crack growth in pipeline steels

Consider a typical "high-pressure" pipeline



Material: *X70*

TS = 586 MPa

YS = 500 MPa

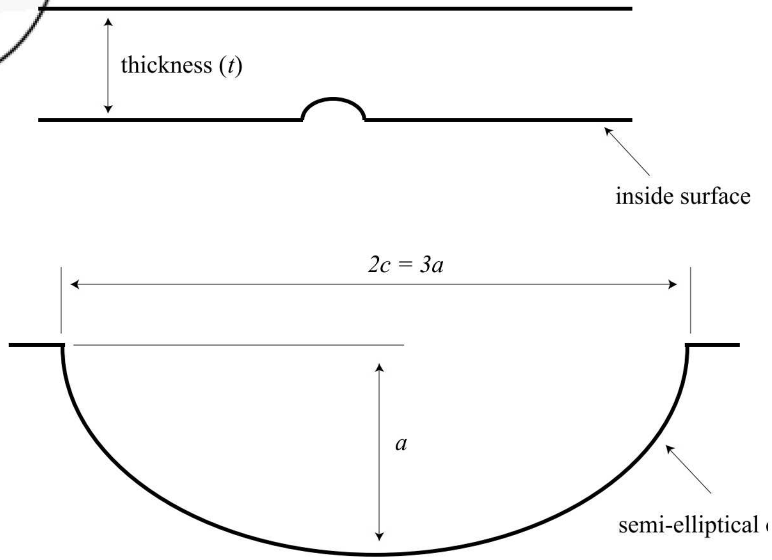
OD = 762 mm

t = 15.9 mm

P_{max} = 7 MPa

P_{min} = 4 MPa

Semi-elliptical crack



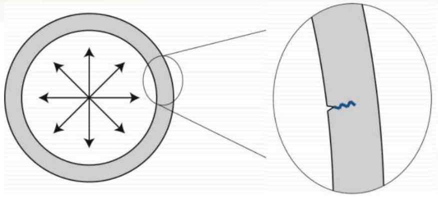
a/t = crack depth

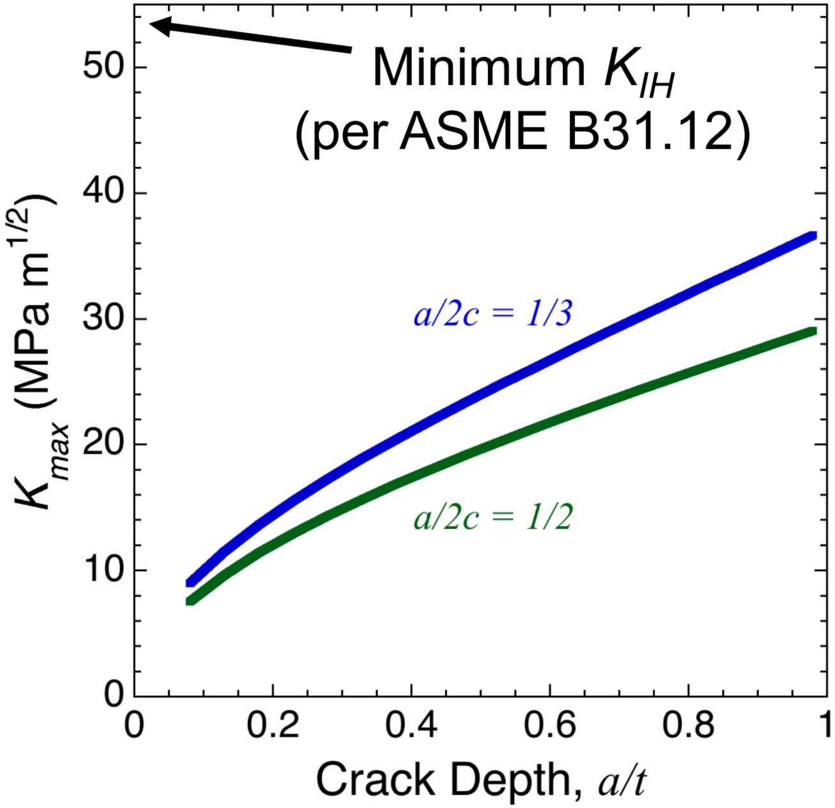
a/2c = depth to length ratio

natural crack shape: *a/2c* = 1/2

ASME crack shape: *a/2c* = 1/3

Stress intensity associated with semi-elliptical crack in “high-pressure” pipeline

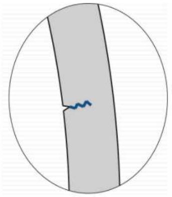




Hoop stress at $P_{max} = 162$ MPa
stress ratio: hoop/$TS = 28\%$

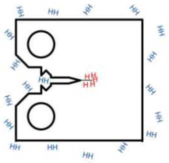
Driving force on semi-elliptical crack:

$$K_{max} < 40 \text{ MPa m}^{1/2}$$



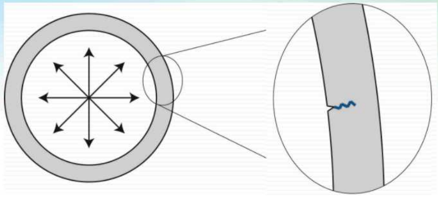
Typical pipeline material fracture resistance:

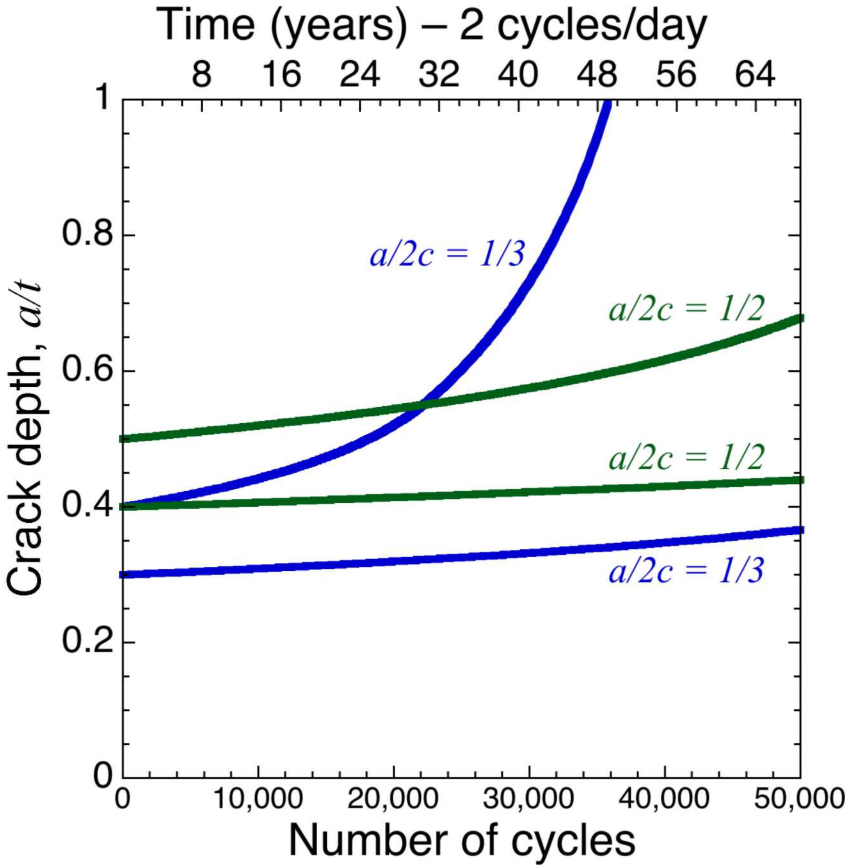
$$K_{JH} > 75 \text{ MPa m}^{1/2}$$



Fracture resistance of pipeline steels in H2 is greater than driving force on semi-elliptical cracks

Predicted lifetime of pipeline with growing fatigue cracks in hydrogen





Assuming

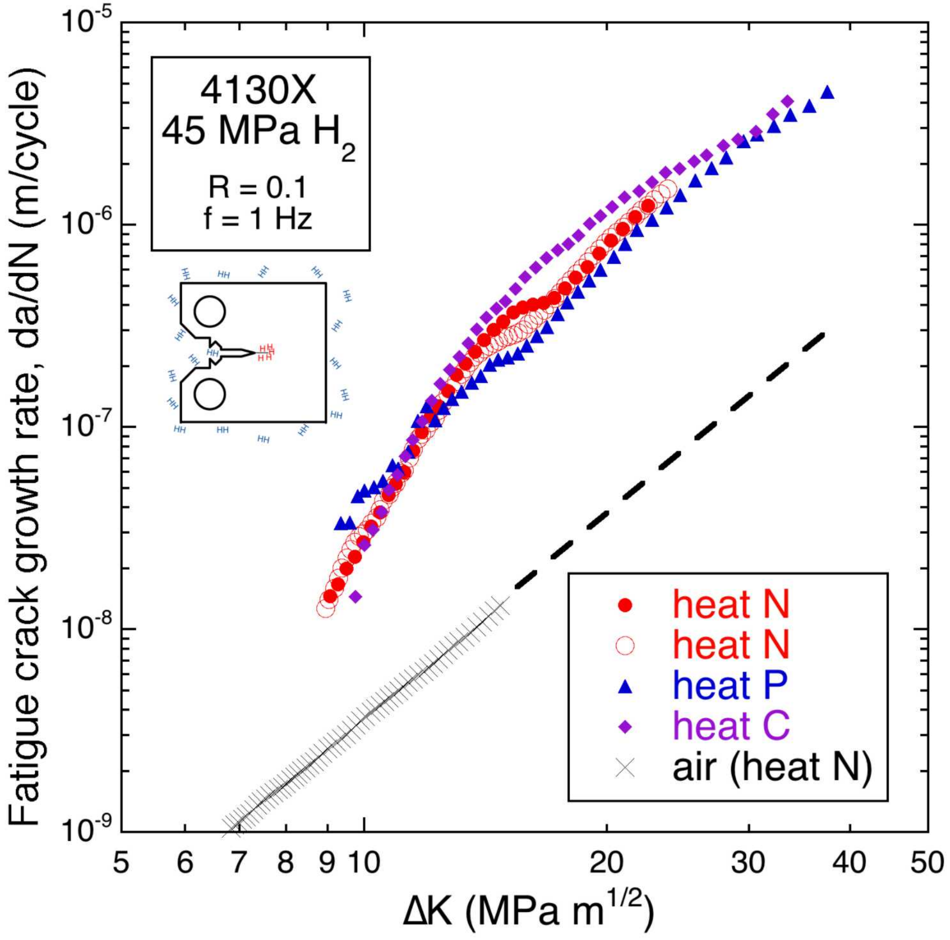
- Pressure cycles between 4 & 7 MPa
- Constant crack shape ($a/2c$)
- Large initial defects
- Fatigue crack growth rates in pure H2 (at higher pressure)

Using:

$$a = a_i + \left({da}/{dN} \right)^{a=a_i} \Delta N$$

- **10,000s of cycles are needed to extend the crack significantly**
- **At 2 cycles per day, decades are needed to advance the crack**

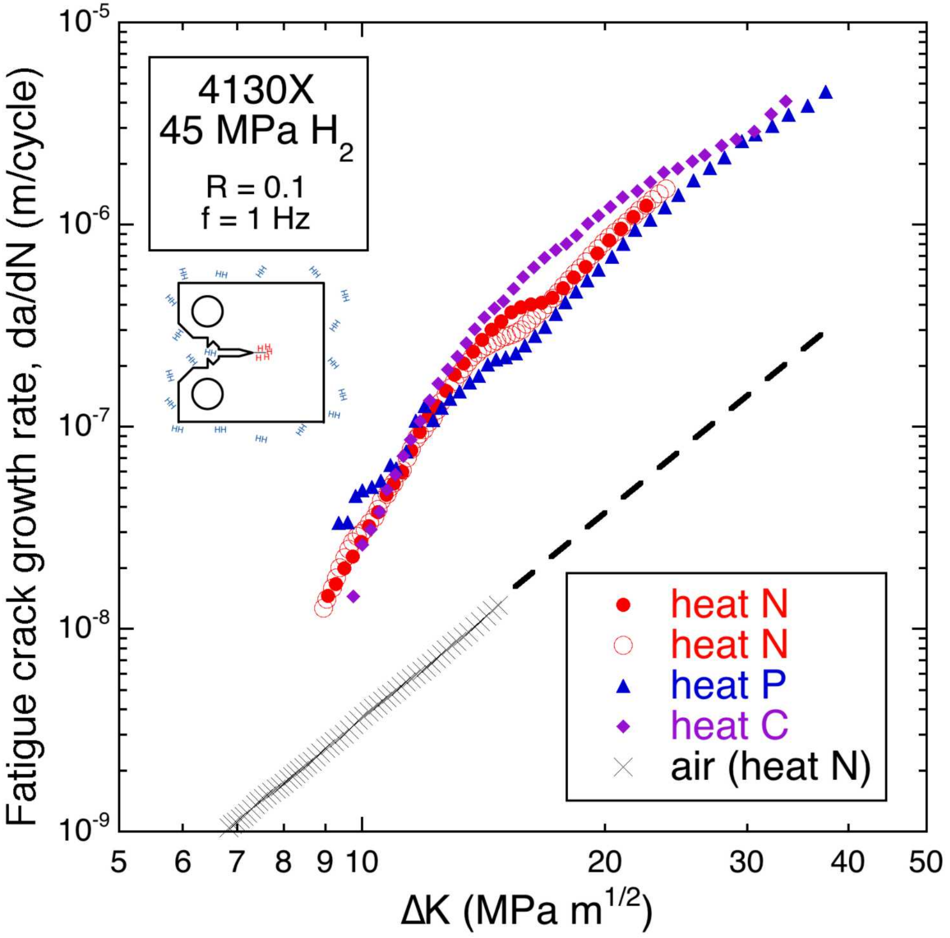
What are the requirements to use a given material in gaseous hydrogen service?



- Fatigue crack growth rate is accelerated by 10X in hydrogen compared to air
- Is this material safe to use in gaseous hydrogen?
  - Yes – No – Maybe

Laboratory gas cylinders are made of this material

What are the requirements to use a given material in gaseous hydrogen service?



Materials requirements depend on the application and the design

- Gas cylinders are made from relatively low strength steels
- Wall stresses are relatively low
- Number of pressure cycles are modest
- Manufacturing defects are well characterized