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Effects of Oxygen Impurities on Long-Term Gaseous Hydrogen Embrittlement of Structural Steels

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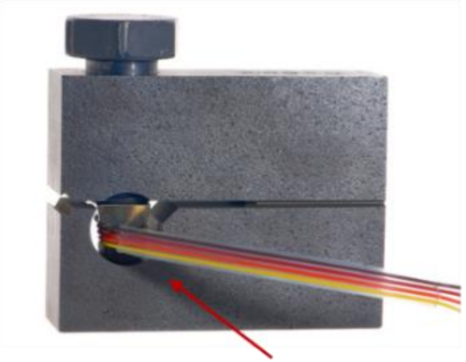
Overview

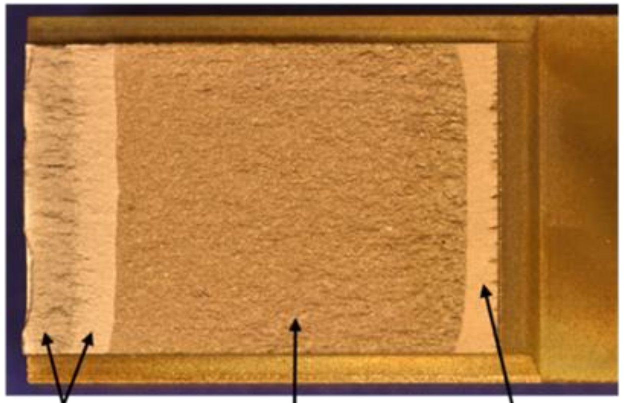
- Background and motivation
  - Examples of the mitigating effects of oxygen impurities on hydrogen embrittlement in laboratory testing
- Experimental methods
  - Long-term, constant displacement fracture tests in high pressure gaseous hydrogen environments
  - Commercial pressure vessel and pipeline steels
- Experimental results
  - Comparison of subcritical crack growth in high-pressure hydrogen and hydrogen with varying degrees of oxygen impurities
- Conclusions and future research

Wedge-opened Loaded (WOL) Sample



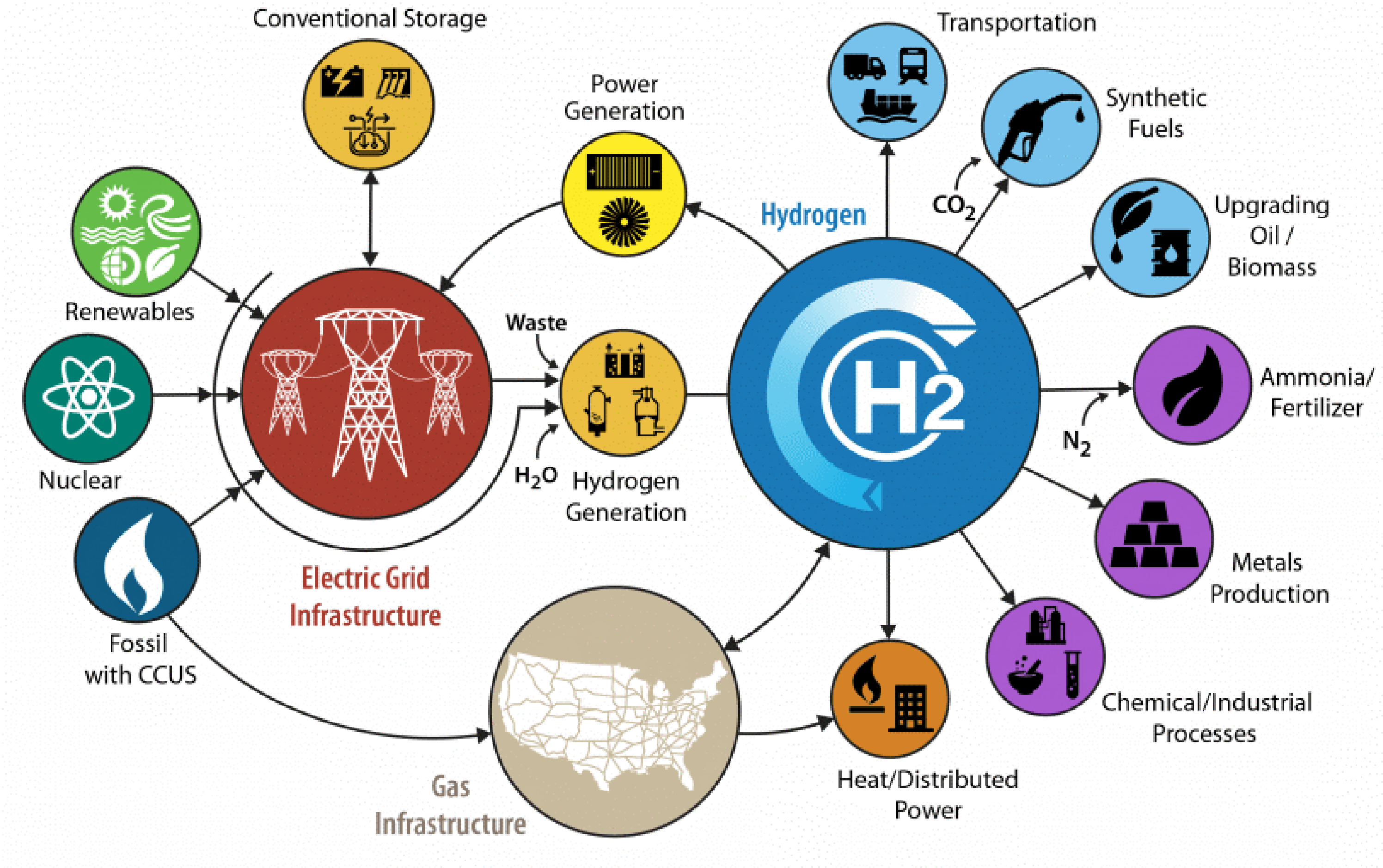
Reaction pin (load tup) with externally monitored strain gauge

Grade L: WOL Fracture Surface



Hydrogen has a key role to play in a sustainable future

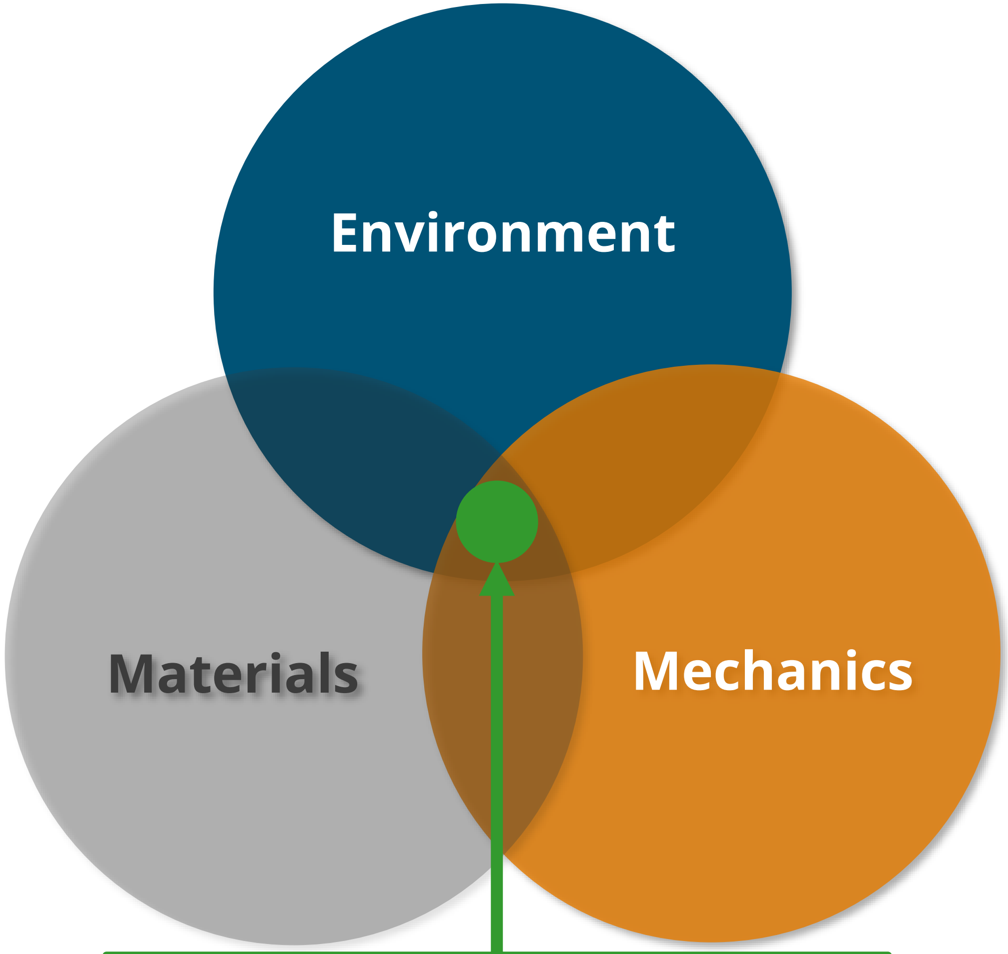
- Hydrogen has many potential avenues for decarbonization across many sectors
  - Energy storage, waste energy conversion
  - Transportation
  - Residential/industrial heating and appliances
  - Steel, cement production



Source: U.S. DOE Hydrogen and Fuel Cell Technologies Office https://www.energy.gov/eere/fuelcells/h2scale

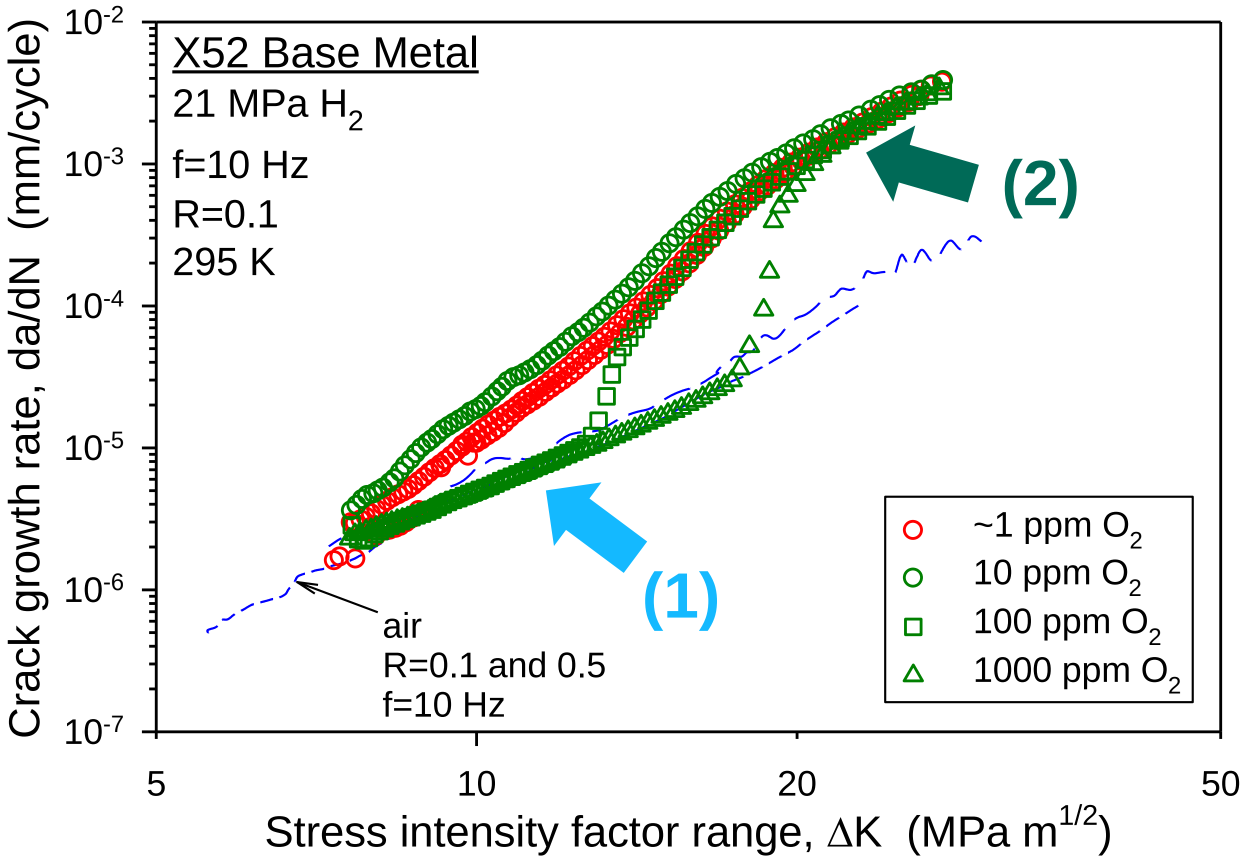
Hydrogen degrades fatigue and fracture resistance

- Hydrogen-assisted fracture and fatigue is influenced by:
  - Materials
    - Yield/tensile strength
    - Microstructure, homogeneity, etc.
  - Environment
    - Partial pressure of hydrogen
    - Impurities (e.g., O_2)
    - Temperature
  - Mechanics
    - Stress state
    - Stress (pressure) cycling
    - Residual stresses/work hardening



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

Oxygen is known to affect measurements of fatigue

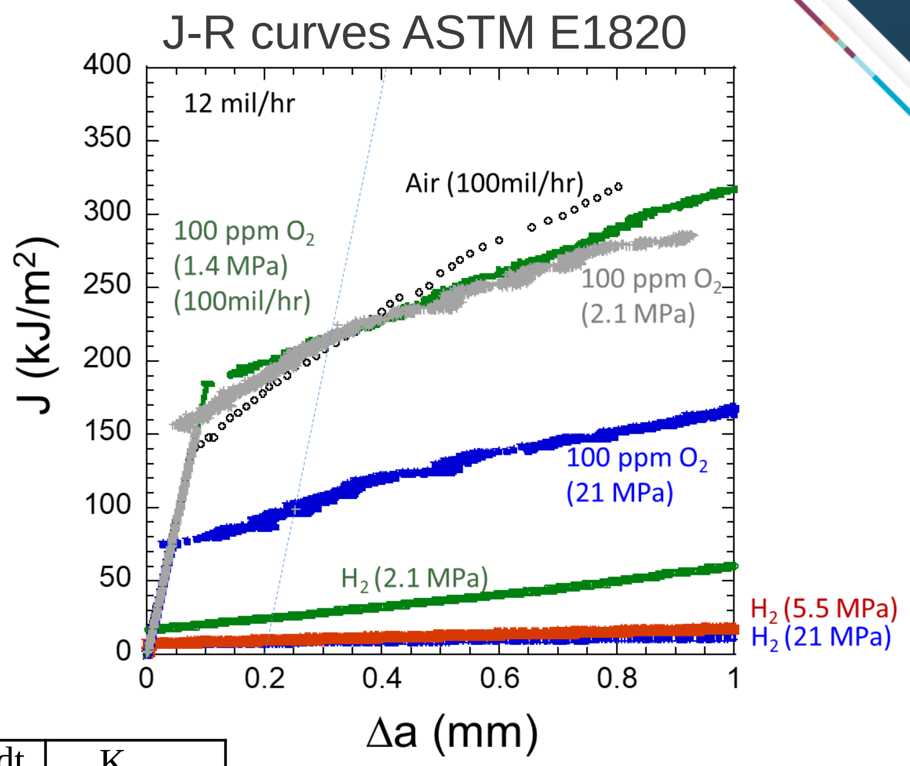


- Numerous examples of trace gases mitigating fatigue crack growth rate (FCGR) in laboratory conditions
- Example:
  - (1) Oxygen reduces FCGR comparable to air
  - (2) Oxygen has no effect on FCGR in H_2

Refs.: Somerday et al, *Acta Mater* 61 (2013) 6153. Nibur et al, SAND2010-4633 (2010).

Oxygen moderated hydrogen-assisted fracture

- Fracture toughness K_{JQH} values decreased by over 60% in pure H_2 at 2.1 MPa
- In 21 MPa mixed gas (100 ppm O_2), fracture toughness decreased by only 30% relative to air
  - In pure H_2 at 21 MPa, relative decrease was 80%
- At lower pressures (1.4-2.1 MPa) in mixed gas, no effect of hydrogen was measured



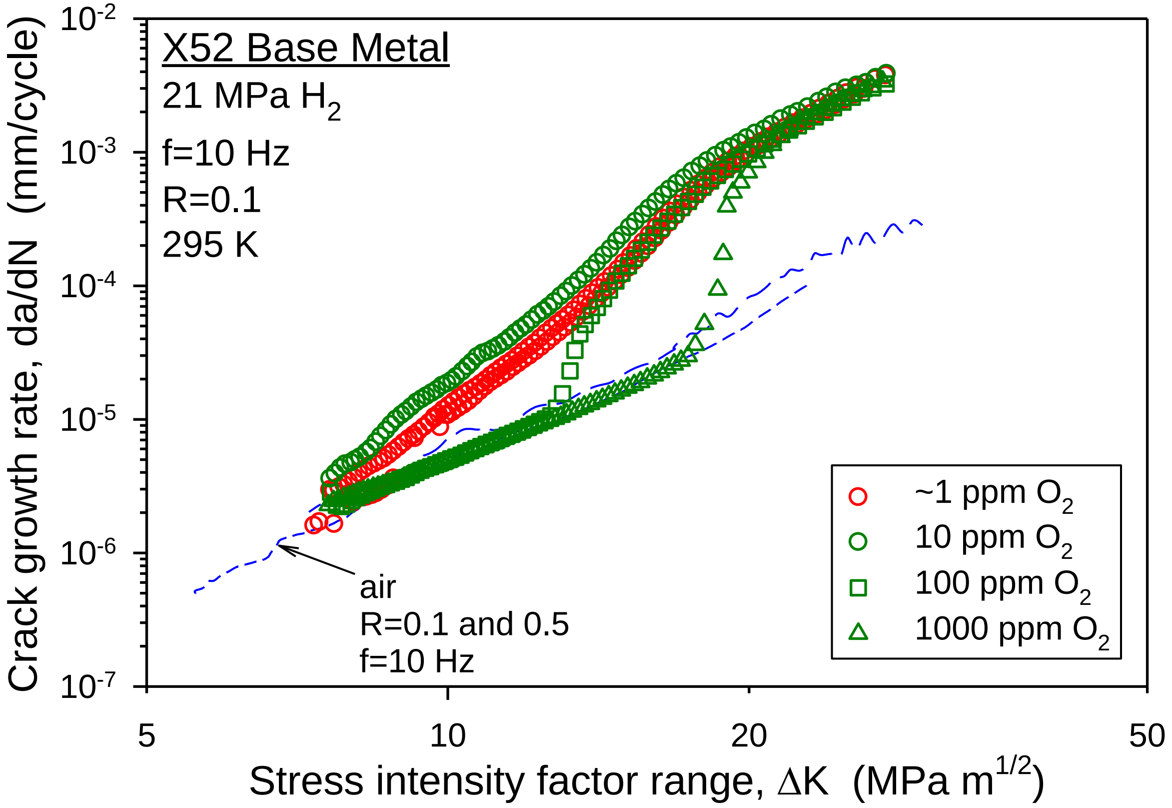
Sample ID	Environment	Test Pressure (MPa)	Actuator rate (mm/hr)	da/dt (m/s)	K_{JQH} (MPa $m^{1/2}$)
X100-51	Air	-	2.5	5.0E-7	217
X100-52	Air	-	2.5	1.4E-7	202
X100-5	H2	21	0.3	8.5E-7	43
X100-6	H2	5.5	0.3	3.6E-7	47
X100-7	H2	2.1	0.3	1.7E-7	75
X100-53	H2 + 100 ppm O2	21	0.3	1.1E-7	151
X100-55	H2 + 100 ppm O2	2.1	0.3	7.4E-8	222
X100-56	H2 + 100 ppm O2	1.4	2.5	1.0E-7	222

60 - 80% reduction

30% reduction

Ref: Ronevich et al, PVP2018-84163

Oxygen has been shown to mitigate hydrogen embrittlement in laboratory tests



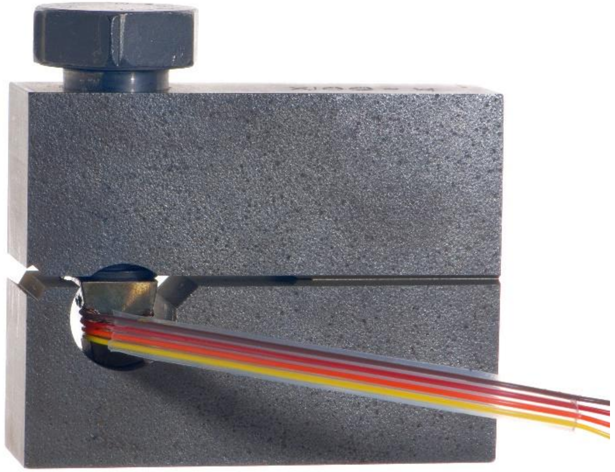
- Fatigue and fracture measurements can be significantly impacted by oxygen impurities
- Fatigue crack growth tests are typically performed at 1 Hz (±decade)
  - da/dN = 10^{-5} mm/cycle
  - Time for Δa = 1mm: ~1 day
  - 1 day = 0.02% of 10 year life
- Are the time scales of a typical laboratory fatigue test sufficient to demonstrate kinetics over decades?
  - More accurately simulate the mechanical/environmental conditions that components see when in use
  - Does trace oxygen have long term mitigation effects on hydrogen embrittlement?

Ref.: Somerday et al, *Acta Mater* 61 (2013) 6153.
Ref.: Nibur et al, SAND2010-4633 (2010).

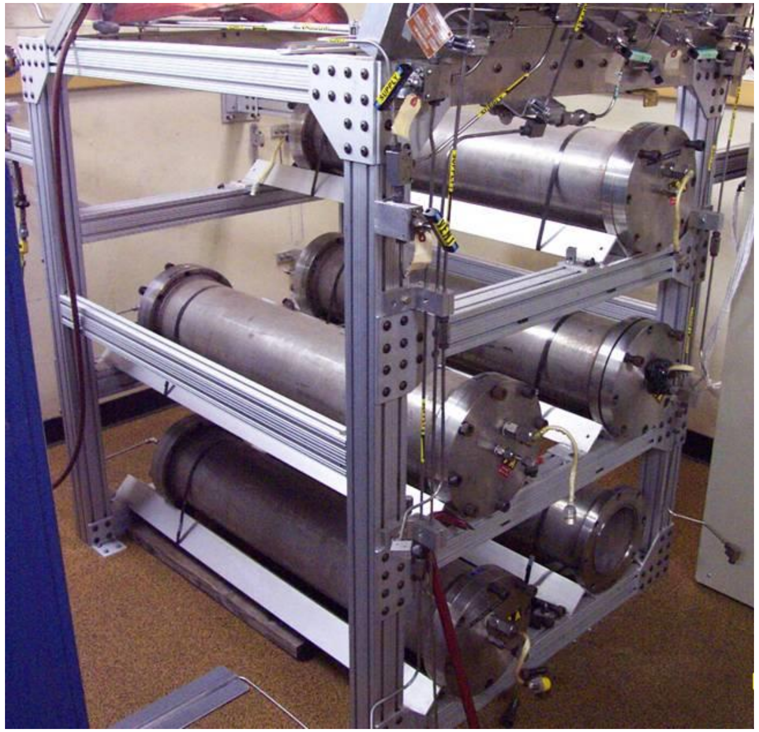
Sustained load testing can be executed over periods of days to weeks to months to years

- Fixed (constant) displacement fracture tests
- Fatigue pre-cracked and loaded in ambient air
- Placed in pressure vessels & pressurized up to 140 MPa gaseous environment
  - Experiments in this study were performed at 103MPa
- Instrumented reaction pins allow for the determination of incubation time
- Directly compare subcritical crack growth in hydrogen and mixed gas environments

Wedge-opened loaded (WOL) test sample



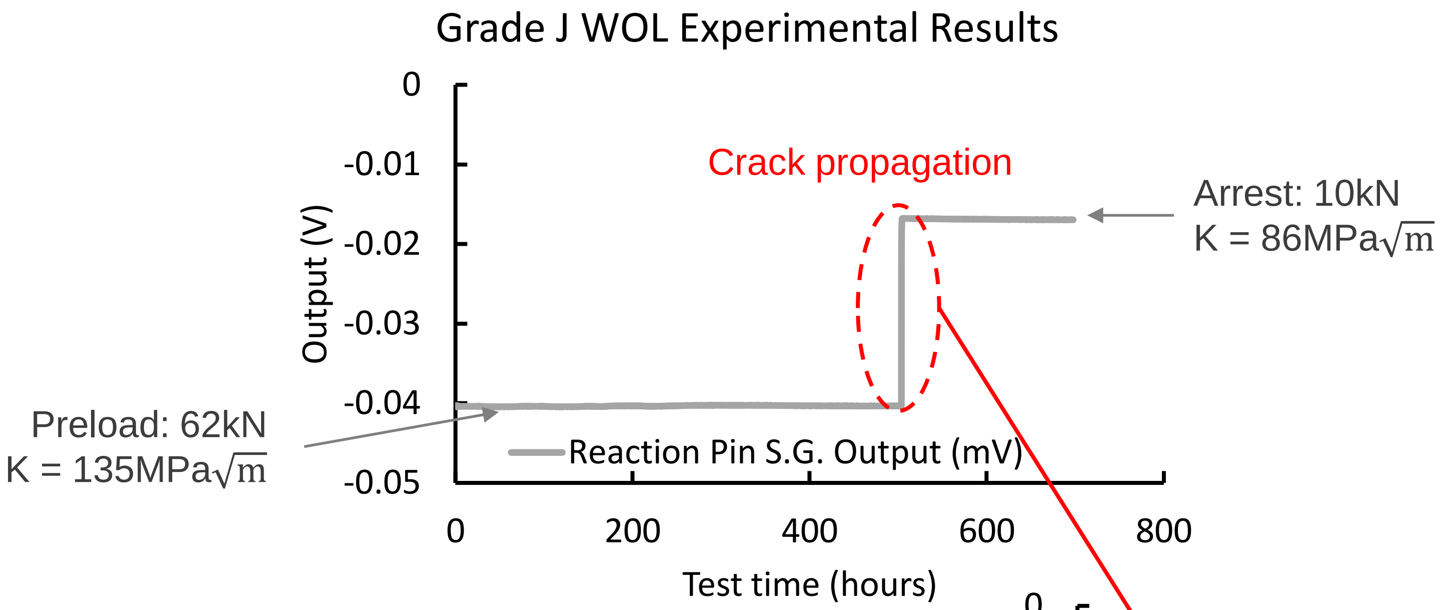
Pressure vessels for medium and long term experiments

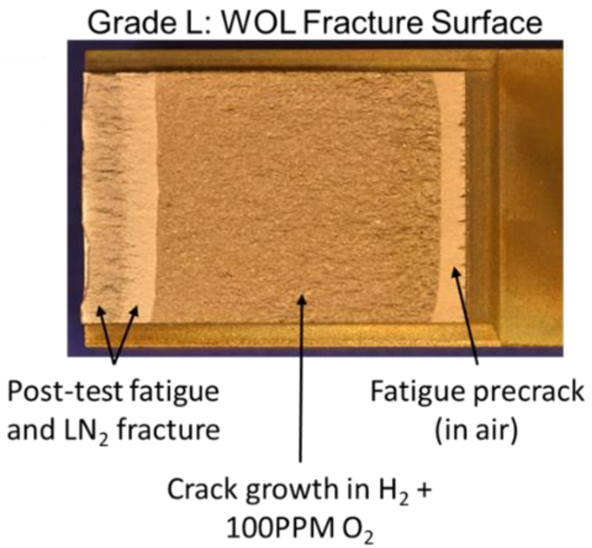


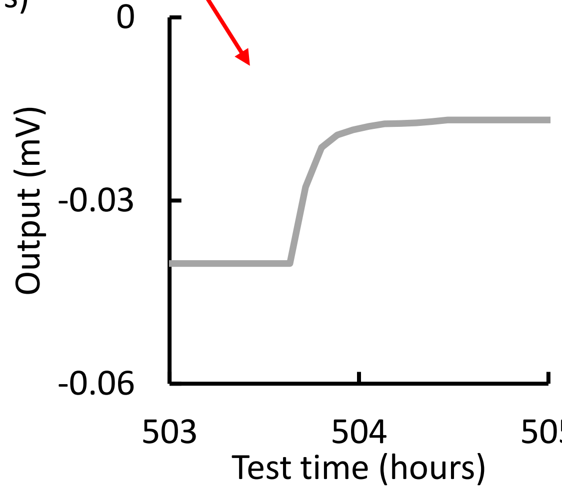
ASTM E1681 – Threshold Stress Intensity Factor for Environment-Assisted Cracking

Crack initiation and growth rates were measured during constant displacement fracture experiments

- Instrumented reaction pins allow for determination of incubation time and crack growth rates
  - Continuous data collection throughout the duration of the experiments
- Time between the initial crack propagation and arrest can range between seconds to hours
  - With a constant displacement, the crack growth rates can be determined from the load on the reaction pin
- Post-test fatigue and heat tinting are used to mark fracture surfaces





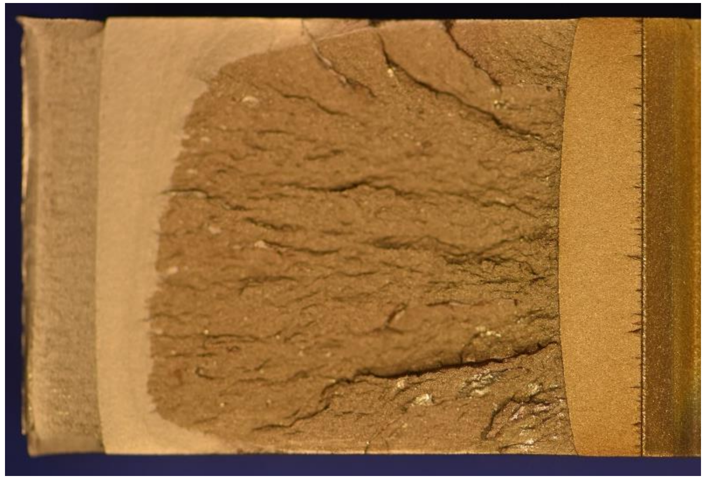


Material selection and fracture surfaces

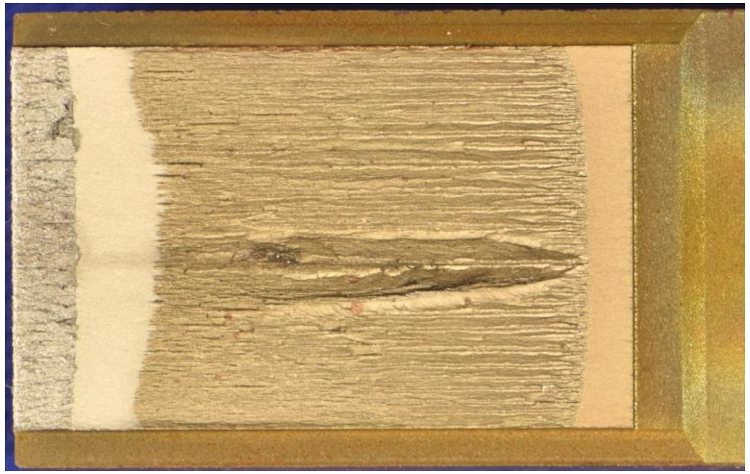
- SA372 Grade J steel
  - Heat A: YS = 700 MPa
  - Heat B: YS = 750 MPa
- SA372 Grade L steel
  - YS = 730 MPa
- X100 pipeline steel
  - YS = 760 MPa
- Precipitation Hardened 13-8 stainless steel
  - YS = 1480 MPa

Grade L

Grade J

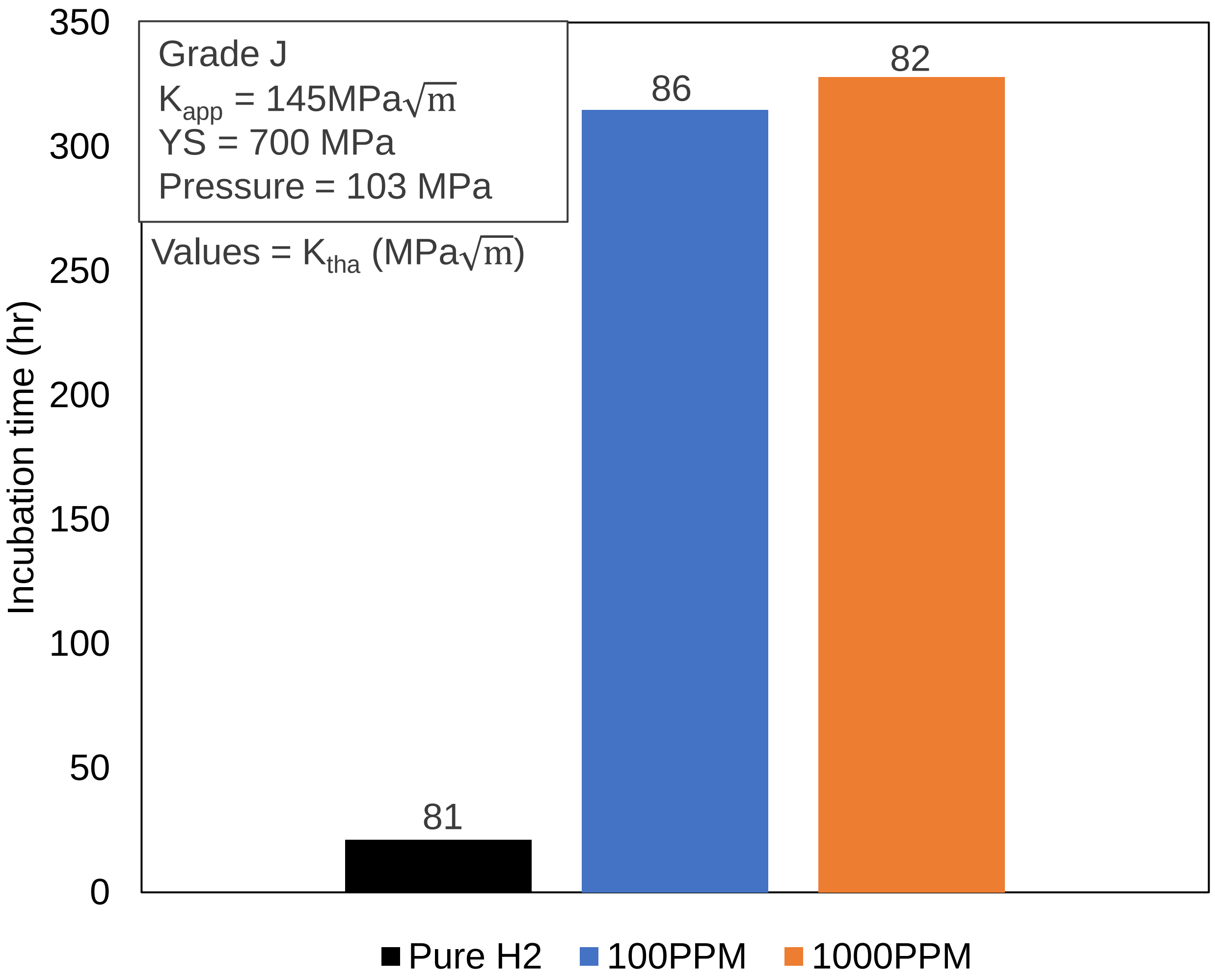


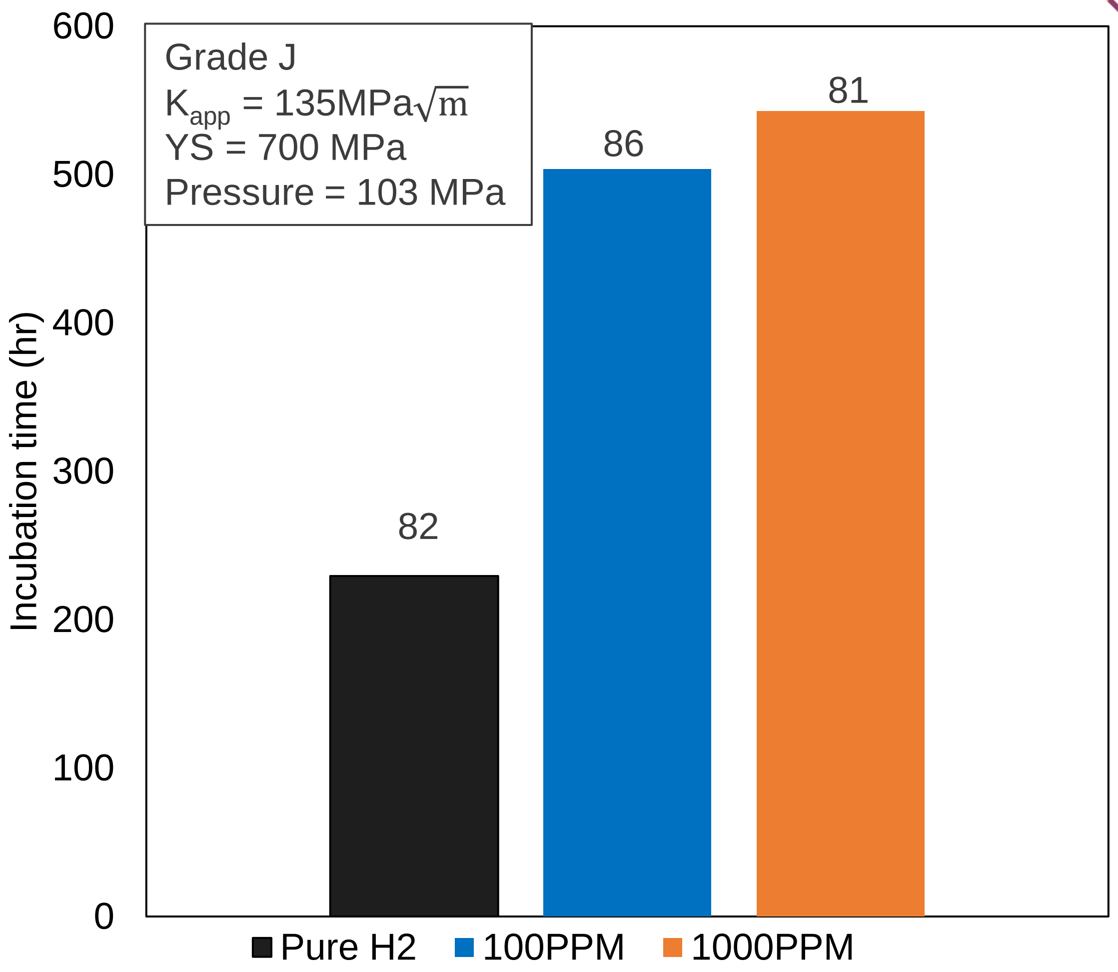
X100



13-8

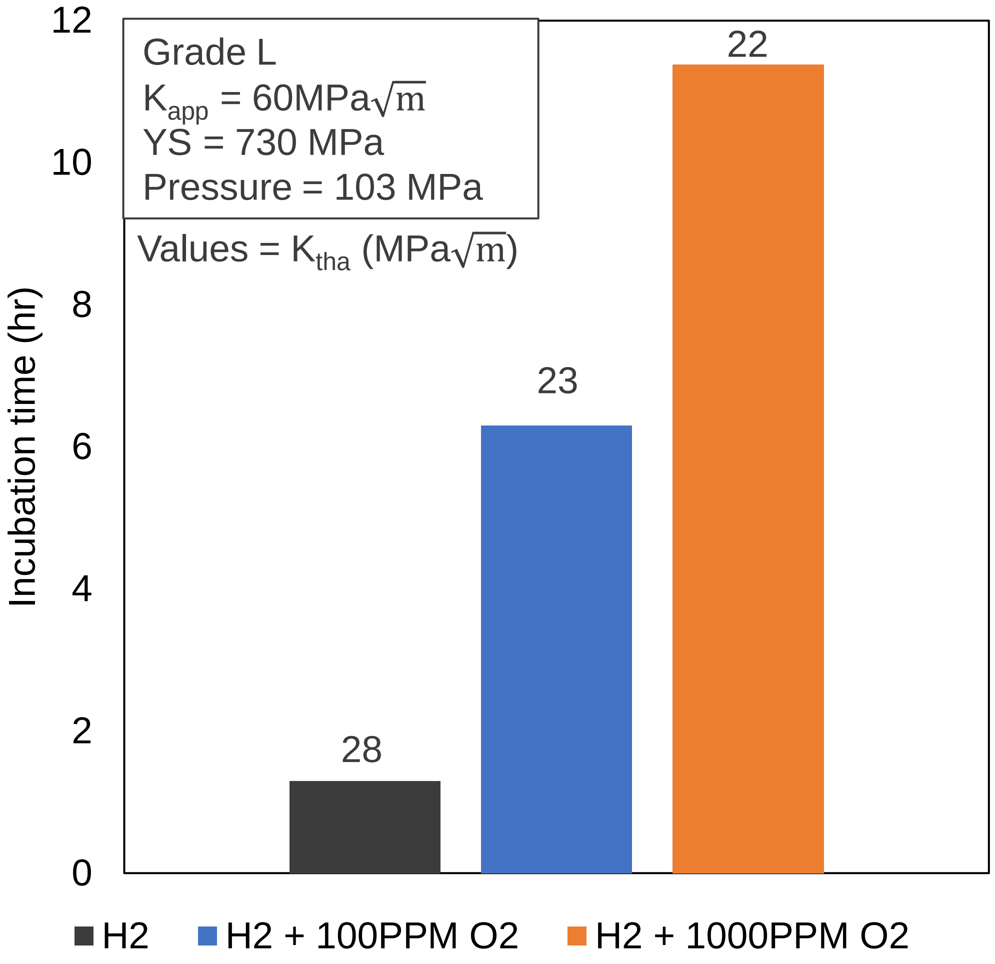
Grade J: 100PPM & 1000PPM O_2 delay incubation time

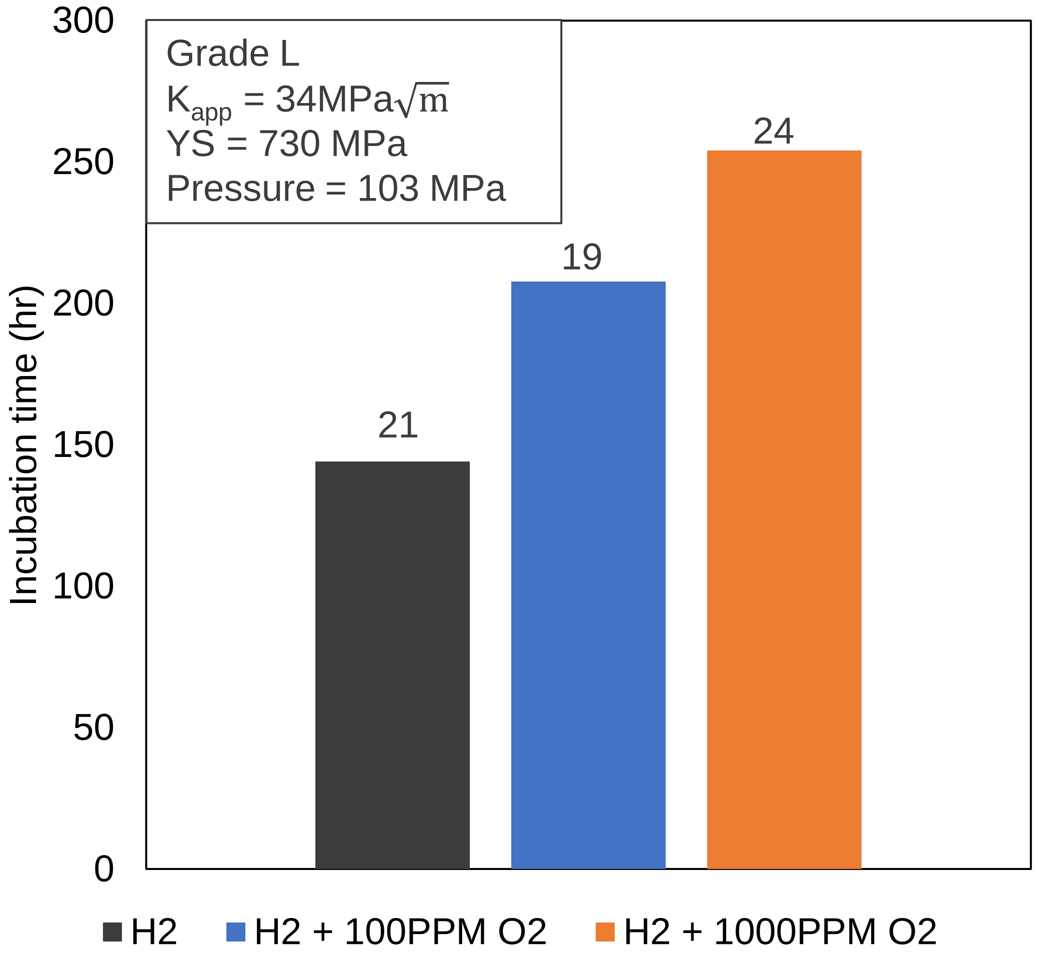




- The Grade J material showed delays of 15x at a higher preload (K_{app} = 145 MPa$\sqrt{m}$) and a 2.2x increase at a lower preload (K_{app} = 135 MPa$\sqrt{m}$)
- K thresholds were within ±5 MPa$\sqrt{m}$ of average for both the pure and mixed gas conditions

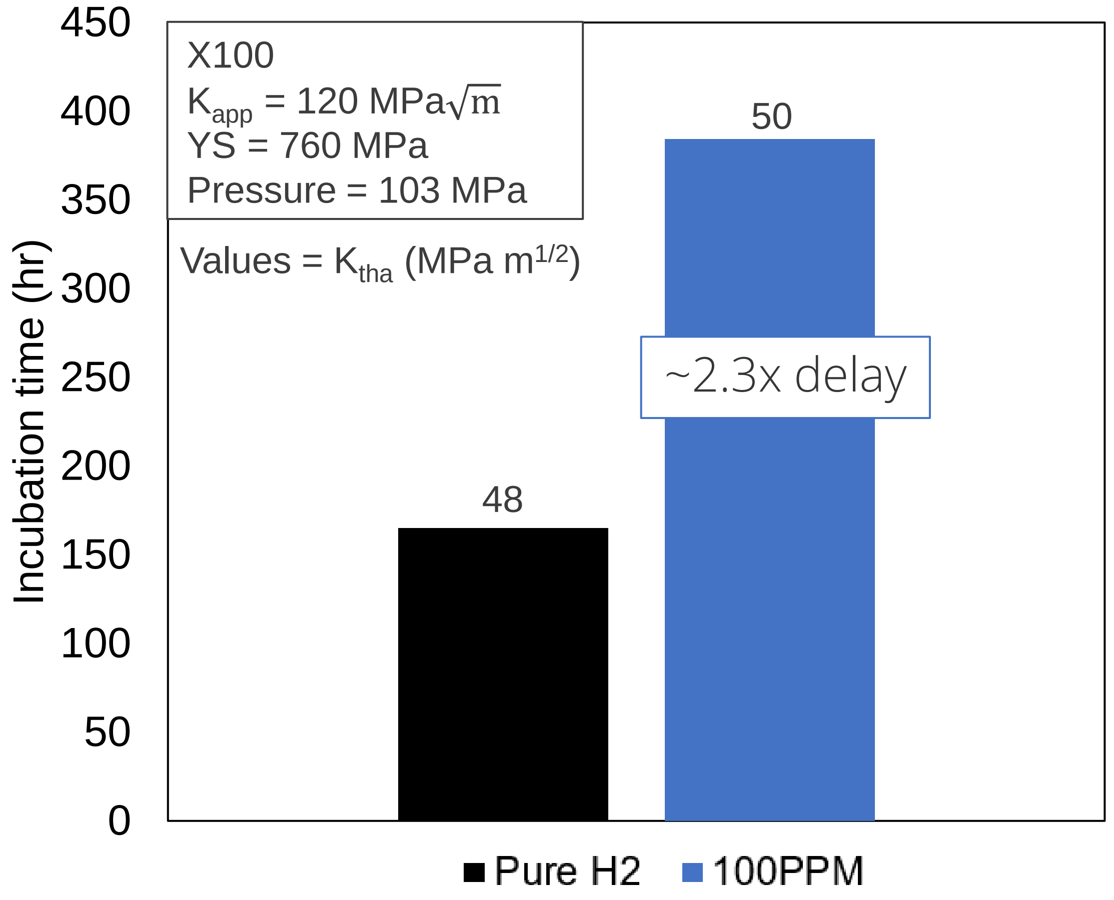
Grade L: 100PPM & 1000PPM O_2 delay incubation time





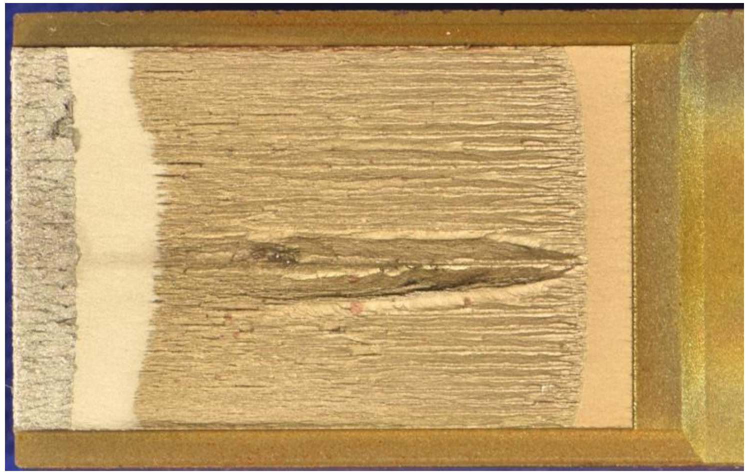
- Grade L had a 5x delay at higher preload (K_{app} = 60 MPa$\sqrt{m}$) and a 1.5x delay at lower preload (K_{app} = 34 MPa$\sqrt{m}$)
- Similar crack arrest thresholds for all test conditions

100PPM O_2 delays incubation time for X100, but 13-8 fractured immediately

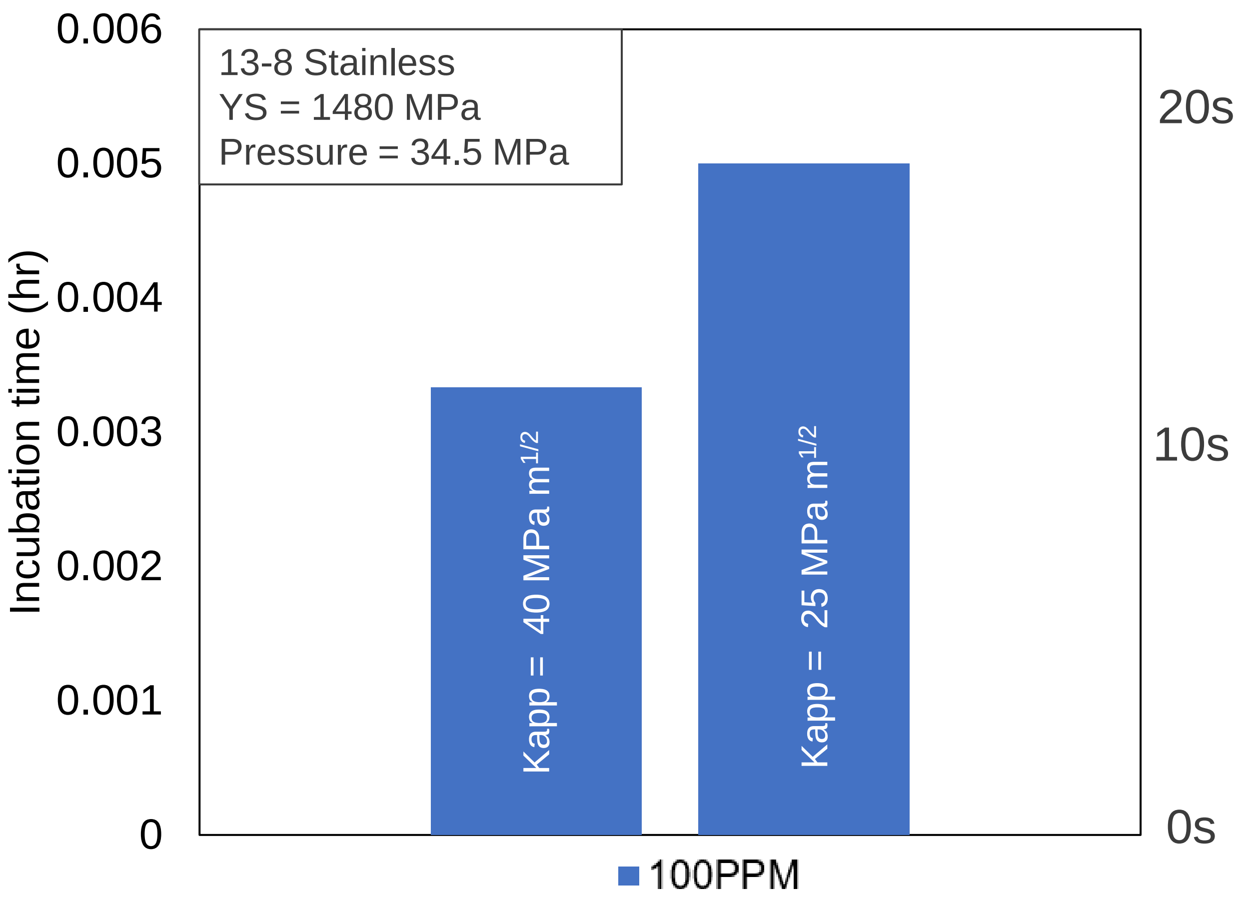


- X100 also saw a significant delay with the addition of 100PPM O_2

X100



100PPM O_2 delays incubation time for X100, but 13-8 fractured immediately

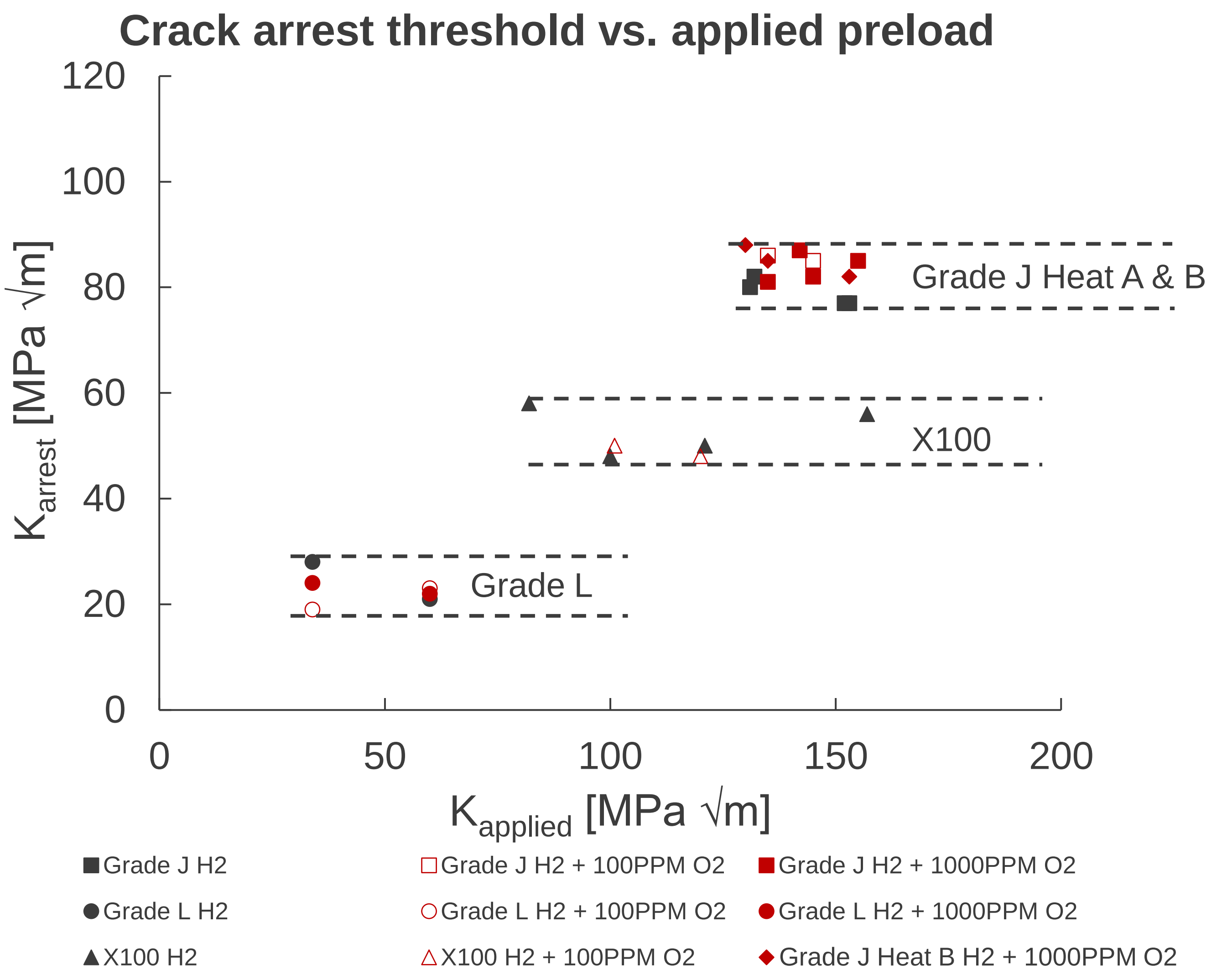


- Both 13-8 samples fractured (a/W > 97%) within seconds of exposure to H_2 + 100PPM O_2
  - At reduced pressures (< 40 MPa)

13-8

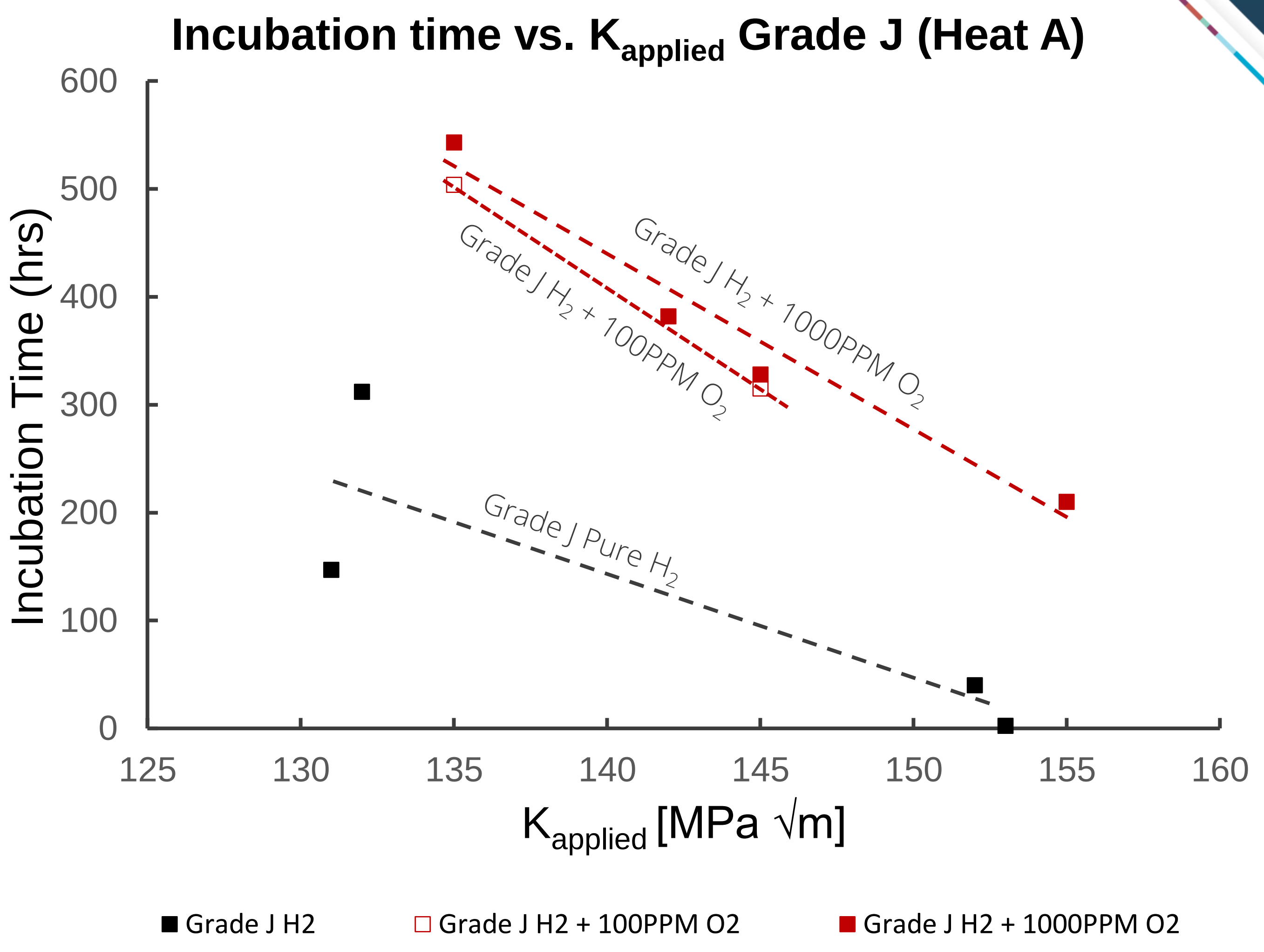
Summary and Conclusions

- Constant displacement fracture tests were carried out in pure hydrogen and mixed gas (100 and 1000PPM oxygen) environments at 103MPa (15ksi)
- K_{arrest} appears to be independent from oxygen content
  - All tests with pure hydrogen and oxygen impurities fall within an apx. 10MPa$\sqrt{m}$ range



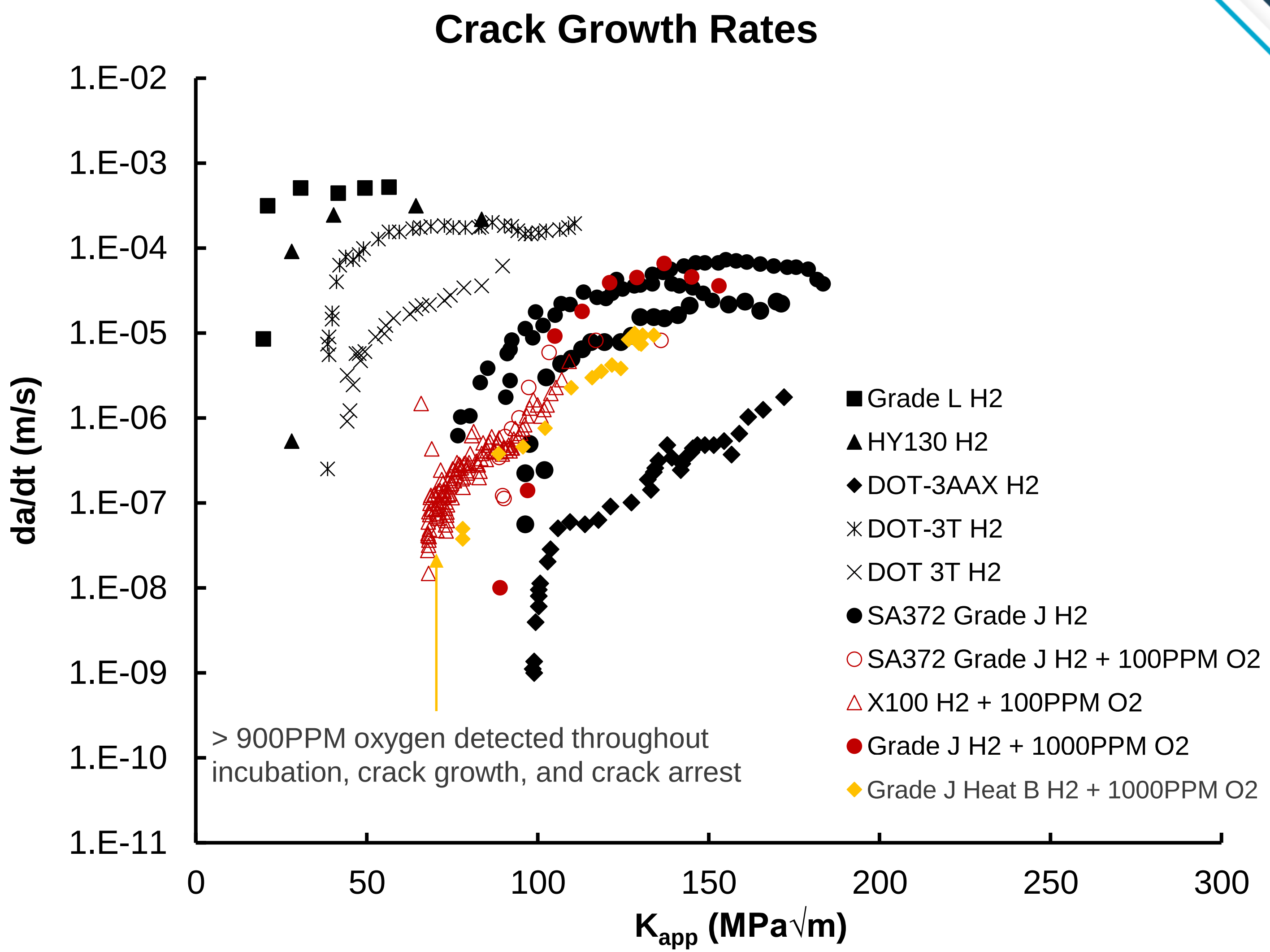
Summary and Conclusions

- Introducing 100PPM oxygen increased the incubation time by factors between 1.5x and 15x, but did not prevent crack propagation
- For the Grade L and Grade J, increasing the oxygen content from 100PPM to 1000PPM further delayed the incubation time, but had a smaller relative effect compared to the delay from pure hydrogen to hydrogen + 100PPM oxygen



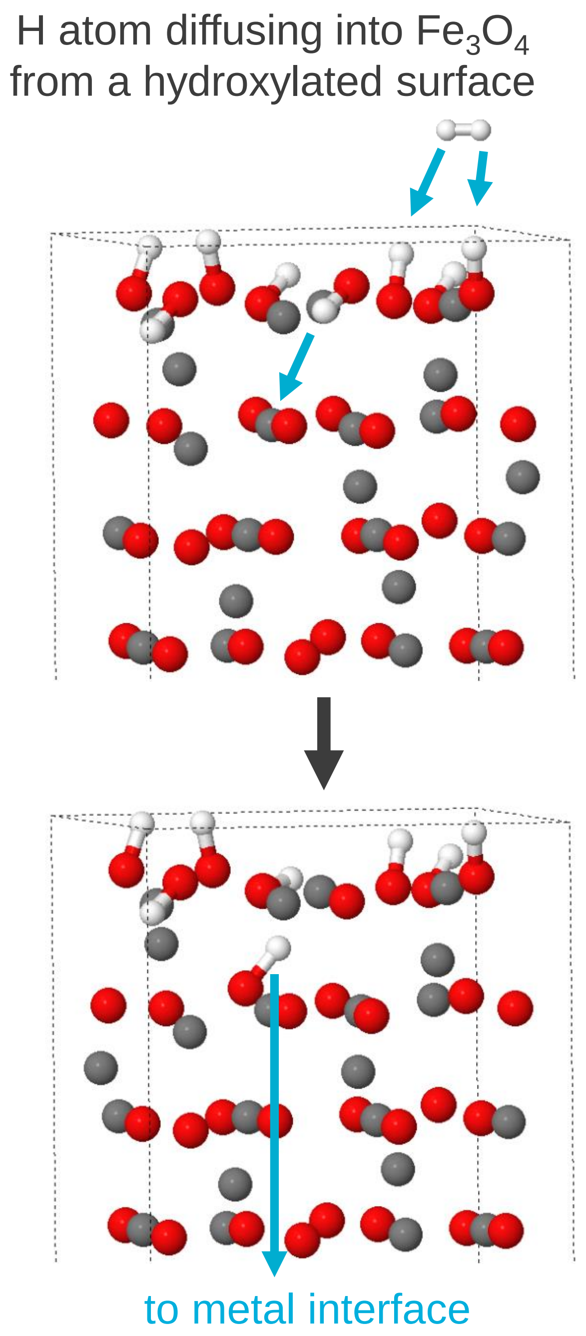
Summary and Conclusions

- Crack growth rates (da/dt) fall within the expected ranges from previous tests in pure hydrogen at similar pressures
- For many commonly used, laboratory testing rates, oxygen impurities can appear to mitigate hydrogen embrittlement
  - Oxygen impurities compete for surface sites with hydrogen, but only slow the uptake of hydrogen and delay the embrittlement (reduction of material properties)
- Based on this data, low oxygen impurities should not be relied upon for long-term mitigation of hydrogen embrittlement
  - Both the gas purity and testing rate are critical in order to determine representative and conservative material properties for the design of gaseous hydrogen infrastructure



Broader Research – Mechanisms

- Ongoing research is looking at determining the mechanisms behind the delay of hydrogen embrittlement in the presence of oxygen impurities
- Surface experiments:
  - Oxides form rapidly on clean steel surfaces (XPS)
  - Hydroxyls form rapidly when oxide surfaces are exposed to hydrogen (XPS)
- Modeling:
  - First principle calculations suggest hydrogen atoms can diffuse through oxides (DFT simulations, right)
- Experimental and computational observations consistently show oxides can impede but not prevent hydrogen-assisted fracture, especially on long time scales (> hours)



Thank you for your attention!

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