Sandia National Laboratories

WPCSOL, LLC

HYSAFE Workshop Materials

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Objective

The purpose of this presentation is to discuss the status on hydrogen-compatible materials selection and its associated research gaps.

The presentation discusses activities at the US national labs and in industry for metals, composites and non-metals.

Each will be discussed in turn.

Overview

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The storage density issues for gaseous fueled hydrogen vehicles is pushing the limits on conventional materials used with hydrogen.

The operating temperature ranges (<-40C to >85C) further complicates the issue.

Metals

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The US has been active in the compatibility of metals for several years. Here are several examples

- SNL has worked to develop a facture mechanics analysis for evaluating materials used for a specific design.
- ASME has incorporated the facture mechanics analysis into the Boiler and Pressure Vessel Code (BPVC) as Article KD-10 in Division 3 of Section VIII.
- D. Stalhiem has investigated the suitability of using current and dated pipeline steels.
- NIST and SNL have been working on fatigue crack growth in pipe line steel.
- ASME is working to incorporate fatigue crack growth into the Section 12 of the B31 Piping Code.
- SNL has investigated the effect of alloy shaving on the 316L class of austenitic steels.

Metals

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- SNL has examined the effect of hydrogen in orthogonal fusion welds in 316L materials.

- SNL is examining other austenitic materials for suitability:

A286;
forge alloy;
15Cr, 26Ni, 2Ti steel;
ASTM A638 grade 660

XM-11;
wrought alloy;
21Cr, 6Ni, 9Mn steel;
ASTM A276 type XM-11 (UNS 21904).

Metals

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Near term trends in data

- Microstructure rather than tensile strength appears to be the key parameter in predicting fatigue crack rates (FCR).
- Banded regions of pearlite through the metal appear to be more resistant to cracking.
- The relative FCR in welds compared to base materials is not clearly established.
- The heat affected zone (HAZ) appears to be more susceptible to cracking. This may be due to the material in this zone might be affecting the amount of pearlite. The effectiveness of a post weld heat treat was not discussed and may not have been investigated yet.

Metals

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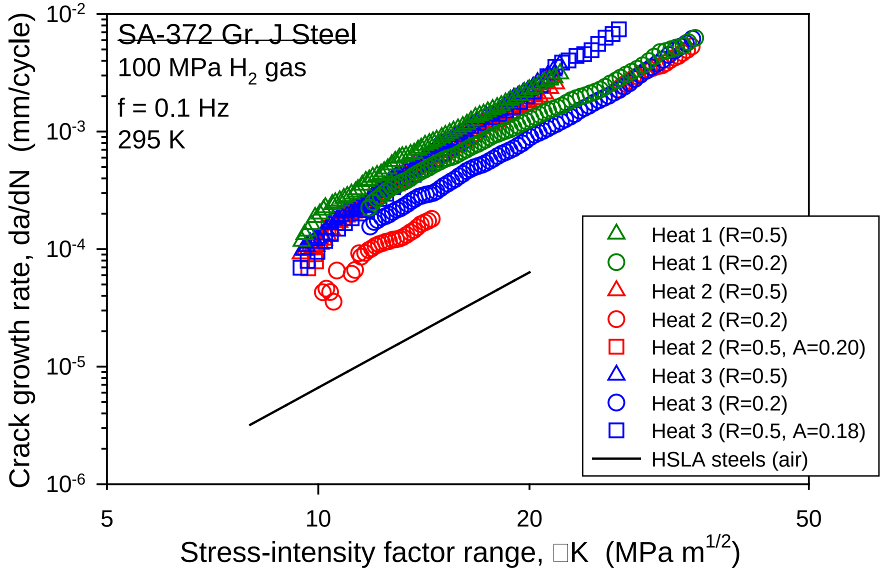
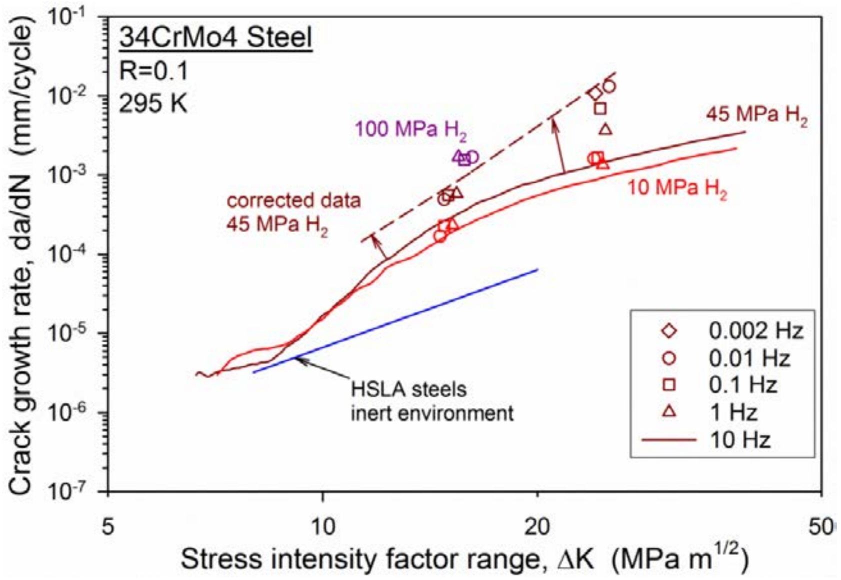
- Alloy shaving of key components in a material formulation results in a change of properties. As an example, the reduction of nickel in 316 results in enhanced hydrogen embrittlement susceptibility.

- Alternative austenitic materials show some promise based on end user cost.

ASME Article KD-10 requires fatigue crack growth relationships in H_2 gas: must balance test duration and data quality

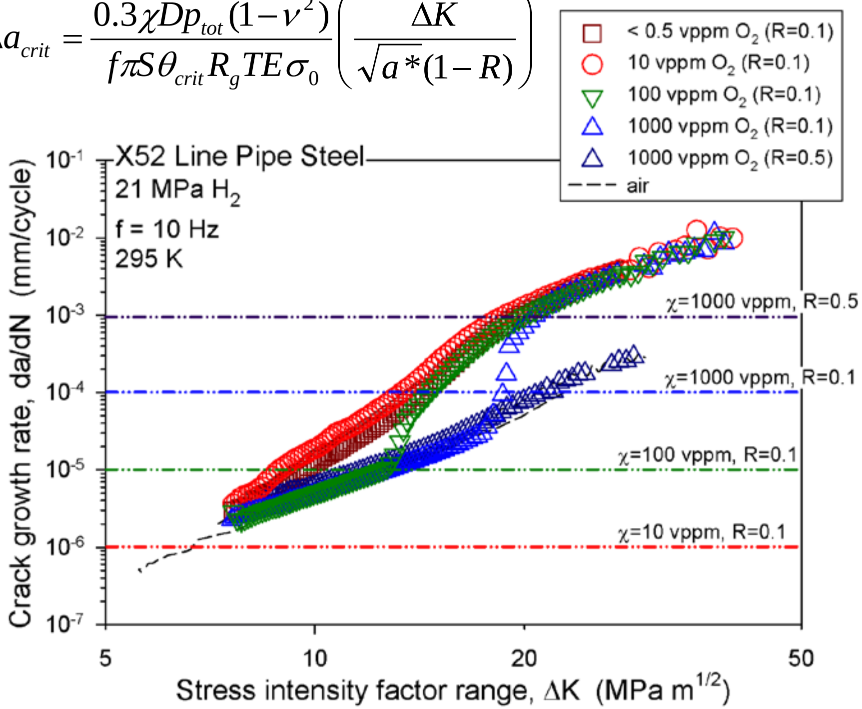


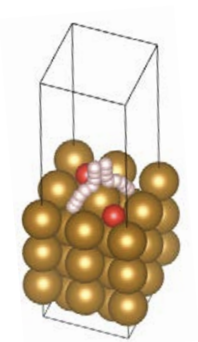


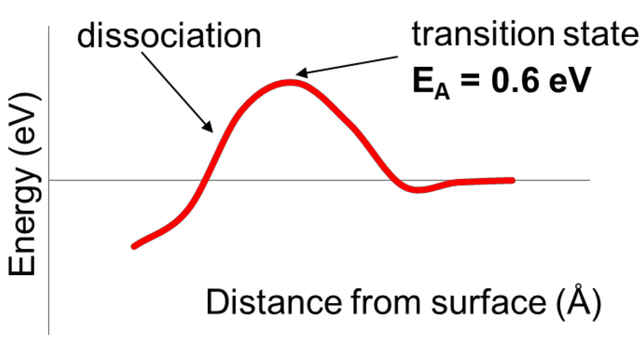
- Fatigue crack growth testing in ASME Article KD-10 currently specifies load-cycle frequency of 0.1 Hz
  - Leads to impractical test durations or incomplete data
  - Cannot simply increase frequency, since this variable affects fatigue crack growth rates in H_2
- Can modified measurement approach capture data at low crack growth rates with reasonable test durations?
  - Measure fatigue crack growth relationship at high frequency (e.g., 10 Hz), apply correction based on upper-bound crack growth rates
  - Need to define upper-bound crack growth rates as a function of stress intensity factor range
  - Upper-bound crack growth rates depend on frequency, material properties (e.g., yield strength), and H_2 pressure

Trace impurities (e.g., O_2) can significantly inhibit H_2-accelerated fatigue crack growth in line pipe steels

$$\Delta a_{crit} = \frac{0.3\chi D p_{tot}(1-\nu^2)}{f\pi S\theta_{crit} R_g T E \sigma_0}\left(\frac{\Delta K}{\sqrt{a^*}(1-R)}\right)^2$$

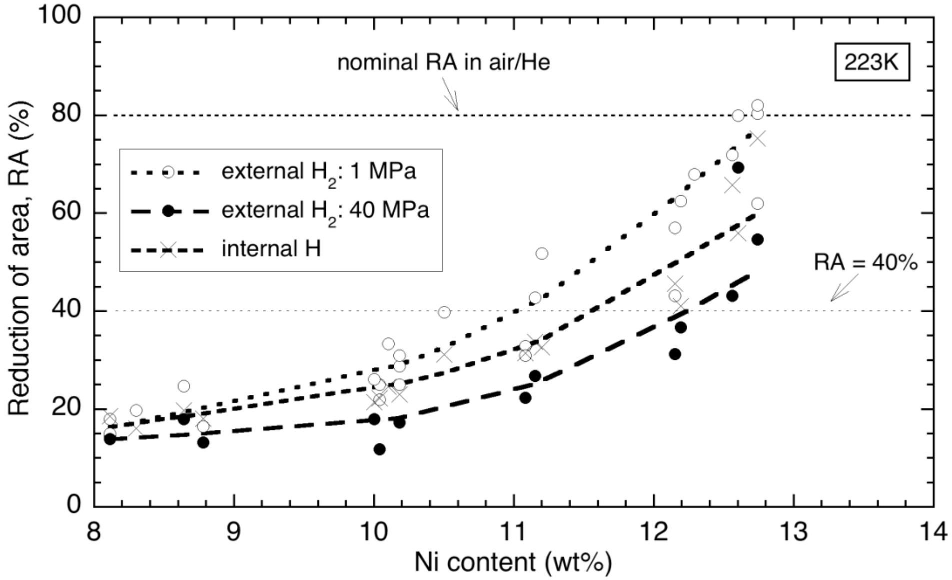




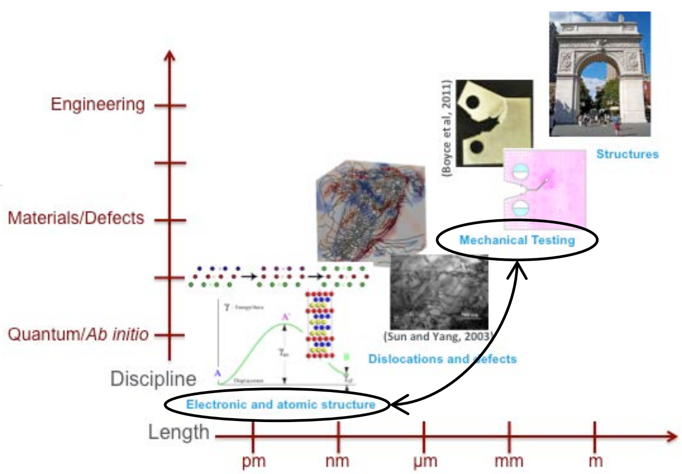


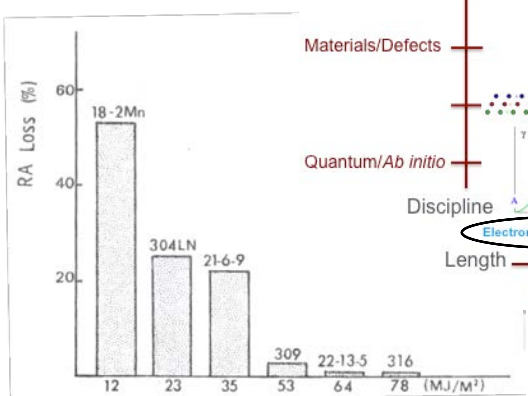
- Oxygen delays onset of H_2-accelerated fatigue crack growth, e.g., increases stress required to activate accelerated crack growth
  - Analytical predictive model developed with one adjustable parameter, i.e., critical oxygen surface coverage for H uptake into steel ($S\theta_{crit}$)
  - Density functional theory modeling demonstrates that O_2 inhibits H_2 dissociation on iron surface
- What is inhibiting potential of other gas impurities?
  - Can inhibiting potential be predicted through theoretical modeling?
- Are gas inhibitors effective for other alloys (e.g., stainless steels)?
- Can critical oxygen surface coverage in predictive model ($S\theta_{crit}$) be independently quantified?

Hydrogen embrittlement susceptibility of austenitic stainless steels depends on Ni content



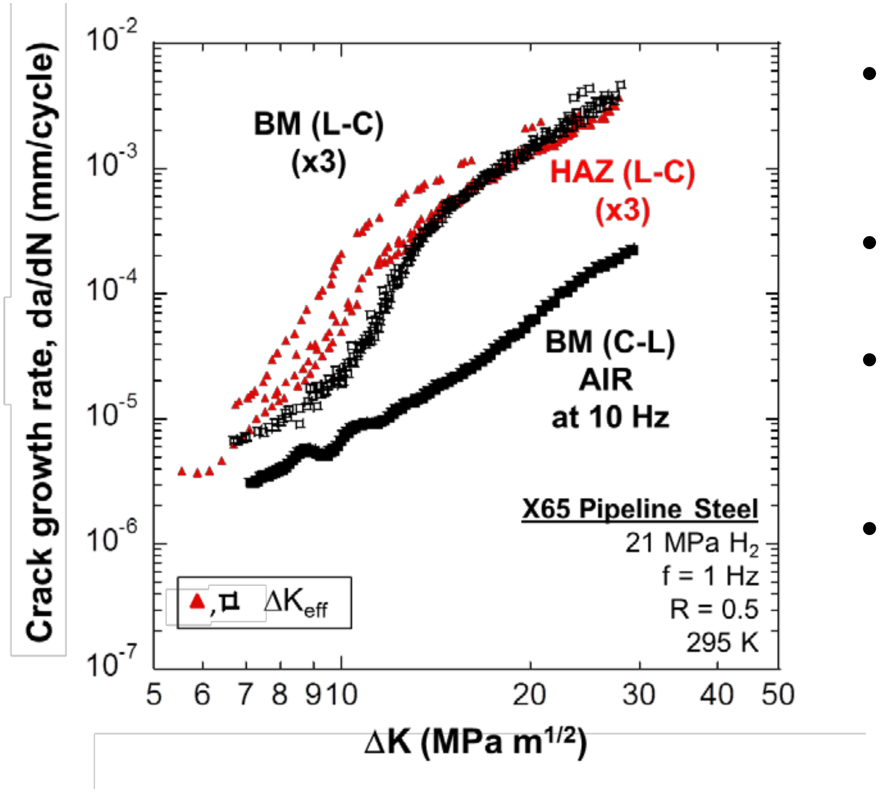
- Reduced Ni content lowers cost but enhances hydrogen embrittlement (HE)
- Can stainless steels be identified with improved balance between cost and performance?
- Can modeling enable alloy selection/development?
  - What is HE mechanism in stainless steels?
  - What fundamental material characteristics (e.g., stacking fault energy) govern HE mechanism and measured properties?
  - Can these fundamental material characteristics be simulated as a function of alloy content?

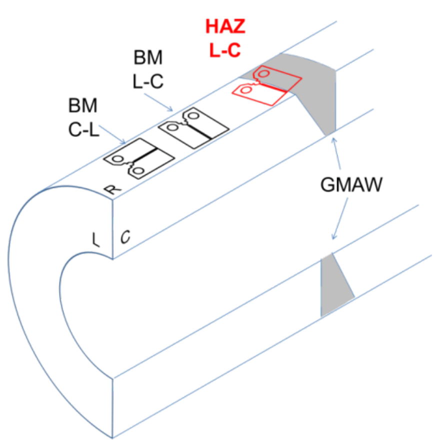




stacking fault energy

H_2-accelerated fatigue crack growth may be more pronounced in pipeline steel welds compared to base metal





- H_2-accelerated fatigue crack growth in welds appears higher than base metal, but several factors complicate interpretation
- What is effect of residual stress on fatigue crack growth measurements for welds?
- What is effect of microstructure on H_2-accelerated fatigue crack growth in pipeline steels?
- What is effect of mode II loading component on H_2-accelerated fatigue crack growth for heat-affected zone measurements?

Near term research opportunities

- Conventional wisdom was to avoid high tensile steels. The indications that micro structure not chemical composition are the issue, leads to re-evaluating the use of HSLA's like a grade from ASTM A656.
- Evaluation of the non-300 series austenitic steels.
  - Applying theoretical modeling to guide this evaluation
- Consideration of non-conventional materials like Al-Li, which is being used in aircraft turbine engines.
  - Material characterization may need to emphasize corrosion and stress-corrosion cracking resistance and not H_2 compatibility
- Cost effective reformer reactor tube materials.

Composites

The US has been active in the suitability of composites for several years. Here are several examples:

- 350 and 700 bar type 3 tanks
- 350 and 700 bar type 4 tanks
- ASME type X and XII tanks

The US design requirements are keeping pace:

- ASME BPVC Section X & XII
- SAE J2579
- CSA NGV 2

Composites

Recently activities

- Cylinder testing defined in UN/ECE GTR 13
- DoE funding of private development of composite vessel reinforcement materials.
- Development of a proprietary reinforced fiber pipe (FRP) for hydrogen pipeline use lead by SRNL.
- SRNL working with ASME on a case study to accept FRP for hydrogen pipeline use.

Composites

Near term research opportunities

- Vessel head materials. Current usage is encountering heat treat limitations due to the required thickness.
- Cost effective options to existing fiberglass and carbon filament selections.
- Development work to generate a cost effective option that would increase the operating temperature range of the tank (or pipe) outside of the limits for polyethylene lined hardware.

“Plastics”

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The US is slowly becoming active with the suitability of plastic in recent years. Here are couple of examples:

- ASME has started a code section to write a “non-metals” piping and vessel code.
- ASME B31 section 3 has a limited “non-metals” section.
- ASME B31 section 12 would like to add “non-metals” suitable for hydrogen section.
- PNNL has started evaluating the suitability of certain “non-metals” for hydrogen. Testing includes explosive decompression of gasket materials.

“Plastics”

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Near term research opportunities

- Suitable, low cost gasket materials for hydrogen fueling pressure systems (~1000 bar).
- Suitable, low cost gasket materials for hydrogen appliance pressure systems (<20 bar).
- Suitable, low cost containment and structural materials for hydrogen appliance pressure systems (<20 bar).
- Composite vessel and pipe liner development for hydrogen at temperatures exceeding the current limited range of -40 to 85C.