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Materials Qualification for Hydrogen Service using CSA CHMC1

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Objectives and Outline of Presentation

- Summarize *guidance* and *standards* relevant to materials selection for hydrogen service
- Identify existing standards for qualifying materials and designs for hydrogen service and their *limitations*
- Describe *general test standard* for qualification of materials for hydrogen service (CSA CHMC1)

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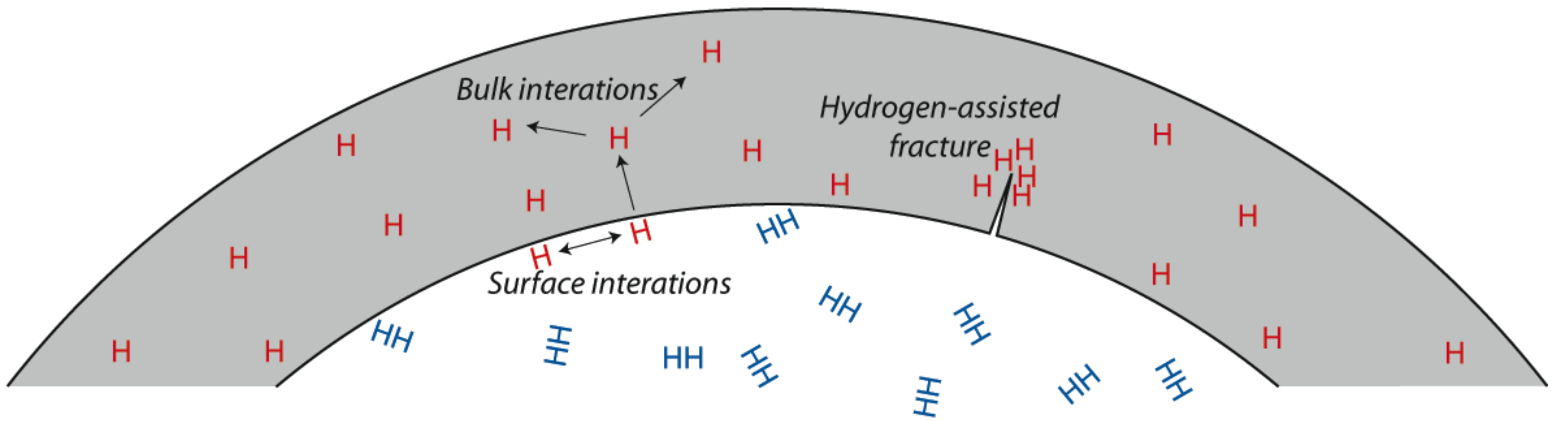
Several physical processes affect observations of hydrogen-assisted fracture

1) *Hydrogen-surface interactions:* molecular adsorption and dissociation producing atomic hydrogen chemisorbed on the metal surface
2) *Bulk metal-hydrogen interactions:* dissolution of atomic hydrogen into the bulk and segregation to defects in the metal (i.e., transport and trapping)
3) *Hydrogen-assisted cracking:* interaction of hydrogen with defects changes local properties of the metal leading to embrittlement and possibly failure



Science-based understanding of embrittlement essential for ensuring safety and reliability of hydrogen technology

Definitions

Hydrogen Compatibility: *materials evaluation*
(commonly described as **Materials Compatibility**)

- Standardized materials testing to determine materials properties for design

Hydrogen Suitability: *component evaluation*

- Generally used in the context of a component level test with gaseous hydrogen
- Can also be design qualification using hydrogen compatibility data

Standard practice for testing and materials selection

- ***Guidance on testing in high-pressure gaseous hydrogen***
  - CSA Group: ***CHMC1-2012***
  - ASTM International: G142 (and G129)
- ***Guidance on materials selection for hydrogen service***
  - American Society of Mechanical Engineers (ASME)
    - B31.12 Hydrogen Piping and Pipelines
    - Hydrogen Standardization Interim Report for Tanks, Piping and Pipelines (STP/PT-003)
  - European Industrial Gases Association (EIGA)
    - IGC Doc 100/03/E Hydrogen Cylinders and Transport Vessels
    - IGC Doc 121/04/E Hydrogen Transportation Pipelines
  - NASA/AIAA (American Institute of Aeronautics and Astronautics)
    - AIAA G-095 Guide to Safety of Hydrogen and Hydrogen Systems
  - Sandia National Laboratories (compilation of data measured in hydrogen)
    - SAND2012-7321 Technical Reference for Hydrogen Compatibility of Materials

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Standards that include materials qualification in high-pressure gaseous hydrogen

- ***ISO 11114-4*** (International Organization for Standardization)
  - Three options for evaluating *compatibility in gaseous hydrogen*
  - Pass-fail criteria
  - Specific to high-strength steels for pressure vessels

- ***ASME KD-10*** (American Society of Mechanical Engineers)
  - Design method using *fracture and fatigue properties measured in gaseous hydrogen*
  - Specific to low-strength steels for vessels steels with high pressure
  - Also adopted for piping and pipelines in ASME B31.12

- ***SAE J2579*** (Society of Automotive Engineers)
  - Several options for materials selection in appendices
  - One option includes materials qualification testing: *fatigue properties measured in gaseous hydrogen*
  - Specific to automotive fuel systems

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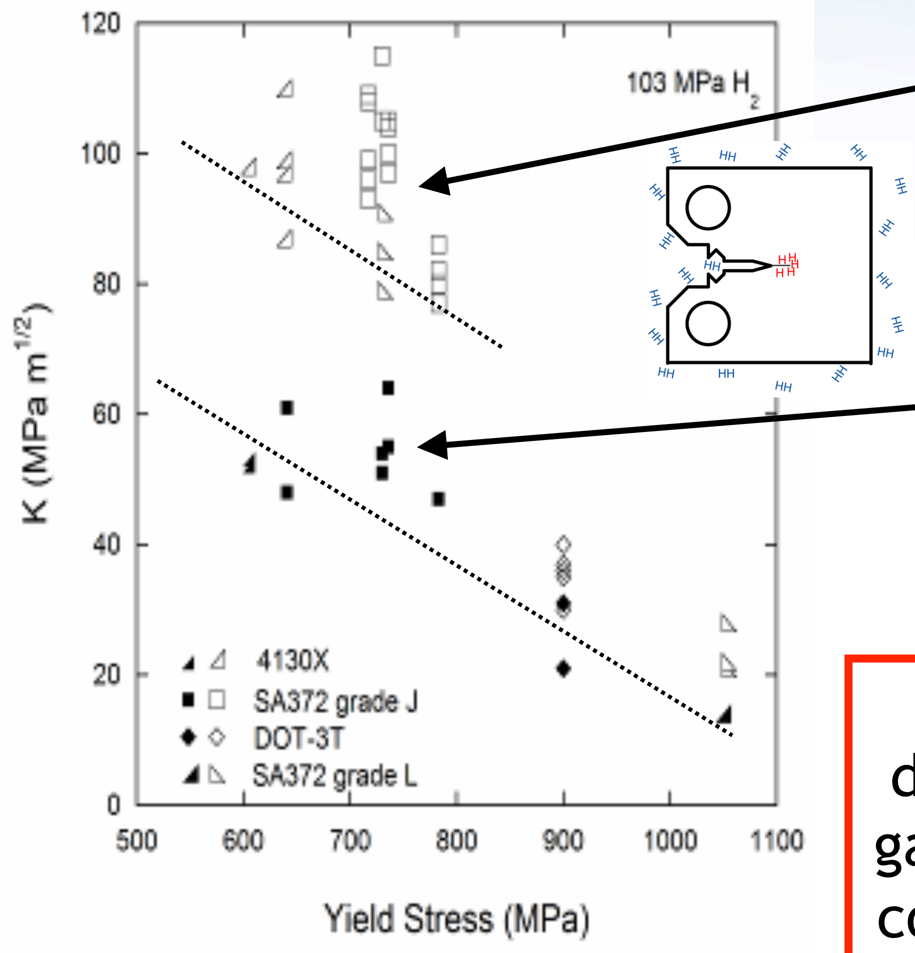
Critical assessment shows need for further development of testing protocols



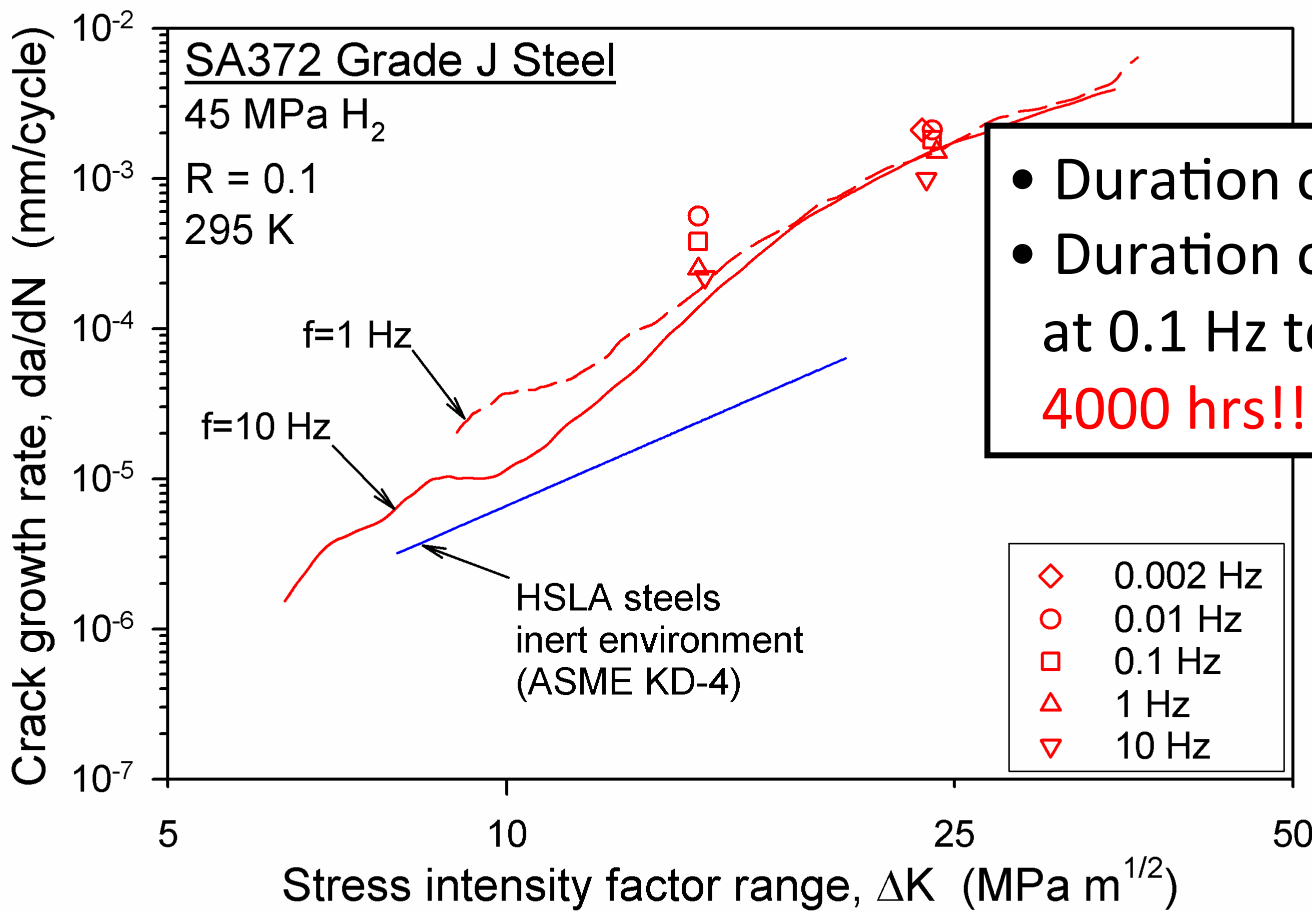
Sustained load cracking, measured according to guidance from ASME Article KD-10 (open symbols); ASTM E1681

Elastic-plastic fracture, measured using ASTM E1820 (closed symbols)

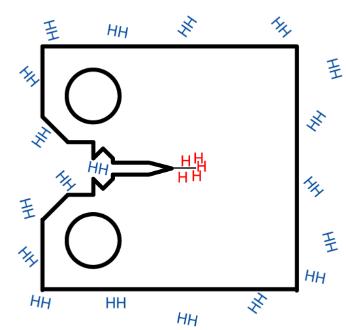
Sustained load procedures for determining fracture resistance in gaseous hydrogen appear to be non-conservative for low-strength steels

Open symbols = *crack arrest threshold*
Closed symbols = *crack initiation threshold*
Ref. SAND2010-4633 (also Nibur et al. *Metall Mater Trans* 44A p.248)

Efficient methods for measuring fatigue crack growth in gaseous hydrogen are necessary



- Duration of 10 Hz test: 40 hrs
- Duration of equivalent test at 0.1 Hz test: estimated at 4000 hrs!! (or 5-6 months)



General standards for qualifying materials for hydrogen service

- ***CSA CHMC1 revision*** (CSA Group)
  - Methodology using *fatigue properties measured in gaseous hydrogen*
  - *Not specific* to application or component
  - Design approach is not specified (provides flexibility)
  - One testing option provides hydrogen safety factor
    - Multiplicative factor incorporated in design safety factors
  - Other testing options require properties measured in hydrogen be used in design
  - Rules for qualification of materials specifications
    - Requires comprehensive definition of material
    - Bounds qualification activity

CSA CHMC1

Test method for evaluating material compatibility in compressed hydrogen applications – Metals

First edition – *published 2012*: definition of procedures for mechanical property evaluation in gaseous hydrogen

Revised document – *draft*: methods for materials qualification

- Screening tests to determine compatibility without special design requirements for hydrogen service
  - Acceptable for aluminum alloys and austenitic stainless steels
- Safety Factor Multiplier Method
  - Fatigue testing determine additional safety factor for hydrogen for wide range of cycle life
- Design qualification method
  - Allows other documented fatigue design methods (eg ASME BPVC) with appropriate testing in gaseous hydrogen

CSA CHMC1 - 2012

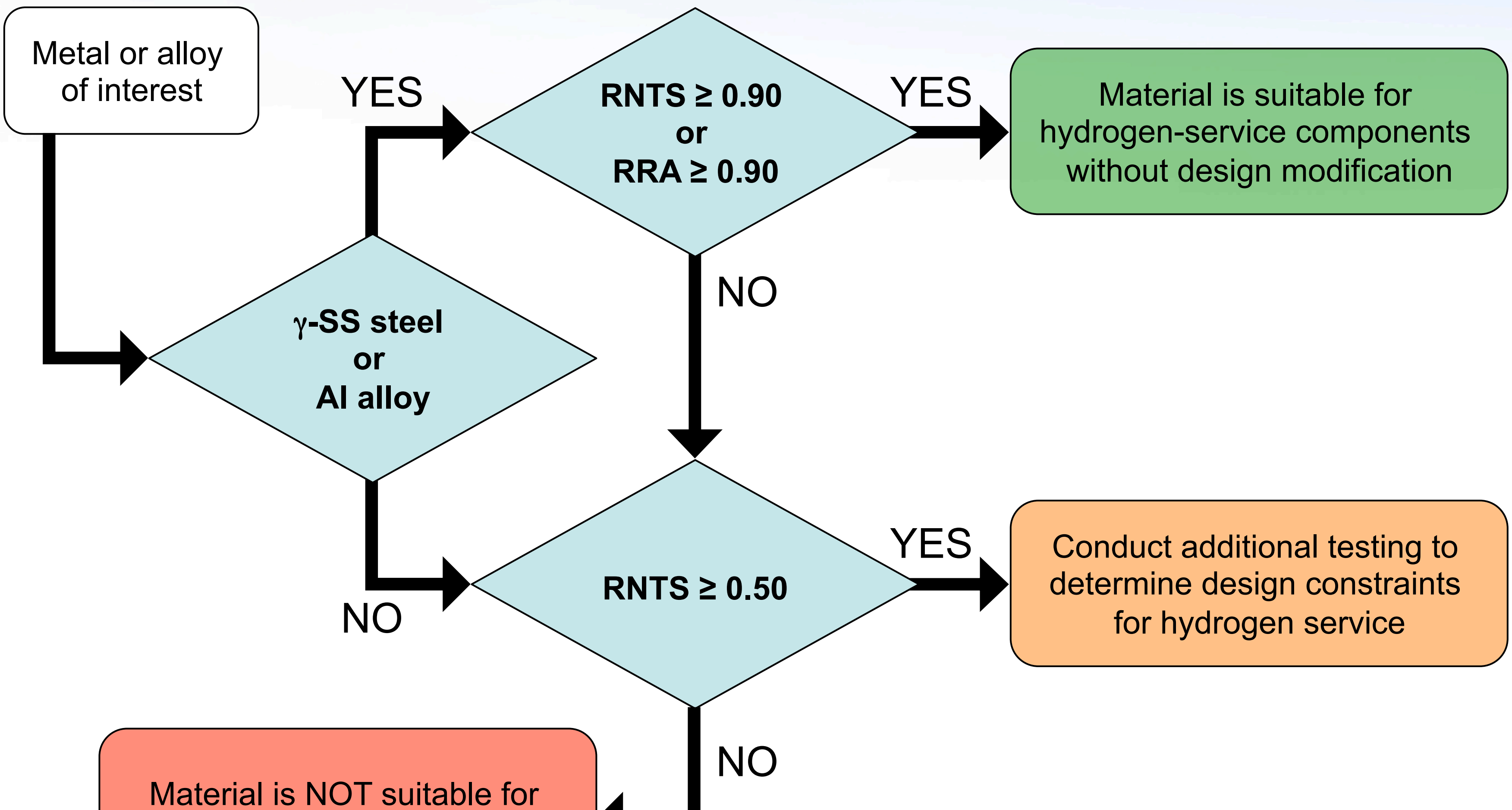
First edition – *published 2012*: definition of procedures for mechanical property evaluation in gaseous hydrogen

- **Part 1: Environment and equipment**
  - Hydrogen gas purity (includes requirements for measuring purity after test)
  - Instrumentation
  - Temperature
  - Pressure

- **Part 2: Test methods**
  (Includes definition of testing parameters such as rate/frequency, specimen geometry, etc)
  - Slow strain rate tensile testing
  - Hydrogen-assisted cracking threshold stress intensity (K_{IH} and J_{IH})
  - Fatigue crack growth rate
  - Fatigue life tests (S-N fatigue methods)

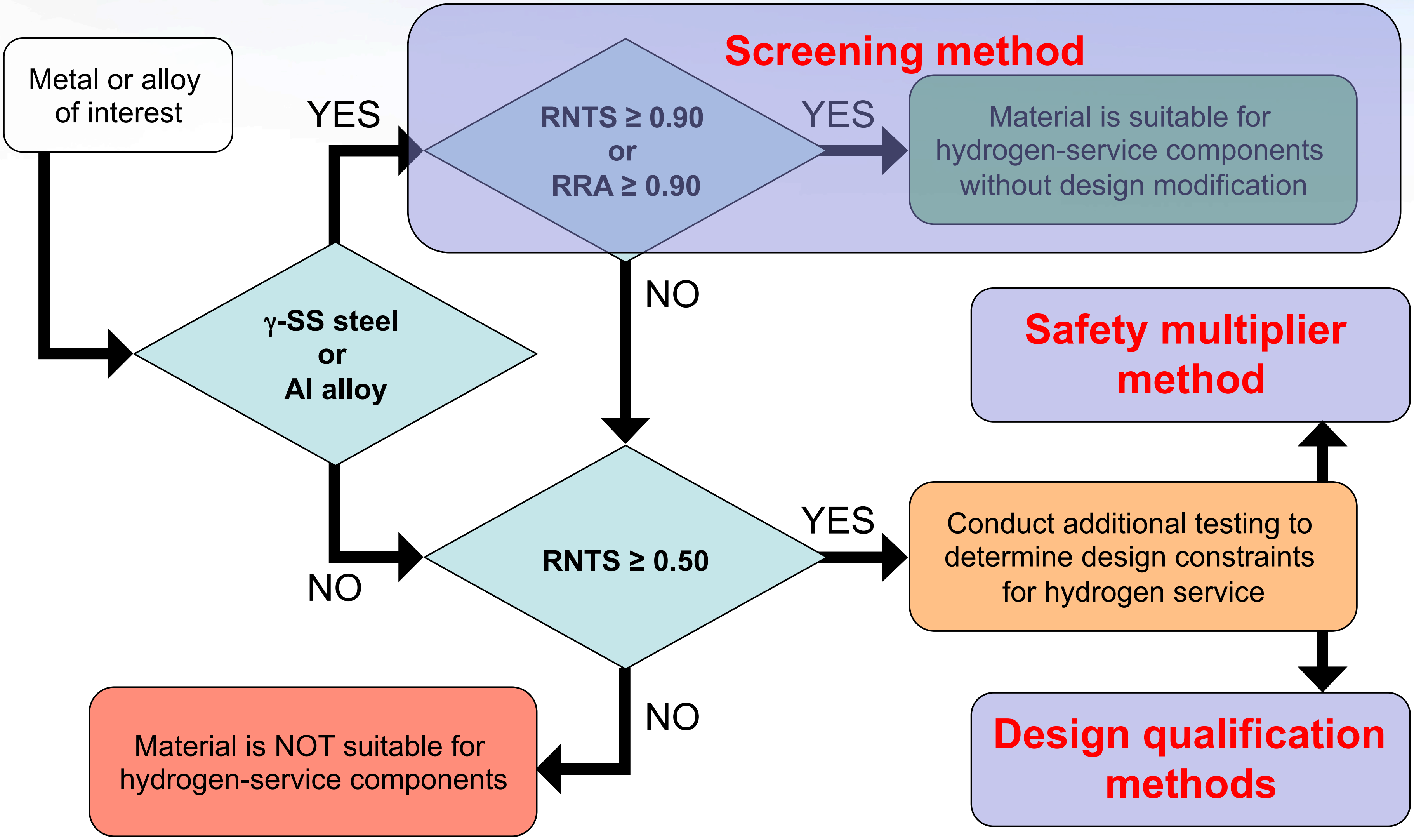
CSA CHMC1 - 2014

Revised document – *draft, adds* **Part 3: Material qualification**



RNTS = Notch Tensile Strength Ratio
RRA = Reduction of Area Ratio (smooth tensile)

CSA CHMC1 - 2014
Three options for material qualification



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CSA CHMC1: Screening Method

- Screening method intended to facilitate certification of commonly-accepted materials with *minimum* testing in gaseous hydrogen environments
  - 316/316L alloys
  - 6061 aluminum alloys
  - Other austenitic stainless steels and aluminum alloys with equivalent behavior in dry gaseous hydrogen (e.g., type 310 and 317 stainless, 2000- and 7000-series aluminum alloys)

- Screening method is *not intended* to establish compatibility with applied loads or external environments (e.g., warm humid air)

CSA CHMC1: Safety Factor Multiplier Method

<u>Notch Tensile Fatigue Tests</u>

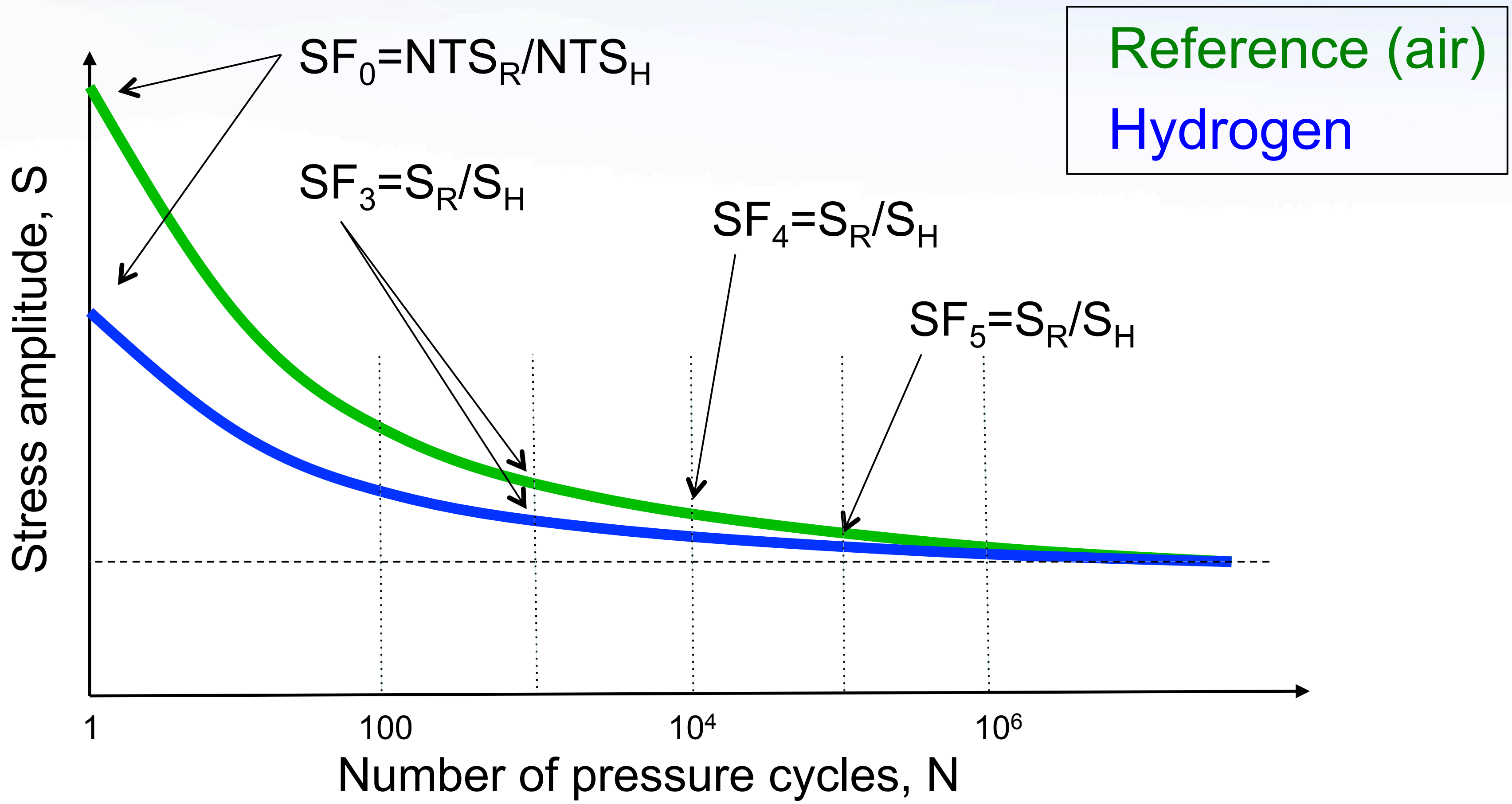
- Measure Wohler curves and determine stress amplitude (S) for number of cycles to failure (N) of 10^3, 10^4 and 10^5 in hydrogen and reference environments
  - $SF_3 = S3_R / S3_H$
  - $SF_4 = S4_R / S4_H$
  - $SF_5 = S5_R / S5_H$
  - $SF_0 = NTS_R / NTS_H$ (tensile test)
- Hydrogen safety factor: $SF_H = \max(SF_0, SF_3, SF_4, SF_5)$

S3 = stress amplitude for failure at N = 10^3
S4 = stress amplitude for failure at N = 10^4
S5 = stress amplitude for failure at N = 10^5

$_R$ = reference environment
$_H$ = hydrogen environment

Safety factor for design ➔ $SF_{design} = SF_{component} \times SF_H$

Schematic representation of Safety Factor Multiplier Method



In this example: $SF_H = SF_0 > SF_3 > SF_4 > SF_5$

Technical basis: Safety Factor Multiplier Method

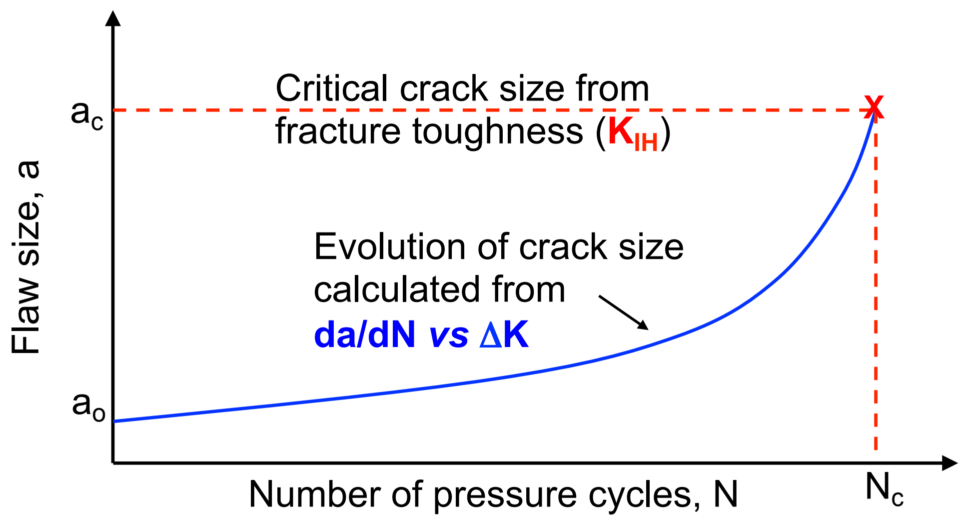
- Pressure hardware is nominally loaded in tension-tension at stresses well below the material's yield strength
  - Stress amplitudes greater than the fatigue limit generally cannot be achieved in tension-tension, if the maximum stress is less than yield
  - Therefore, fatigue in pressure hardware must initiate at stress concentrations
- Notches simulate stress concentrations/defects in real hardware
  - Circumferential notches:
    - probe relatively large volumes of material
    - mitigate surface effects
    - are axial symmetric
  - Limited data suggest that:
    - notch sensitivity saturates in fatigue for $K_t \approx 3$
    - fatigue limit is relatively insensitive to R-ratio (for positive values)

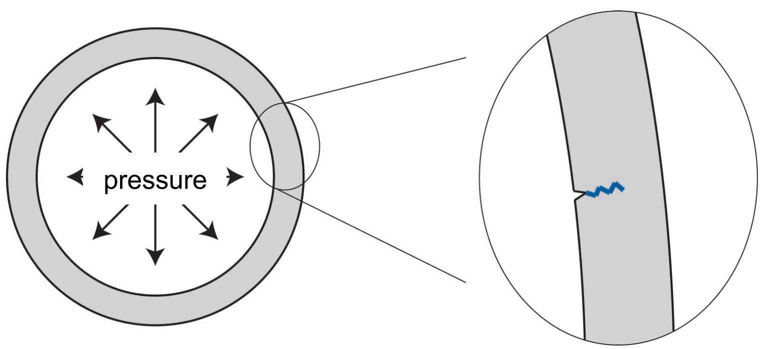
CSA CHMC1: Design Qualification Method

Design qualification method is

1. "any documented design rules appropriate for the component… considers… failure by fatigue" and
2. uses material properties measured in the appropriate gaseous hydrogen environments

One example of established design qualification for hydrogen service: ASME BPVC VIII.3 article KD-10





Fracture mechanics-based methodology codified in KD-4 of ASME BPVC VIII.3 using measured *fatigue crack growth rates*

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Summary of CSA CHMC1

- True material qualification test
  - Not specific to component or application
  - Specific to environment and material form
- Three routes to qualify a material for hydrogen service
  - Screening Method
  - Safety Factor Multiplier Method (stress-based fatigue method)
  - Design Qualification Methods
- Qualification of generic material designation (e.g. type 310) requires a materials specification that defines the material
  - Compositional ranges
  - Mechanical properties, minimum and maximum values
  - Product form, processing route, etc
- Qualification of the materials specification requires testing of materials from 3 batches (or heats)
  - Additional testing is required when the materials specification changes

Summary of standards for qualifying materials for hydrogen service

- Several standards exist for hydrogen pressure vessels
  - *ISO 11114-4* and *ASME BPVC VIII.3 KD-10*
    - Limited scope
    - Opportunity to improve test methods; existing methods may not result in conservative design values
- Standard for fuel systems on vehicles: *SAE J2579*
    - Limited scope; does not define material
    - Provides framework for materials testing and metrics for evaluating testing results
- General standard for qualifying materials for hydrogen service: *CSA CHMC1*
    - General rules for qualifying materials
    - Specific requirements: *safety factor multiplier method*
    - Includes qualification of material specifications