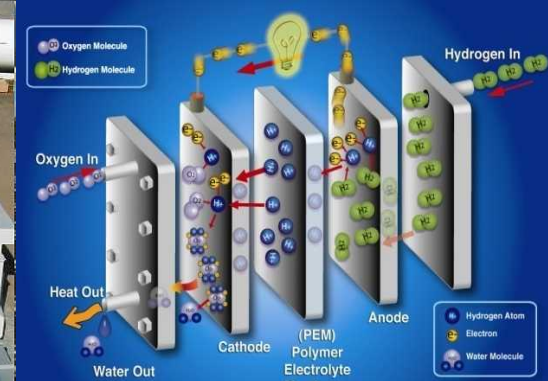


Assessing Steel Pipeline and Weld Susceptibility to Hydrogen Embrittlement

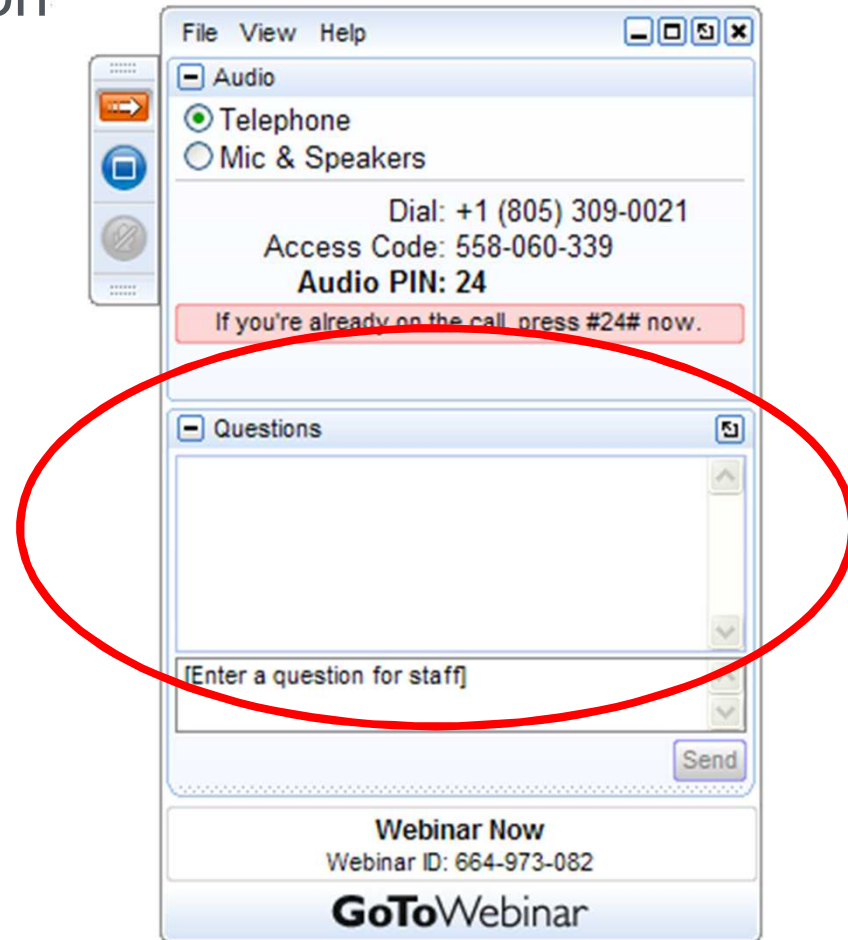


Presenters:
Joe Ronevich (presenter) and Brian Somerday
Sandia National Laboratories

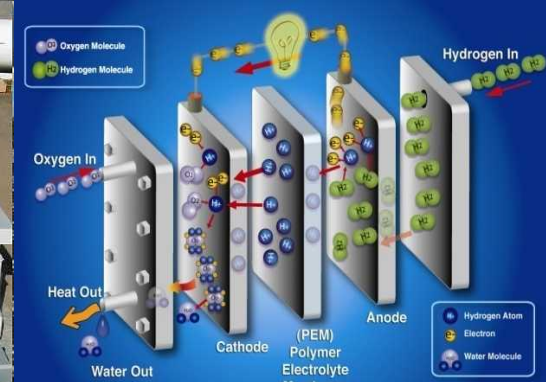
DOE Host:
Neha Rustagi – Technology Manager

**U.S. Department of Energy
Fuel Cell Technologies Office
January 12th, 2016**

- Please type your question into the question box



Assessing Steel Pipeline and Weld Susceptibility to Hydrogen Embrittlement



Presenters:

Joe Ronevich (presenter) and Brian Somerday
Sandia National Laboratories

DOE Host:

Neha Rustagi – Technology Manager

U.S. Department of Energy
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Assessing Steel Pipeline and Weld Susceptibility to Hydrogen Embrittlement

Joe Ronevich (presenter) and Brian Somerday
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Funded by:

U.S. Department of Energy,
Office of Energy Efficiency and Renewable Energy,
Fuel Cell Technologies Office

January 12th, 2016

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Partners and Acknowledgements

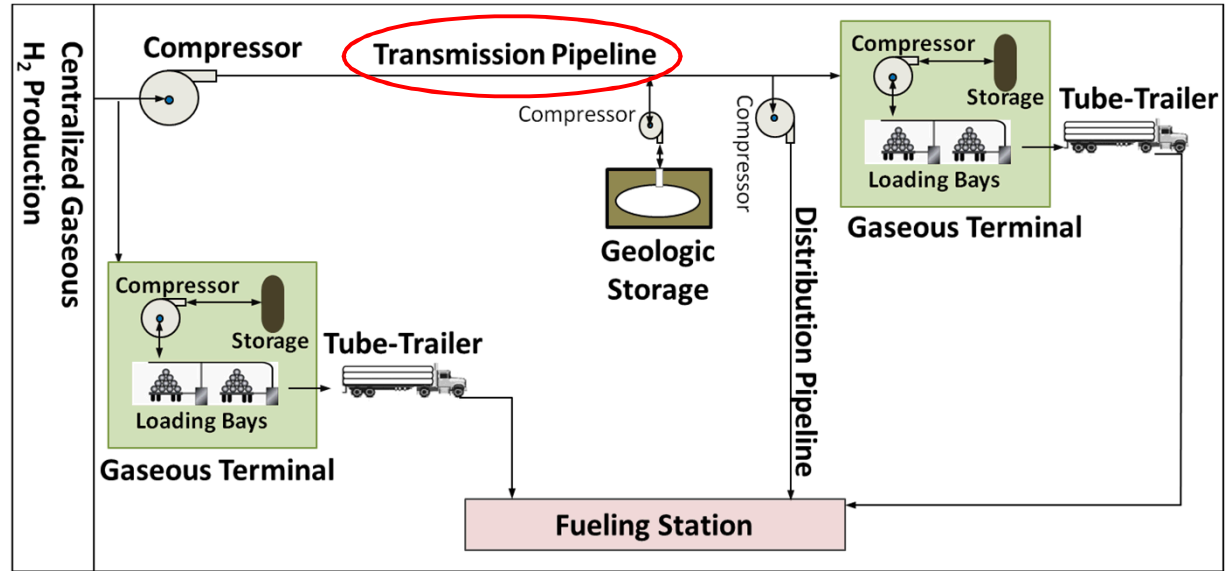
- Hydrogen Effects on Materials Laboratory (SNL)
 - Chris San Marchi
 - Jeff Campbell
 - Brendan Davis
 - Ken Lee
 - Kevin Nibur (currently at Hy-Performance Materials Testing)
- Federal Labs: ORNL, NIST
- Academia: International Institute for Carbon-Neutral Energy Research (I²CNER)
- Industry: ExxonMobil
- Standards Development Organizations: ASME

Agenda

- **Background**
Why steel hydrogen pipelines?
- **Research Objectives**
Variables being analyzed, and target outcomes
- **Approach**
Experimentation and analysis completed
- **Results**
- **Conclusions**
- **Related and Future Work**

Background

Gaseous Delivery Pathways



Liquid Delivery Pathway

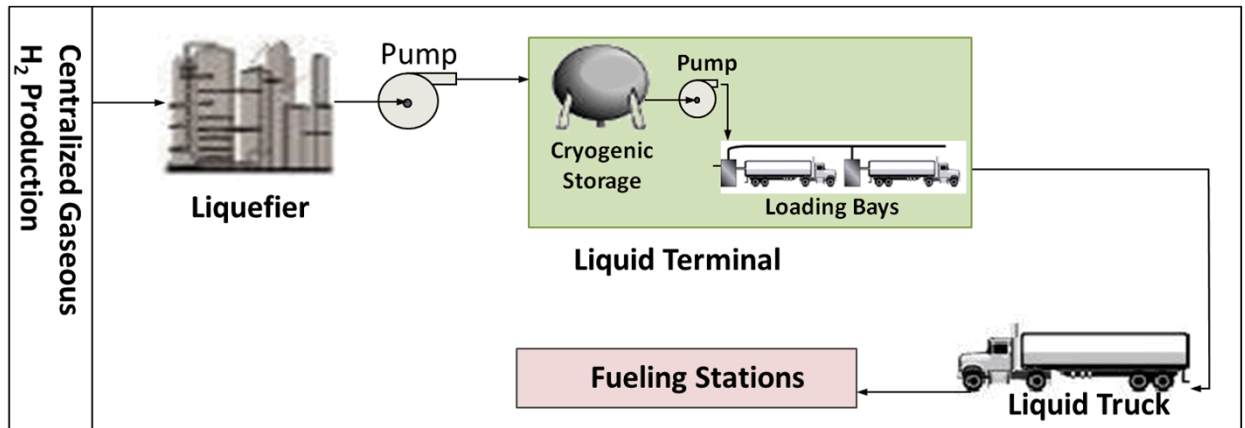


Image:
A. Elgowainy, ANL

Structural materials are central to the cost and reliability of H₂ infrastructure.

Background: Pipeline Installation & Operation



X52 or X65 Line Pipe
(i.e. base metal)

Microstructure of base metal affects crack growth rates



Friction Stir Welding (FSW)

Gas Metal Arc Welding (GMAW)

Welding to join or repair pipe

Welds may be more susceptible to embrittlement

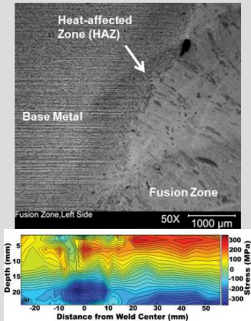


Can gas impurities mitigate embrittlement effect?

Daily pressure fluctuations can result in fatigue loading which can affect embrittlement

Images used with permission from U.S Pipeline, and Canadian Energy Pipeline Association

Background



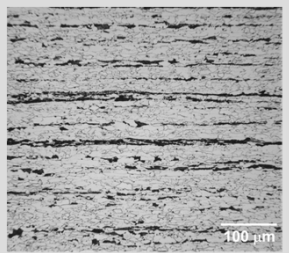
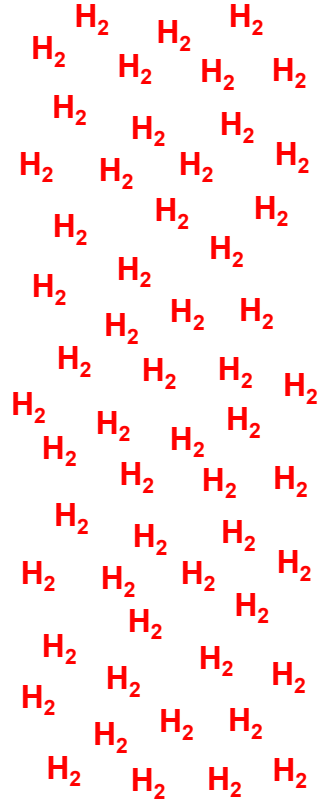
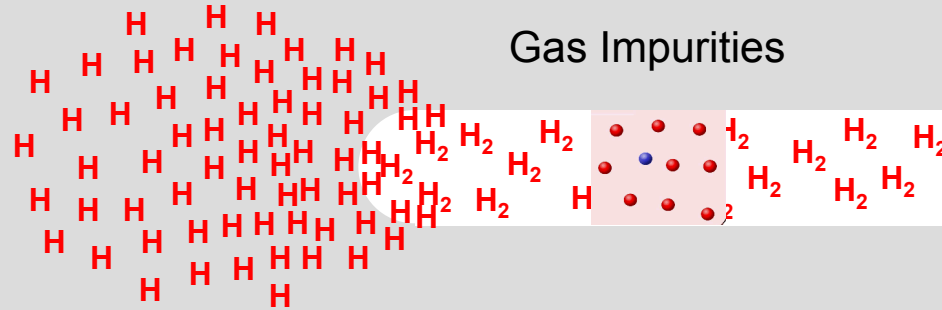
- Microstructure
- Weld
- Residual stress

$\sigma_{local}, \epsilon_{local}$

↑

$\sigma_{remote} \rightarrow K$

↑



Banding

↓

$\sigma_{local}, \epsilon_{local}$

↓

$\sigma_{remote} \rightarrow K$

Hydrogen-assisted cracking trends depend on microstructure, stress, and hydrogen uptake, but may be dominated by one variable.

Objectives/Relevance

Why should steel hydrogen pipelines be used?

- Operation of steel pipelines, and resistance to 3rd party damage is well-understood
 - Hydrogen pipelines function safely under *constant pressure* load
 - 1,500 miles of steel hydrogen pipelines already in use in the U.S.

Project Purpose:

- Assess steel pipeline performance under conditions expected in mature hydrogen market
 - Determine resistance of **base metal and welds to fluctuating loads**
 - Experimental data and analysis can guide the **optimization of design codes and standards** to lower pipeline cost while maintaining reliability
 - Establish **models that predict pipeline behavior as a function of microstructure** to guide future developments of novel steels

Research on hydrogen embrittlement will enable risk-informed design of lower cost hydrogen pipelines.

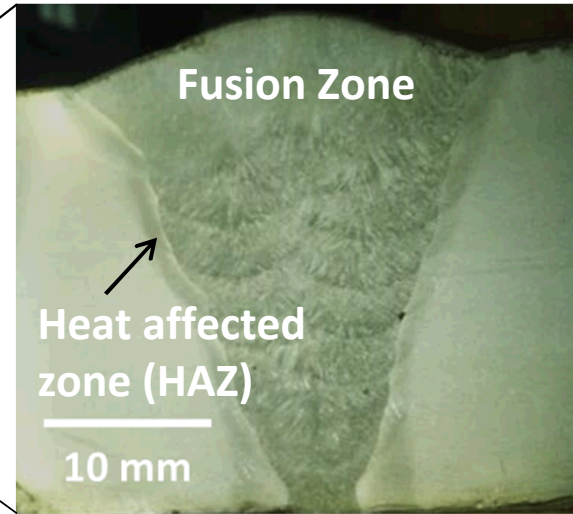
Approach: Base Metal and Welds

- Apply core capability (HEML) to measure fatigue crack growth in steels in high-pressure H₂ gas
 - Industrially relevant pipeline grades
 - Representative service environment
 - Fatigue crack growth data will be the basis for requirements of the ASME B31.12 code
- Assess variables that influence hydrogen embrittlement in pipeline steels
 - Welds
 - Microstructural banding
 - Gas impurities



Approach: Base Metal and Welds

X65



Gas metal arc weld (GMAW)

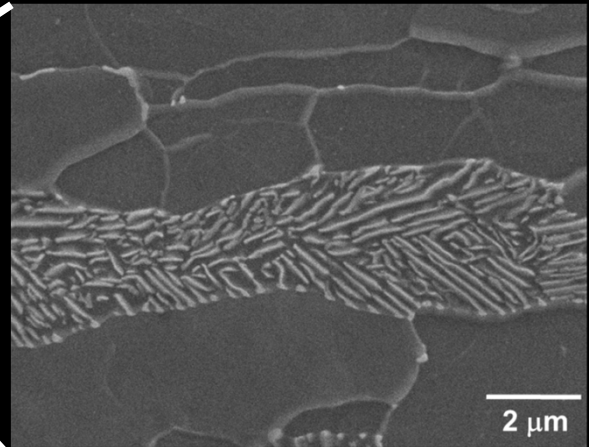
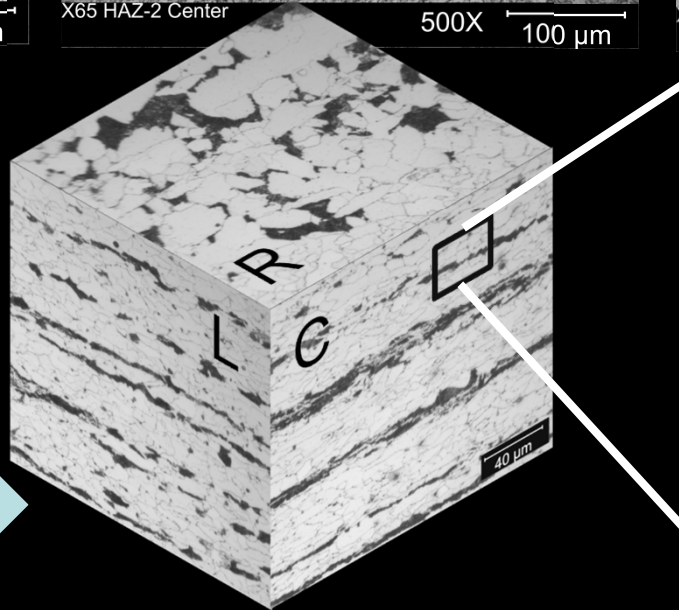
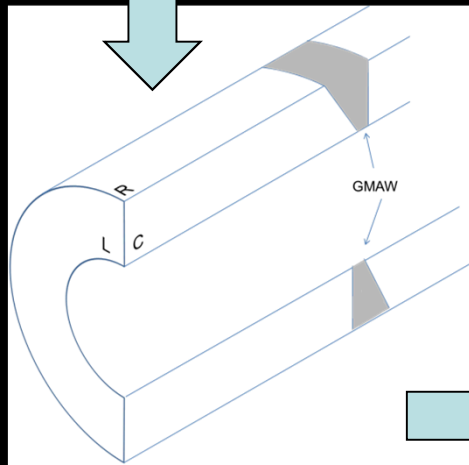
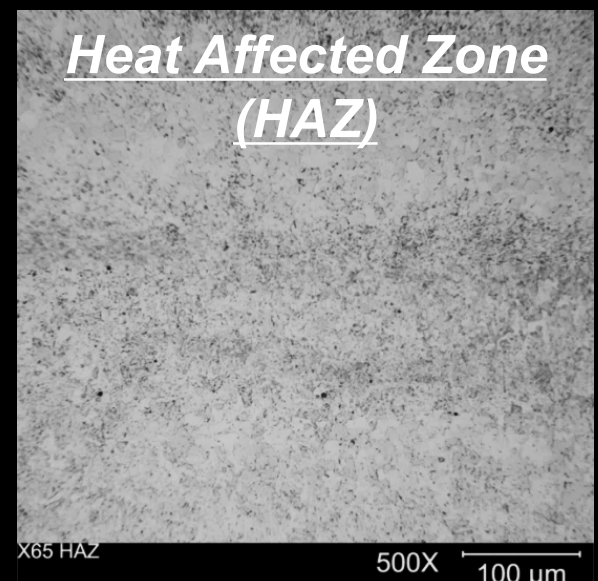
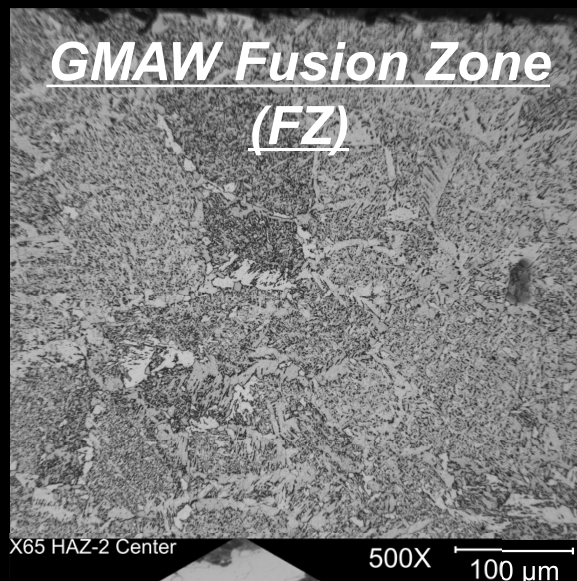
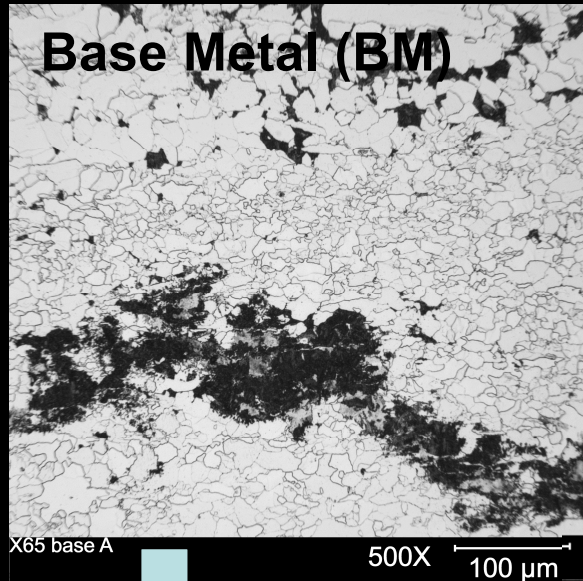
X52



Friction Stir Weld (FSW)

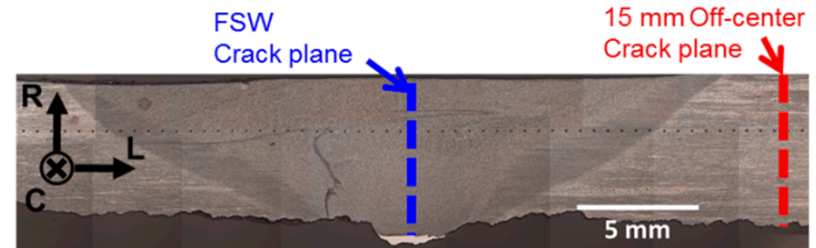
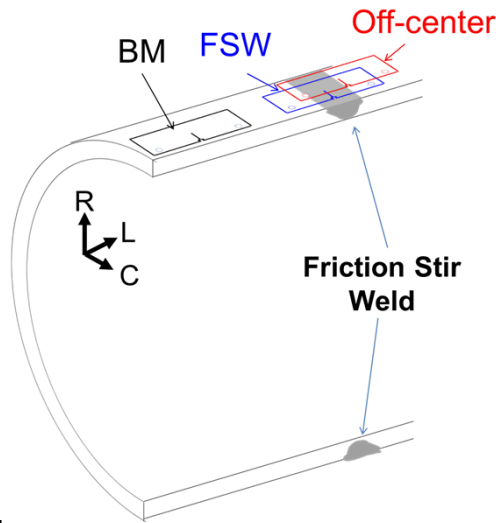
Welding process generates different microstructures and stresses than the base metal.

Approach: X65 Base Metal and Welds



Experimentation completed on base metal, fusion zones, and heat affected zones for X65 steel.

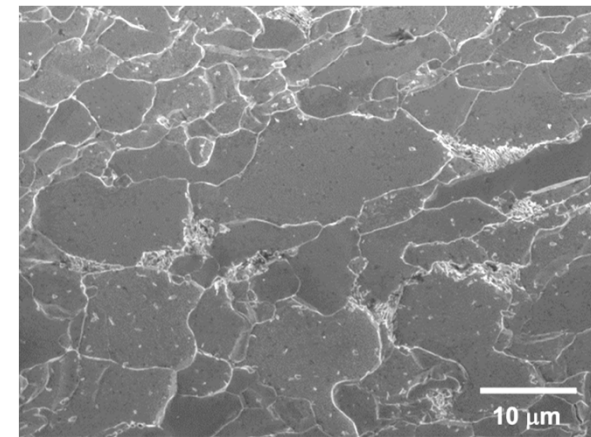
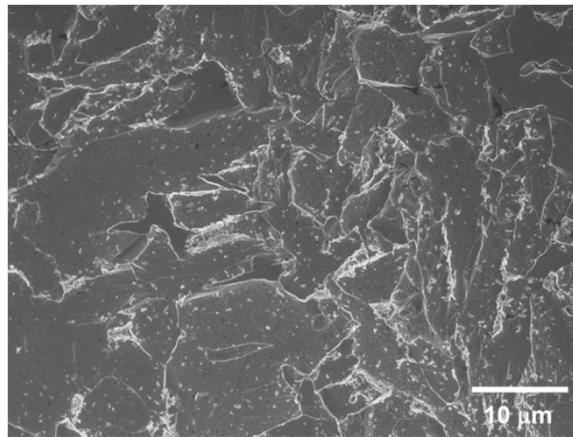
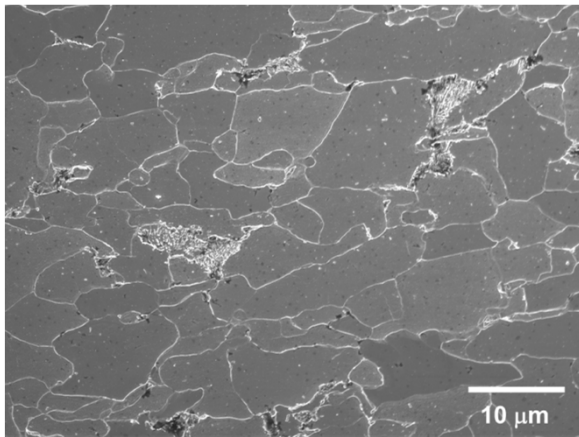
Approach: X52 Friction Stir Welds (FSW)



BM

FSW

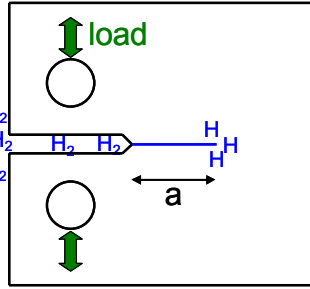
Off-Center



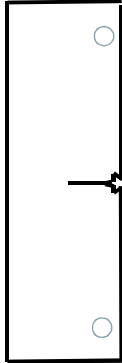
Two different regions of FSW were analyzed to account for potential differences in microstructure.

Approach: Testing Apparatus and Procedures

Compact Tension
(C(T))



ESE(T)



- Instrumentation

- Internal load cell in feedback loop
- Crack-opening displacement measured internally using LVDT or clip gauge
- Crack length calculated from compliance

- Mechanical loading

- Triangular load-cycle waveform
- Constant load amplitude
- $R = \frac{P_{min}}{P_{max}} = 0.5$ $freq = 1 Hz$

- Environment

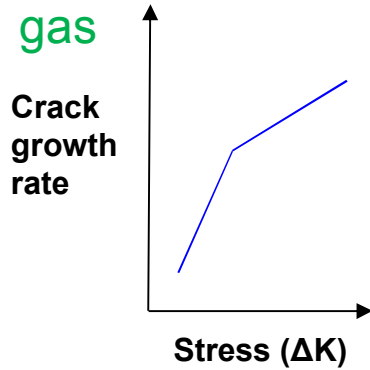
- Supply gas: 99.9999% H₂
- Pressure = 21 MPa (3 ksi)
- Room temperature



Fatigue crack growth measured in high-pressure H₂ gas

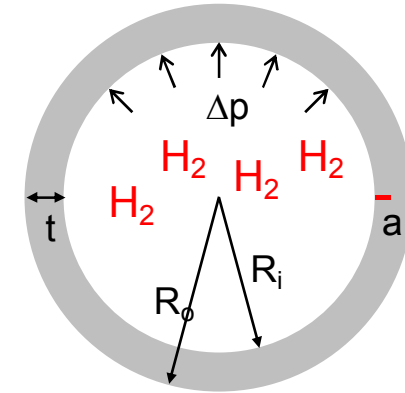
Approach: Optimization of Design

Experimentation:
measurements in H₂
gas

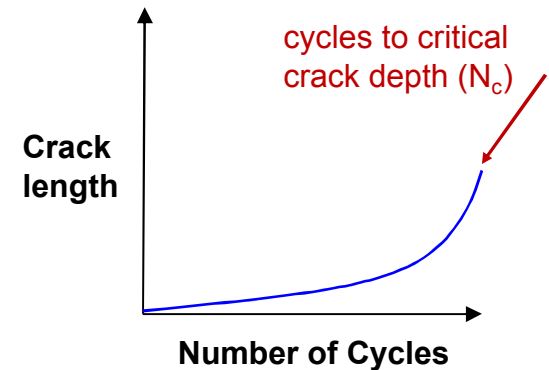


Fracture Mechanics Analysis

$$\Delta K = \Delta p [f(a, t, R_o, R_i)]$$



Assuming
steel
thickness,
calculate:

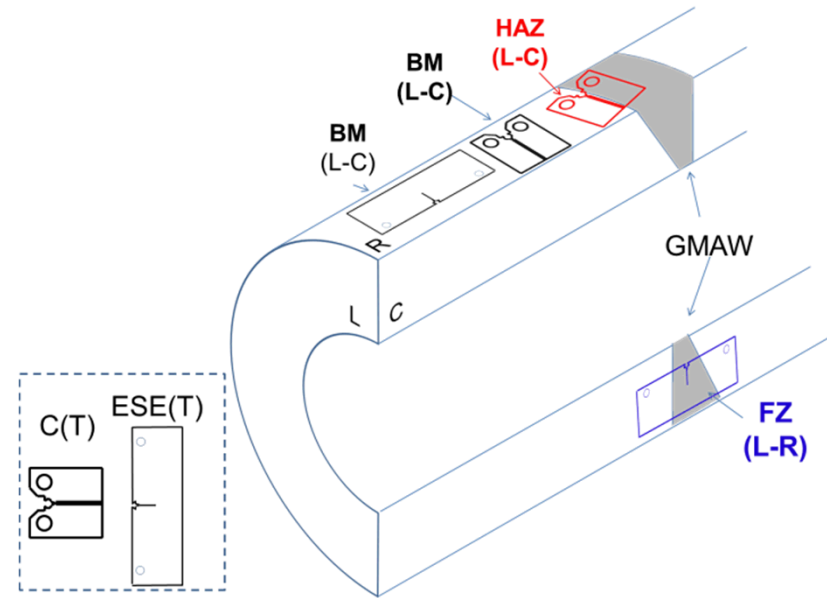
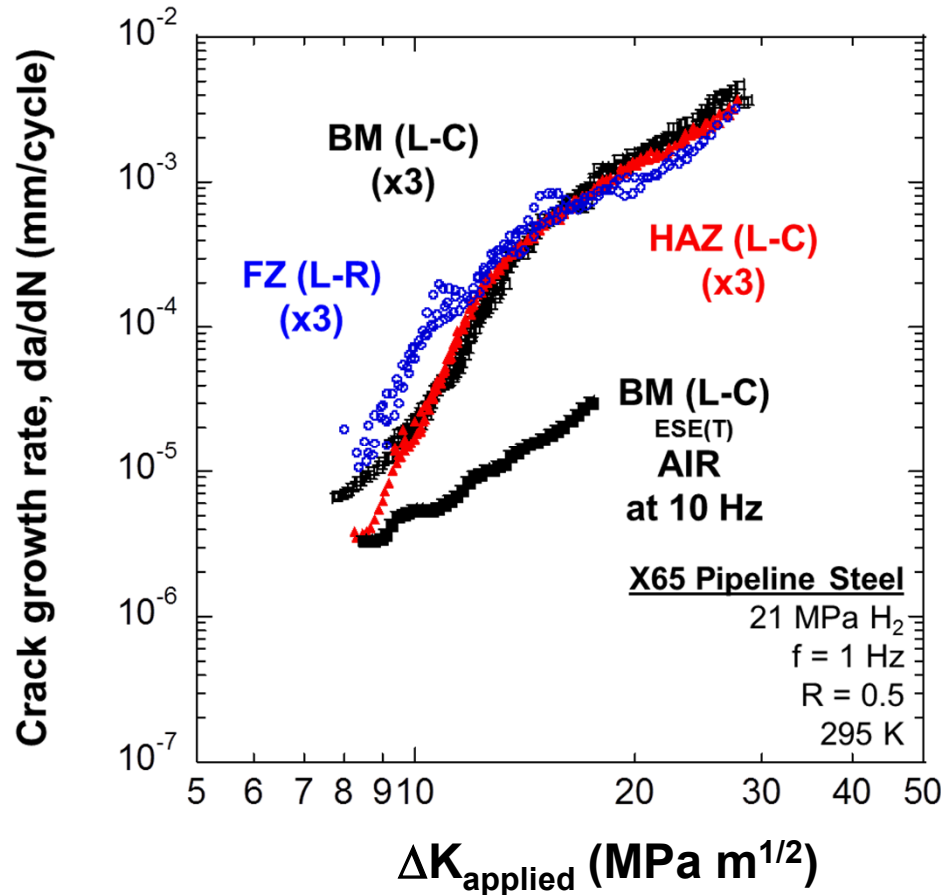


Design Analysis

Is steel pipeline life sufficient given expected service conditions, and ASME code requirements (life = $0.5 N_c$)?

Fracture mechanics analysis to characterize steel reliability in H₂ gas.

Results: X65 Gas Metal Arc Weld (GMAW)

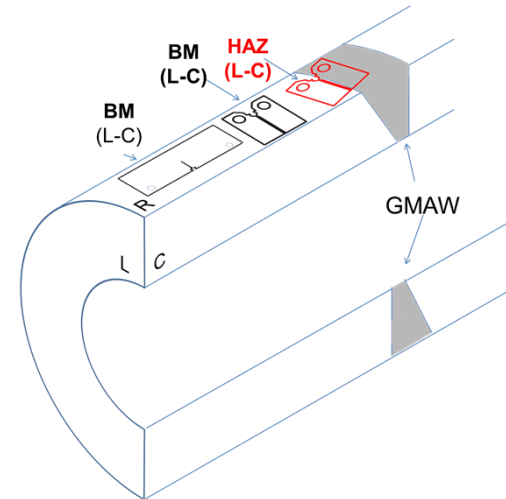
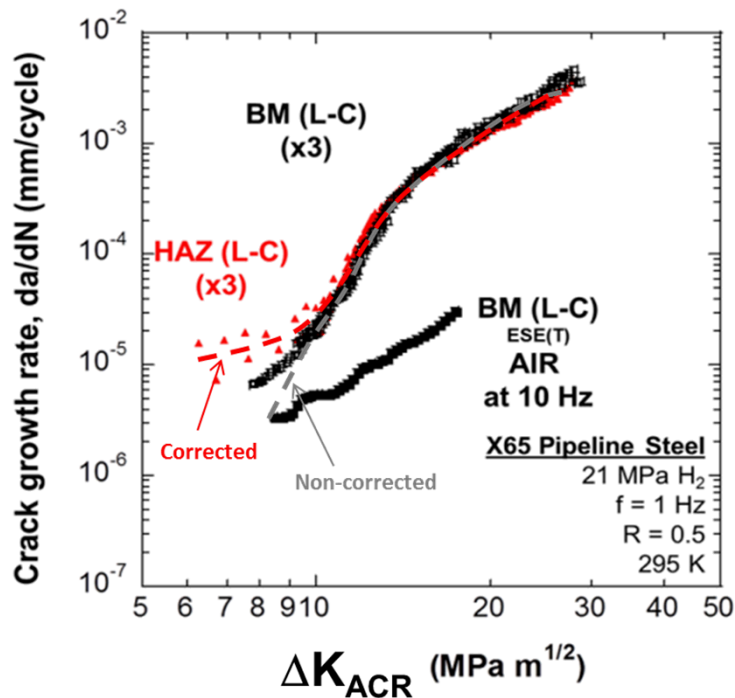


- Triplicate tests revealed repeatable results
- Results did not account for “residual stress” resulting from welding

Must perform analysis to account for contribution of residual stress to driving force, ΔK .

Results: X65 Gas Metal Arc Weld (GMAW)

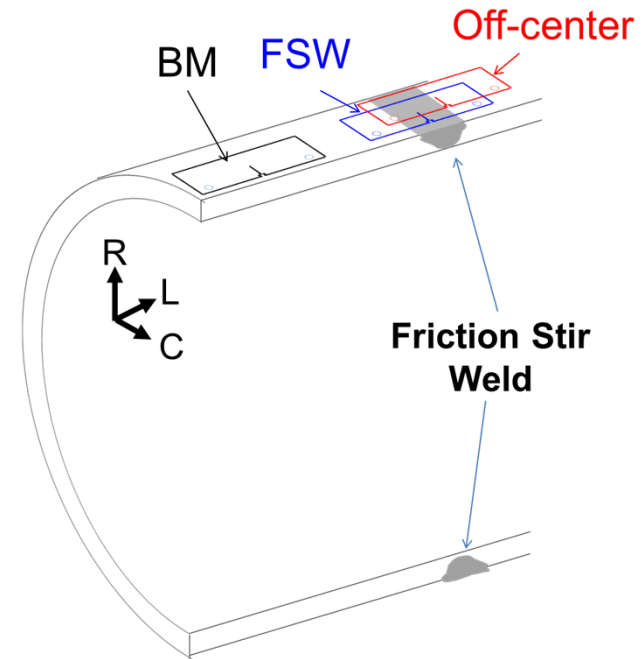
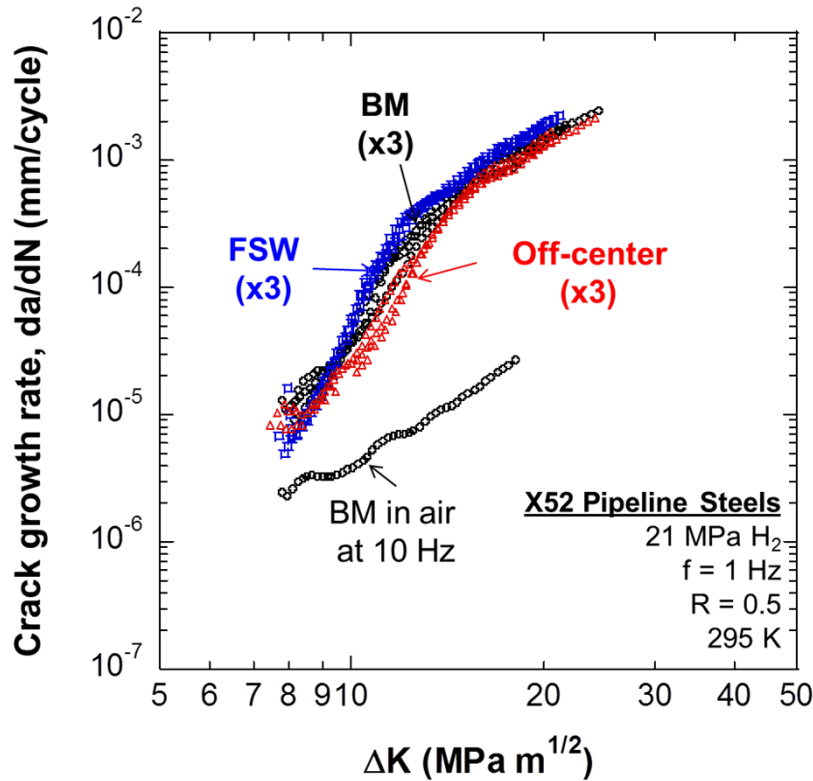
Analysis to account for residual stress in driving force leads to more reliable da/dN vs. ΔK curves.



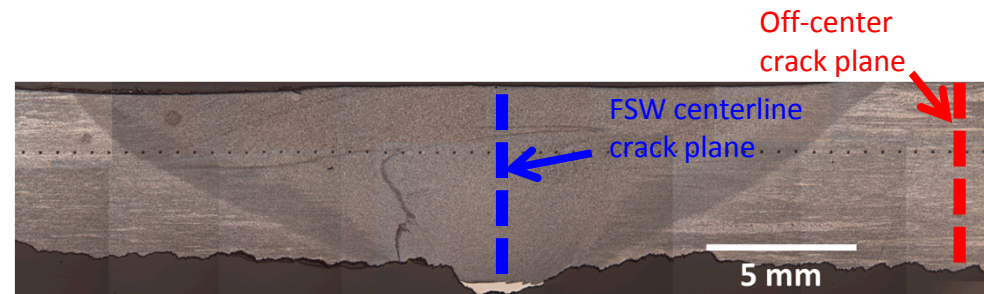
- Corrections show faster crack growth at lower ΔK than previously determined.

X65: Crack growth faster in weld heat affected zone than in base metal.

Results: X52 Friction Stir Welds (FSW)

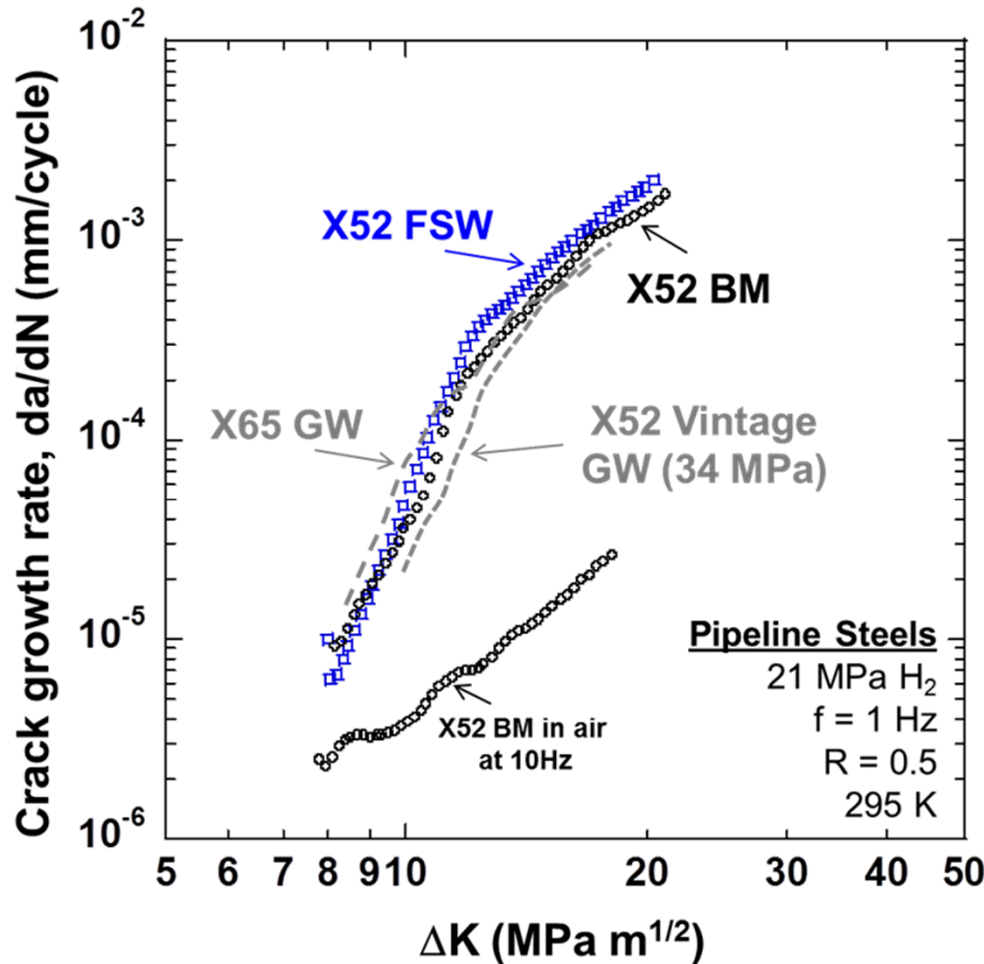


- Crack growth rate measurements in FSW are repeatable (triplicate results obtained)



X52: crack growth faster in center of FSW than in base metal, and faster in base metal than in off-center position.

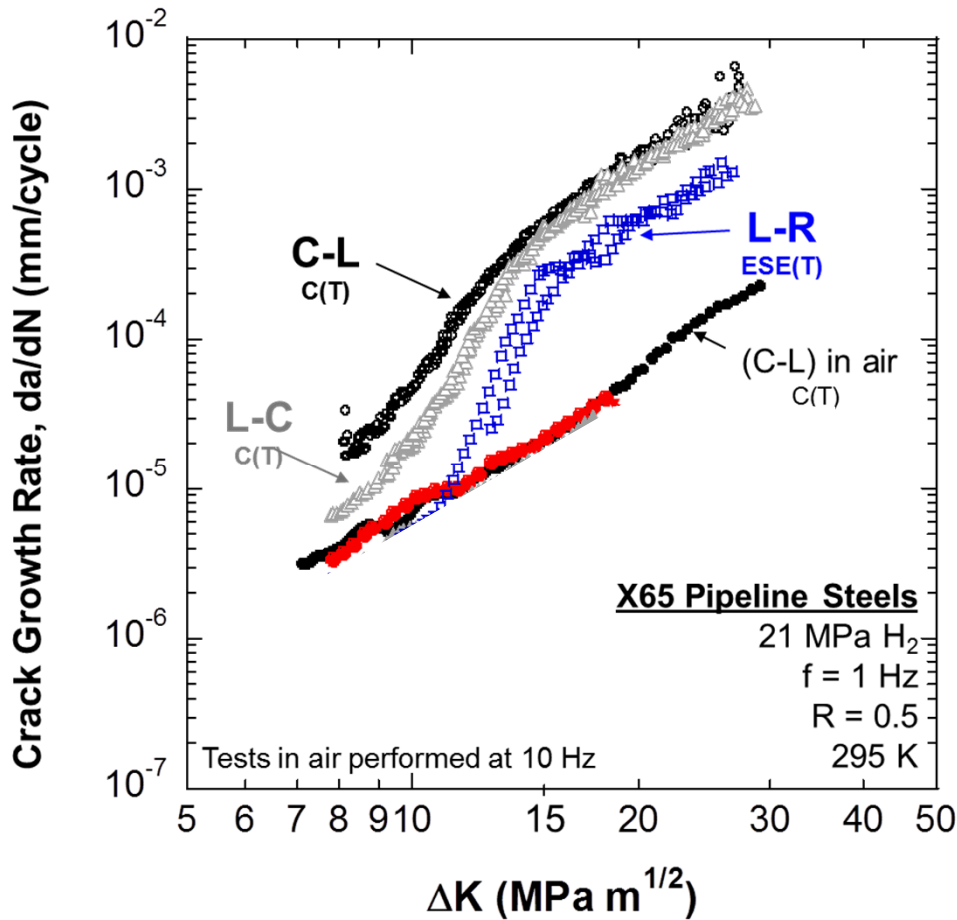
Conclusions: Welds



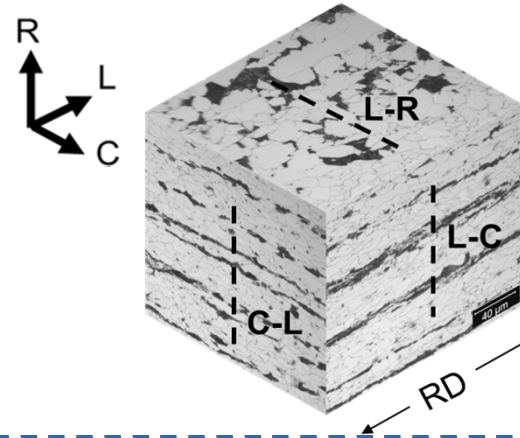
*X52 Vintage GW is work from NIST [Slifka *et al.* PVP2015]

Friction stir welds and conventional gas metal arc welds exhibit similar crack growth rates in hydrogen.

Results: Microstructural Banding



J. Ronevich et al., *Int. J. Fatigue*, 2015.



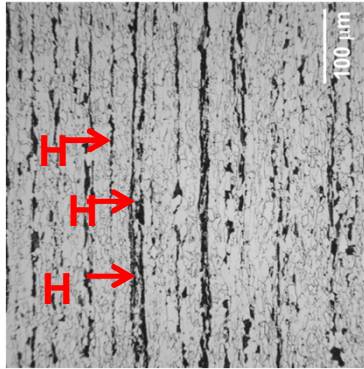
Data obtained compared to data from other specimen orientations:

- Cracks in L-C and C-L direction encounter consistent microstructure (primarily ferrite), and had similar crack growth rates
- Cracks in in L-R direction encountered alternating bands of ferrite-pearlite, and grew much more slowly.

Bands of pearlite significantly slow crack growth.

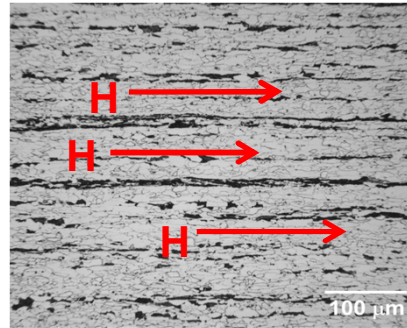
Conclusions: Microstructural Banding

Hydrogen diffusion in L-R orientation vs. C-L orientation



L-R

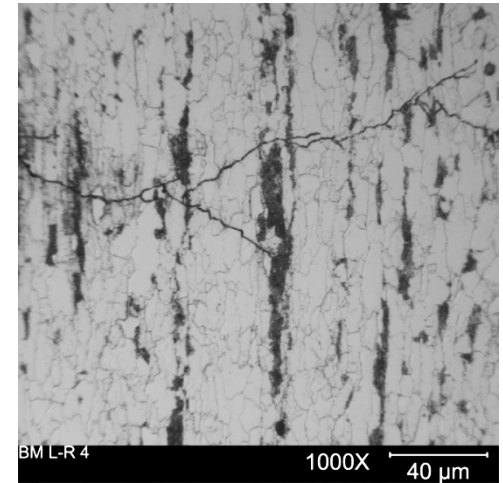
Hydrogen diffusivity
across banded
structure



C-L

Hydrogen diffusivity
along banded
structure

<

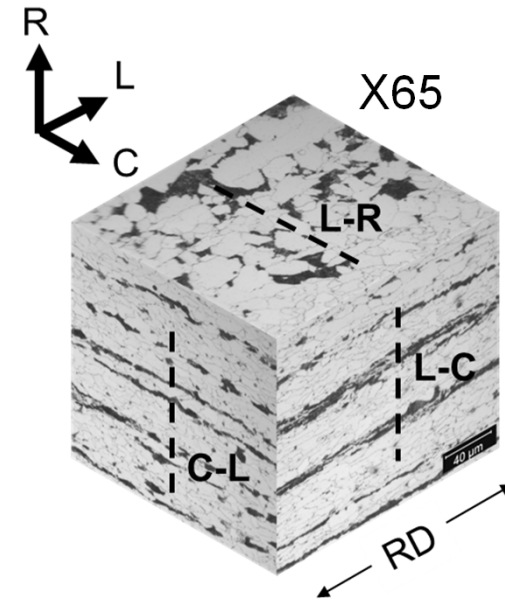
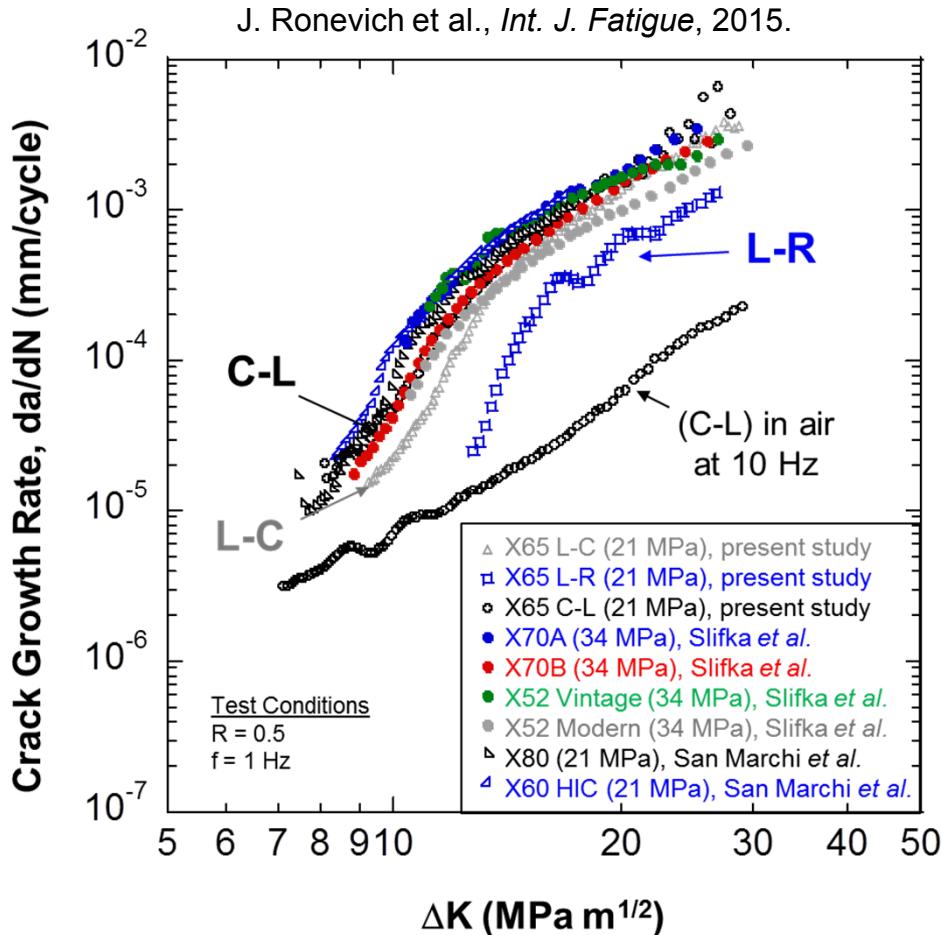


Crack-tip branching in L-R orientation

Slower rates of crack growth perpendicular to pearlite bands may be because:

- 1) hydrogen diffusion is slower, and**
- 2) Hard pearlite results in crack branching (which reduces driving force).**

Conclusions: Microstructural Banding



X60 and X80 data:
San Marchi et al., ASME PVP, 2010

X52 and X70 data:
Slifka et al., ASME PVP, 2014
Drexler et al., Proceedings of SteelyHydrogen, 2014

Examining multiple pipeline steels demonstrates that most pronounced microstructure effect is banded ferrite-pearlite in L-R orientation

Conclusions: H₂ Pipeline Design

H₂ Pipeline Wall Thickness Necessary*		
Pressure cycle (psi)	Initial flaw depth: 3% wall thickness	Initial flaw depth: 5% wall thickness
1500 to 3000	0.62 in (15.7 mm)	0.81 in (20.7 mm)
300 to 3000	1.37 in (34.9 mm)	1.83 in (46.5 mm)

*Thickness determined by $0.5N_c$, in which $N_c = 73,000$ cycles
 ($0.5N_c = 36,500$ cycles = 50 yr at 2 cycles/day)

- NG pipeline thickness necessary calculated based on ASME B31.8

Thickness: 0.96 in (24.4 mm)

$$P = \frac{2St}{D} FET$$

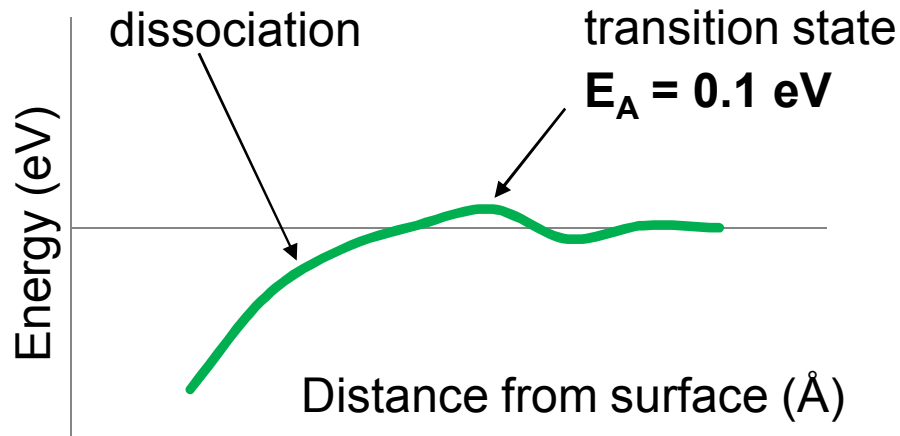
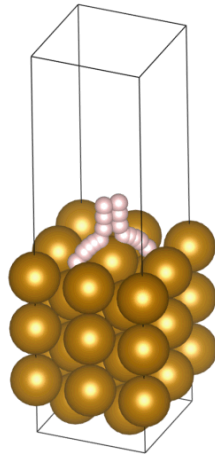
P = design pressure = 21 MPa
 S = SMYS = 52 ksi (X52)
 t = thickness
 D = outside diameter = 24 in.
 F = design factor = 0.72 (Class 1)
 E = longitudinal joint factor = 1
 T = temp derating factor = 1

H₂ pipelines may not require a thickness premium relative to current natural gas codes.

Related Research: Embrittlement Mitigation

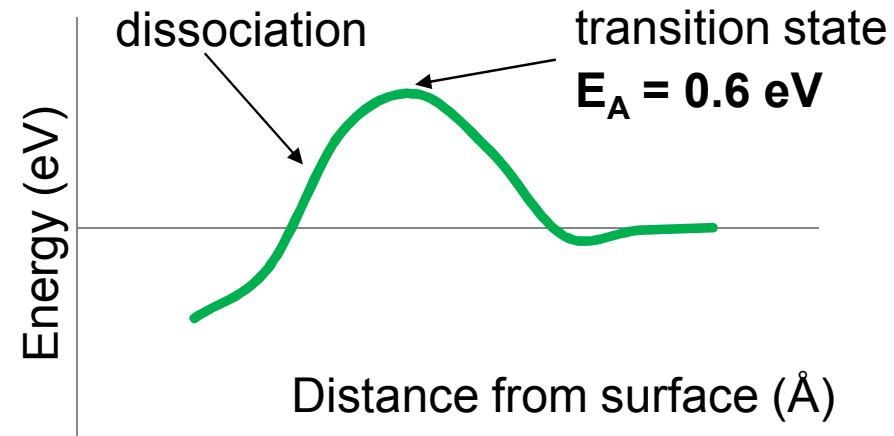
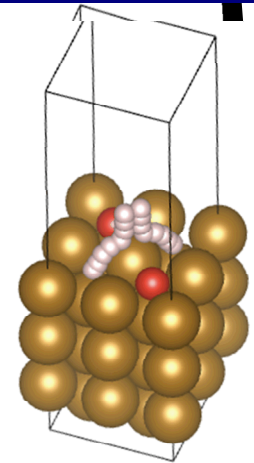
Potential energy surface scan for H₂ approaching Fe(100) surface

H₂ molecule approaches directly on top Fe atom



Potential energy surface scan for H₂ approaching Fe(100) surface **with preadsorbed O atoms**

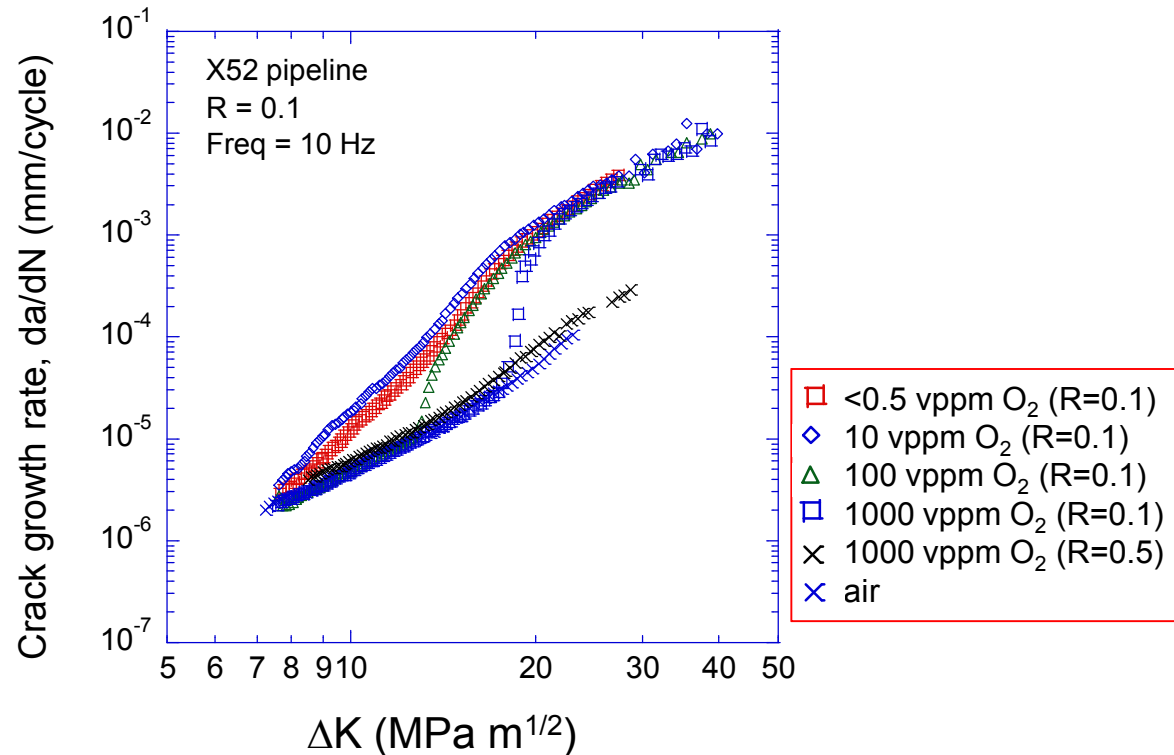
H₂ molecule approaches directly on top Fe atom



Staykov et al., *Int J Quantum Chemistry*, 2014

DFT simulations show that pre-adsorbed oxygen inhibits H₂ dissociation.

Related Research: Embrittlement Mitigation



- At lower ΔK , crack growth rates in H₂ environments same as rates in air
- At R=0.1, hydrogen-accelerated crack growth observed at higher ΔK
 - da/dN at onset of hydrogen-accelerated crack growth depends on O₂ concentration
- At R=0.5, hydrogen-accelerated crack growth not observed

B.P. Somerday et al., *Acta Mater*, 2013

Mitigation depends on several variables: O₂ conc, R-ratio, da/dN, and load cycle frequency.

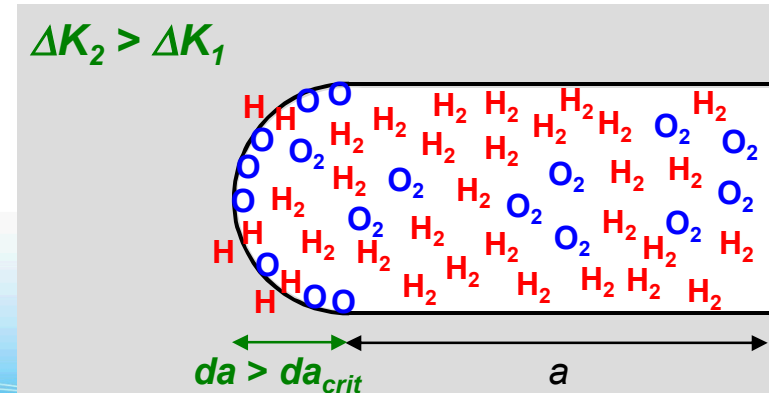
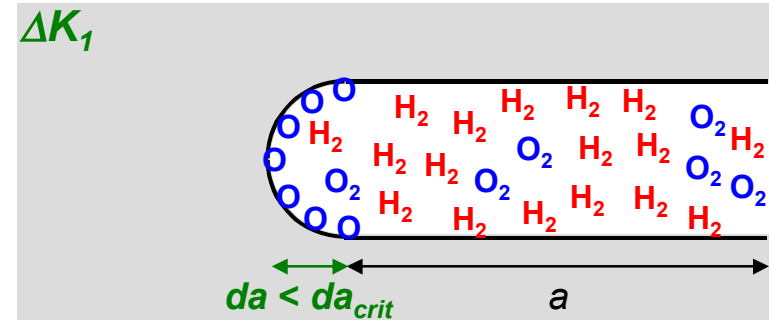
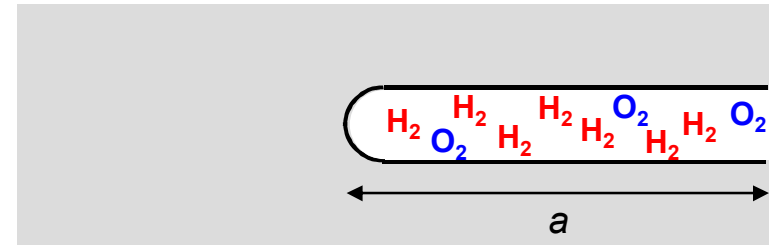
Related Research: Modeling H₂ Embrittlement with Oxygen Impurities

B. Somerday et al., *Acta Mater*, 2013

Assumptions

- Initial inert-environment crack growth modeled by blunting-resharpening
- Oxygen out-competes hydrogen for adsorption sites on freshly exposed crack-tip surface
- Extent of oxygen adsorption depends on crack-tip area, proportional to crack-growth increment (da)
 - when $da < da_{crit}$, crack tip *fully passivated* by oxygen
 - when $da > da_{crit}$, crack tip *not fully passivated* → **H uptake**

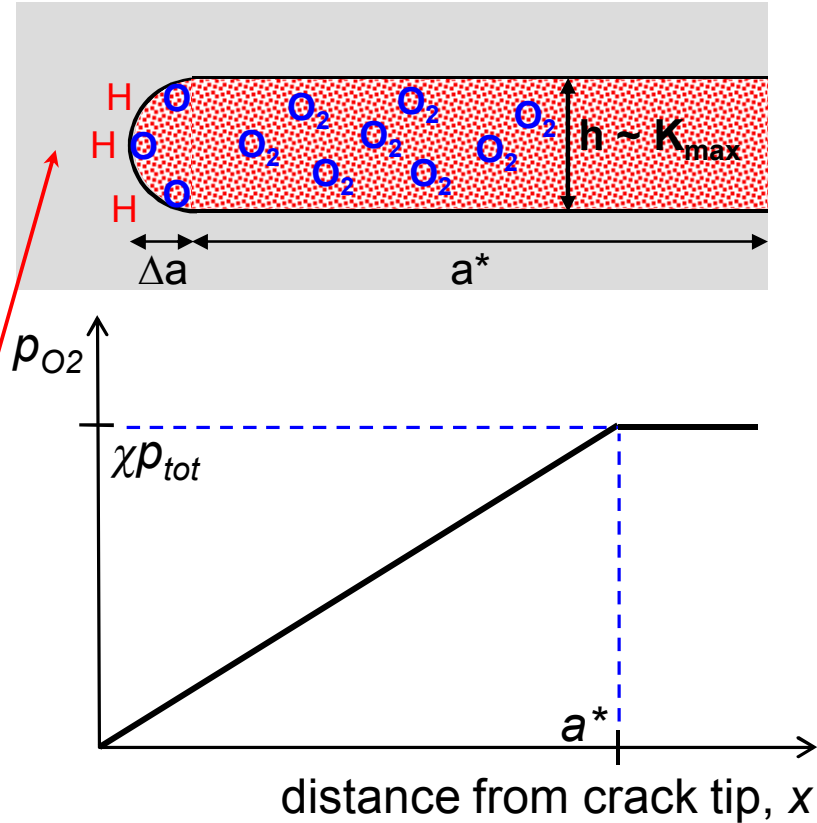
Developed model that relates oxygen adsorption to hydrogen uptake.



Model developed based on idealized crack geometry and diffusion-limited oxygen adsorption

Somerday et al., *Acta Mater*, 2013

- *Goal*: quantify amount of adsorbed oxygen (n) during load-cycle time (Δt)
- *Key assumption*: adsorption rate-limited by O₂ diffusion in crack channel
 - constant crack-channel height (h) during diffusion
 - steady state p_{O_2} profile
- Model foundation: oxygen delivered to crack tip ($Jh\Delta t$) = oxygen adsorbed on crack tip ($S\theta\pi\Delta a$)



$$J = \text{flux} = D \frac{\chi p_{tot}}{R_g T a^*}$$

$$h = \text{channel height} = 0.6(1 - \nu^2) \frac{\sigma_0}{E} \left(\frac{\Delta K}{\sigma_0(1 - R)} \right)^2$$

$$\Delta t = 1 / f$$

$$\theta = \text{oxygen coverage} \quad S = \text{surface site density}$$

H uptake and accelerated crack growth when $\theta = \theta_{crit}$

$$\theta = \frac{0.3 \chi D p_{tot} (1 - \nu^2)}{\Delta a f \pi S R_g T E \sigma_0} \left(\frac{\Delta K}{\sqrt{a^*} (1 - R)} \right)^2$$

Summary

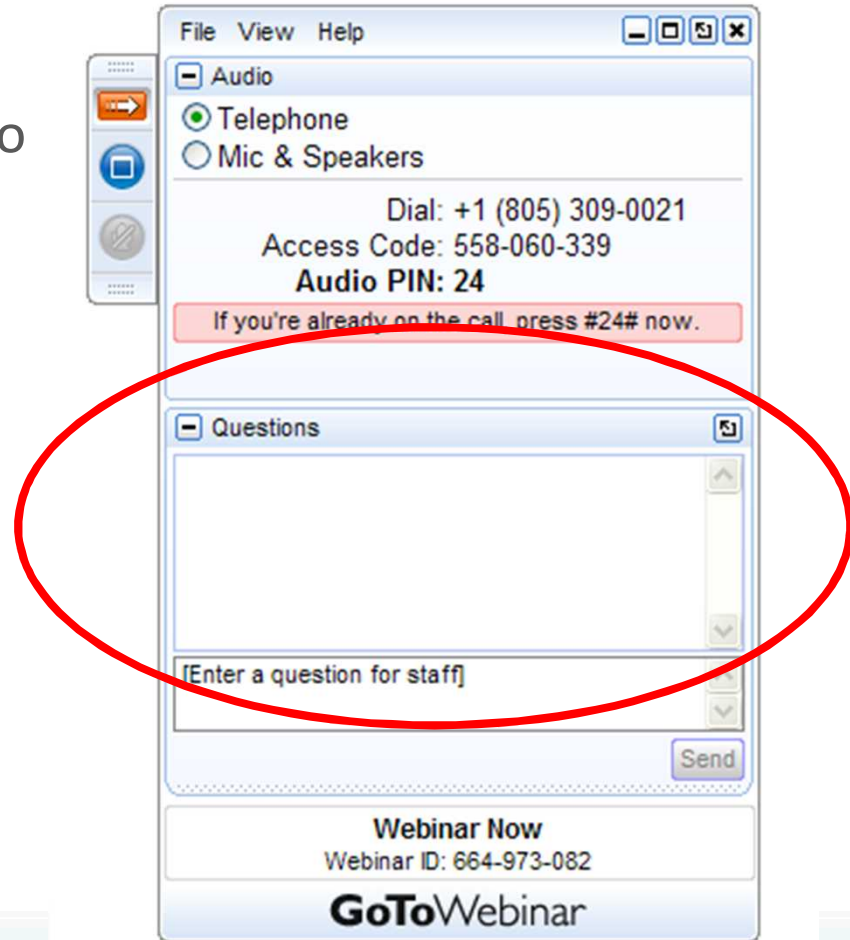
- Base Metal:
 - Resistance to hydrogen assisted fatigue depends on microstructure, not just strength.
- Welds:
 - Friction stir welds and gas metal arc welds have similar resistance to hydrogen embrittlement
 - Friction stir welding is often an economical alternative
 - Welds have slightly faster crack growth than base metal
- Design Codes:
 - Thickness premiums on hydrogen pipelines may be over-conservative
- Embrittlement mitigation:
 - Low levels (ppm) of gas species such as O₂ can enhance safety margins for steel H₂ pipelines

Remaining Challenges and Barriers

- Establish data-informed safety factors for steel H₂ pipelines, particularly for high-strength steels (e.g. X80 or X100)
 - Realistic safety factors can lower cost of steel H₂ pipelines
- Reduce testing burden for qualifying steel base metal and welds for H₂ pipelines by developing microstructure-performance (i.e., fatigue crack growth behavior in H₂ gas) relationships
 - Microstructure-performance relationships are foundation for predictive, physics-based model of H₂-accelerated fatigue crack growth

Question and Answer

- Please type your questions into the question box



Thank You

Presenters:

- Joe Ronevich - Sandia National Laboratories
 - jaronev@sandia.gov
- Brian Somerday - Sandia National Laboratories
 - bpsomer@sandia.gov

DOE Host:

- Neha Rustagi – Technology Manager, Hydrogen Production and Delivery Program
 - Neha.Rustagi@EE.Doe.Gov

Webinar Recording and Slides:

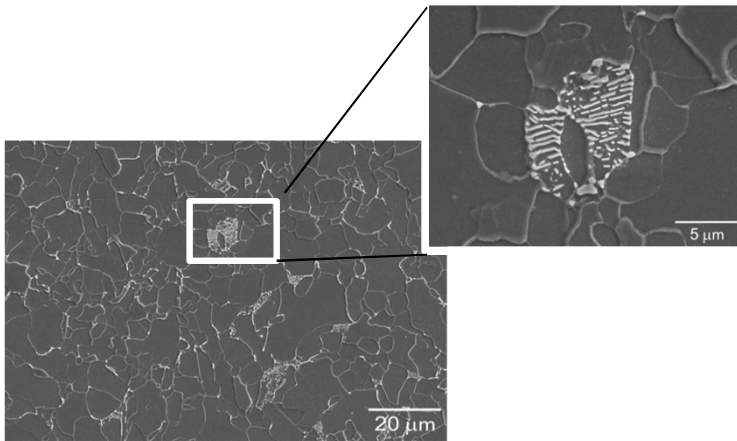
(<http://energy.gov/eere/fuelcells/webinars>)

Newsletter Signup

(<http://energy.gov/eere/fuelcells/subscribe-news-and-financial-opportunity-updates>)

Technical Back-Up Slides

Related Research: Embrittlement Mechanisms



ferrite + 8
vol% pearlite



324 mm OD x 12.7 mm WT

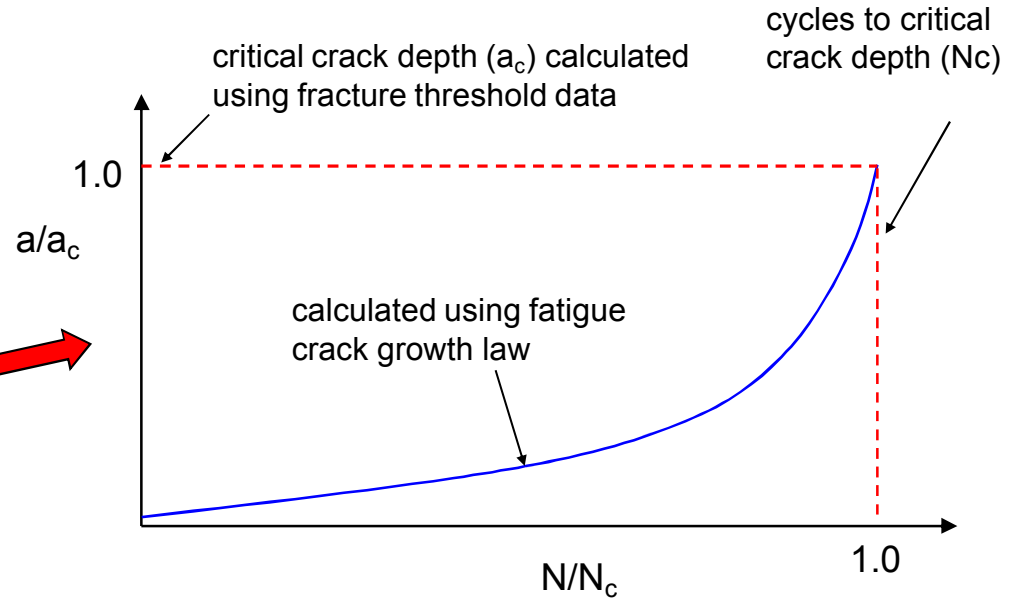
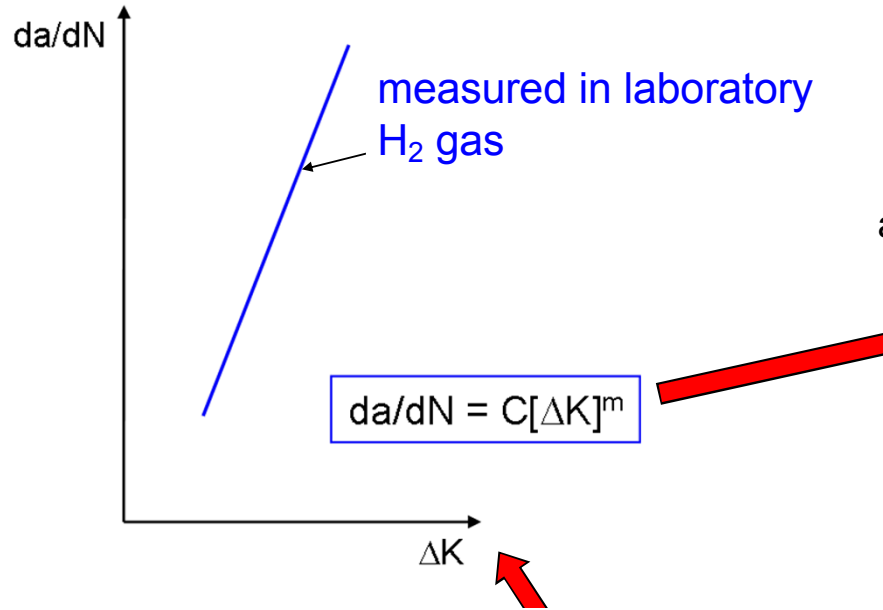
- Tensile properties
 - Yield strength: 428 MPa
 - Ultimate tensile strength: 483 MPa
- Alloy composition

C	Mn	P	S	Si	Cu	Ni	Cr	V	Nb	Al	CE
0.06	0.87	0.011	0.006	0.12	0.03	0.02	0.03	0.002	0.03	0.034	0.11

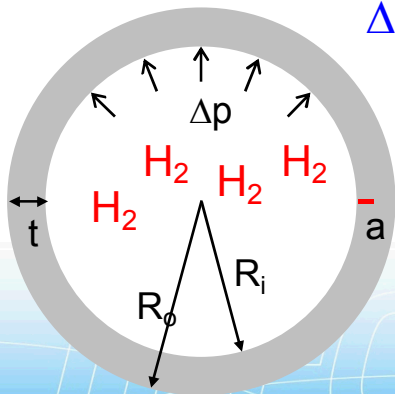
Measurements performed on technologically relevant steel: API 5L X52 (PSL 2).

Approach

Fracture mechanics analysis to characterize steel reliability in H₂ gas



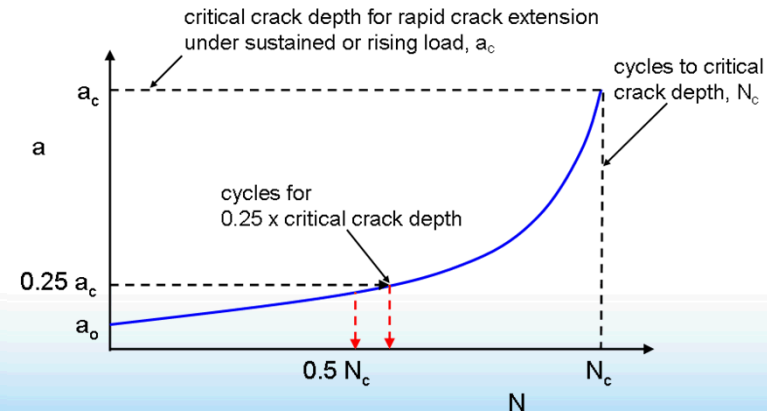
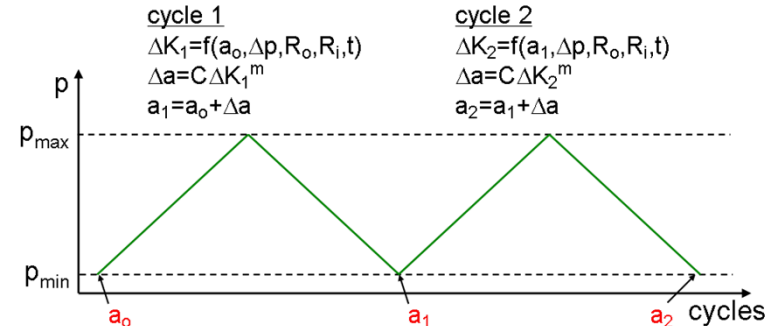
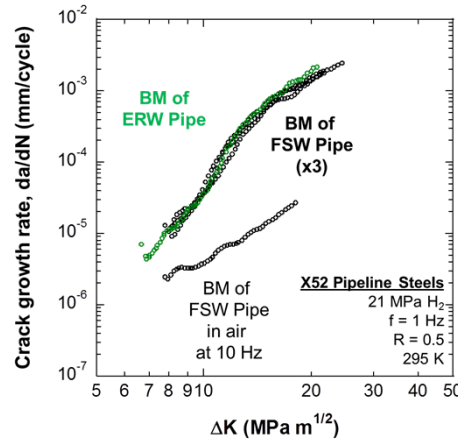
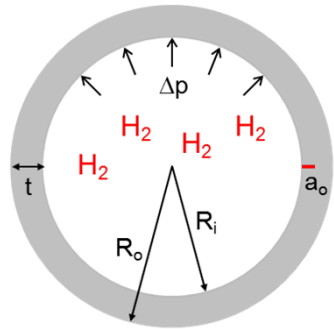
$$\Delta K = \Delta p[f(a, t, R_o, R_i)]$$



- Two fracture properties in H₂ needed
 - Fatigue crack growth curve
 - Fracture threshold
- Fatigue life analysis framework accommodates H₂ embrittlement

Conclusions: H₂ Pipeline Design

Measured fatigue crack growth behavior can be used to calculate minimum wall thickness for steel H₂ pipelines.

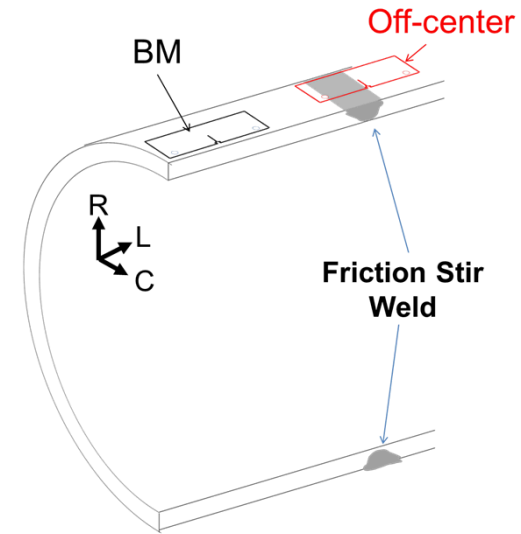
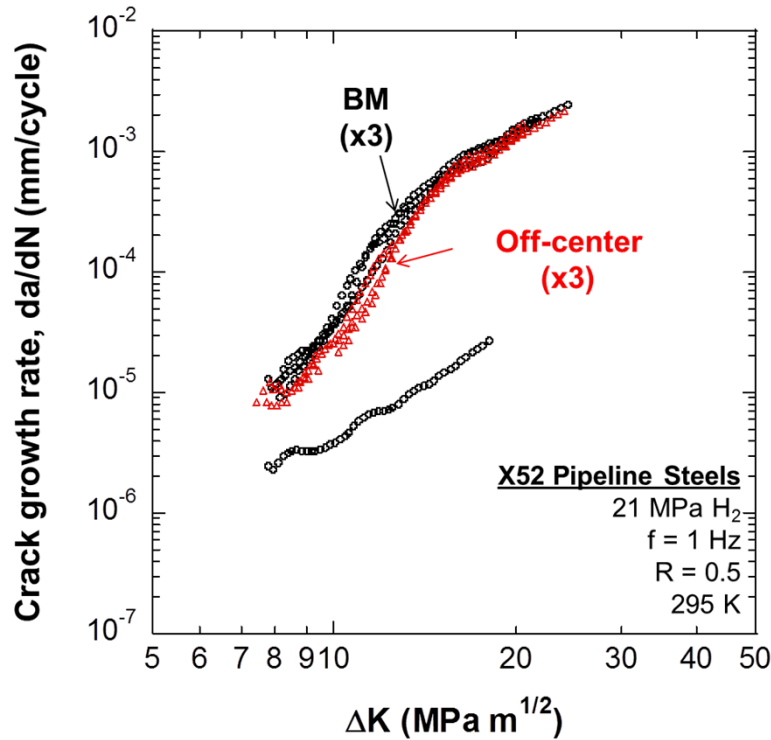


$$\Delta K = \Delta p [f(a, t, R_o, R_i)]$$

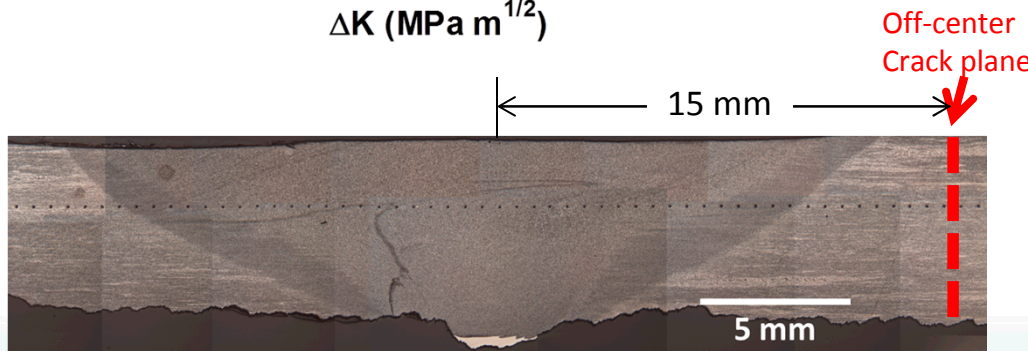
$$da/dN = C \Delta K^m$$

- ASME fatigue life calculation: structural analysis + fatigue crack growth law
- Inputs:
 - pressure cycle range (Δp)
 - initial flaw depth (a_o)
 - pipe outer diameter ($2R_o$)
 - fatigue crack growth law ($da/dN=C\Delta K^m$)
- Goal:** Calculate wall thickness (t) required to attain fatigue life of $0.5N_c$

Results: X52 Friction Stir Welds (FSW)



- Crack growth rate measurements at off-center position in friction stir weld are repeatable
- Crack growth rates at off-center position are modestly lower than rates for base metal (BM)



Triplicate fatigue crack growth rate measurements at off-center position in friction stir weld completed.

Results: X65 Steel and GMAW, Non-Uniform Crack Fronts

Non-uniform crack fronts rendered initial data unusable.

Compact Tension C(T)

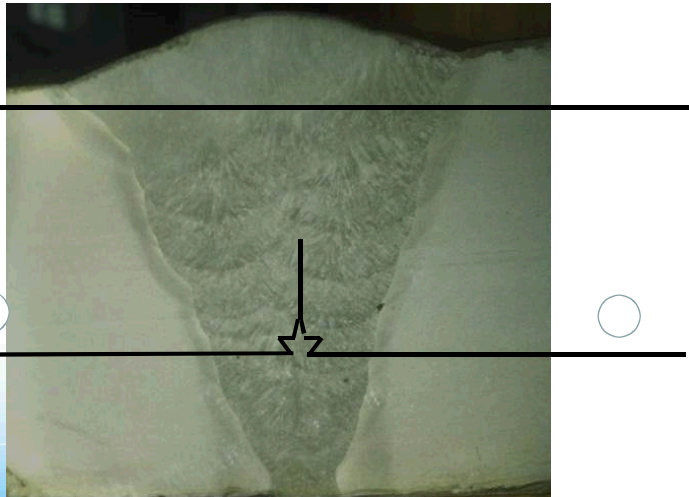
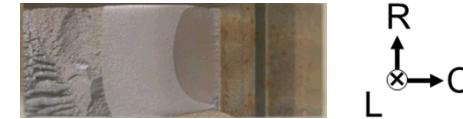
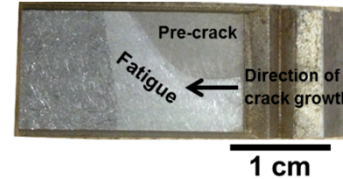
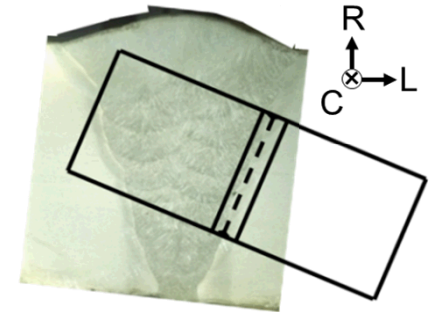
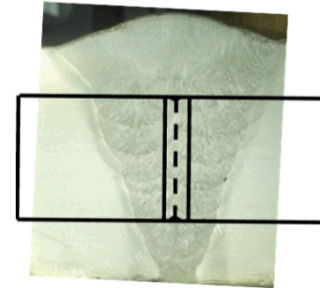
specimens extracted from pipe

- Entire crack plane contained in FZ or HAZ
- Non-uniform crack fronts observed
- Attributed to residual stress

BM

FZ

HAZ



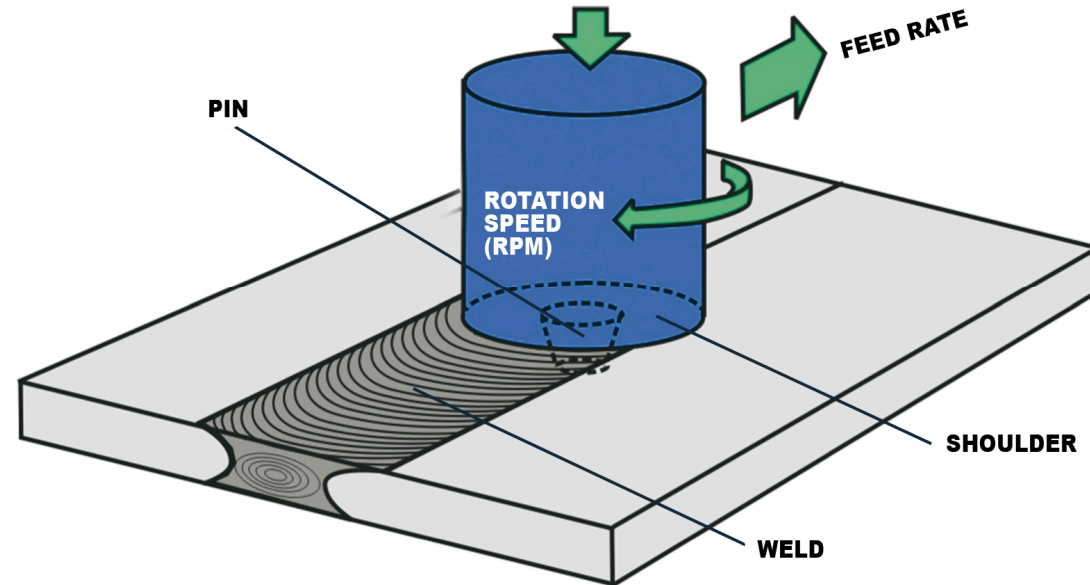
Alternate standardized test specimen geometry necessary for weld FZ testing: ESE(T)

Experimentation

Friction stir welding offers cost and reliability advantages over conventional welding

How it works:

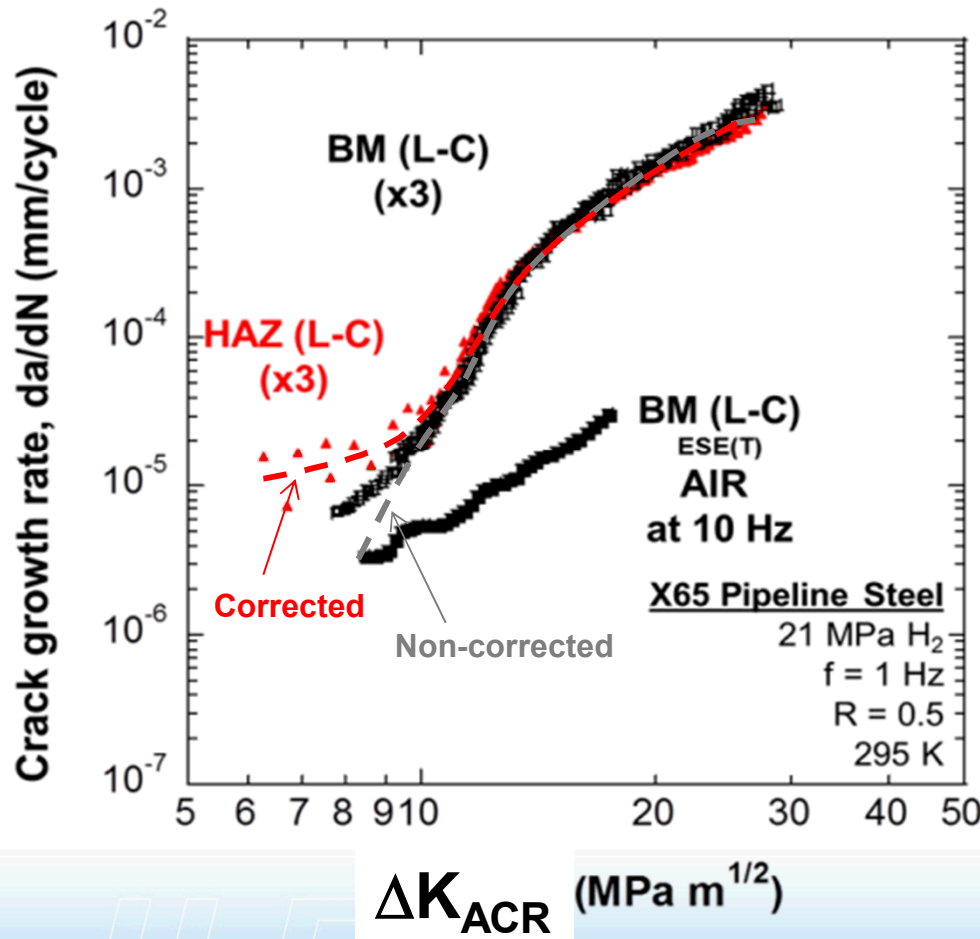
- 1) Tool is inserted into joint under high compression
- 2) Tool is rotated at high rpm
- 3) Metal softens and is stirred to form weld



Advantages

- No consumables (e.g. filler wire, shielding gas) are needed:
- No melting of metal
 - Reduces residual stress
 - Reduces heat affected zone
 - Prevents solidification cracking

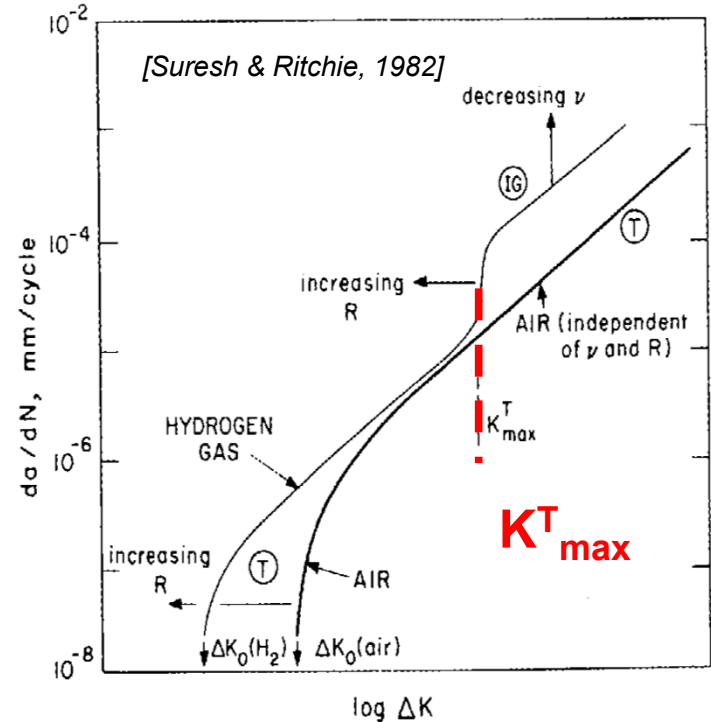
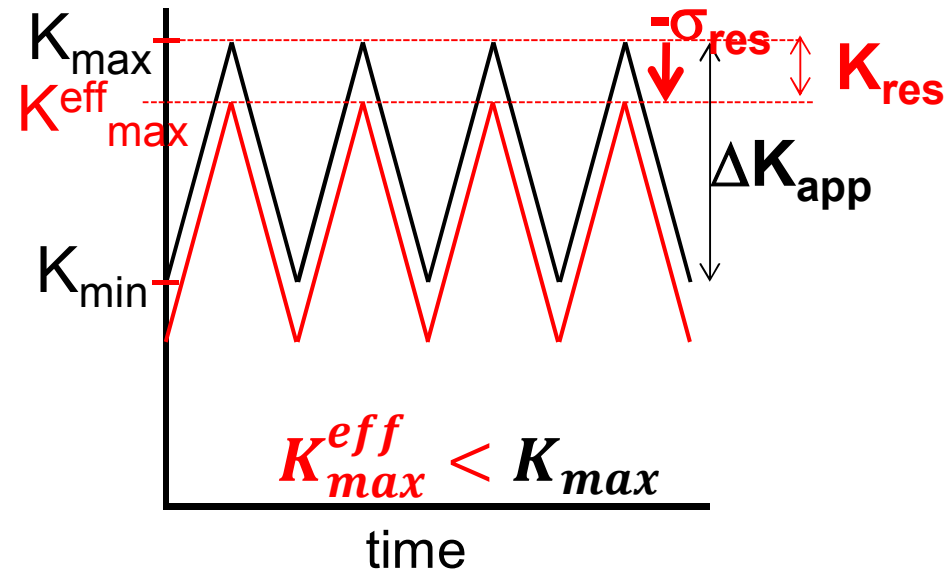
Corrections for crack closure suggests that FCGR for HAZ is higher than BM



- Adjusted Compliance Ratio (ACR) method implemented to remove effects of closure
 $\rightarrow \Delta K_{ACR}$

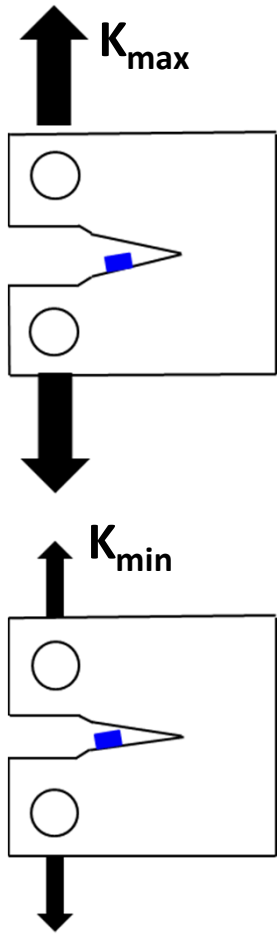
Removal of closure effects highlights importance in comparing intrinsic fatigue behavior

Compressive residual stress can reduce K_{max}

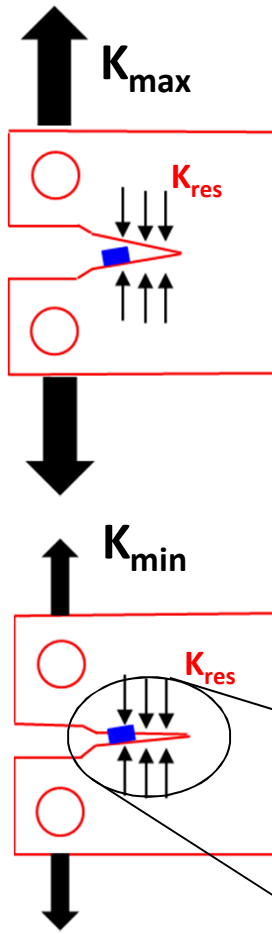


$K_{max}^T \sim$ onset of hydrogen accelerated FCG

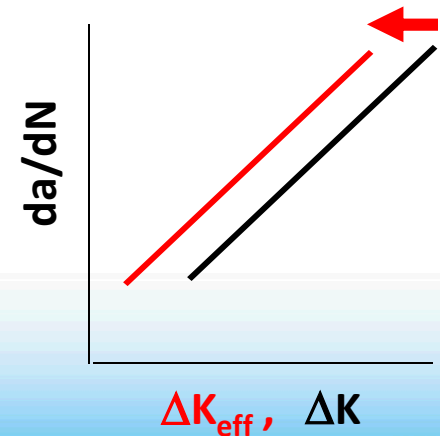
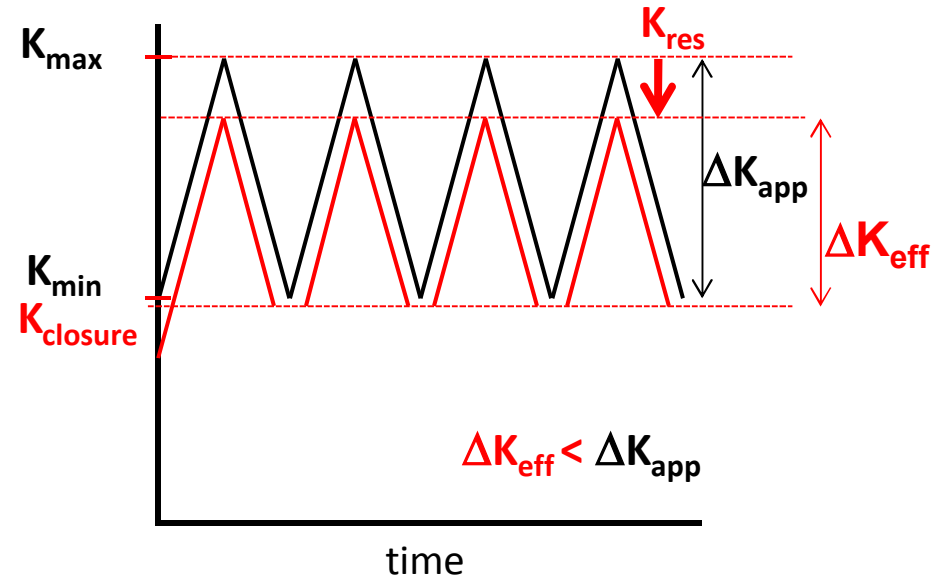
Analysis performed to account for effect of residual stress on crack-driving force



No residual stress



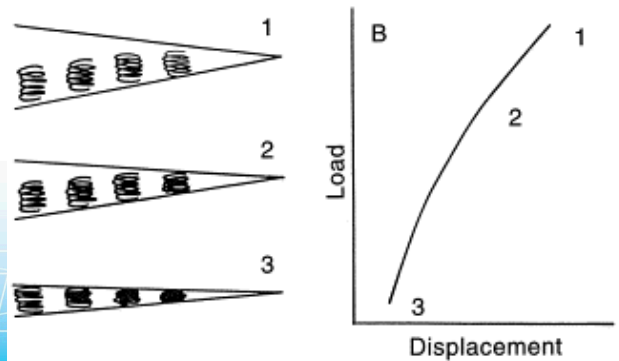
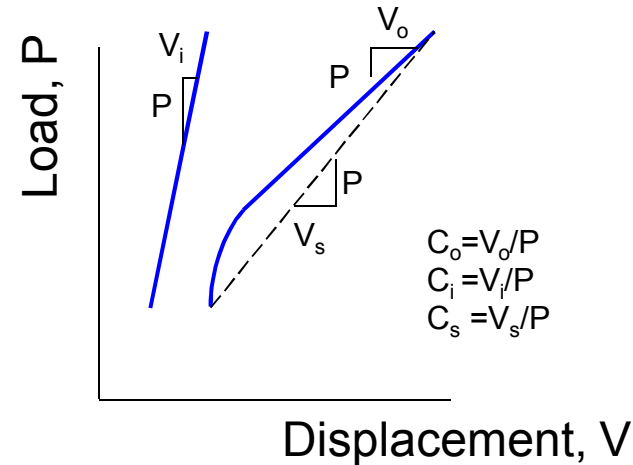
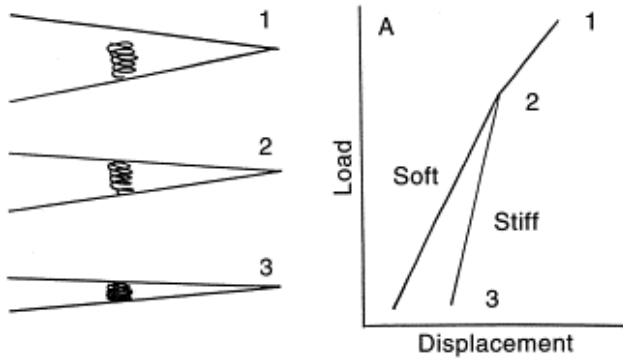
Compressive residual stress



- Compressive residual stress induces “crack closure”, reducing crack-driving force from ΔK to ΔK_{eff}

Crack closure analysis employed adjusted compliance ratio (ACR) method

- Adjusted compliance ratio (ACR): ASTM E647-13a approved method
- Alternative method is ASTM 2% Compliance Offset
- Both methods are used to calculate $\Delta K_{\text{effective}}$
- $\Delta K_{\text{applied}} > \Delta K_{\text{effective}}^{ACR}$



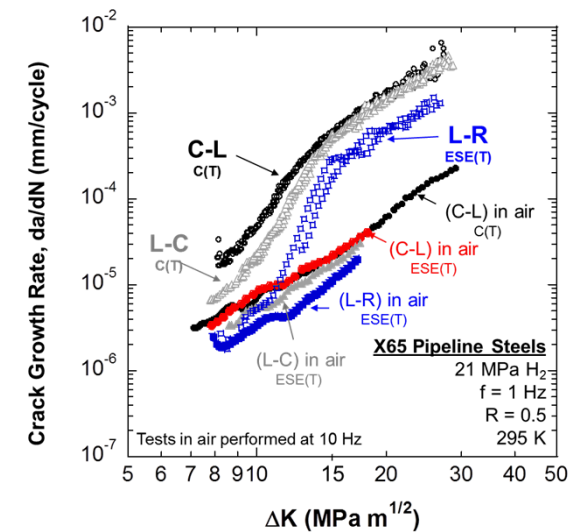
$$ACR = \frac{C_s - C_i}{C_o - C_i}$$

$$\Delta K_{\text{effective}} = \Delta K_{\text{app}} \times ACR$$

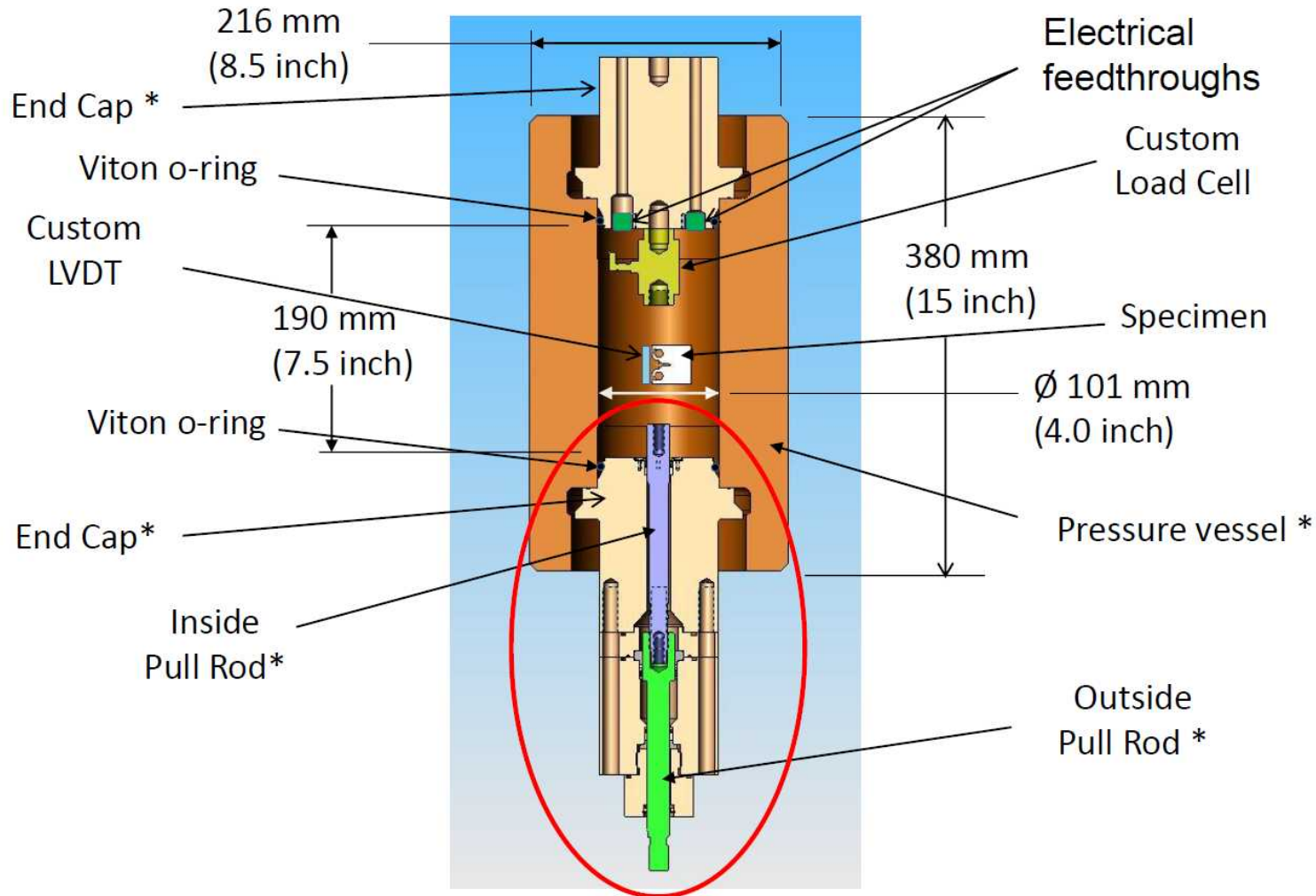
Microstructure-sensitive hydrogen transport

Crack growth rate, da/dN (x 10⁻⁵ mm/cycle) at select ΔK

Orientation (Environment)	10 MPa m ^{1/2}	12 MPa m ^{1/2}	15 MPa m ^{1/2}	20 MPa m ^{1/2}
C-L (Air)	0.745	1.13	2.14	6.37
L-R (Air)	0.350	0.447	1.15	N/A*
L-C (Air)	0.543	0.927	1.73	N/A*
Perpendicular				
Ratio in Air, $\frac{da/dN_{C-L}}{da/dN_{L-R}}$	2.1	2.5	1.9	N/A*
Parallel				
Ratio in Air, $\frac{da/dN_{C-L}}{da/dN_{L-C}}$	1.4	1.2	1.2	N/A*
C-L (H ₂)	4.60	17.6	61.5	159
L-R (H ₂)	0.519	2.16	29.0	69.4
L-C (H ₂)	2.30	11.6	51.5	139
Perpendicular				
Ratio in H ₂ , $\frac{da/dN_{C-L}}{da/dN_{L-R}}$	8.9	8.1	2.1	2.3
Parallel				
Ratio in H ₂ , $\frac{da/dN_{C-L}}{da/dN_{L-C}}$	2.0	1.5	1.2	1.1



Design concept of pressure vessel



* Material: A286 Precipitation hardened austenitic stainless steel