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Influence of Hydrogen Compatibility Research on Codes & Standards

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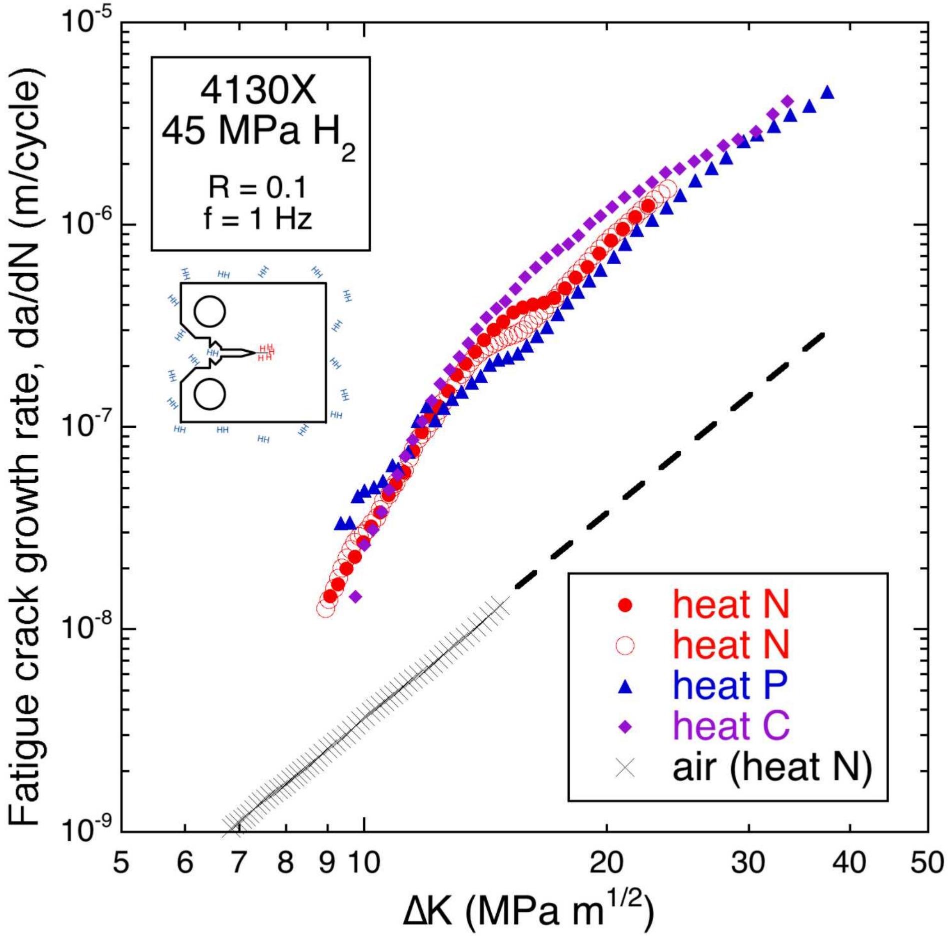
What are the requirements to use a given material in gaseous H2 service?



- **Fatigue crack growth rate is accelerated by 10X in H2 compared to air**
- **Is this material safe to use in gaseous hydrogen?**
  - **Yes – No – Maybe**

Laboratory gas cylinders are made of this material

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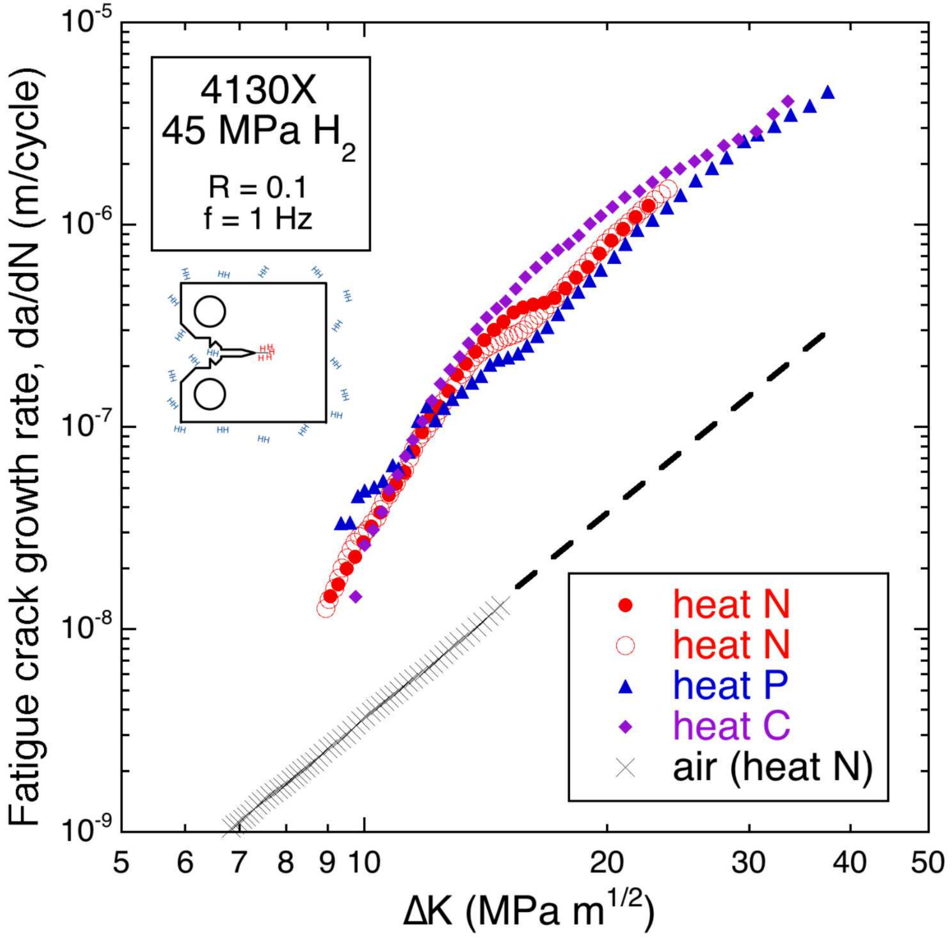

Materials requirements depend on the application and the design

- **Gas cylinders are generally made from relatively low strength steels**
- **Wall stresses are relatively low**
- **Manufacturing defects are well characterized**

In today's talk, I will cover

- Key differences between standardized material selection methods
  - Performance-based
  - Design-based
- Example of performance-based methods
  - High pressure vehicle fuel system
- Example of design-based methods
  - Development of Master curves for stationary pressure vessel in ASME Code Case 2938

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

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

- **Performance-based method**

Example - high-pressure vehicle fuel system

  - Establish materials *performance metrics*
  - Consider mechanics of the service condition
  - Explore relevant environments and determine dominant conditions

- **Design-based method**

Example - stationary pressure vessel

  - 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

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- Development of Master curves for design-based methods
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Question: What is limiting performance metric to establish conservative material behavior for application?

Example: High-pressure vehicle fuel system

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

Critical, but how to define relevant weld geometry?

- Tensile properties
  - Tensile tests in hydrogen do not provide much new information relative to tests in air
    - Yield strength is generally not changed
    - Tensile ductility requirements (elongation, RA)
      - No consensus on criteria
      - Criteria are generally arbitrary
      - Not used quantitatively in design

What value do tests in H_2 add?

- **Fatigue performance**
  - **Deep stress cycles associated with refueling**

Critical limiting behavior

Performance-based testing *is not intended* and *should not* be used for design. Keep it simple but sufficient.

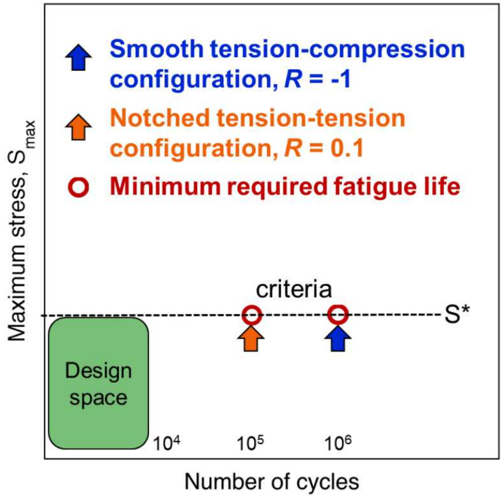
Critical assessment of limiting fatigue behavior

Example: High-pressure vehicle fuel system

In vehicle application, 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

- Fatigue life performance criteria, established to be conservative
  - *Two options:*
    - 100,000 stress cycles when subjected to stress concentration (*notched*)
      - Conservative stress state
      - Conservative number of cycles
    - 200,000 stress cycles for tension-compression cycle (*smooth*)
      - Conservative stress amplitude: 2x typical for stress relieved component
      - Conservative number of cycles

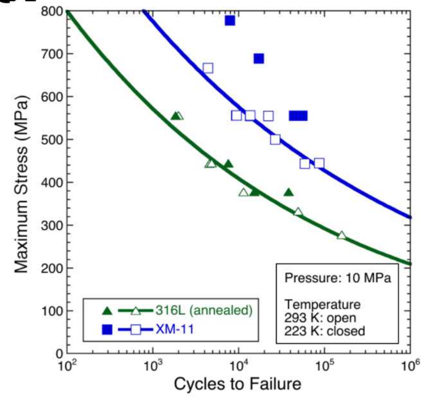


Simple performance requirements established for SAE J2579 based on relevant design space (proposed to GTR IWG)

Example: High-pressure vehicle fuel system

Test configuration		Evaluation parameter	Requirements of tests performed in H2
Fatigue life tests (must satisfy 1 of 2 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 > 100,000 cycles**

- **Test requirements have substantially evolved to simple performance-based metrics to demonstrate suitability for application**
  - **Discussion to remove Slow Strain Rate Tension (SSRT) test**
  - **Fatigue life test conducted at room temperature only (i.e., low-temperature, high-pressure tests removed)**
    - **Data show that the fatigue life of austenitic stainless steels is greater at low temperature than at room temperature**



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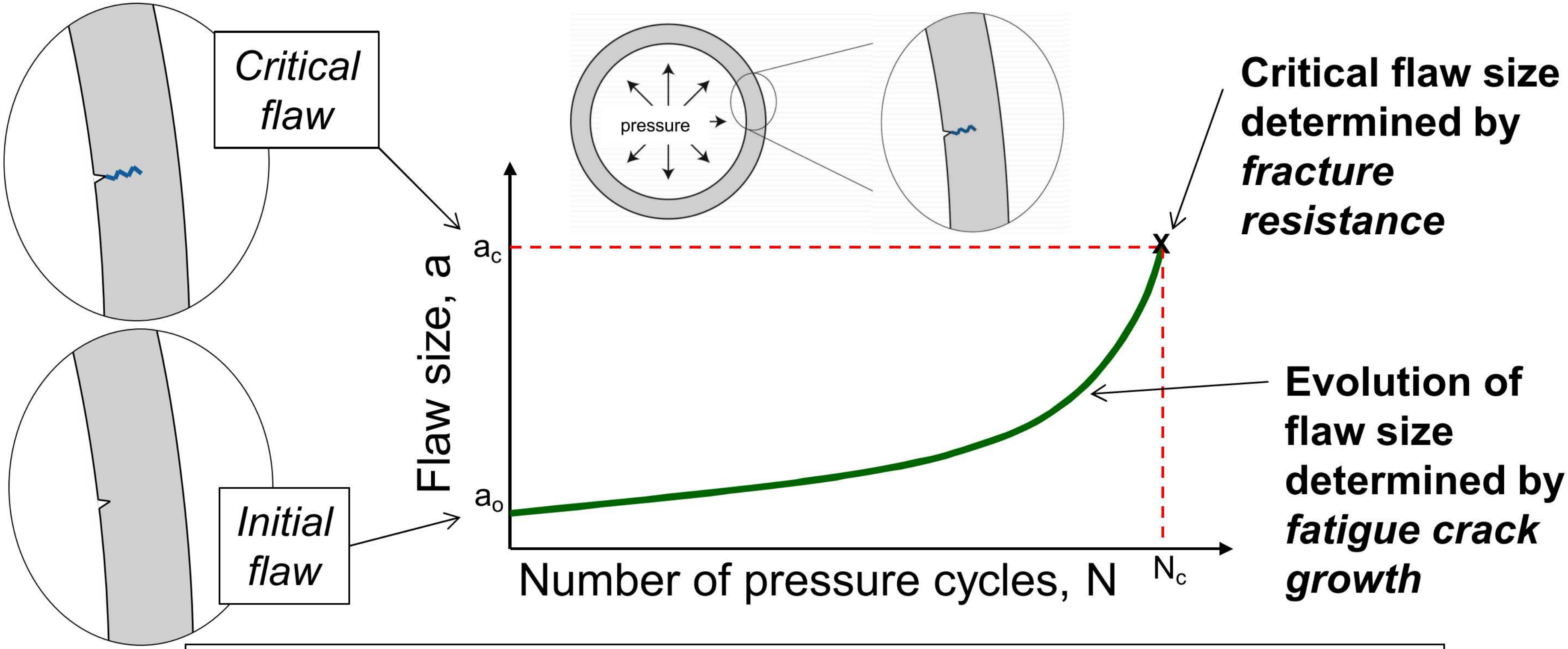
Motivation for fatigue design curves for hydrogen pressure vessels

- **Storage vessels for high-pressure hydrogen require fracture mechanics-based design: BPVC VIII.3.KD-10**



Critical flaw size determined by *fracture resistance*

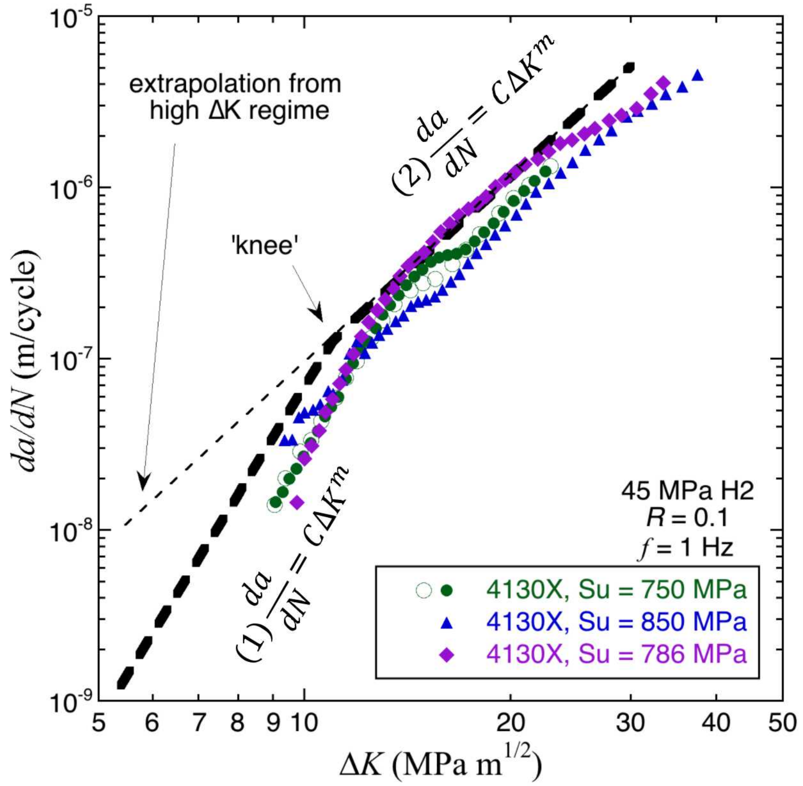
Evolution of flaw size determined by *fatigue crack growth*

Generation of fatigue and fracture data in gaseous hydrogen is very expensive and time consuming

Fatigue crack growth rates in gaseous hydrogen can be characterized by two slopes (or power laws)

Example: Stationary pressure vessel

- **Fatigue crack growth is characterized by a knee in the *da/dN*–Δ*K* curve**
- **Transition regime at “*low* Δ*K*” with a steep slope and large exponent *m***
- **Crack growth rate at “*high* Δ*K*” with slope similar to air, but significantly higher rate by 10x or more**



Much of the data fell within a narrow band suggesting potential development of “master” curves

Pressure vessel steels tested at Sandia in gaseous H_2 at pressure of ≥103 MPa (15 ksi)

Example: Stationary pressure vessel

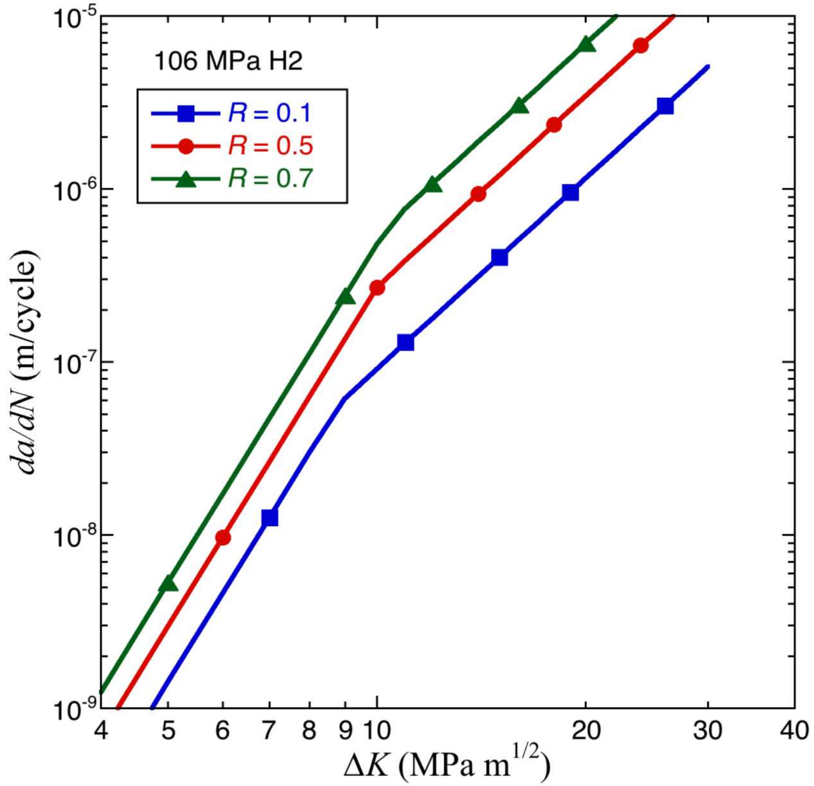
Designation	Tensile strength (MPa)	Yield Strength (MPa)
Cr-Mo steels		
SA-372 Grade J (A71)	839	642
SA-372 Grade J (B50)	871	731
SA-372 Grade J (A72)	908	784
SA-372 Grade J (AV60Z)	890	760
34CrMo4	1045	850
Ni-Cr-Mo steels		
SA-372 Grade L	1149	1053
SA-372 Grade L-LS †	873 †	731 †
SA-723 Grade 1 – Class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

† Does not meet SA-372 (low strength)

Code Case 2938: Simple relationship was developed to capture fatigue crack growth rates in hydrogen and account for load ratio (*R*)

$$\frac{da}{dN} = C\left[\frac{1 + C_H R}{1 - R}\right]\Delta K^m$$

	da/dN_{low}	da/dN_{high}
C (m/cycle)	3.5×10^{-14}	1.5×10^{-11}
m	6.5	3.66
C_H	0.4286	2.00



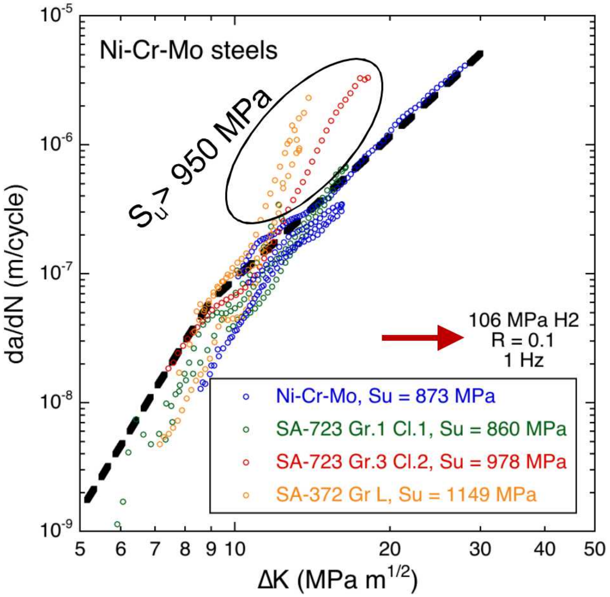
ASME Code Case 2938 approved for Master Curves in 2018!

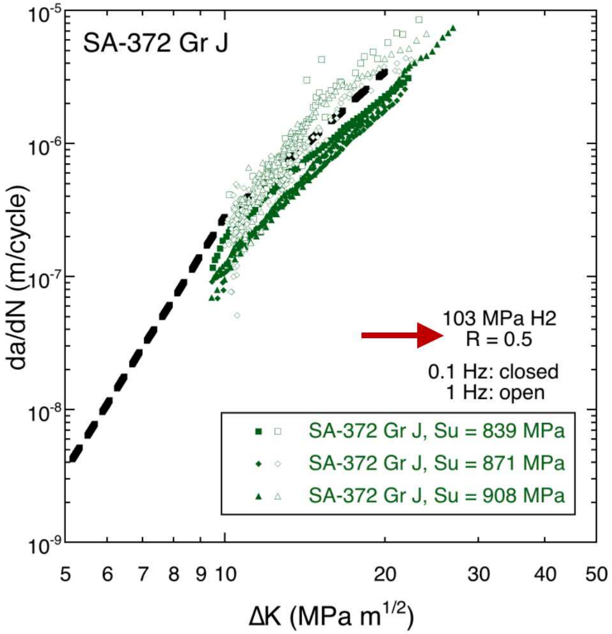
Requirements:

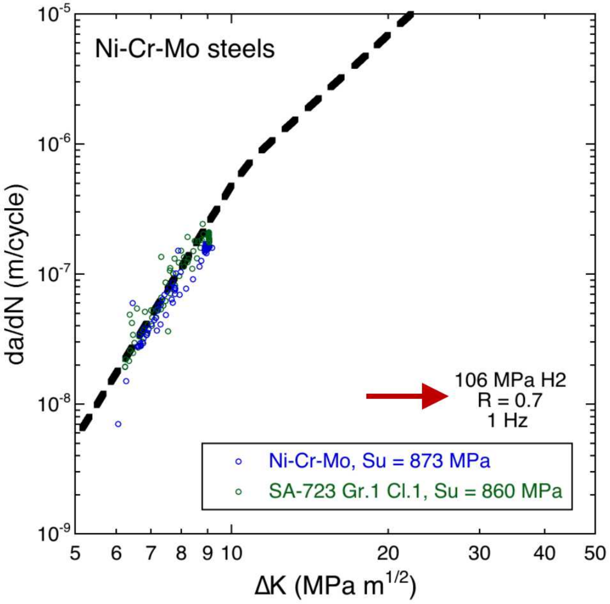
1) Crack growth rate calculated by equation and table
2) For $K_{I,MIN} < 0$, set $K_{I,MIN} = 0$
3) $S_u < 915$ Mpa
4) $K_{I,MAX}$ shall not exceed 40 MPa $m^{1/2}$

Master curves captured trends of all pressure vessel steels tested below strength of 950 MPa tensile strength

Example: Stationary pressure vessel

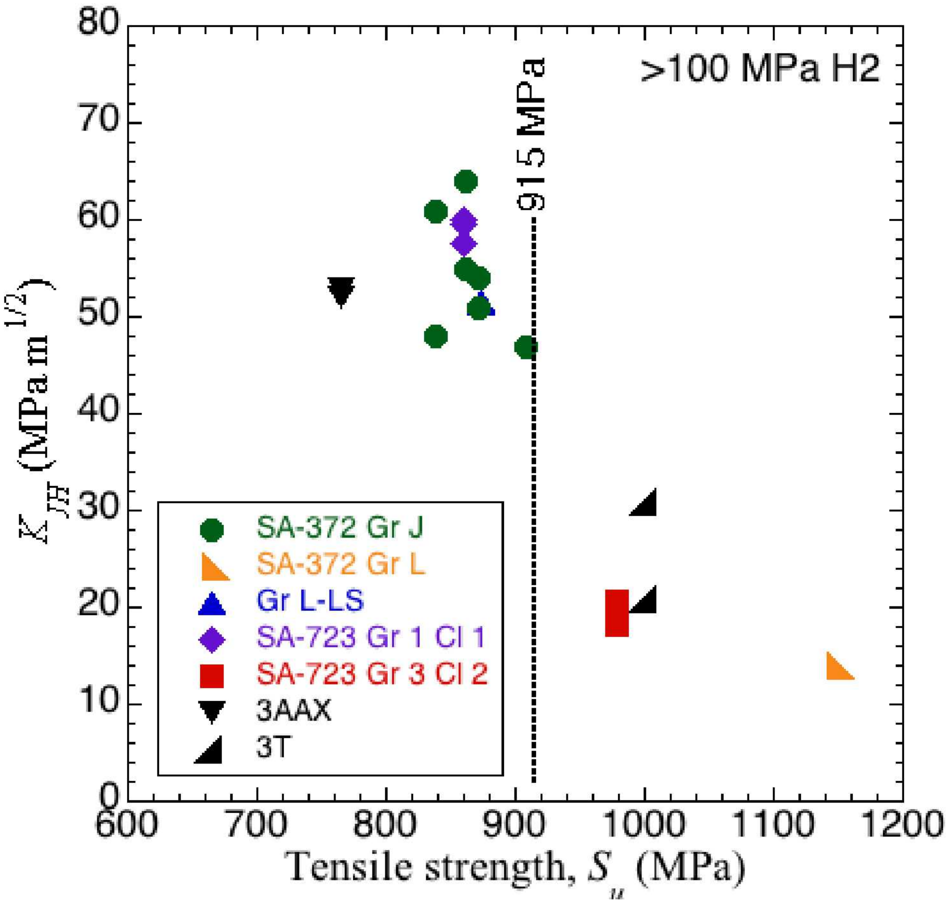






Utilization of master curves for design, in lieu of requiring tests in high pressure gas = Significant cost savings

Fracture resistance in gaseous hydrogen is low for high strength Pressure Vessel steels



PV steels display low resistance to hydrogen-assisted fracture in high strength condition

- **For tensile strength < 915 MPa**
  - **$K_{JH} > 45$ MPa m$^{1/2}$**
- **For tensile strength > 975 MPa**
  - **$K_{JH} < 20$ MPa m$^{1/2}$**

K_{JH} = elastic-plastic plane-strain fracture toughness in gaseous hydrogen (ASTM E1820)

Design curves based on best available data, however a few questions remain (in progress)

- **High-strength steels show low fracture resistance in H2**
  - **Fracture resistance becomes uncomfortably low, when tensile strength is >950 MPa**
  - **Code Case limits TS ≤ 915 MPa**

> - *Steels with S_u between 915-950 MPa are being re-evaluated*
> - *High-strength steels considered in H-Mat*

- **Fatigue behavior is pressure sensitive**
  - **Empirical pressure term fits data for pipeline steels at low pressure**

> *Testing is being considered to evaluate broader applicability of design curves*

- **Fatigue behavior near threshold and with negative load ratio are not well documented**
  - **Code Case assumes that a fatigue threshold does not exist in H2**
  - **Code Case allows assumption that for $R < 0$, $K_{min} = 0$**

> *Hardware and methods are being developed for high-pressure testing at low K_{max} and negative K_{min}*

Summary

- Motivation for R&D on materials compatibility
  - Establish science-based test methodologies consistent with the requirements of relevant applications as well as tools for engineering
- Performance-based methods
  - Used to qualify materials (i.e. high-pressure vehicle fuel system)
  - Harmonization of simple metrics for materials testing are being developed (SAE J2579, UN GTR no.13)
- Design-based methods
  - Used to establish bounding behavior for environment
  - Master curves for stationary pressure vessels ASME Code Case 2938 drastically simplifies design process