Hydrogen Embrittlement of Structural Steels

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Overview

Timeline

- Project start date Jan. 2007
- Project end date Oct. 2012*
- Percent complete 60%

Budget

- Total project funding (to date)
  - DOE share: $1000K
- FY11 Funding: $200K
- FY12 Funding: $100K

*Project continuation and direction determined annually by DOE

Barriers & Targets

- Pipeline Reliability/Integrity
- Safety, Codes and Standards, Permitting
- High Capital Cost and Hydrogen Embrittlement of Pipelines

Partners

- DOE Pipeline Working Group
  - Federal Labs: Sandia, Oak Ridge, Savannah River, NIST
  - Universities: Univ. of Illinois
  - Industry: Secat, industrial gas companies, ExxonMobil
  - Standards Development Organizations: ASME

Objectives/Relevance

- Why steel hydrogen pipelines?
  - Safety of steel pipelines well understood (e.g., third-party damage tolerance, vulnerability of welds)
  - Hydrogen pipelines safely operated under *static pressure*
- Demonstrate reliability/integrity of steel hydrogen pipelines for *cyclic pressure*
  - Address potential fatigue crack growth aided by hydrogen embrittlement, particularly in welds
- Enable pipeline reliability/integrity framework that accommodates hydrogen embrittlement
  - Ensure relevance to H_2 pipeline code ASME B31.12
- FY11-FY12: quantify effects of O_2 impurities on fatigue crack growth laws for X52 steel in H_2 gas

Approach

- Apply unique capability for measuring fracture properties of steels in high-pressure H_2
  - Fracture properties serve as inputs into reliability/integrity assessment as specified in ASME B31.12 pipeline code
  - Milestone: Determine the threshold level of O_2 concentration required to mitigate accelerated fatigue cracking for X52 steel in 21 MPa H_2 gas (~100% complete)
  - Milestone: Measure the fatigue crack growth law for X65 pipeline girth weld in H_2 gas (10% complete)
- Emphasize pipeline steels and their welds identified by stakeholders as high priority
  - Provide feedback to stakeholders through DOE Pipeline Working Group

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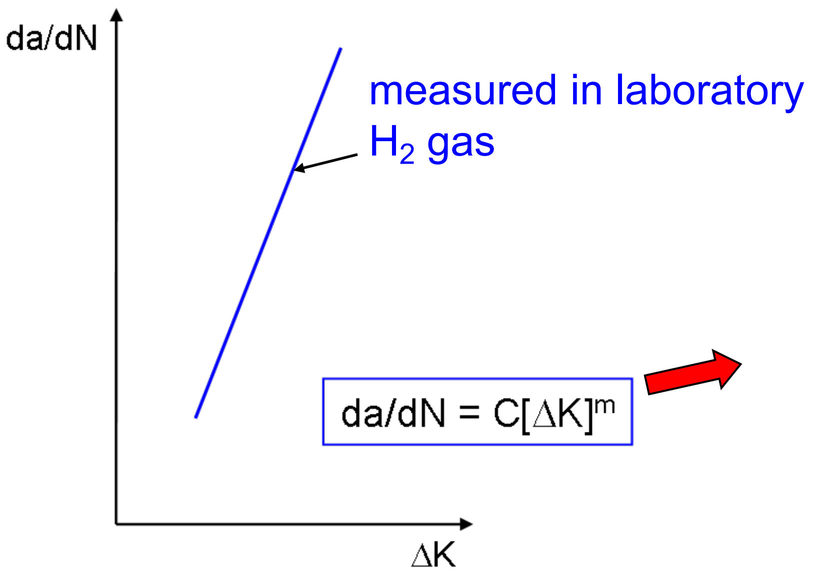
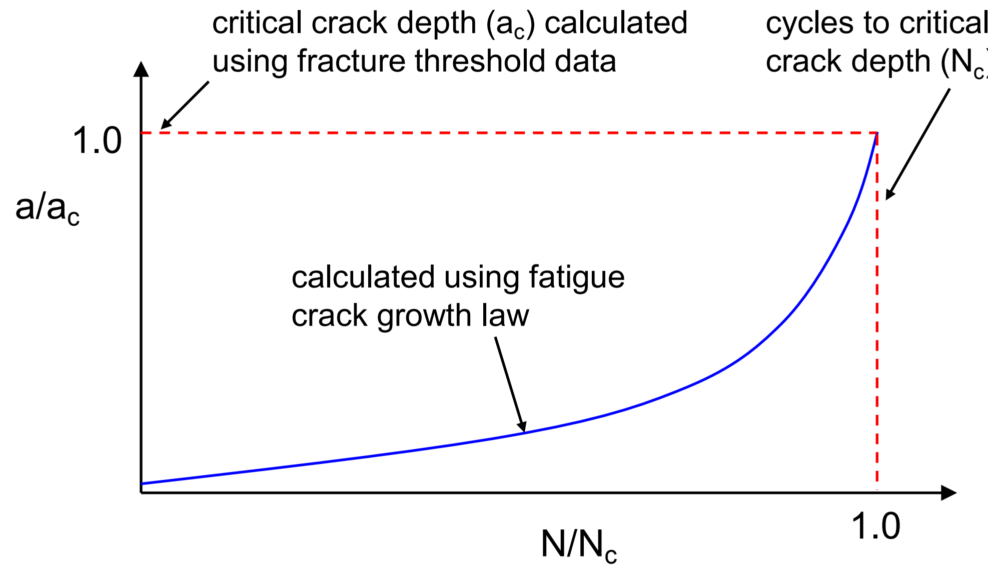
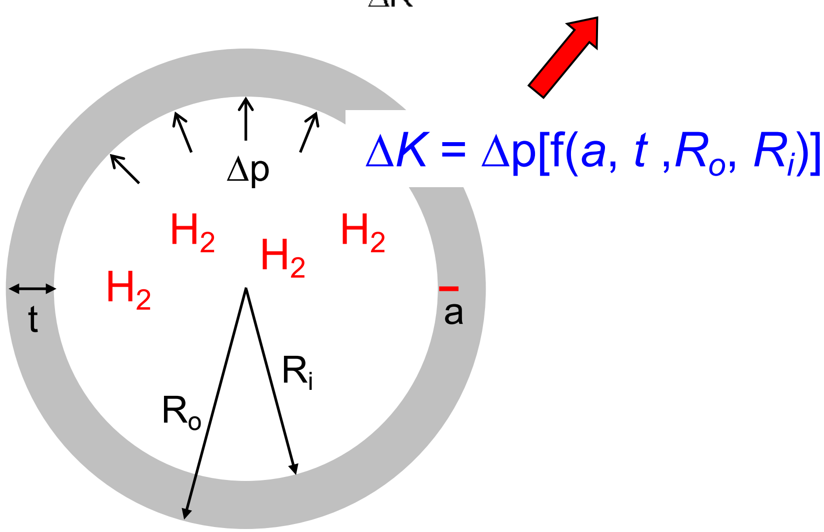
Reliability/integrity assessment framework in ASME B31.12 requires fracture data in H_2







- Two fracture properties in H_2 needed
  - Fatigue crack growth law
  - Fracture threshold
- Reliability/assessment framework accommodates H_2 embrittlement

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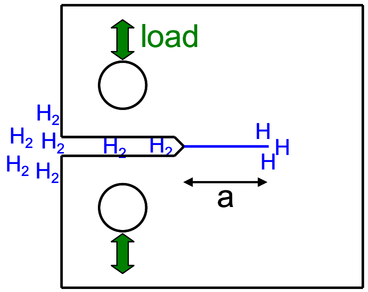
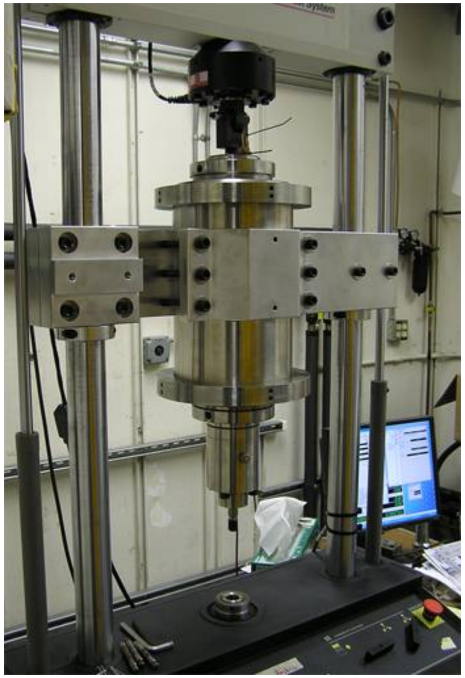
Fracture data in H_2 measured using specialized lab capabilities: fatigue crack growth

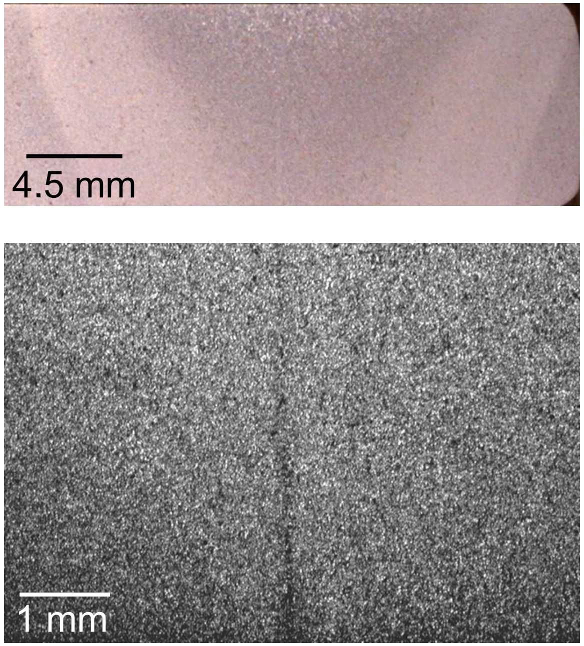




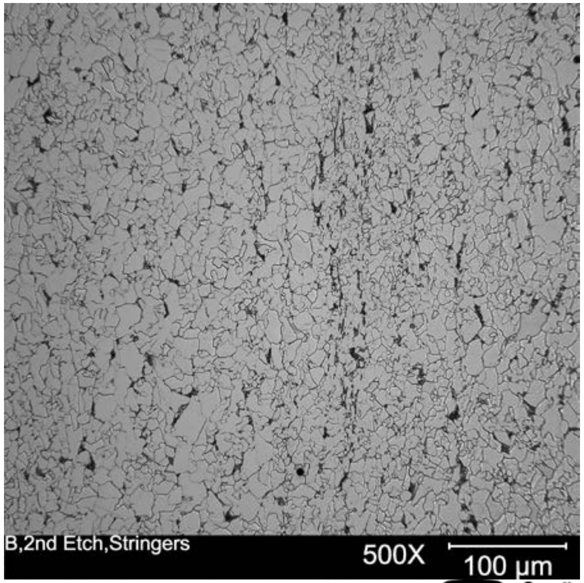
- Material
  - X52 ERW pipeline steel
- Instrumentation
  - Internal load cell in feedback loop
  - Crack-opening displacement measured internally using LVDT
  - Crack length calculated from compliance
- Mechanical loading
  - Triangular load-cycle waveform
  - Constant load amplitude (increasing ΔK)
- Environment
  - Primary supply gas: 99.9999% H_2
  - Other supply gases: H_2 with 10-1000 ppm O_2
  - Pressure = 3,000 psi (21 MPa)
  - Room temperature

Measured fracture properties of technologically relevant steel: API 5L X52

- Tested same X52 steel from DOE Pipeline Working Group tensile property round robin
  - Stakeholders expressed interest in X52 steel
- Tensile properties
  - Yield strength: 62 ksi (428 MPa)
  - Ultimate tensile strength: 70 ksi (483 MPa)



base metal



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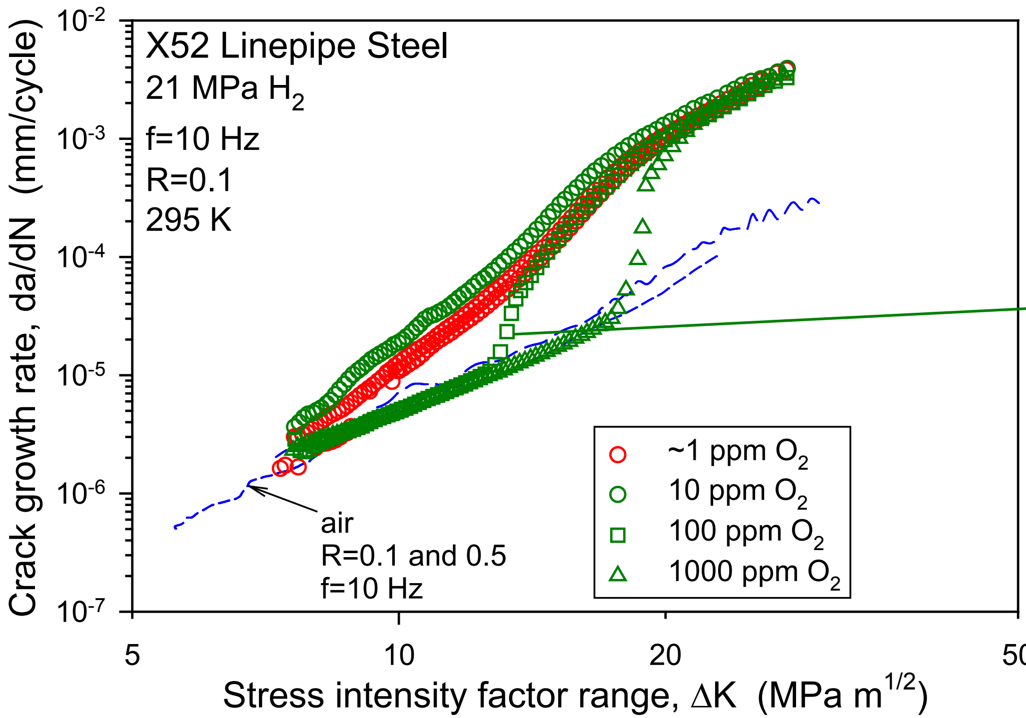
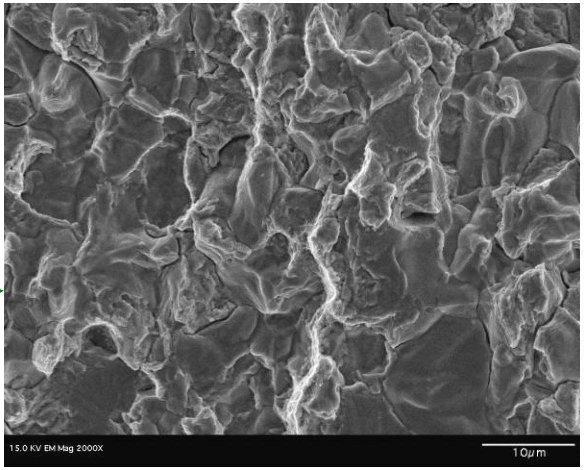
Accomplishment:

Measured onset of H_2-accelerated fatigue cracking as function of ΔK and O_2 concentration





SEM image showing hydrogen-induced intergranular cracking

- Increasing O_2 concentrations systematically mitigate H_2-accelerated fatigue crack growth
  - Onset of H_2-accelerated fatigue crack growth displaced to higher ΔK
- At O_2 concentrations <100 ppm, H_2-accelerated cracks propagate along grain boundaries
- O_2-affected fatigue crack growth laws lead to enhanced reliability/integrity for steel H_2 pipelines

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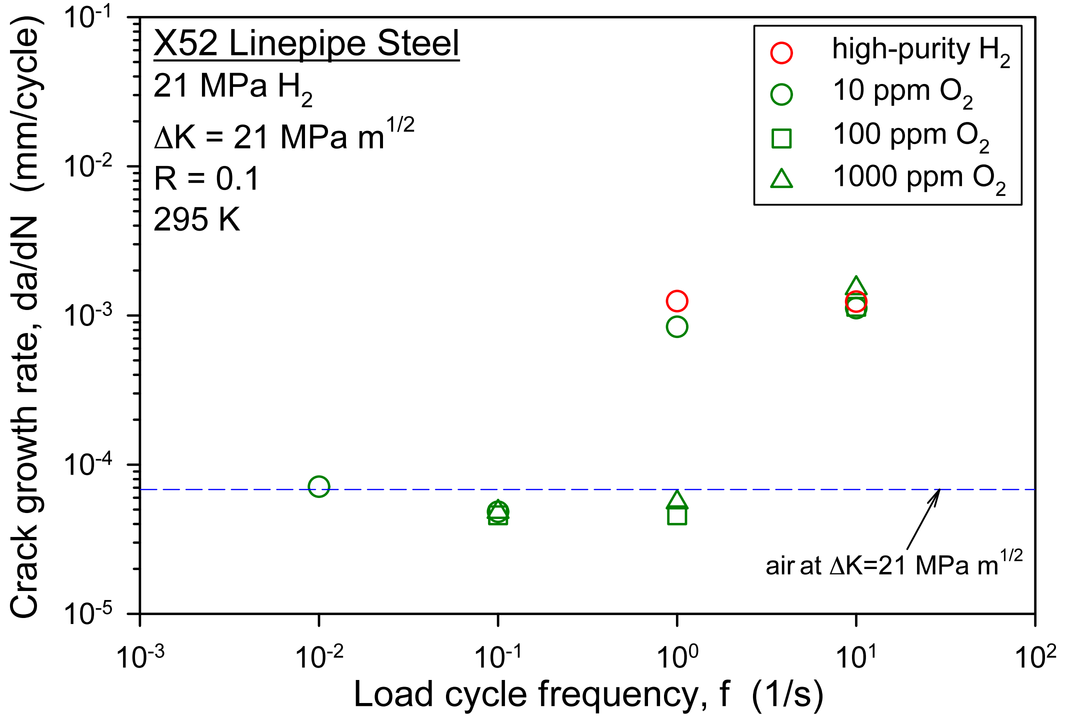
Accomplishment:

Quantified effects of load-cycle frequency on O_2-modified, H_2-accelerated fatigue cracking



- Inhibiting effect of O_2 more pronounced at lower load-cycle frequencies
- Threshold level of O_2 concentration required to mitigate accelerated fatigue cracking depends on load-cycle frequency
  - H_2-accelerated fatigue cracking effectively suppressed for all O_2 concentrations >10 ppm when frequency <0.1 Hz

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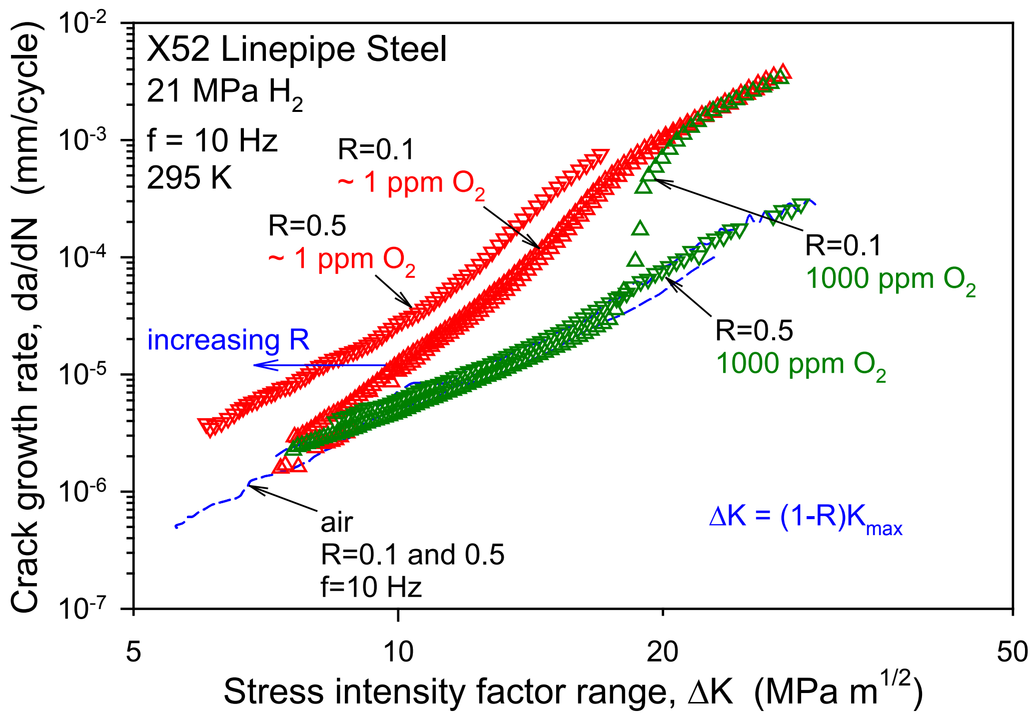
Accomplishment:

Quantified effect of load ratio ($R=K_{min}/K_{max}$) on O_2-modified, H_2-accelerated fatigue cracking



- At higher O_2 concentrations, increasing R ratio magnifies retarding effect of O_2 on H_2-accelerated fatigue cracking
  - No accelerated cracking observed in H_2 + 1000 ppm H at higher R ratio
- Effect of O_2 on enhancing reliability/integrity more pronounced if H_2 pipeline operated at higher pressure ratios (i.e., p_{min}/p_{max})

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Accomplishment:

Developed model for role of mechanical crack growth rate in stimulating H_2-accelerated cracking

- K_{max} governs crack-tip stresses that activate intergranular cracking
- da/dN governs rate of bare-metal exposure and atomic hydrogen uptake

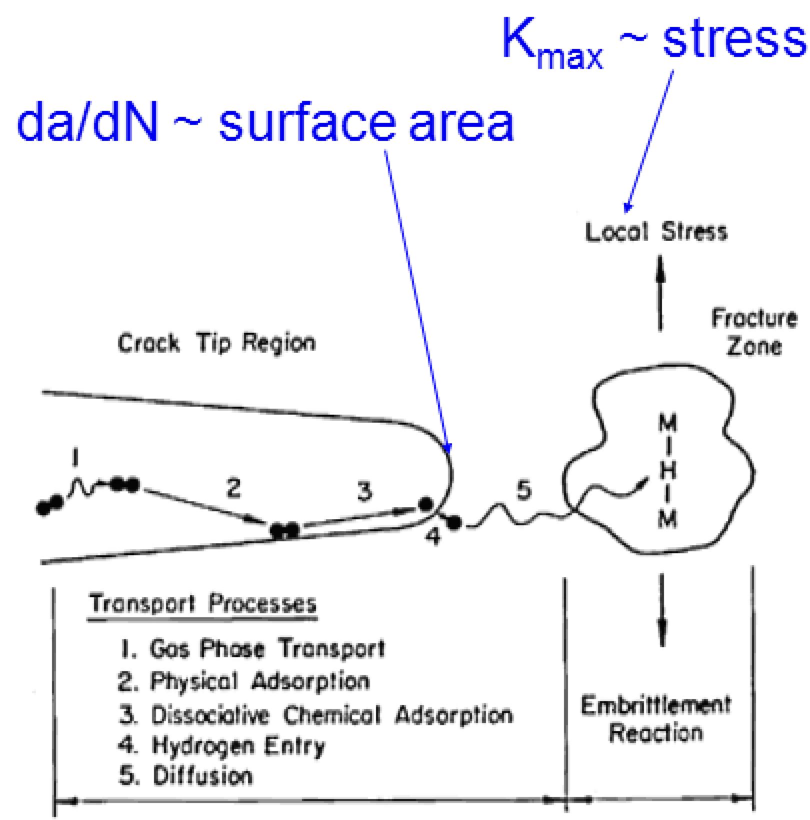
$$\frac{d[H]}{dN} \propto \theta_H = (1-\theta_O)$$

$$\theta_O \propto \frac{1}{da/dN}$$

θ = fractional surface coverage of hydrogen (θ_H) or oxygen (θ_O)

Assume $\theta_H + \theta_O = 1$

(Wei and Simmons, Fatigue: Environment and Temperature Effects, 1983)



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Physics-based model presumes that cracking accelerates when threshold levels of K_{max} and "mechanical" da/dN exceeded

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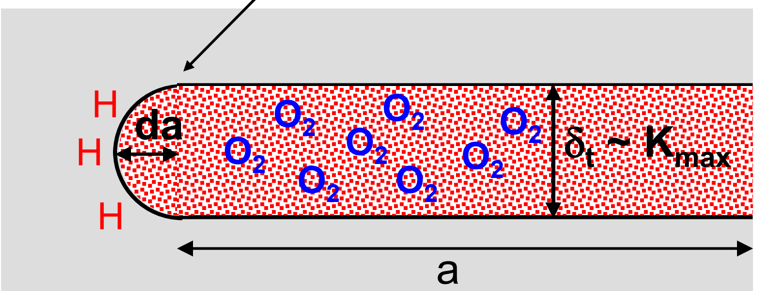
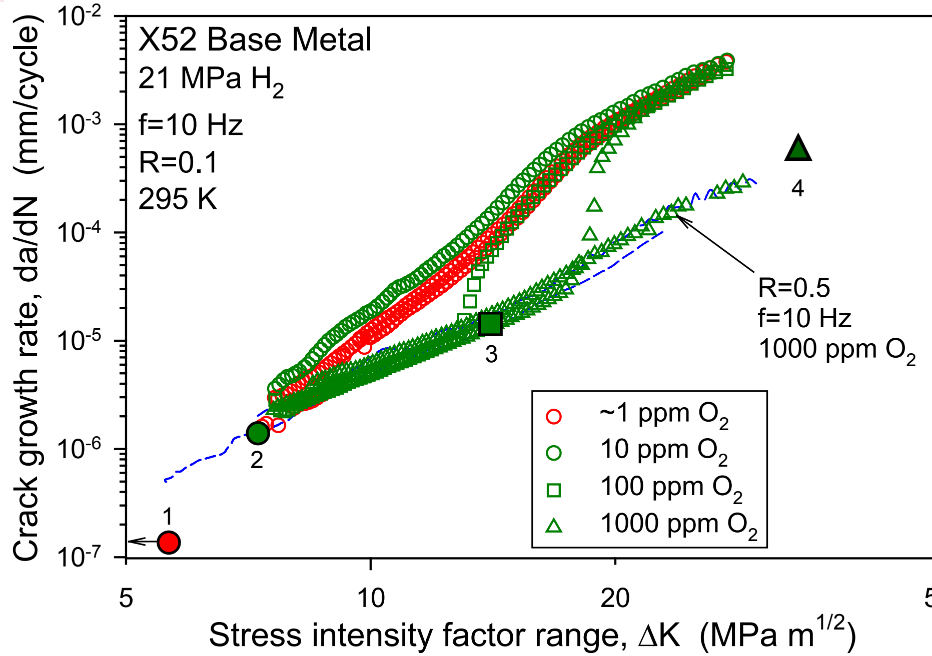
Accomplishment:

Model based on rate-limiting O_2 diffusion predicts effects of O_2 concentration, R ratio, and frequency

Assumptions: H uptake when $\theta_O < 1$

O_2 diffusion rate limiting





- O_2 diffusion model assumptions:
  - steady state
  - $p_{O2} = 0$ at crack tip
- Mass balance between O_2 flow in gas during one cycle and O_2 adsorbed on fresh crack-tip surface yields:

$$\frac{da}{dN} = \frac{Dp_{O2}}{\theta_o \pi \nu RT} \frac{0.6(1-\nu_P^{\ 2})}{E\sigma_0} \left(\frac{\Delta K}{\sqrt{a}(1-R)} \right)^2$$

- Predictions of "mechanical" da/dN required for $\theta_O < 1$
  - Point 1: 1 ppm O_2
  - Point 2: 10 ppm O_2
  - Point 3: 100 ppm O_2
  - Point 4: 1000 ppm O_2, R=0.5
- Model enables extrapolation of laboratory data to predict effects of O_2 in pipeline

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Collaborations

- DOE Pipeline Working Group (PWG)
  - Participants funded by DOE FCT Program
    - Federal Labs: Sandia, Oak Ridge, Savannah River
    - Universities: Univ. of Illinois
    - Industry: Secat
  - Participants not funded by DOE FCT Program
    - Federal Labs: NIST
    - Industry: industrial gas companies, ExxonMobil
    - Standards Development Organizations: ASME
  - Extent of collaborations include:
    - PWG meetings (up to 2 times/year)
    - Supplying materials (e.g., ExxonMobil-Sandia)
    - Coordinating testing (e.g., NIST-Sandia)
- International Institute for Carbon-Neutral Energy Research (I^2CNER), Fukuoka, Japan (e.g., O_2 diffusion model)

Proposed Future Work

Remainder of FY12

- Measure fatigue crack growth law of girth weld fusion zone from X65 steel in H_2 gas (Milestone: June 2012)

FY13

- Measure fatigue crack growth law of girth weld heat-affected zone (HAZ) in H_2 gas
- Conduct reliability/integrity analysis of X52 H_2 pipeline using operating parameters supplied by industry partner
- Expand pipeline steel testing beyond X52, e.g., transition to higher-strength steels such as X70 and X80

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Summary

- Measured fracture thresholds and fatigue crack growth laws allow evaluation of reliability/integrity of steel H_2 pipelines
  - Hydrogen embrittlement accommodated by measuring fracture properties in H_2 following ASME B31.12 design standard
- Measurements on X52 steel in H_2 gas with O_2 impurities reveal the following trends:
  - O_2 systematically retards H_2-accelerated fatigue crack growth as concentration increases from 10 ppm
  - Inhibiting effect of O_2 more pronounced at high load ratio
  - Threshold level of O_2 concentration required to mitigate accelerated fatigue cracking depends on load-cycle frequency
- Effects of O_2 concentration, R ratio, and frequency on O_2-modified, H_2-accelerated fatigue can be predicted from model