Proposed test method to establish hydrogen compatibility of materials for fuel cell vehicles

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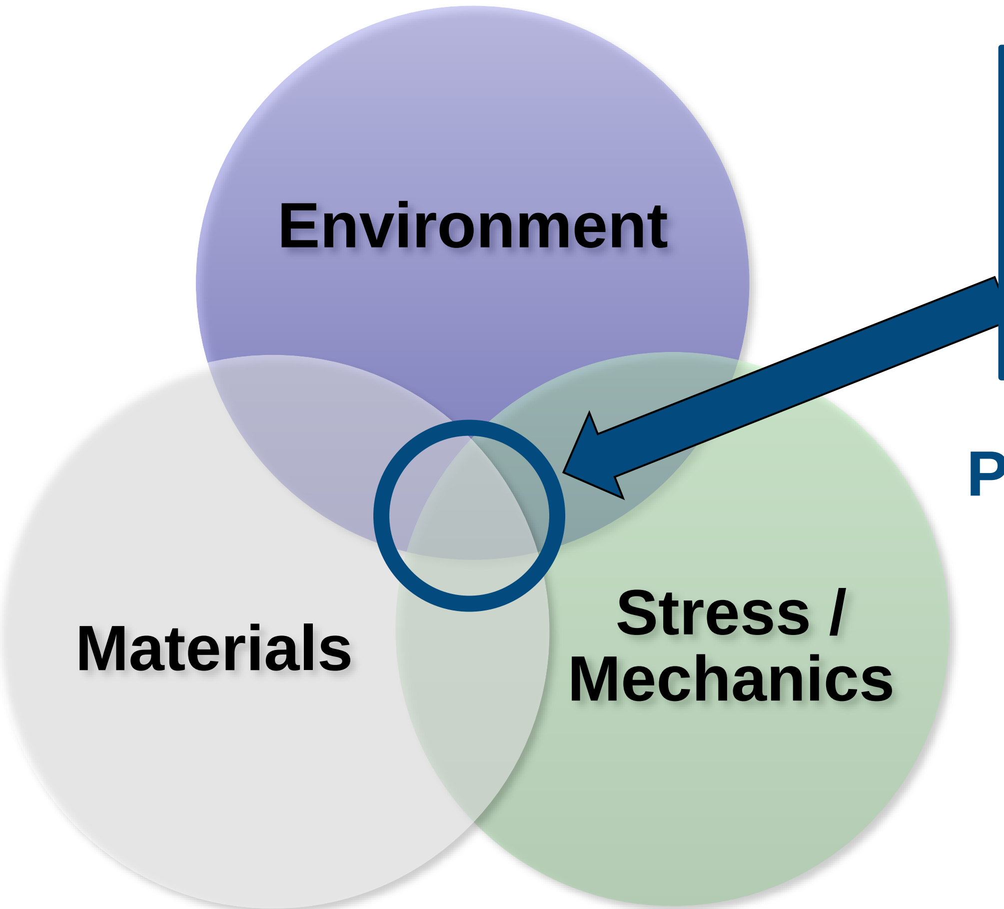
How do we standardize materials selection methods for high-pressure H_2 service?

- **Design-based method:** *ASME pressure vessels*
  - Measure reliable ***design data***
  - Prescribed component design methodology
  - Data often included in the code or standard
- **Performance-based method:** *vehicle systems*
  - Establish materials ***performance metrics***
  - Design information/method is not specified
  - Often used in the context of system performance and specific application requirements

Goal: Establish performance-based test metrics consistent with the requirements of fuel-cell vehicles

Performance evaluation requires assessment of *materials*, *environmental*, and *mechanics* variables



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

Performance method should

- Document *Materials* characteristics
- Establish *Environmental* conditions
- Measure relevant *Mechanical* properties

Determine relevant performance metrics for fuel-cell vehicle application

- What are the characteristics of the hydrogen fuel system in this application?
  - What characteristics are relevant for the materials of construction?

materials

- High-pressure hydrogen storage: 700 bar system
  - High stress
  - Hydrogen compatibility

environment

- Deep pressure cycles: refueling
  - Fatigue loading

mechanics

Hydrogen pressure cycles due to refueling are typically in the 100s, but theoretically up to ~11,250 refuelings
- 11,000 cycles = refuel once per day for 30 years

What are the necessary elements of a performance test method in this context?

- **Material definition**
  - Microstructure, strength, etc
  - Performance of welds

Critical, but how to define relevant weld geometry?

- **Environment**
  - Gas purity, pressure, temperature
- **Mechanical properties**
  - *Tensile properties*
    - Yield strength is generally not changed in H2
    - Tensile ductility requirements (elongation, RA)
      - No consensus on criteria
      - Criteria are generally arbitrary
      - Not used quantitatively in design
  - *Fatigue performance*
    - Deep stress cycles associated with refueling

Do tensile tests in H2 add value?

Critical limiting behavior

Organization of materials testing protocol

- **Material definition**
  - Materials specification must define the material
  - If welded construction, the welding procedure must be specified
- **Environmental test conditions**
  - *Gas purity*: baseline fuel-cell grade
  - *Pressure*: 1.25 NWP (nominal working pressure)
  - *Temperature*
    - Fatigue life: 293K (room temperature)
    - Tensile (SSRT): 228K
- **Mechanical properties**
  - Two options:

Notched (option 1)	*Smooth* (option 2)
• Fatigue life	• Fatigue life • Tensile (SSRT)

Materials testing protocol: material definition

1. Materials definition
   1.1. Materials must be defined by a materials specification
      - Can be nationally-recognized or company-defined
      - Must include compositional ranges
      - Must specify yield strength, tensile strength and elongation to failure
   1.2. Material should be tested in the final product form, whenever possible
   1.3. S* is tensile strength at room temperature
      - measured or from mill certification

Materials testing protocol: material definition

1. Materials definition

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1.4. Welds and metallurgically bonded materials

- Welded specimens must also be tested
- Joining process must be defined by a Welding Procedure Specification (WPS)
  - Must also include definition of tensile properties (yield, tensile and elongation)
- Specimens should be extracted from joined structure, whenever possible
  - Representative welds can be used, if necessary
- Welded specimens must satisfy the same requirements in gaseous hydrogen as base materials

Materials testing protocol: environment

2. Environmental test conditions

2.1. Gas purity

- Source gas shall satisfy Table 2.1 (source gas)
- Purity of gas in the testing chamber shall be verified to satisfy Table 2.1 (sampled gas)
- Once established by 3 consecutive evaluations, verification of gas purity can occur on a yearly basis

Table 2.1

Species	Source gas requirements	Sampled gas requirements
H_2	99.999% min	–
O_2	≤ 1	< 2
H_2O	≤ 3.5	< 10
$CO + CO_2$	≤ 2	–

Materials testing protocol: environment

2. Environmental test conditions

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2.2. Pressure

- Testing shall be conducted in gaseous hydrogen at minimum pressure of 1.25 X NWP
  - [note: NWP = nominal working pressure, which is typically 700 bar for vehicle storage]

2.3 Temperature

- Fatigue life testing
  - Temperature = 293 ± 5K
- Slow strain rate tensile (SSRT) testing
  - Temperature = 228 ± 5K

Materials testing protocol: mechanics

3. Testing requirements

3.1. Two options

- Notched specimen methodology (option 1)
- Smooth specimen methodology (option 2)
- It is *not* necessary to satisfy both methods

Materials testing protocol: mechanics

3. Testing requirements

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3.2. Notched specimen methodology (option 1)

- Notch shall have an elastic stress concentration factor (Kt) of ≥ 3
- Minimum of 3 specimens
- Force-controlled fatigue life test
  - Constant load amplitude
  - Maximum net section stress ≥ 1/3 S*
  - Load ratio (R) = 0.1 (minimum/maximum)
  - Frequency = 1 Hz

***Requirement*: all specimens must display >10^5 cycles before failure (or test termination)**

Materials testing protocol: mechanics

3. Testing requirements

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3.3. Smooth specimen methodology (option 2)

3.3.1. Fatigue life (smooth)

- Use internationally-recognized standards
- Minimum of 3 specimens
- Force-controlled fatigue life test
  - Constant load amplitude
  - Maximum net section stress ≥ 1/3 S*
  - Load ratio (R) = -1 (fully reversed tension-compression)
  - Frequency = 1 Hz

***Requirement*: all specimens must display >2x10^5 cycles before failure (or test termination)**

Materials testing protocol: mechanics

3. Testing requirements

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3.3. Smooth specimen methodology (option 2)

…

3.3.2. Slow strain rate tension (SSRT) test

- Use internationally-recognized standards
- Minimum of 3 specimens
- Tensile test
  - Strain rate ≤ 5×10^{-5} s^{-1}

***Requirement*: all specimens must display yield strength >80% of yield strength measured in air at same temperature (228 ± 5 K)**

Materials testing protocol: summary

4. Summary of tests and requirements

test and requirements		Notched method (option 1)	Smooth method (option 2)
Fatigue life	Test conditions	• H2 pressure = 1.25 NWP • Temperature = 293 ± 5K • Net section stress ≥ 1/3 S* • Frequency = 1 Hz	• H2 pressure = 1.25 NWP • Temperature = 293 ± 5K • Net section stress ≥ 1/3 S* • Frequency = 1 Hz
	# of tests	3	3
	Requirement	$N > 10^5$	$N > 2x10^5$
SSRT	Test conditions	Not required	• H2 pressure = 1.25 NWP • Temperature = 228 ± 5K • Displacement ≤ $5x10^{-5}$ s^{-1}
	# of tests		3
	Requirement		Yield strength > 0.80 yield strength in air at same temperature

Rationale: material definition

1. Materials definition

- Materials must be defined by a materials specification
  - For the purposes of the performance-based approach, materials are assumed to be insensitive to materials variables
- Material should be final product form, whenever possible
  - The product form for the application must be defined and controlled
- S* is tensile strength at room temperature
  - Tensile strength is an important characteristic that correlates with fatigue life (and common design practice)

Rationale: material definition

1. Materials definition

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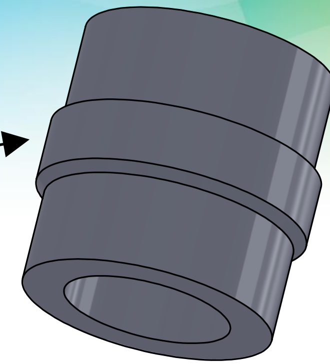
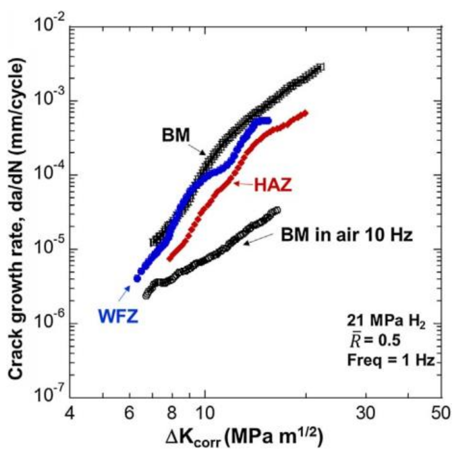
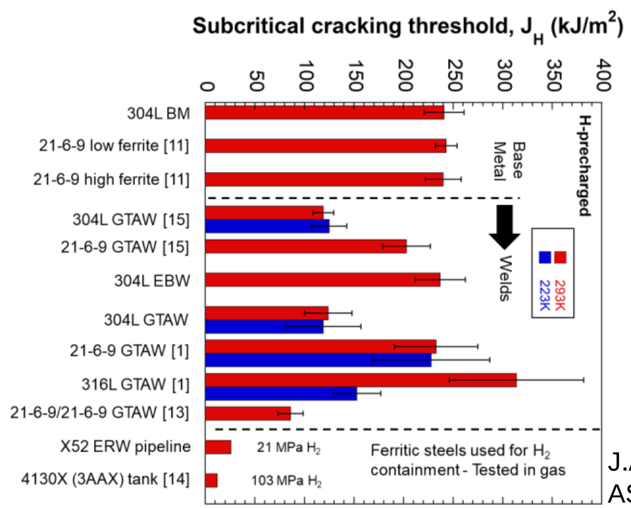
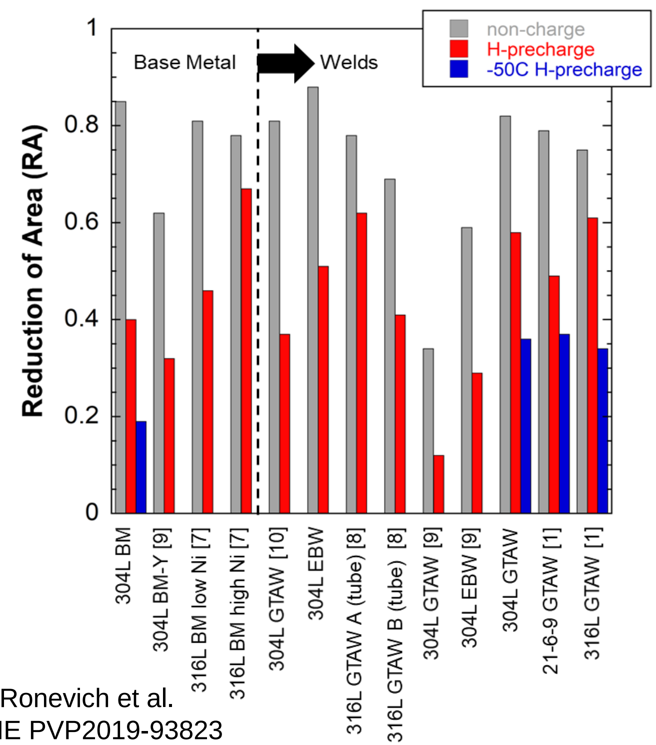
- **Welds and metallurgically bonded materials**
  - Welds are technologically important
  - However, all weld configurations are impossible to predetermine and specify
  - Quality welds generally behave similarly to base materials





Ronevich et al, Eng Fract Mech 194 (2018) 42-51.



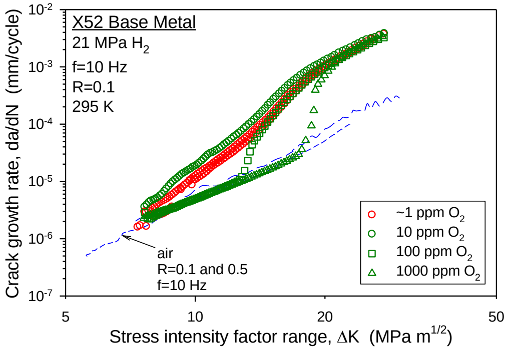


J.A. Ronevich et al. ASME PVP2019-93823

Rationale: environment

2. Environmental test conditions

- **Gas purity**
  - Oxygen impurities can have substantial effect on measurements
  - Gas in the test chamber is never as ‘clean’ as the source gas (due to purging process), thus the quality of test environment must be verified
    - Not practical to verify every test, but as long as purge processes are consistent, yearly verification is adequate



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

Rationale: environment

2. Environmental test conditions

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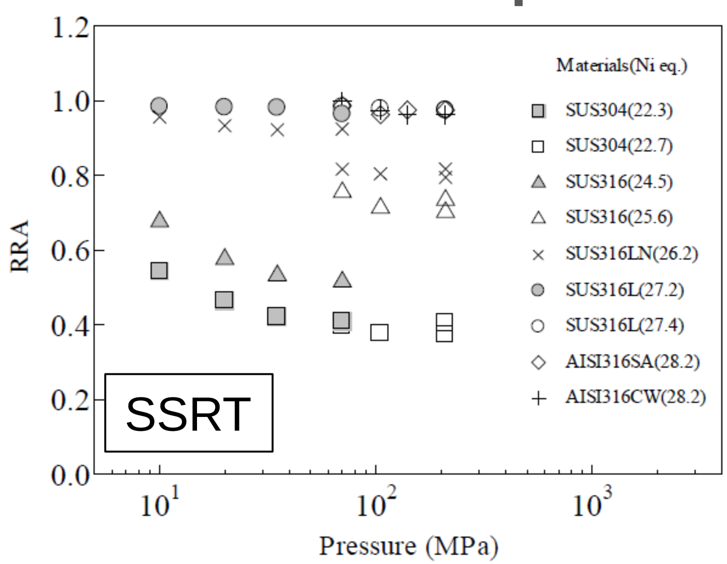
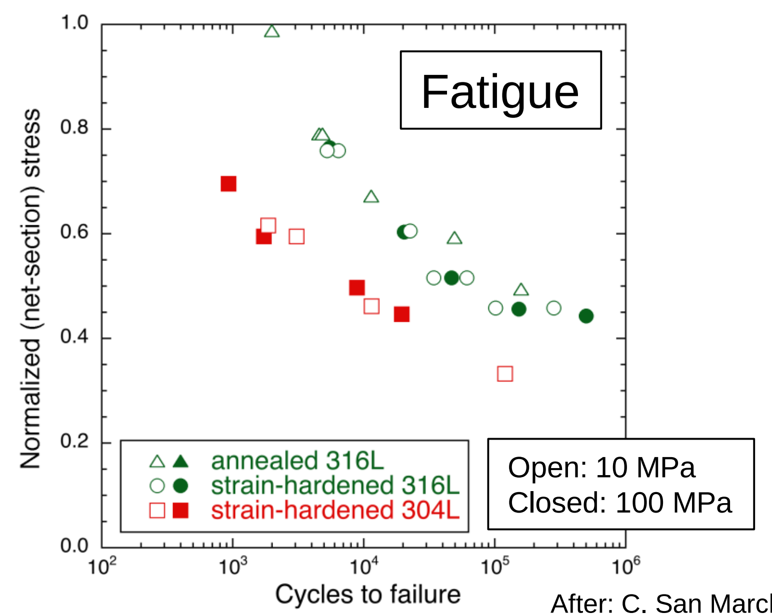
- **Pressure**
  - Off-normal operations have the potential to expose systems to > 1.25 x NWP
  - However, mechanical properties are not a strong function of pressure



H. Kobayashi et al. ASME PVP2016-64033

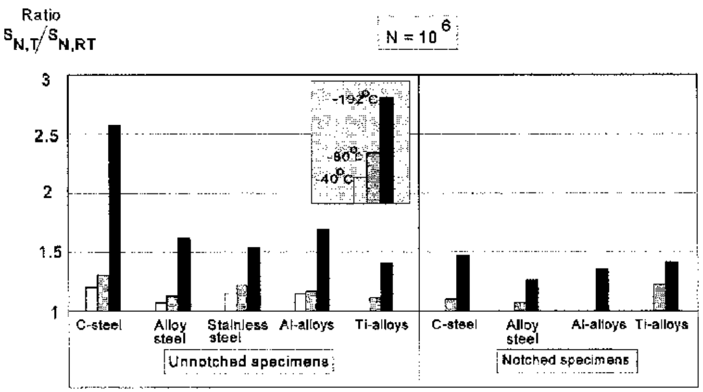


After: C. San Marchi et al., 43rd MPA Seminar, 2017.

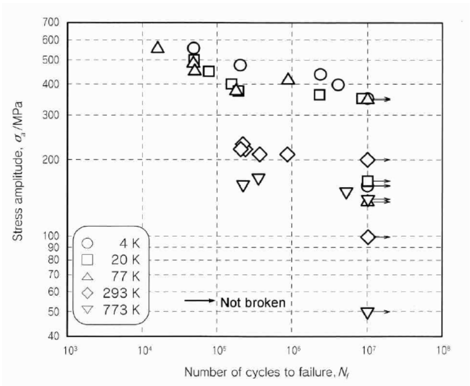
Rationale: environment

2. Environmental test conditions …

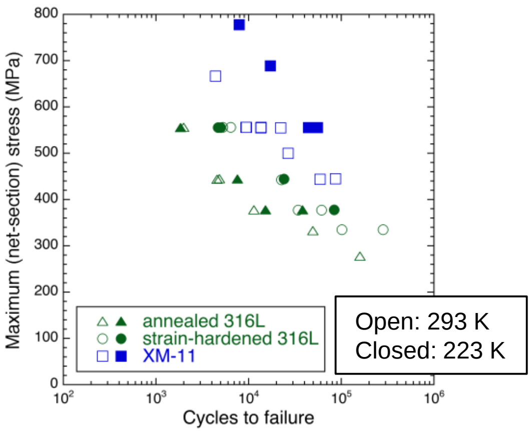
- **Temperature**
  - Environmental temperature range for automotive is usually considered to be -40 to +85˚C
  - Fatigue life: 293 ± 5K
    - Fatigue strength is generally increased at low temperature (data support this in hydrogen also)



J. Schijve, Fatigue of Structures and Materials, 2nd ed., Springer 2009.



NIMS space use materials strength data sheet, No. 7 (2006)



After: C. San Marchi et al., 43rd MPA Seminar, 2017.

Rationale: environment

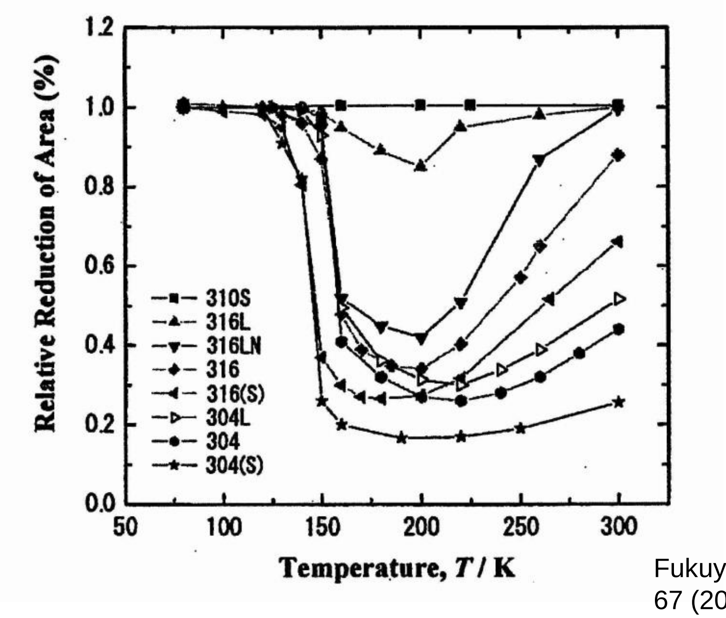
2. Environmental test conditions

…

- **Temperature**

  …

  - Slow strain rate tensile (SSRT) testing: 228 ± 5K
    - SSRT shows greater ductility loss at low temperature

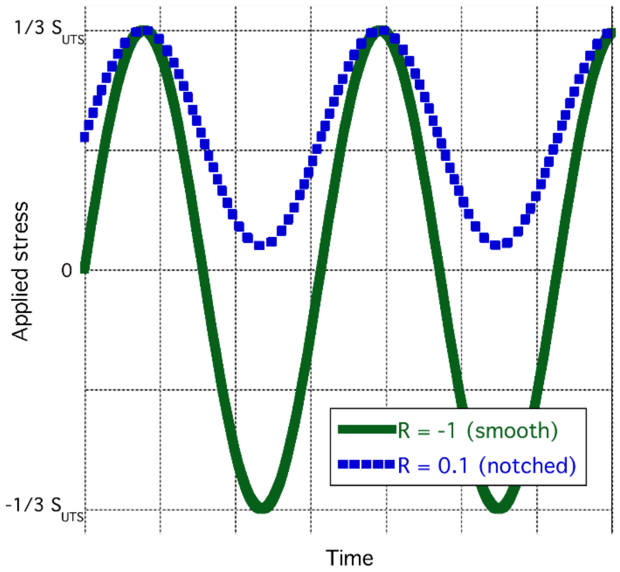


Fukuyama et al, J. Japan Inst. Met. 67 (2003) 456-459

Rationale: mechanics

3. Testing requirements

- Two options
  - Notched specimen methodology (option 1)
  - Smooth specimen methodology (option 2)



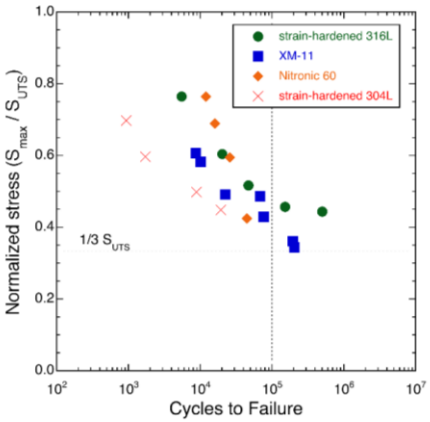
- For same maximum (net-section) stress, the load cycles are different for:
  - Notched (R = 0.1) and
  - Smooth (R = -1)
- Stress concentration amplifies affects of stress cycle
  - Notched (Kt ≥ 3)
  - Smooth (Kt = 1)

Rationale: mechanics

3. Testing requirements

…

- **Notched specimen methodology (option 1)**
  - Demonstrate that the fatigue life in the presence of stress concentration (>100,000) exceeds the design life requirement (11,250) by large safety factor
    - Typical design stress for pressure systems is < 1/3 S*
    - Pressure applications are typically tension-tension (i.e., R > 0)



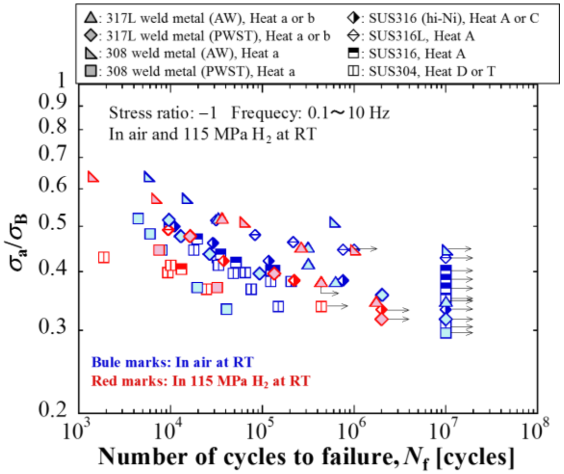
After: C. San Marchi et al., 43rd MPA Seminar, 2017.

Rationale: mechanics

3. Testing requirements

…

- **Smooth specimen methodology (option 2)**
  - **Fatigue life (smooth)**
    - Demonstrate that fatigue limit is not changed by hydrogen
      - Fatigue limit generally is > 1/3 S*



Nakamura et al, M&M2017 Conference, 2017.

Rationale: mechanics

3. Testing requirements

…

- Smooth specimen methodology (option 2)
  …
  - Slow strain rate tension (SSRT) test
    - Verify yield strength is maintained in hydrogen
      - 80% criteria is based on using ‘crosshead’ displacement to estimate yield strength (preferred method measures extension in gauge length of specimen with extensometer)
    - Strain rate limit is intended to allow for slow kinetics of hydrogen uptake during test
      - Strain rate studies suggest limiting behavior at strain rate $<10^{-4}$ s^{-1}

Omura et al., Zairyo to Kankyo/Corros. Eng. 55 (2006) 139–145 (in Japanese).

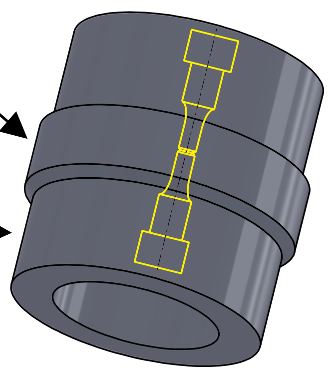
Additional considerations for notched configuration: Application of notched fatigue life testing to welds and welded components

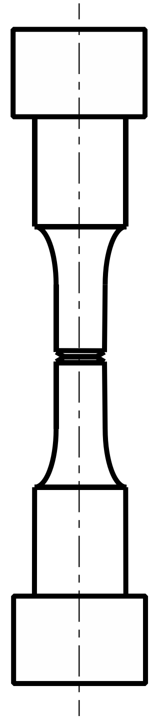
Notched fatigue specimen
Kt ≥ 3

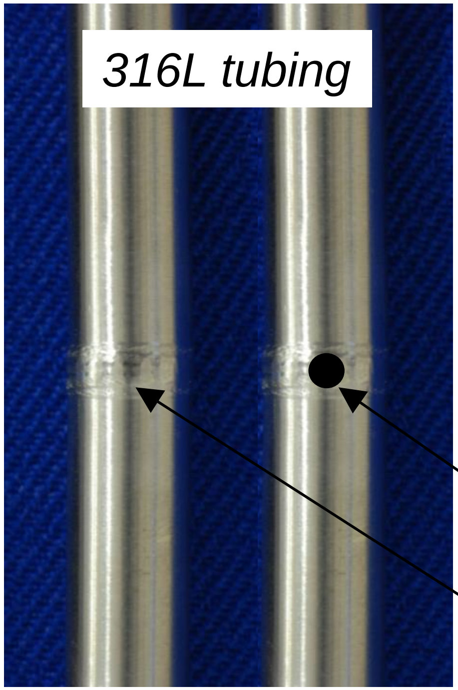
Notch can bias failure to desired region (eg, weld)

weld

Base metal ring







through hole

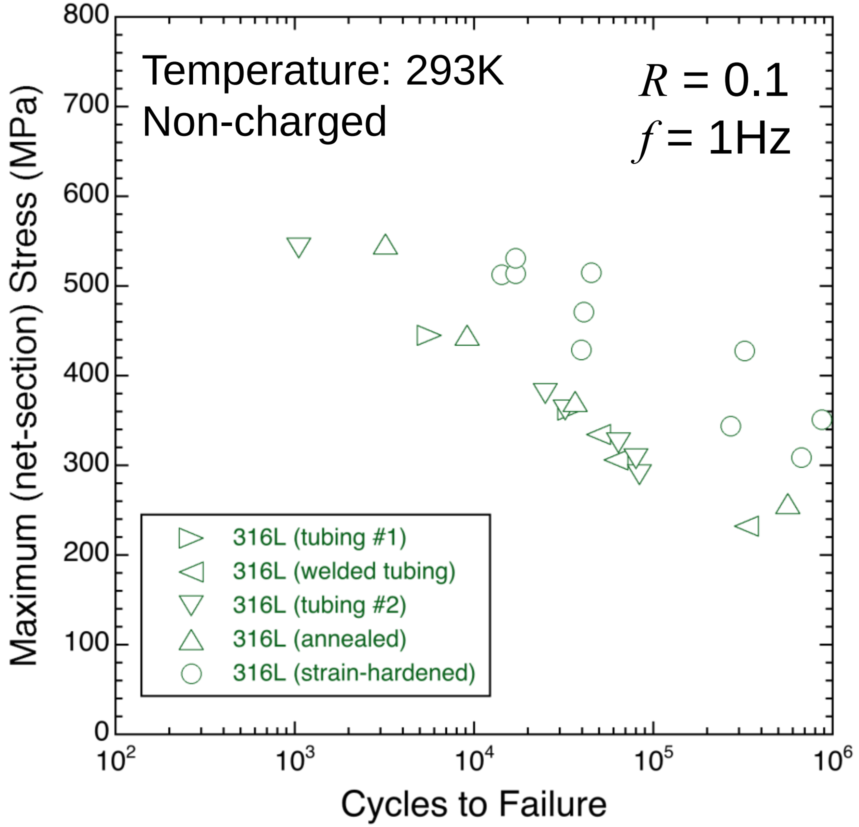
Orbital tube weld

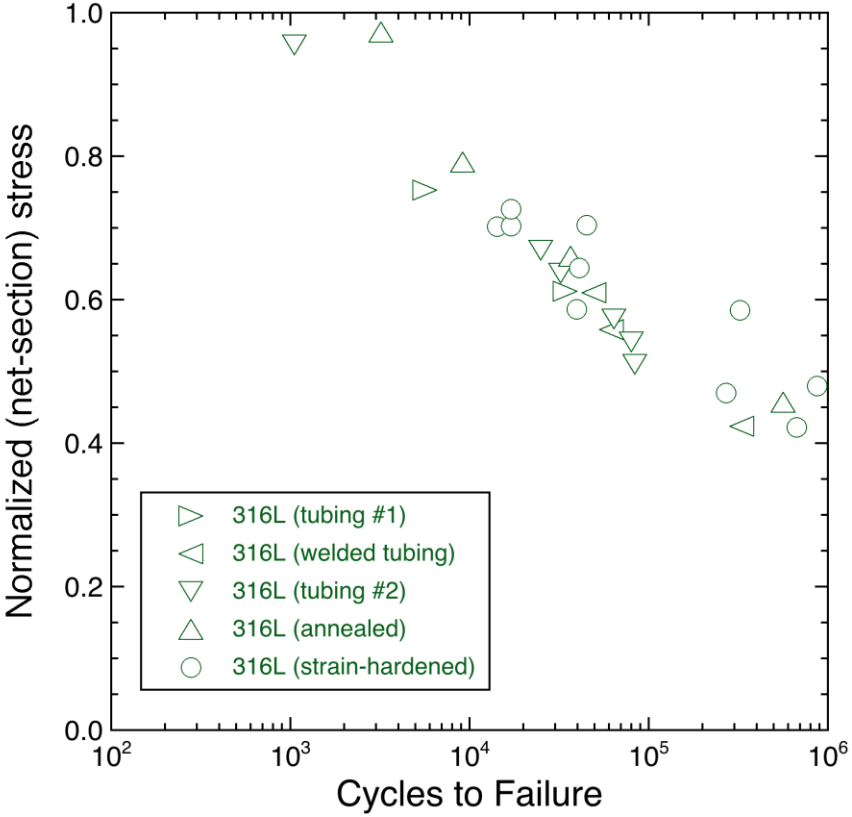
Hole-drilled tubular fatigue specimen
Kt ~ 3

Behaves nominally the same as bulk specimen

Concept can be applied to more complex weld configurations

Additional considerations for notched configuration: Fatigue life of hole-drilled tubular specimens are consistent with baseline materials





Orbital tube welds behave similarly to base materials in the hole-drilled tube configuration

Summary

GOAL: Establish performance-based test metrics consistent with the requirements of fuel-cell vehicles

test and requirements		Notched method (option 1)	Smooth method (option 2)
Fatigue life	Test conditions	• H2 pressure = 1.25 NWP • Temperature = 293 ± 5K • Net section stress ≥ 1/3 S* • Frequency = 1 Hz	• H2 pressure = 1.25 NWP • Temperature = 293 ± 5K • Net section stress ≥ 1/3 S* • Frequency = 1 Hz
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