Sandia National Laboratories

H2FC Hydrogen and Fuel Cells Program

R&D for Safety, Codes and Standards: Materials and Components Compatibility

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2018 DOE Hydrogen and Fuel Cells Annual Merit Review

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Project ID# SCS005

Overview

Timeline

- Project start date: Oct 2003
- Project end date: Sept 2018*

* Project continuation and direction determined by DOE annually

Budget

- Total Project Budget: $9.7M
  - FY17 DOE Funding: $560K
  - Planned FY18 Funding: $450K

Technical Barriers

A. Safety Data and Information: Limited Access and Availability

F. Enabling national and international markets requires consistent RCS

G. Insufficient technical data to revise standards

Partners

- **SDO/CDO participation:** CSA, ASME, SAE, ISO
- **Industry:** FIBA Technologies, Tenaris-Dalmine, Japan Steel Works, BMW, Opel, GM, Swagelok
- **International engagement:** AIST-Tsukuba (Japan), I2CNER (Kyushu University, Japan), MPA Stuttgart (Germany), KRISS (Korea)

Relevance and Objectives

Objective: Enable technology deployment by **performing and applying foundational research toward the development of science-based codes and standards** that enable the deployment of hydrogen technologies

Barrier from 2013 SCS MYRDD	Project Goal
A. Safety Data and Information: Limited Access and Availability	Develop and maintain material property database and informational resources to aid materials innovation for hydrogen technologies
F. Enabling national and international markets requires consistent RCS	Develop science-based materials test methods, working with SDOs and the international community to validate and incorporate methods in globally harmonized testing specifications
G. Insufficient technical data to revise standards	Execute materials testing to address *targeted* data gaps and critical technology deployment • Coordinate activities with international stakeholders

Project Approach and Milestones

MYRD&D 2013 Barrier	FY18 Milestone	Status
A. Safety Data and Information: Limited Access and Availability	Advance state-of-the-art materials database for hydrogen compatibility	Sandia Hydrogen Effects Database (Granta MI) is publically accessible and populated with literature data
F. Enabling national and international markets requires consistent RCS	Complete "round robin" testing with Kyushu University and MPA Stuttgart to inform SAE J2579 and proposal for GTR	Fatigue life tests at SNL and KU have been completed and results are consistent; SSRT (tensile) tests at SNL are underway
G. Insufficient technical data to revise standards	Evaluate effect of temperature on fatigue life of austenitic stainless steels in high-pressure hydrogen	Fatigue testing in low-temperature and high-pressure hydrogen was demonstrated
	Aggregate fatigue behavior for PV steels and identify trends	• A master curve for fatigue crack growth was developed for PV steels (basis of ASME code case) • Tensile strength limit of 950 MPa was confirmed as practical limit in most cases

Approach: Establish science-based test methodologies consistent with the requirements of applications

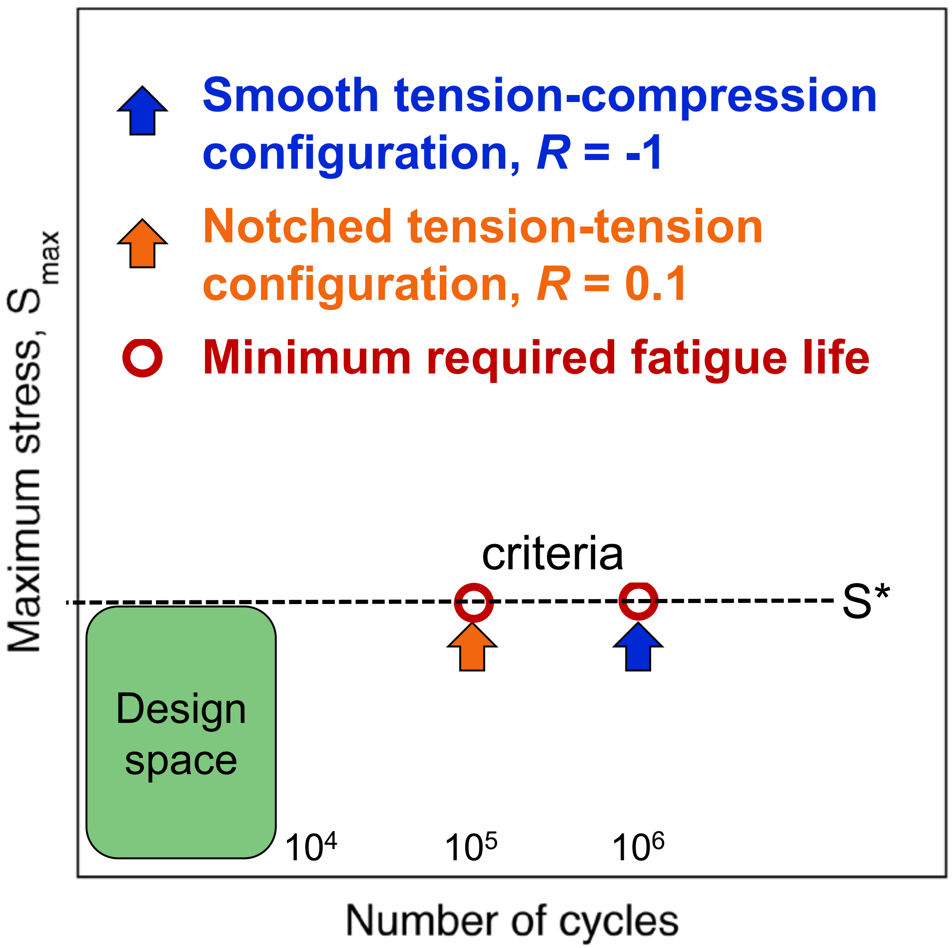
How do we standardize selection methods for materials for H_2 service?

- **High-pressure vehicle fuel system**: *performance-based method*
  - Establish materials *performance metrics*
  - Consider mechanics of the service condition
  - Explore relevant environments and determine dominant conditions
- **Stationary pressure vessel**: *design-based method*
  - Measure reliable *design data*
  - Establish bounding behavior for environment and mechanics
    - balance between testing efficiency and meaningful data
  - Assess data in aggregate to establish global behavior

National Laboratory role: ***Develop and deploy foundational scientific framework to establish and evaluate methods***

Approach: high-pressure vehicle fuel system

Determine relevant performance metrics to establish conservative material behavior for application



Smooth tension-compression

Infinite life assessment

- Single point assessment of infinite fatigue life
- Assumes stresses in application are fully reversed
- No stress concentrations with maximum stress ≤ S*

Notched tension-tension

Conservative assessment

- Assesses performance life that is conservative for the intended application
  - but not overly conservative
- Assumes mechanics of notch are consistent with application
  - or bound the application

Approach: high-pressure vehicle fuel system

Evaluate a wide range of austenitic stainless steels in hydrogen to study method and measure trends of fatigue response with strength, composition, and environment

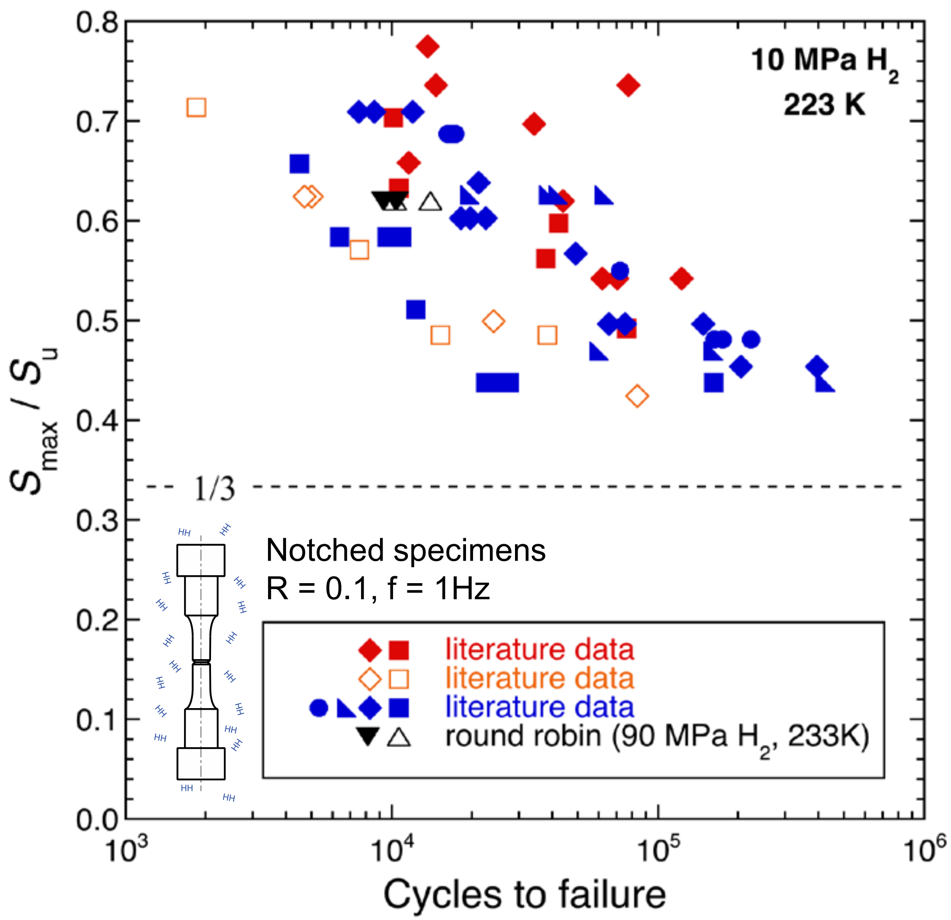
material	S_y (MPa)	S_u (MPa)	Cr	Ni	Mn	N
316L	280	562	17.5	12	1.2	0.04
CW 316L	573	731	17.5	12	1.2	0.04
304L	497	721	18.3	8.2	1.8	0.56
XM-11	539	881	20.4	6.2	9.6	0.26
Nitronic 60	880	1018	16.6	8.3	8.0	0.16
SCF-260	1083	1175	19.1	3.3	17.4	0.64

Wide range of strength (i.e., weight)

Wide range of Ni content (i.e., cost)

Accomplishment: high-pressure vehicle fuel system

"Round robin" fatigue testing initiated under auspices of SAE to aid harmonization of testing methodologies



- Fatigue life tests in high-pressure (90 MPa) and low temperature (233K) hydrogen have been completed by SNL and KU (6 tests)
  - Results are consistent between labs
  - Results from MPA expected soon
- Fatigue life measurements are consistent with data from the literature at lower pressure
- SSRT (tensile) tests and smooth fatigue are not yet completed by SNL and MPA

Accomplishment: high-pressure vehicle fuel system

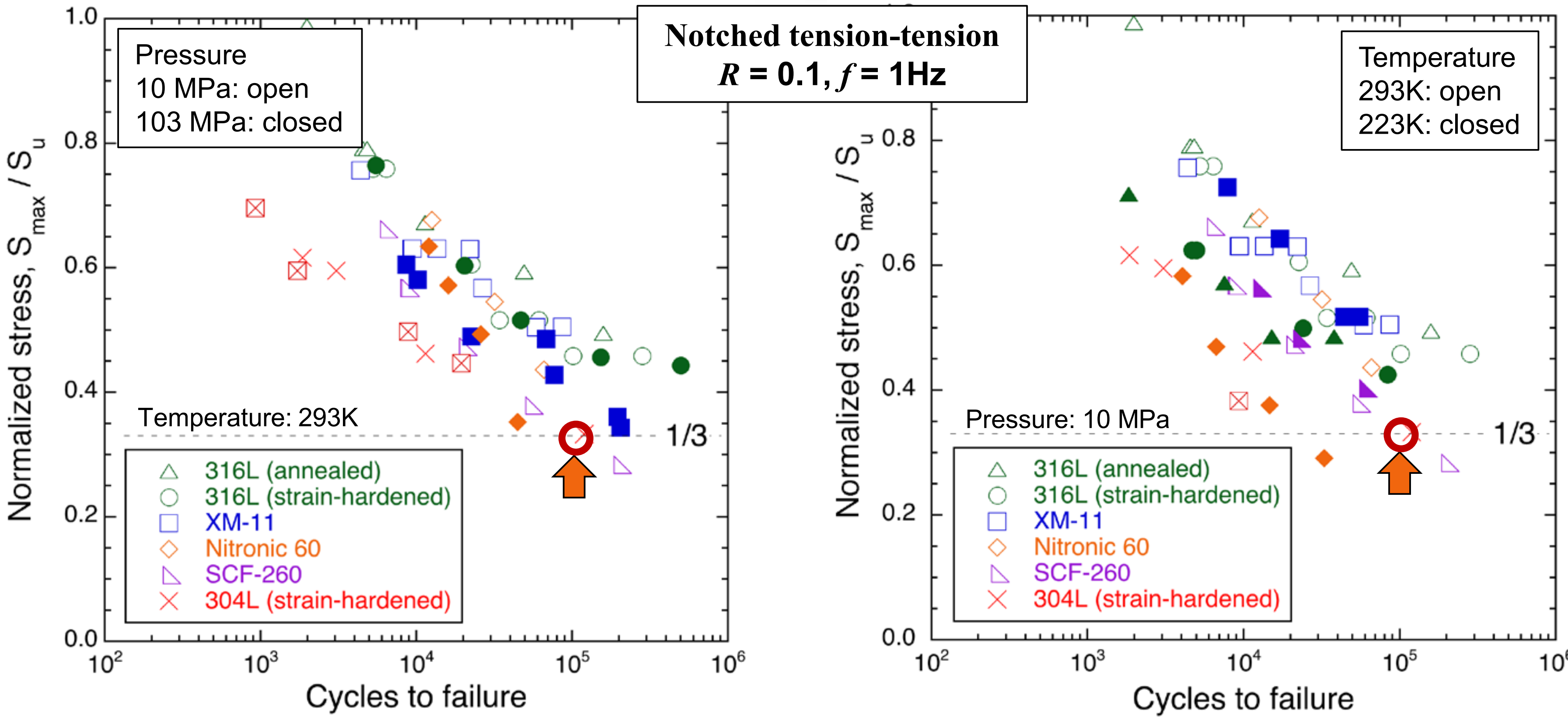
Simple performance requirements established for SAE J2579 based on relevant design space (proposed to GTR IWG)

Test configuration		Evaluation parameter	Requirements of tests performed in H2
Slow strain rate tension tests – SSRT (3 tests)		Yield strength	Average ≥ Sy
		Tensile strength	Average ≥ Su
		Strain hardening capacity	Average > 1.07
		Elongation	Average ≥ 12%
Fatigue life tests (must satisfy 1 of 3 options)	Option 1 (**3 tests**): **Smooth, R= -1**	Cycles to failure	Each > 200,000 cycles
	Option 2 (**3 tests**): **Notched, R = 0.1**	Cycles to failure	Each > 200,000 cycles
	Option 3 (**5 tests**): **Notched, R = 0.1**	Cycles to failure	Each > 100,000 cycles

Note: Sy and Su are specified minimum yield and tensile strength respectively from materials definition or standard

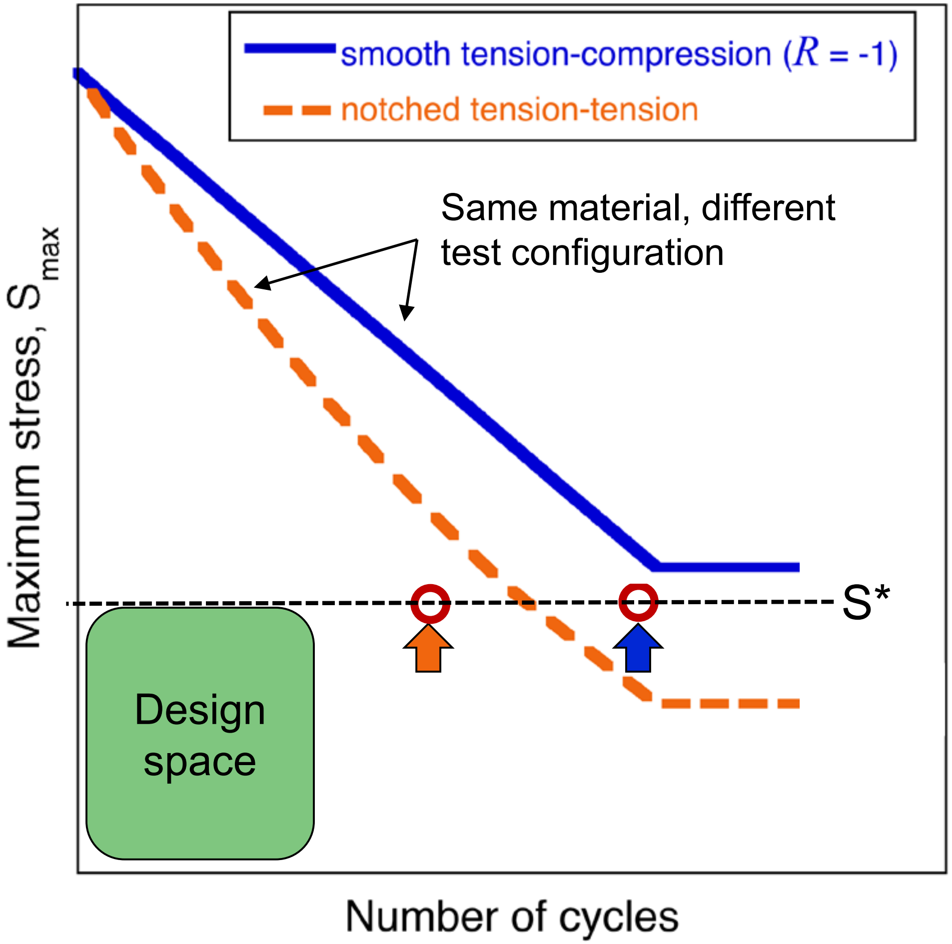
Accomplishment: high-pressure vehicle fuel system

Assessment of trends for austenitic stainless steels shows less variability of fatigue life than tensile ductility



- 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

Background: high-pressure vehicle fuel system
While the assessment of materials for vehicle fuel systems is blind to the fatigue life *curves,* the metrics are designed to consider the performance of the material in the respective test configurations



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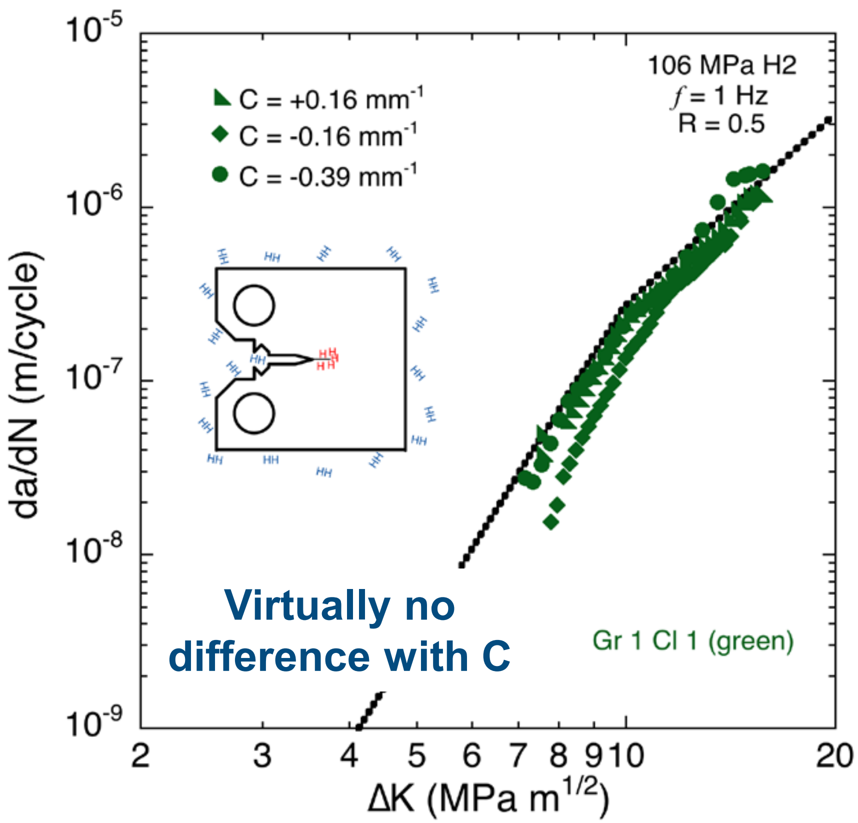
Approach: stationary pressure vessels

Accelerate testing by innovative fracture mechanics approach



- C is the rate at which K is changed during the test
- Time to collect data for a given ΔK range scales approximately with C
- For a (conventional) constant load test C ~ 0.1 mm^{-1}
- For segments shown
  - Constant load is estimated to be 14 ~hr
  - C = -0.16 mm^{-1} is ~8 hr
  - C = -0.39 mm-1 is ~5.5 hr
- For ΔK range of 5–6 MPa $m^{1/2}$
  - C = +0.16 mm^{-1} is ~47 hr
  - C = -0.39 mm-1 is ~27 hr

Fatigue tests at low ΔK can be greatly accelerated by using negative values of C (and within guidance of ASTM standard methods)

Approach: stationary pressure vessels

Diverse set of pressure vessel steels provide a global picture of performance for this product form

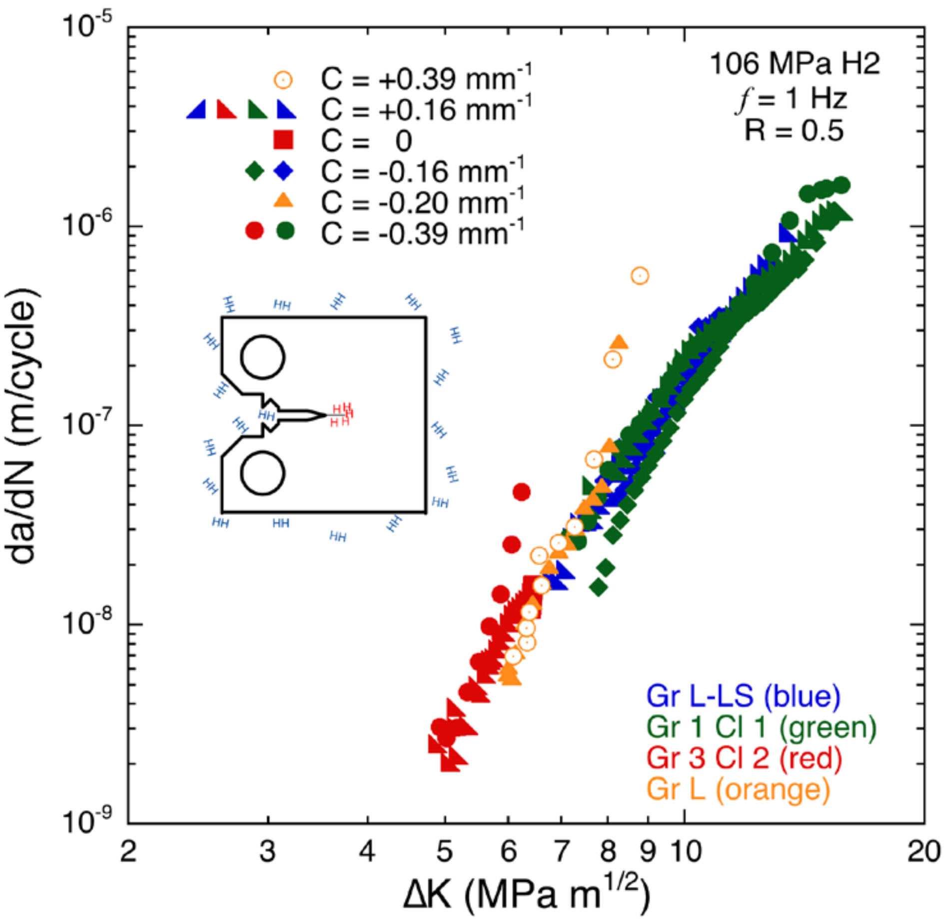
Designation	Tensile strength (MPa)	Yield Strength (MPa)
Cr-Mo steels		
SA-372 Grade J (A71)	839	642
SA-372 Grade J (B50)	871	731
SA-372 Grade J (A72)	908	784
SA-372 Grade J (AV60Z)	890	760
34CrMo4	1045	850
Ni-Cr-Mo steels		
SA-372 Grade L	1149	1053
SA-372 Grade L-LS †	873 †	731 †
SA-723 Grade 1 – Class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

† Does not meet SA-372 (low strength)

Tensile strength > 950 MPa (highlighted)

Accomplishment: stationary pressure vessels

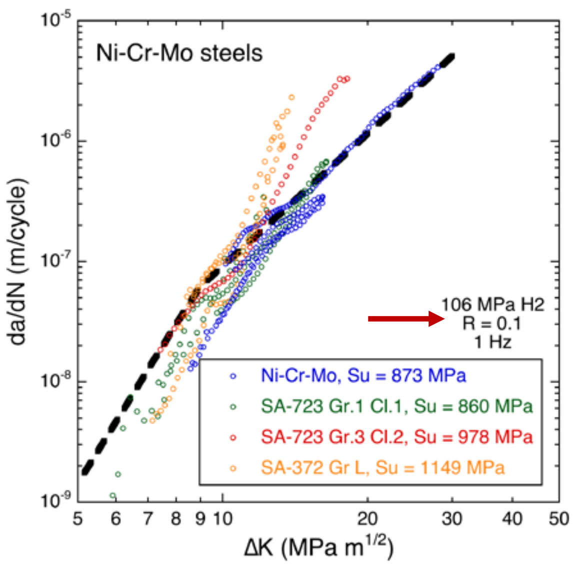
Fatigue crack growth tests can be significantly accelerated by managing C

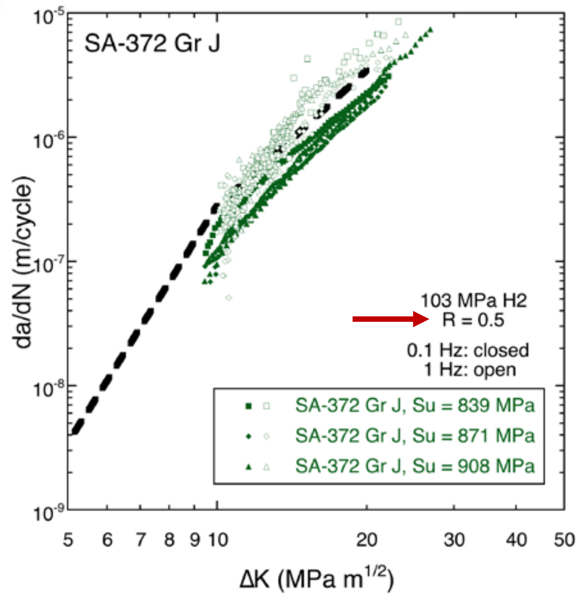


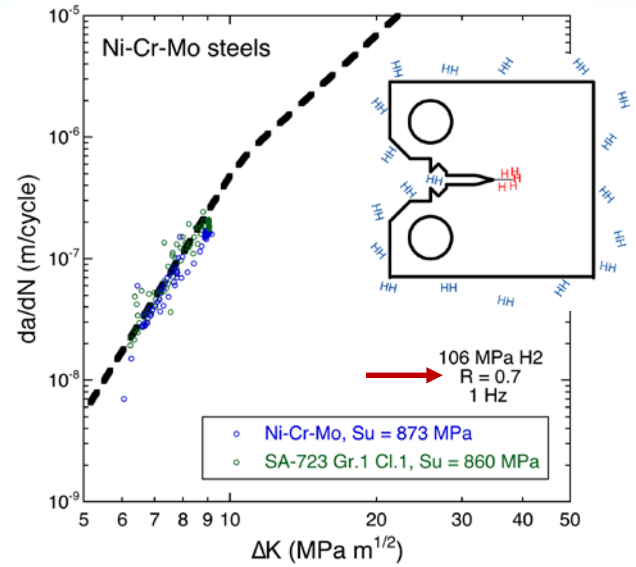
- The measured fatigue crack growth rate is not affected by C for these tests
  - Therefore, test time can be reduced by a factor of 2 to 3, while capturing the same information
- These steels represent a wide range of strength and composition for Ni-Cr-Mo pressure vessel steels
- Deviations from from the basic trend are only apparent in high-strength steels (tensile strength > 950 MPa)

Accomplishment: stationary pressure vessels

A generic fatigue crack growth curve was developed to capture the general behavior of pressure vessel steels





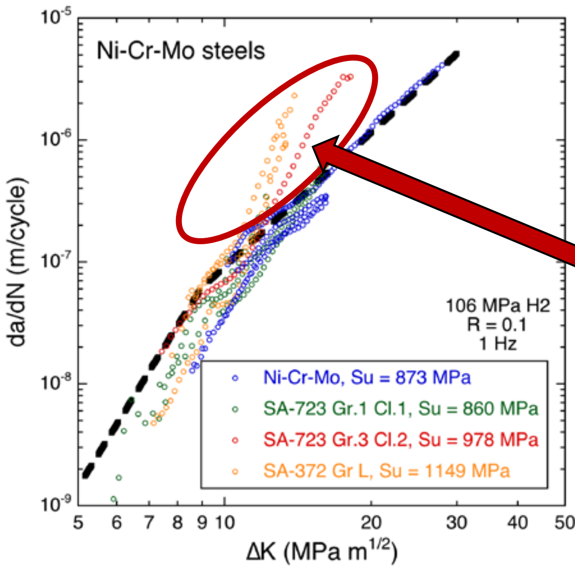


- The dashed lines capture fatigue performance of pressure vessels as a function of R and pressure (or fugacity, f)
- ASME BPVC committee is preparing a code case to allow design with this curve fit

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

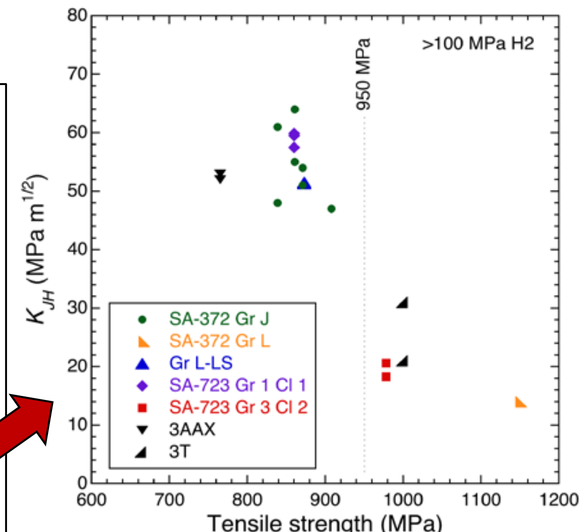
Accomplishment: stationary pressure vessels
PV steels with tensile strength >950 MPa are especially sensitive to hydrogen-assisted fatigue and fracture

- High-strength PV steels should only be used with extreme caution
  - All significant deviations from general fatigue trends can be attributed to high tensile strength (>950 MPa)
  - Fracture resistance becomes uncomfortably low, when tensile strength is >950 MPa



For PV steels with tensile strength > 950 MPa

- Accelerated fatigue crack growth rate is observed
- K_{JH} < 30 MPa $m^{1/2}$ (which leads to the accelerated fatigue)



(where K_{JH} is measured as J_{IC} from ASTM E1820 in gaseous hydrogen)

Response to Previous Year Reviewers' Comments

- *FY17 Reviewer Comment: several comments about comparison to NIST data*
  - NIST has not published any data on pressure vessel steels measured in hydrogen (pipeline steels are a different project). Unpublished results have been shared with ASME, and represent just a handful of tests in limited ranges of ΔK and R. Nevertheless, the limited NIST data for PV steels is consistent with the assessment provided here (see SAND2019-1098PE).
  - On the other hand, there is healthy amount of data on PV steels from Japan. This data is in qualitative agreement with the data presented here and is being acquired for the database, which will enable quantitative comparison in the future.
- *FY17 Reviewer Comments:* "More documentation through ASME, ASTM, and SAE International is recommended. Standardized, published test methods and direct comparisons of data on samples exposed to hydrogen and samples exposed to air are recommended"
  - The meaning of "more documentation" is unclear. If this means more codes and standards, the goals of this project are not to write code. If documentation means participation, as one example, we actively participate in R&D with ASME, organizing the hydrogen effects sessions at ASME PVP conference. Additionally, the materials expert team (SAE Fuel Cell Safety Task Force) is led out of this project. More specific examples where there are gaps would be helpful for project definition.
  - Philosophically, I do not like comparisons of results in air and in hydrogen because the focus becomes the difference and not the materials performance.

Collaborations

- Standards Development Organizations (SDOs)
  - Sandia technical staff participate on committees engaged in materials testing and selection for hydrogen service when the SDOs are active
  - Low-temperature fatigue studies are being actively being shared with the FC Safety Task Force at SAE
  - Fatigue curves are being incorporated into ASME BPVC
- Industry partners
  - Partners communicate materials testing gaps/needs and provide technology-relevant materials (FIBA Technologies, Tenaris-Dalmine, JSW, BMW, Opel, Swagelok)
  - International MOU for evaluation of Ni-Cr-Mo PV steels informs development of advanced high-pressure storage
- International research institutions
  - Fatigue testing at low temperature is focus of R&D collaboration within the context of SAE and international participants with complementary programs in Japan (Kyushu Univ) and Germany (MPA Stuttgart)
    - shared learning on capability deployment and testing methods
    - Joint publication for ASME PVP conference (July 2018)

Remaining Challenges and Barriers

- Demonstrate low-temperature, high-pressure capability for standardized materials characterization
  - Extremely challenging tests
  - While initial tests have been performed, more work is necessary to improve robustness of system and efficiency of testing (international interactions and shared learning improve confidence on results)
- Establish internationally-harmonized metrics for materials selection (US, Europe and Asia embrace different test methodologies)
  - Significant progress on conservative criteria for fatigue life, but many questions remain (e.g., specimen geometry)
  - Relevant fracture test methods are still disputed (rising load, statically loaded, step loaded)
- Next generation materials/microstructures cannot be identified without fundamental understanding of the physical processes
  - Advanced scientific computing, coupled with controlled experimentation are needed to develop mechanistic understanding of hydrogen effects and inform materials design hypotheses

Proposed Future Work

Any proposed future work is subject to change based on funding levels

Remainder of FY18

- ***Low-temperature, high-pressure testing capability for fuel systems and refueling infrastructure***
  - Evaluate the hypothesis that low temperature is not the limiting condition for fatigue life of austenitic stainless steels for high-pressure vehicle fuel systems
  - Continue harmonization discussions in SAE task force and GTR IWG
    - Aluminum alloys, welds, etc. (will require activity beyond FY18)
- ***Advanced stationary storage options***
  - Develop procedures to extract fatigue crack growth rates at multiple R ratios from same specimen to further reduce testing burden

FY19 (project continuation and direction determined by DOE annually)

- ***Advancing design tools and harmonized methods***
  - Develop deeper understanding of mechanics of notches in fatigue testing to enhance international consensus on test methods and develop framework for crack initiation and short crack behavior
  - Develop hardware designs for reverse loading and strain-based methods to extend test method development to negative load ratios
- ***Scientific basis for next generation microstructures***
  - Develop experimental and computational studies to probe fundamental behaviors at microstructural length scales

Summary

- Definitive *database tools* for materials selection
  - Database provides relevant data to public and enables quantitative comparison of data from different sources
- *High-pressure vehicle fuel system*: performance-based method
  - Harmonized materials acceptance criteria SAE J2579
    - Methods and criteria presented to GTR No. 13 IWG
  - Fatigue life data in high-pressure hydrogen at low temperature are emerging
    - Collaboration with Japan and Germany suggest low temperature is not limiting condition for austenitic stainless steels
- *Stationary pressure vessels:* design-based methods
  - Fatigue crack growth tests can be significantly accelerated by managing the C parameter during fatigue testing (test time reduction of factor of 2-3)
  - A generic fatigue crack growth curve was developed to capture the general behavior of pressure vessel steels and high-strength limits confirmed
    - This relationship is the basis of a code case applicable to ASME BPVC VIII.3.KD-10
- Extensive *international partnerships*
  - Research institutions: AIST (Japan) , Kyushu University (Japan), KRISS (Korea), MPA Stuttgart (Germany)
  - Industry: Japan Steel Works, Tenaris-Dalmine (Italy), FIBA Technologies (US)

Technical Back-Up Slides

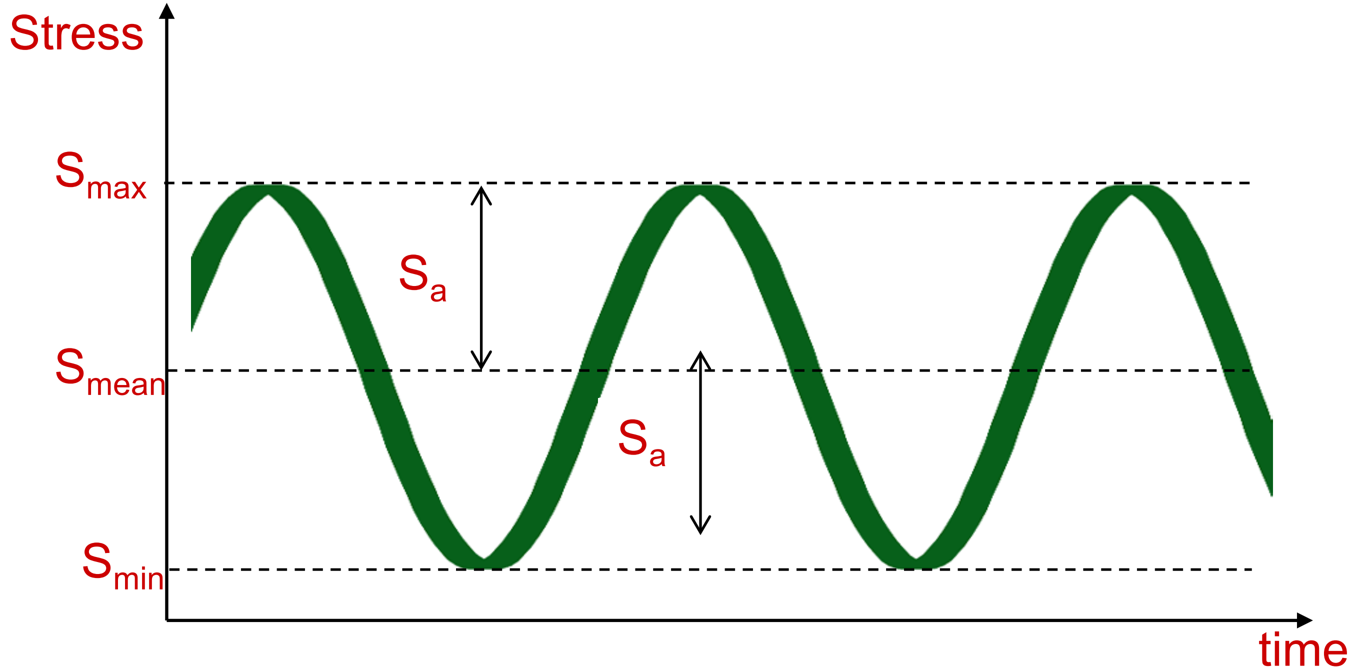
Background/Approach: high-pressure vehicle fuel system

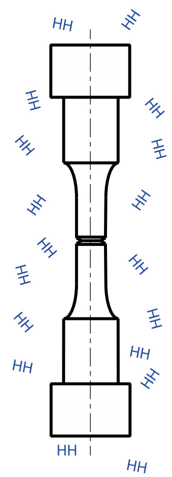
Fatigue life testing is a standard methodology for assessing fatigue performance of materials when fracture mechanics cannot be applied

- Stress-based methods determine the fatigue life as a function of design stress
- Two forms of stress-based fatigue testing are actively being pursued by international community:

Conventional fatigue life testing
- "smooth" specimens
- Fully reversed loading (R = -1)

Hydrogen fatigue life testing
- "notched" specimens
- Tension-tension loading (R = 0.1)





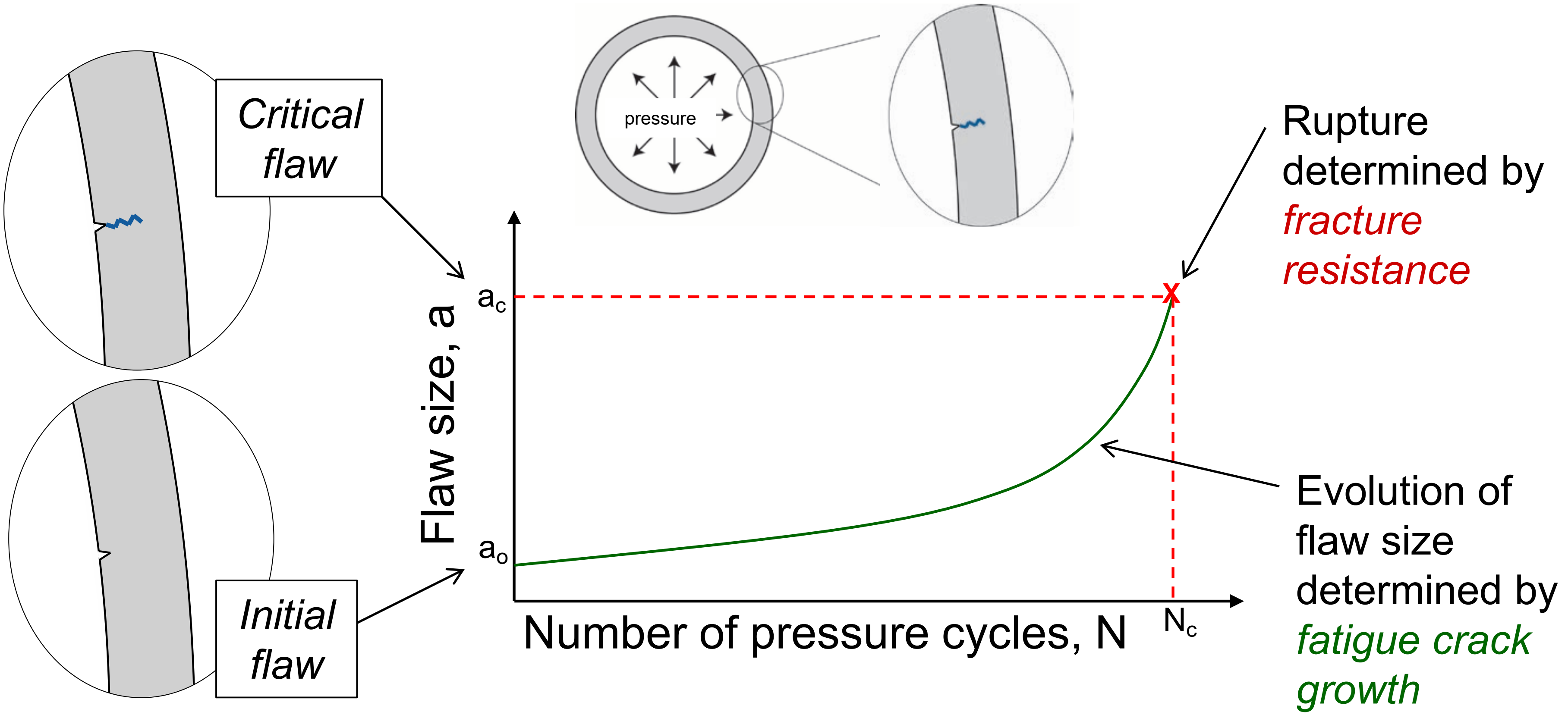
$R = S_{min} / S_{max}$

$S_{max} = 2S_a/(1-R)$

Background: high-pressure vehicle fuel system
Test plan for collective learning activity (”round robin”) with Kyushu University and MPA Stuttgart; coordinated through SAE Fuel Cell Safety Task Force

Test	Test conditions	Environment	Number of tests, each lab
Slow strain rate tension (SSRT)	$\leq 5 \times 10^{-5}\ s^{-1}$	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

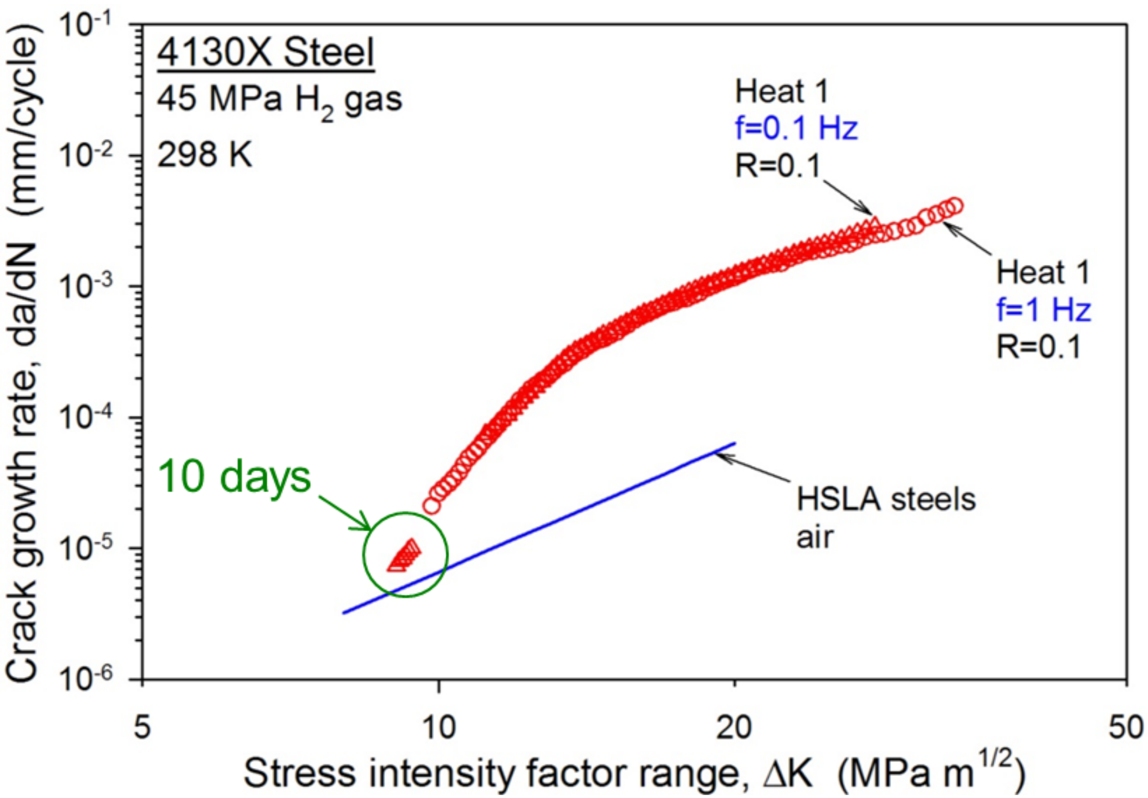
Background/Approach: stationary pressure vessels
Fracture mechanics based methods for fatigue crack growth and fracture resistance are the basis for high-pressure hydrogen pressure vessel design (ASME BPVC VIII.3 Article KD-10)

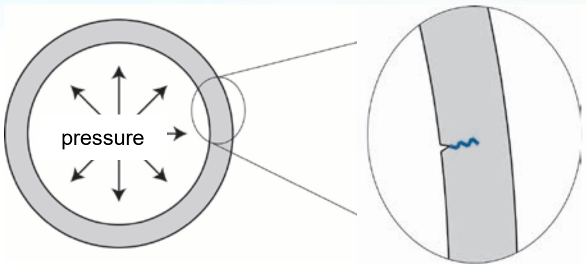


Industry needs and uses fracture mechanics to optimize pressure vessel designs for stationary storage

Background/Approach: stationary pressure vessels

Fatigue crack growth measurements impose a cyclic driving force (ΔK) on a crack to determine the rate at which a crack will grow; the data is transferrable to component design





$$\Delta K = \Delta P \times f(a, t, R)$$

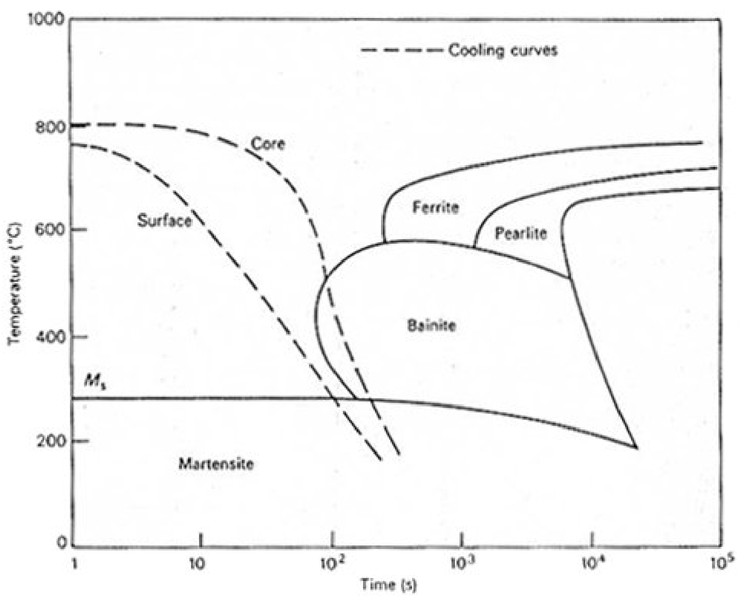
$$da/dN = C \Delta K^m$$

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

Efficient methods for generating fatigue crack growth data are needed to enable conservative predictions

Background/Approach: stationary pressure vessels

International partnership provides common basis for development of advanced storage options



- Pressure vessel steels are quenched to achieve uniformity of desired properties through the wall thickness
- "Hardenability" of Cr-Mo steels limited to <38mm wall thickness

- Ni-Cr-Mo pressure vessel steels provide superior hardenability
  - Reduces variability in thick-walled steel vessels
  - Enables design with greater inner diameter (greater volume)
- International MOU established for evaluating Ni-Cr-Mo pressure vessels
  - Fiba Technologies (US)
  - Tenaris-Dalmine (Europe)
  - Japan Steel Works (Asia)

Scientific objective: ***Establish scientific basis for fracture mechanics assessment***

Engineering objective: ***Increase storage volume of stationary pressure vessels***