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Hydrogen Compatibility of Materials

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DOE EERE Fuel Cell Technologies Office Webinar

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Sandia National Laboratories

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Webinar Objectives

- Provide context for hydrogen embrittlement and hydrogen compatibility of materials
  - Distinguish embrittlement, compatibility and suitability
  - Examples of hydrogen embrittlement
- Historical perspective
  - Previous work on hydrogen compatibility
  - Motivation of “Materials Guide”
- Identify the landscape of materials compatibility documents
  - Motivation of the content of the Technical Reference
- Technical Reference for Hydrogen Compatibility of Materials
- Important strengths and limitations of the Technical Reference
  - Next steps: Tools for data management (database)

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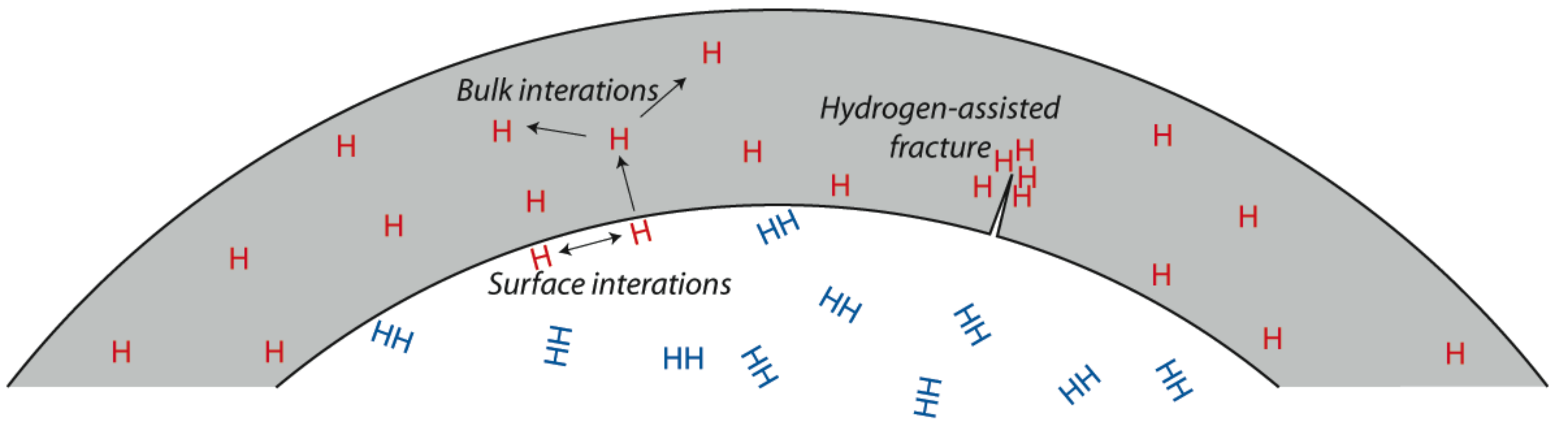
Hydrogen embrittlement results from hydrogen dissolving into metals and affecting their properties

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 enables innovation of hydrogen technology

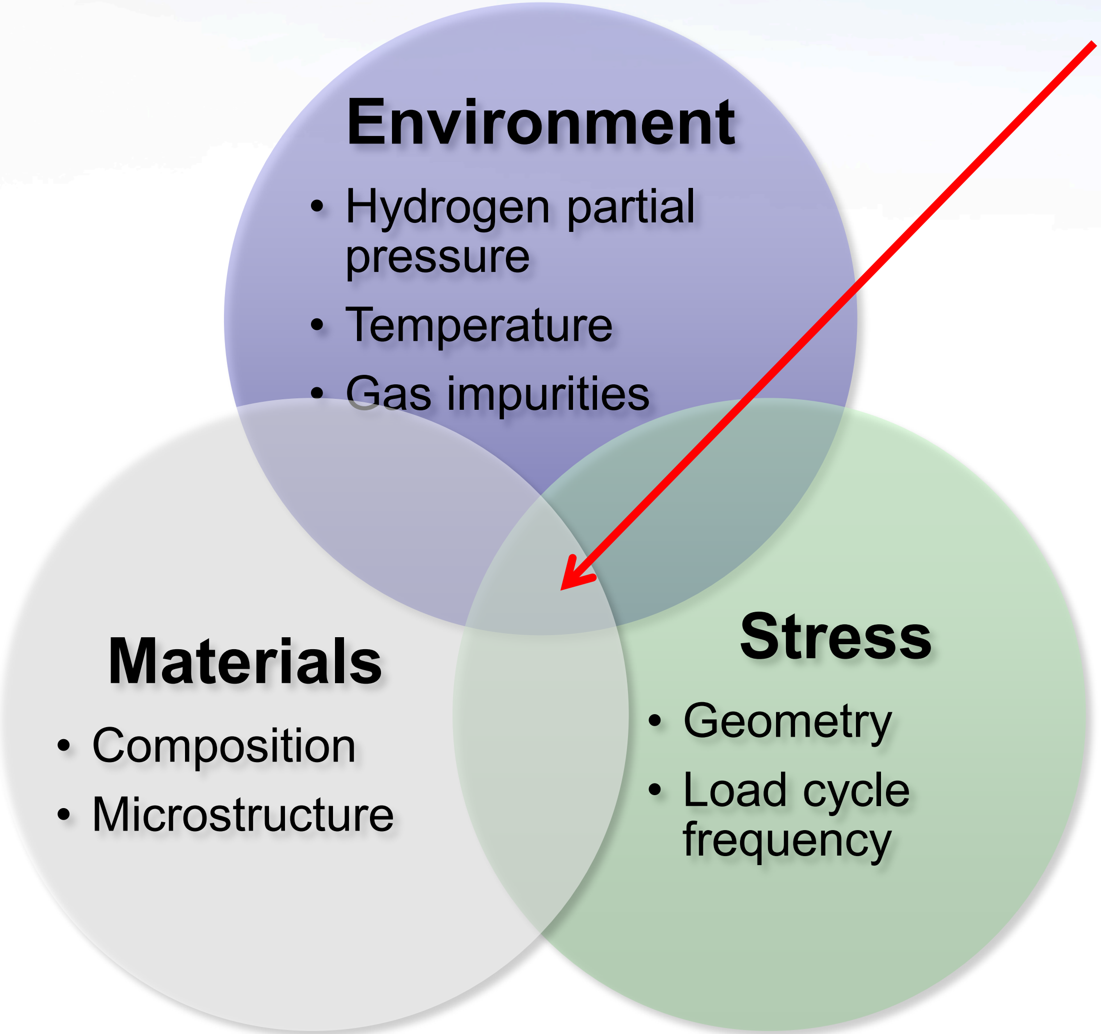
What is hydrogen compatibility of materials?

- ***Hydrogen compatibility***: materials evaluation
  - Standardized testing to determine materials properties for design

- ***Hydrogen suitability***: component evaluation

  There are multiple methods for establishing suitability:
  - Performance test with gaseous hydrogen to verify integrity of the component design or subsystem integration
  - Design analysis to show structure accommodates the effects of hydrogen on materials properties

Hydrogen embrittlement is a degradation; hydrogen compatibility establishes suitability



Hydrogen embrittlement occurs at the intersection of variables representing:

- Environment
- Materials
- Stress / Mechanics

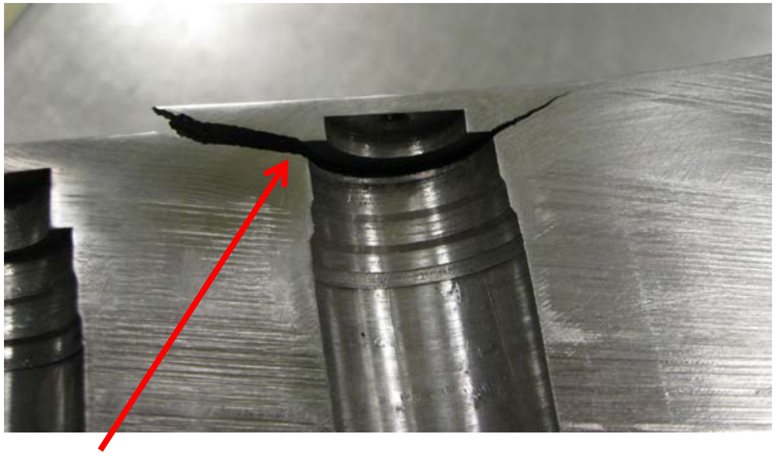
Hydrogen compatibility is the evaluation of the behavior of the materials

Hydrogen suitability is the management and control of these variables

Example: hydrogen embrittlement in diaphragm compressor

High-volume, two-stage diaphragm compressor
- Maximum output pressure: 70 MPa
- Used in *hydrogen 'containing' environments*

Compressor adapted for *high-purity hydrogen* system
- Second stage head failed after ~10^3 cycles



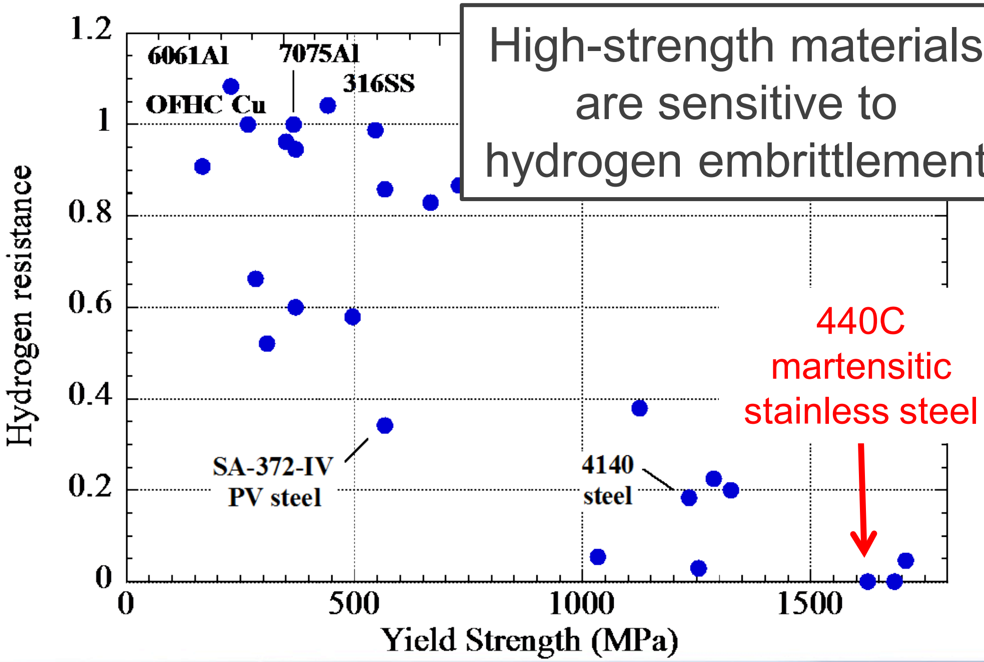
Hydrogen-assisted fatigue crack initiated at site of stress concentration

Root cause analysis
- *Material of construction*: known to be very sensitive to hydrogen embrittlement
- *Service environment changed*: high-purity hydrogen ≠ hydrogen with impurities (e.g., oxygen)

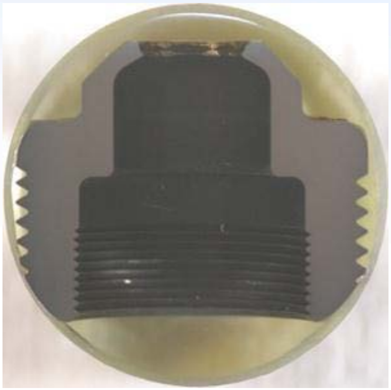
Example: hydrogen embrittlement of pressure relief device

Pressure relief device/valve (PRD)
- Activation pressure of ~54 MPa
- Operated successfully for many months
- System contains 17 identical valves

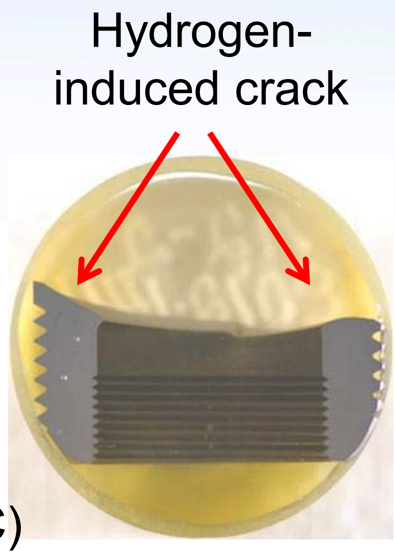
No change in service environment
- Sudden failure of nozzle within PRD



High-strength materials are sensitive to hydrogen embrittlement



Cross section of undamaged nozzle (material: type 440C)



<u>Root cause analysis</u>
- *Material of construction*: known to be very sensitive to hydrogen embrittlement
- *Material did not meet specification*: too hard/strong

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Historical perspective: large volume of work on hydrogen by NASA contractors

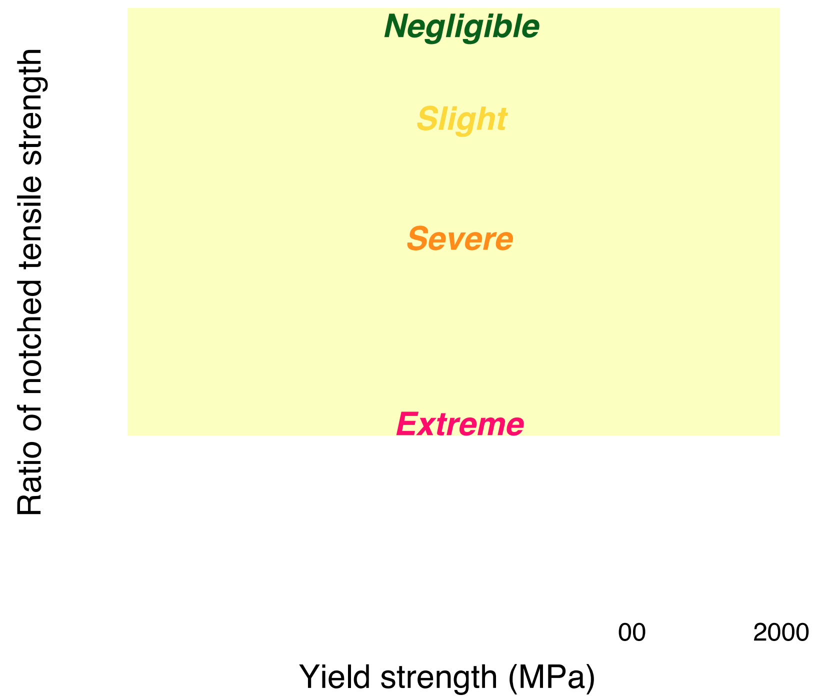
NASA contractors developed method for ranking materials based on notched tensile strength

- Data for a range of materials captured in AIAA G-095, *Guide to Safety of Hydrogen and Hydrogen Systems*†
- Extensively referenced for hydrogen safety as well as materials selection (compatibility)

<u>Does not</u>:

- provide explicit recommendation of materials for hydrogen
- address usage of materials ranked ‘severe’ or ‘extreme’
- account for fatigue

Data from: RP Jewitt et al, NASA report no. CR-2163

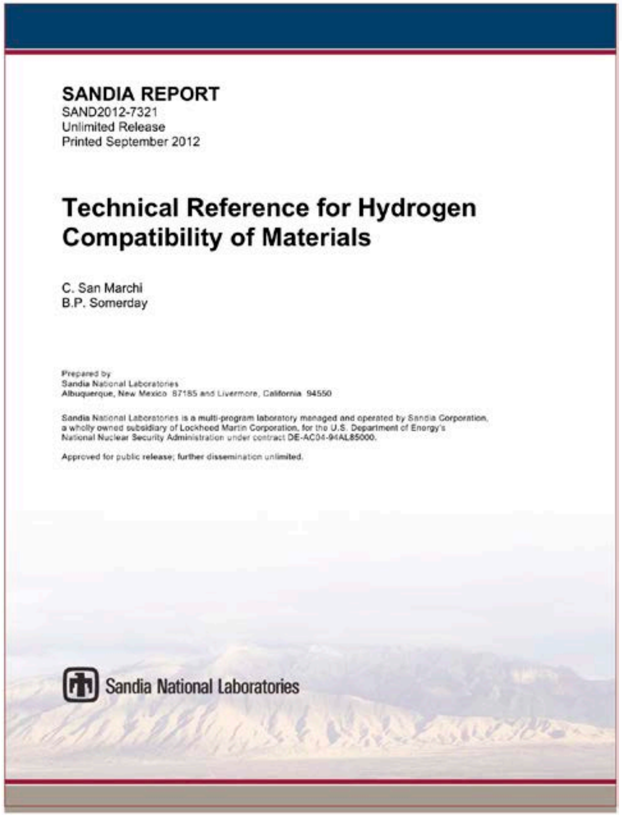


† also: PM Ordin, NASA report no. NSS 1740.1

Historical perspective: investment in fuel cell technologies establishes new needs

DOE Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Project Plan 2003 identified the need for a materials guide for “proper selection of materials for hydrogen service”

- Motivation for structural materials work in hydrogen program
- Hydrogen Effects in Materials Laboratory at Sandia National Laboratories, Livermore CA
  - Operational for several decades
  - Unique mission, expertise and facilities
- Genesis of *Technical Reference for Hydrogen Compatibility of Materials*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Technical Reference for Hydrogen Compatibility of Materials

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Sandia National Laboratories

http://www.sandia.gov/matlsTechRef

Sandia's objectives for studying structural materials for hydrogen energy

- Enable *widespread commercialization* by providing data for standards and technology applied to components for hydrogen service
  - Create materials reference guide ("Technical Reference") and identify material property data gaps
  - Execute materials testing to meet immediate needs for data in standards and technology development
    - Examples: measure properties of hydrogen-exposed welds and Al alloys
  - Improve efficiency and reliability of materials test methods in standards
    - Example: optimize fatigue crack growth testing in ASME Article KD-10 tank standard

- Participate directly in standards development
  - Design and safety qualification standards for components
    - SAE J2579, CSA HPIT1, ASME Article KD-10 (BPVC VIII.3)
  - Materials testing standards
    - CSA CHMC1 (Compressed Hydrogen Materials Compatibility)

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Recommendations for testing and materials selection

- ***Guidance on testing in high-pressure gaseous hydrogen***
  - CSA Group: *CHMC1-2012*
  - ASTM International: G142 (and G129)

- ***General 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*

Standards that include materials qualification in high-pressure gaseous hydrogen

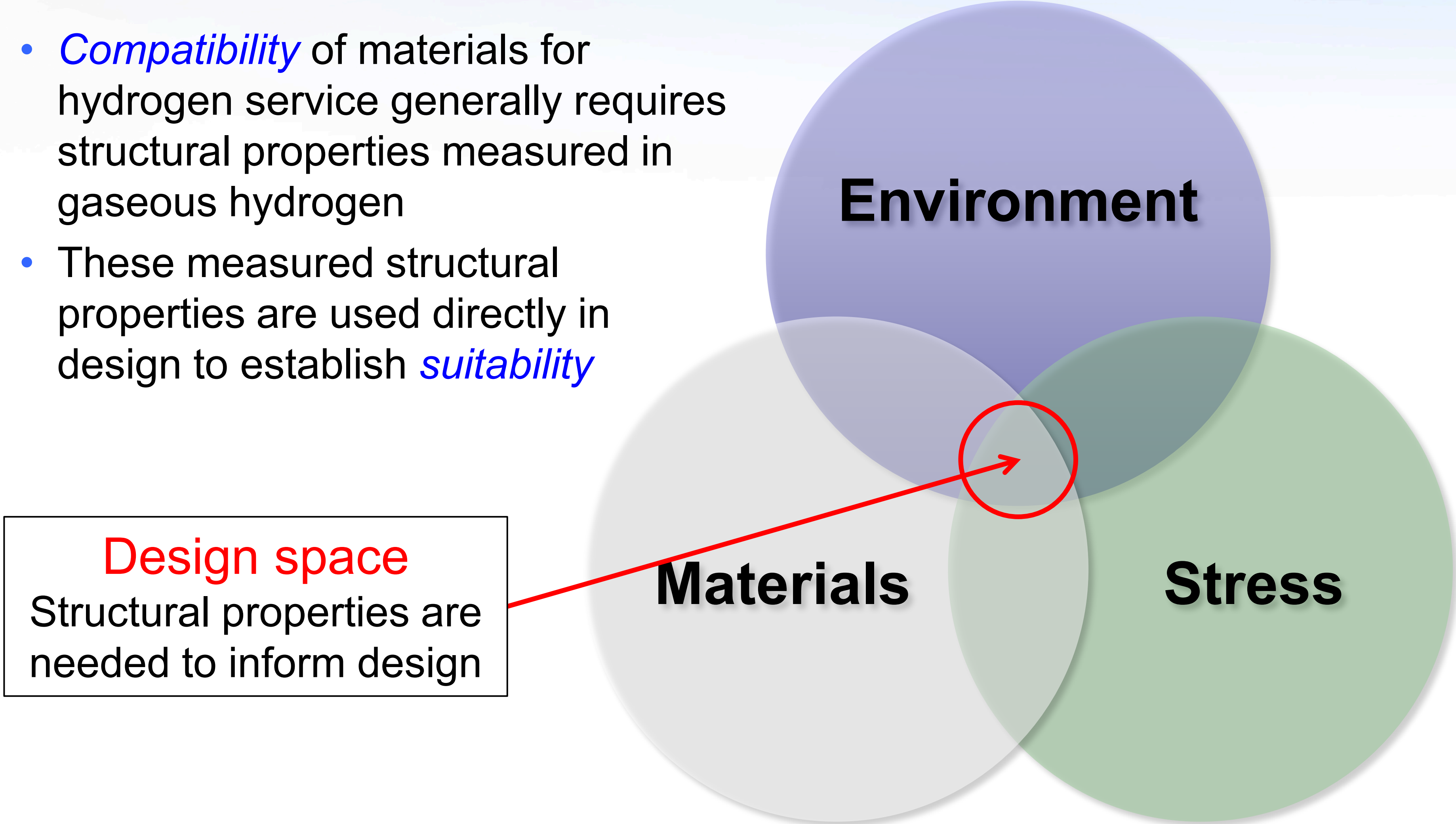
- ***ISO 11114-4*** (International Organization for Standardization)
  - Three options for evaluating *compatibility in gaseous hydrogen*
  - Pass-fail criteria
  - Specific to high-strength steels for pressure vessels
- ***ASME KD-10*** (American Society of Mechanical Engineers)
  - Design method using *fracture and fatigue properties measured in gaseous hydrogen*
  - Specific to low-strength steels for vessels 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

Standards specifically for qualifying materials for hydrogen service

- ***CSA CHMC1 revision*** (CSA Group)
  - Screening test to qualify alloys resistant to hydrogen embrittlement
    - Uniquely for aluminum alloys and austenitic stainless steels
  - 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 measured properties be used in design
  - Rules for qualification of materials specifications
    - Requires comprehensive definition of material
    - Bounds qualification activity

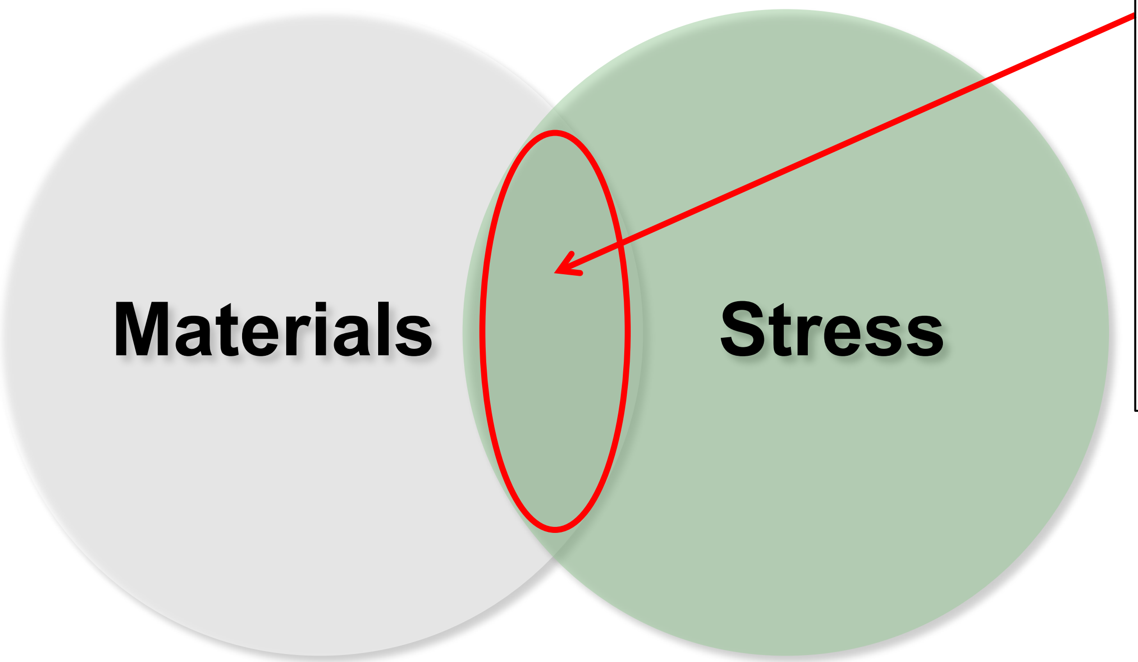
Structural properties must be measured in gaseous hydrogen

- *Compatibility* of materials for hydrogen service generally requires structural properties measured in gaseous hydrogen
- These measured structural properties are used directly in design to establish *suitability*



Designers require structural properties of materials of construction

- In the absence of environmental effects, structural design requires:
  - Definition of materials
  - Knowledge of structural properties

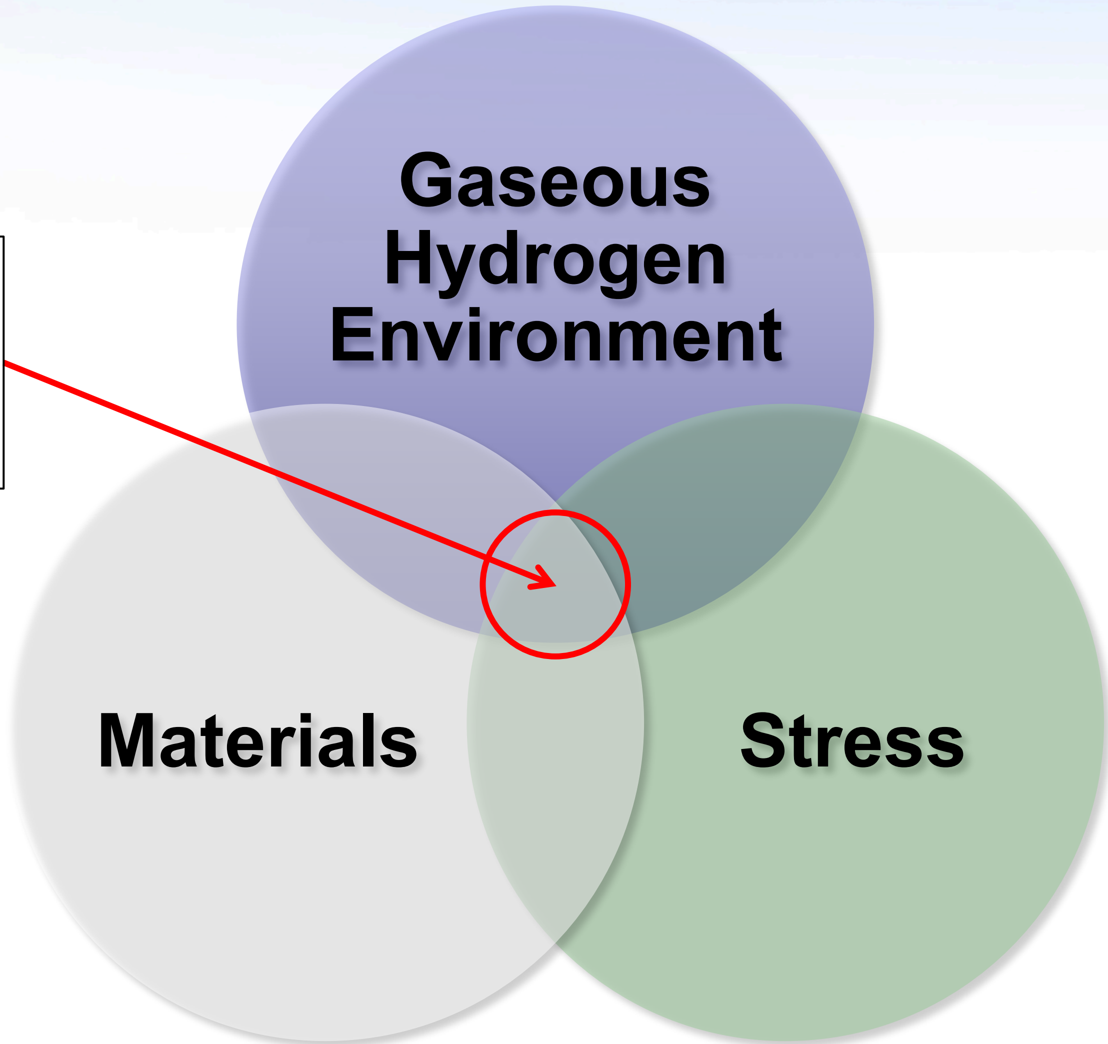


Design space

- Structural properties are needed to inform design
- Properties are often tabulated in *handbooks of properties*

The Technical Reference is primarily a handbook of structural properties

Technical Reference for Hydrogen Compatibility of Materials



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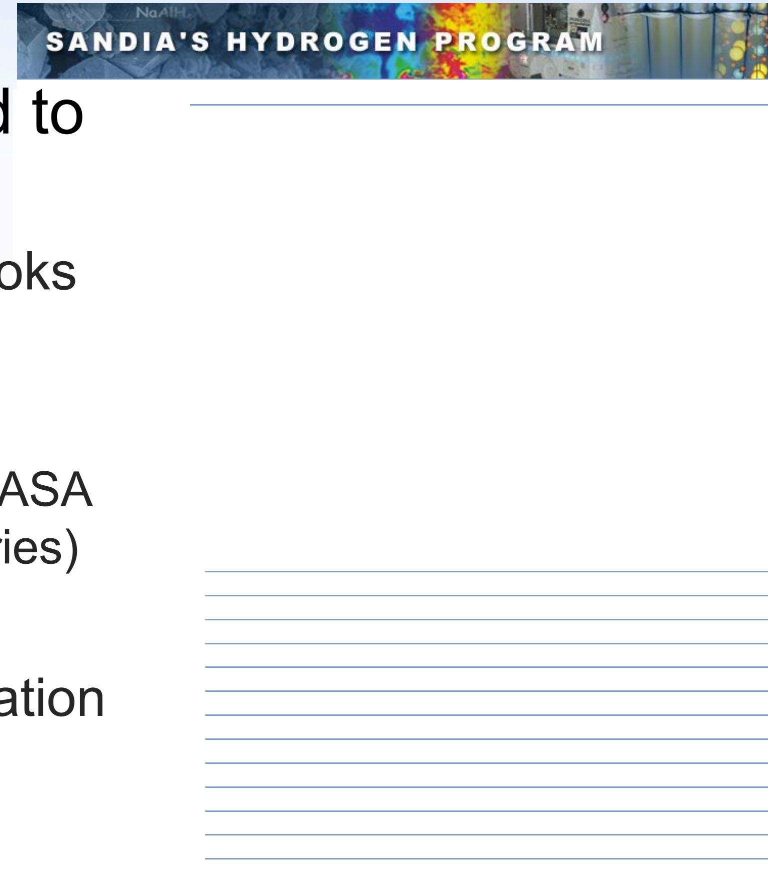

- Summarizes materials data related to hydrogen embrittlement
  - Modeled after existing metals handbooks
  - Data culled from open literature
    - Peer-reviewed scientific articles
    - Public institutional reports (primarily NASA and US government national laboratories)
  - Organized by material
  - Objective summary of relevant information
    - Limited recommendations
    - Vetted by cognizant experts
- Easily and publicly accessible
  - http://www.sandia.gov/matlsTechRef
  - http://en.openei.org/wiki/Gateway:Hydrogen

Outline of the Technical Reference for Hydrogen Compatibility of Materials

1. Introduction	
2. Steels	
1) Carbon steels	1100
2) Low-alloy steels	12xx
3) High-alloy ferritic steels	14xx-18xx
3. Austenitic steels	2xxx
4. Aluminum alloys	
1) Non-heat treatable	31xx
2) Heat treatable	32xx
5. Copper alloys	4001
6. Nickel alloys	5110
7. Nonmetals	8100

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Technical Reference for Hydrogen Compatibility of Materials

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Available at
http://www.sandia.gov/matlsTechRef

The Technical Reference is composed of stand-alone material-specific chapters

General structure of each chapter

1. Background on material(s) described in chapter
2. Hydrogen transport properties
   - permeability, diffusivity and solubility
3. Mechanical properties in gaseous hydrogen
   1) Strength properties
   2) Fracture properties
   3) Fatigue properties
4. Microstructure and Fabrication (including properties of welds)
5. References
6. Figures and tables of data

The Technical Reference consists of text with references, as well as tables and plots of data

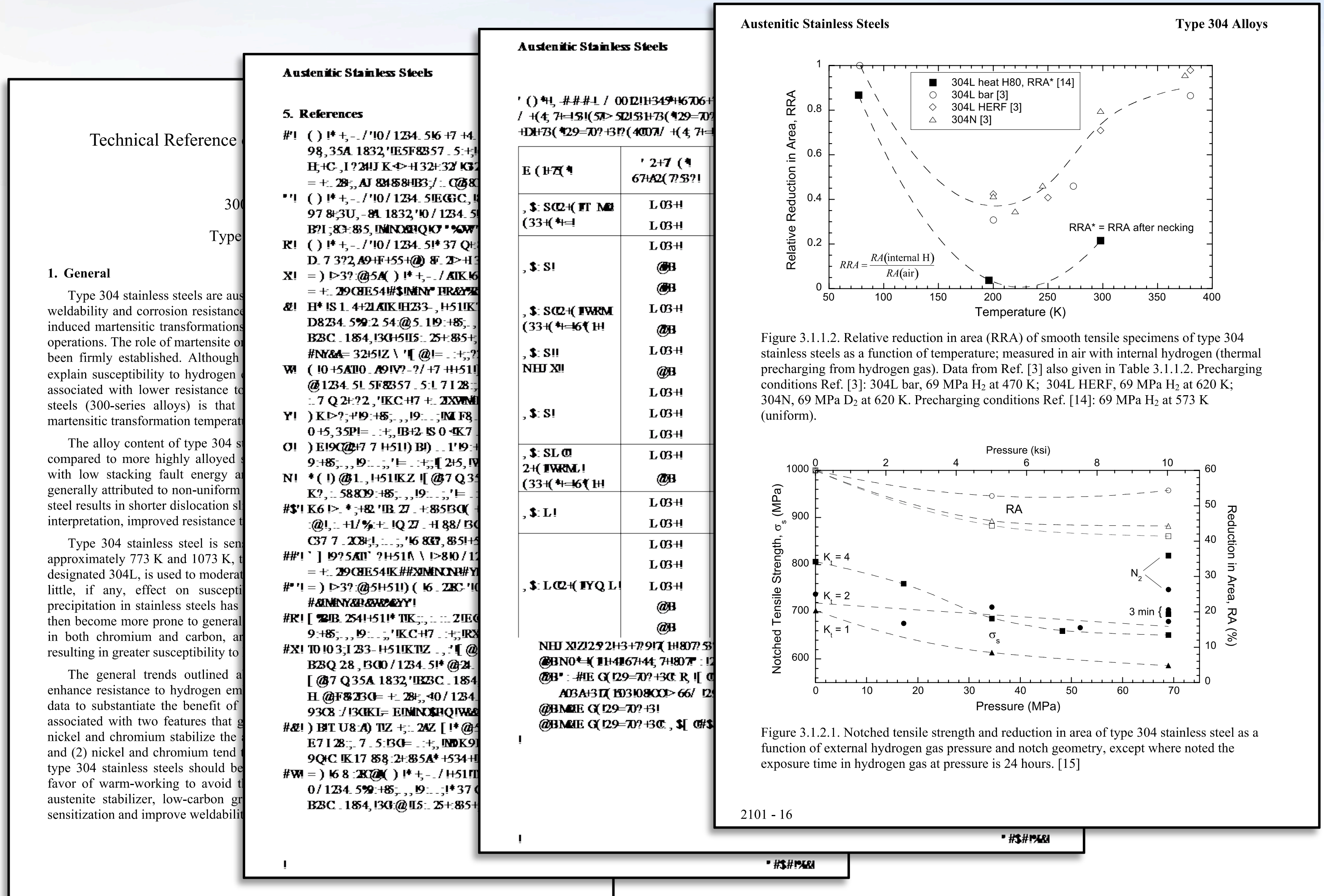

Figure 3.1.1.2. Relative reduction in area (RRA) of smooth tensile specimens of type 304 stainless steels as a function of temperature; measured in air with internal hydrogen (thermal precharging from hydrogen gas). Data from Ref. [3] also given in Table 3.1.1.2. Precharging conditions Ref. [3]: 304L bar, 69 MPa H_2 at 470 K; 304L HERF, 69 MPa H_2 at 620 K; 304N, 69 MPa D_2 at 620 K. Precharging conditions Ref. [14]: 69 MPa H_2 at 573 K (uniform).

Figure 3.1.2.1. Notched tensile strength and reduction in area of type 304 stainless steel as a function of external hydrogen gas pressure and notch geometry, except where noted the exposure time in hydrogen gas at pressure is 24 hours. [15]

2101 - 16

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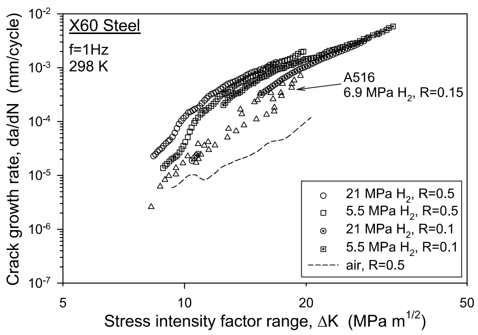
In principle, data from *TR* can be used in design and qualification of materials

Plain Carbon Ferritc Steels

C-Mn Alloys



s from Figure 3.3.2.1.

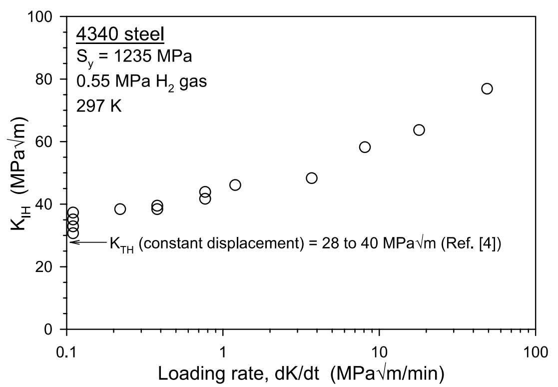
1100 - 29

- ASME BPVC VIII.3 Article KD-10 requires measurement of fatigue crack growth rates in gaseous hydrogen
- Fatigue data is included in the *TR*
- However, the pedigree of the tested materials and the parameters of the tests may not satisfy the requirements of any standard
  - Article KD-10 requires fatigue testing at frequency of 0.1Hz
  - Data shown here were acquired with load frequency of 1 Hz

The *TR* reveals general trends with materials, environmental and stress variables

Low-Alloy Ferritic Steels

Tempered Ni-Cr-Mo Alloys



340 [6].

1212 - 14

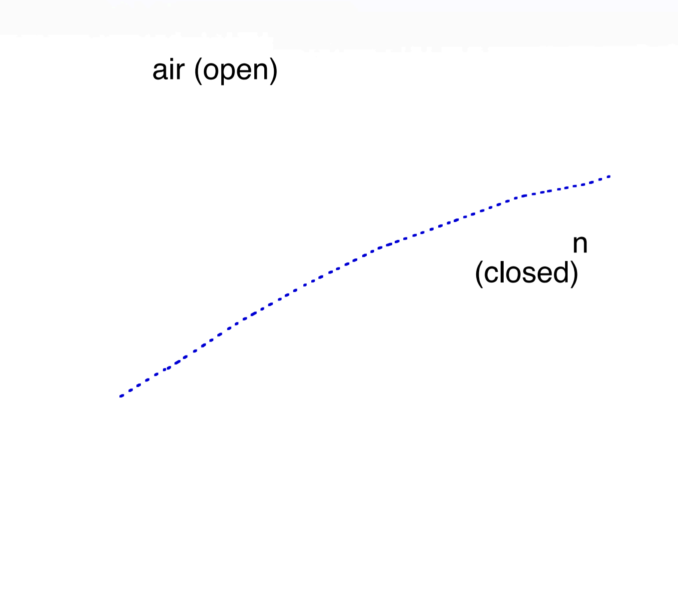
- Measurements can depend on parameters of the test
  - e.g., loading rate and frequency dependencies
- Established materials trends can be amplified by hydrogen
  - e.g., dependence of fracture toughness on materials strength
- Characteristics that are normally insensitive to variation can be very sensitive to hydrogen
  - e.g., small compositional differences of equivalently certified material

Hydrogen embrittlement is sensitive to materials, environmental and stress variables

The *TR* exposes gaps of existing standards, fundamental understanding and available data

- Significant amount of data generated in gaseous hydrogen does not inform design
  - Very high-strength materials: not appropriate for pressure systems
  - Low-pressure testing: cannot be extrapolated to high pressure
- Data relevant to design is limited in scope and completeness
- Challenges with standardizing materials qualification are highlighted by documented trends (e.g. nickel in SS)

Tensile ductility of type 316 austenitic stainless steels



Hydrogen embrittlement varies significantly over the range of allowable nickel content for type 316/316L austenitic stainless steel

The *TR* is valuable tool for general guidance, but has some important limitations

- The *TR* provides basic information on materials and their behavior in gaseous hydrogen environments
  - Provides general guidance on selection of materials for hydrogen service
  - Aids identification of trends, sensitive parameters, gaps
- Limitations of the current formulation of the *TR*
  - Difficult to cross-reference information
    - Materials pedigree
    - Testing pedigree
    - Data
  - Challenge to keep text-based documents up-to-date and manageable
  - Information is not sufficient to *qualify* materials or designs

Question remains: ***How do we qualify materials for hydrogen service?***

Materials qualification requires a significant investment in evaluating materials

- Existing materials standards are largely insufficient for specifying materials for hydrogen service
  - Type 316/316L austenitic stainless steel is ***one known*** example of material that is very sensitive to hydrogen within the allowable compositional range
  - Implicit bounds on the strength of a material may need to be made explicit (hydrogen embrittlement is sensitive to strength)
- Standards that attempt to qualify a material require *multiple tests* on *multiple specimens* from *multiple batches* of material certified to the same designation
  - Quantification of a specific parameter (e.g., tensile ductility) usually requires a minimum of 9 tests (and could require more than 30)
  - In comparison, reports in the literature often represent single tests
  - Standards often require multiple parameters (eg fracture and fatigue)
  - Welds must be additionally qualified (testing x3 per ASME KD-10)
  - This is a lot of data!!

A mechanism is needed to manage and disseminate materials qualification information

- Testing in gaseous hydrogen is expensive and time-consuming; few facilities exist
  - Access to materials properties measured in gaseous hydrogen should not be allowed to become a roadblock to commercialization of hydrogen technologies
- Databases aid qualification activities, materials selection and engineering analysis; however,
  - Text-based data presentation does not enable efficient communication of information (e.g. paper reports)
  - Paper reports limit comparison and integration of multiple data sets
- Robust software tools exist for managing databases of materials properties, as well as the pedigrees of the materials and the testing methods

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Materials databases are evolving into sophisticated data management tools

- Many institutions and industries are adopting sophisticated tools for data management
  - Warehouse and disseminate data from numerous sources
  - Analyze data sets and improve quality control
  - Harmonize the structural properties and materials used in design of engineering systems
  - Automatically populate engineering tools with design data
  - Minimize redundant testing activities
  - Aid materials innovation
- Sandia National Laboratories is a member of the Material Data Management Consortium (MDMC)
  - Other members include ASM, Boeing, NASA, Raytheon, Oak Ridge National Laboratory, Los Alamos National Laboratory and several others
  - Potential leverage for building tools to facilitate qualification of materials for hydrogen service

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Summary

- Hydrogen embrittlement depends sensitively on environment, materials and applied stress
- The *Materials R&D* element of Sandia's hydrogen program addresses the need for technical guidance on materials selection and materials testing for hydrogen service
- The *Technical Reference for Hydrogen Compatibility of Materials* is a handbook of structural materials data
- The *TR* is also an instrumental tool for managing hydrogen compatibility of materials, and aids identification of :
  - Important trends in the response of materials
  - Testing parameters that are sensitive to hydrogen
  - Gaps in our fundamental understanding of hydrogen embrittlement and gaps in the available data
- A database component of the *TR* will enable qualification of materials for hydrogen service
  - Requires collaboration of stakeholders and sharing of information

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Acknowledgements

- The *Technical Reference for Hydrogen Compatibility of Materials* is supported by the Fuel Cell Technologies Office (FCTO) of the Office of Energy Efficiency and Renewable Energy (EERE) at the U.S. Department of Energy (DOE)
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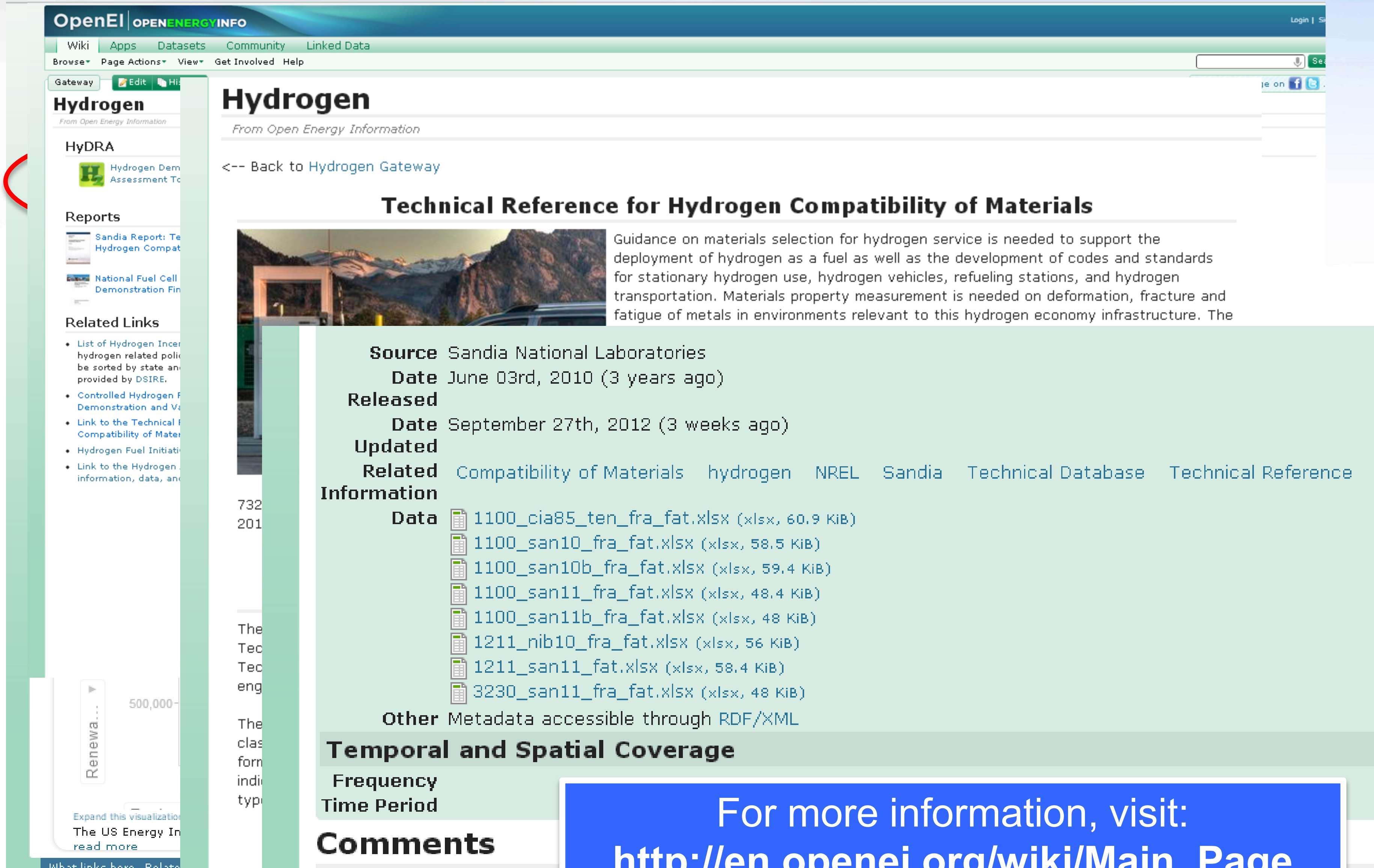

For more information, visit:
http://en.openei.org/wiki/Main_Page