Dispelling Myths about Gaseous Hydrogen Environmental Fracture and Fatigue

Chris San Marchi and Joe Ronevich

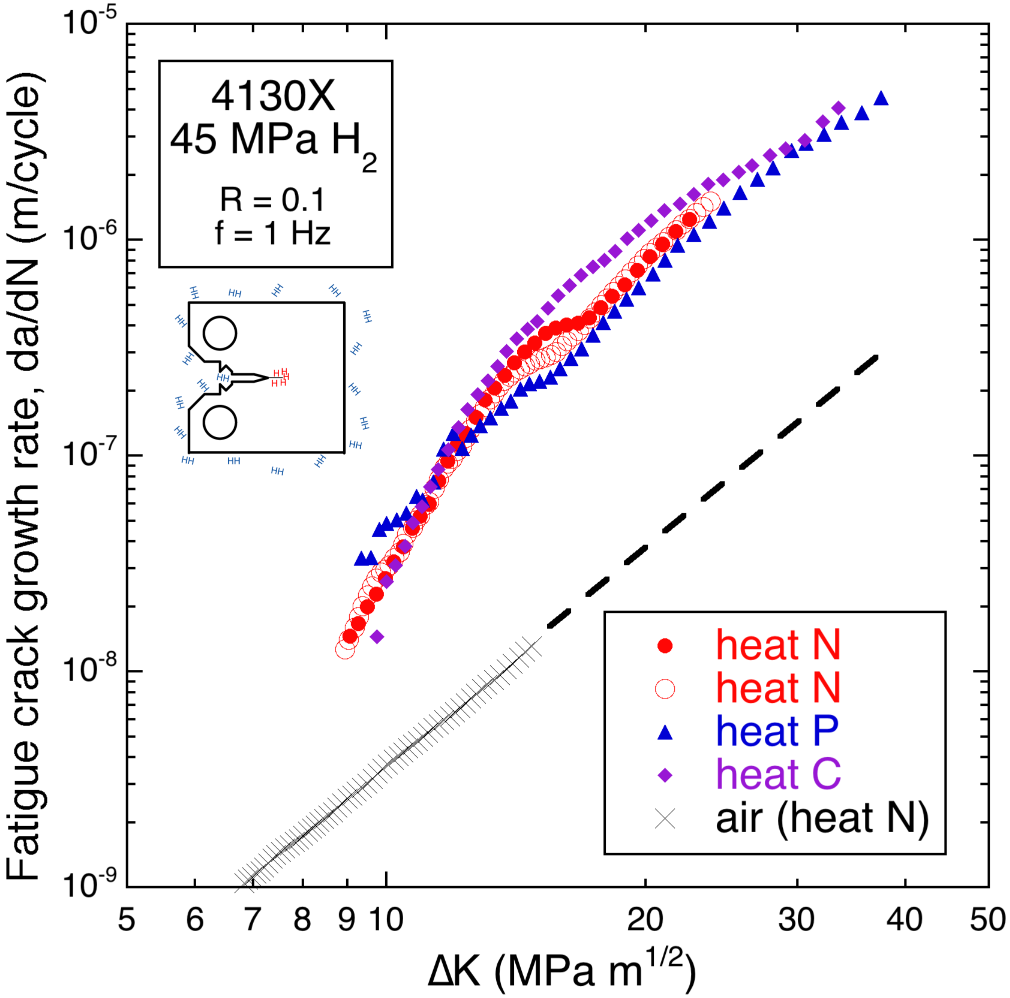
Sandia National Laboratories

TMS, March 2018

Phoenix AZ

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525

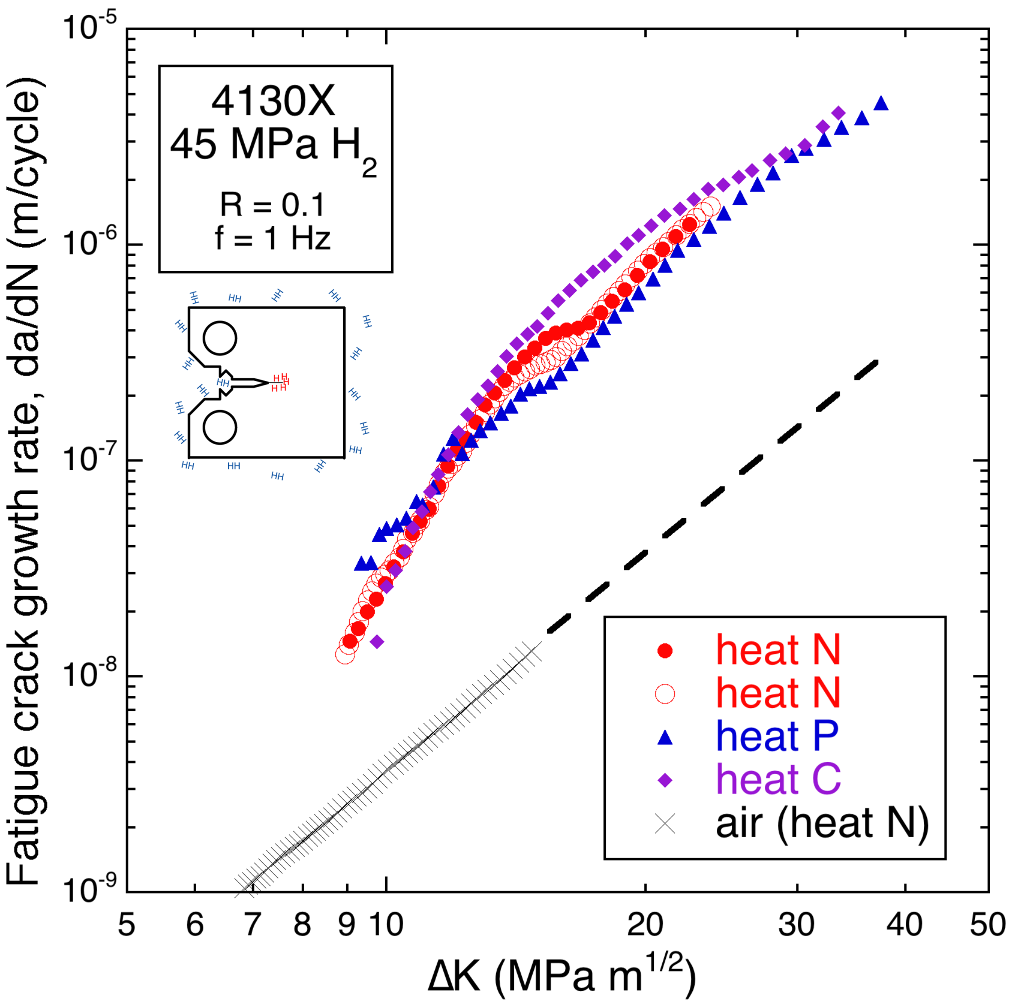
What are the requirements to use a given material in gaseous H2 service?



- **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

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



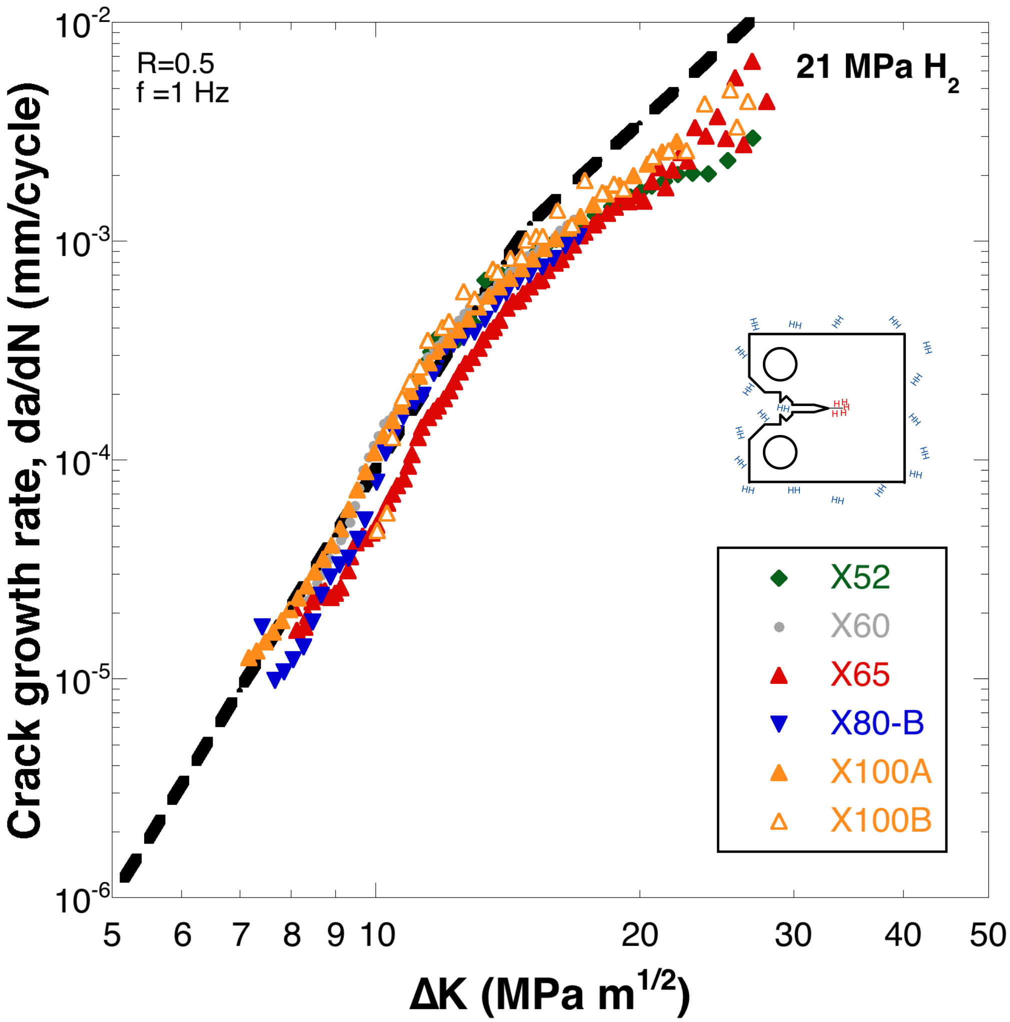
Materials requirements depend on the application and the design

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

Outline

- Materials
  - The effects of H2 depend on microstructure of ferritic steels
  - Austenitic stainless steels can be immune to H2
  - Aluminum alloys are immune to H2
- Environment
  - Stainless steels are sensitive to H2 at low temperature
  - Low pressure H2 has negligible effect on performance
  - Impurities can mitigate effects of H2
- Mechanics
  - High-strength alloys have low fracture resistance in H2
  - Suitability for H2 service can be assessed with tensile tests

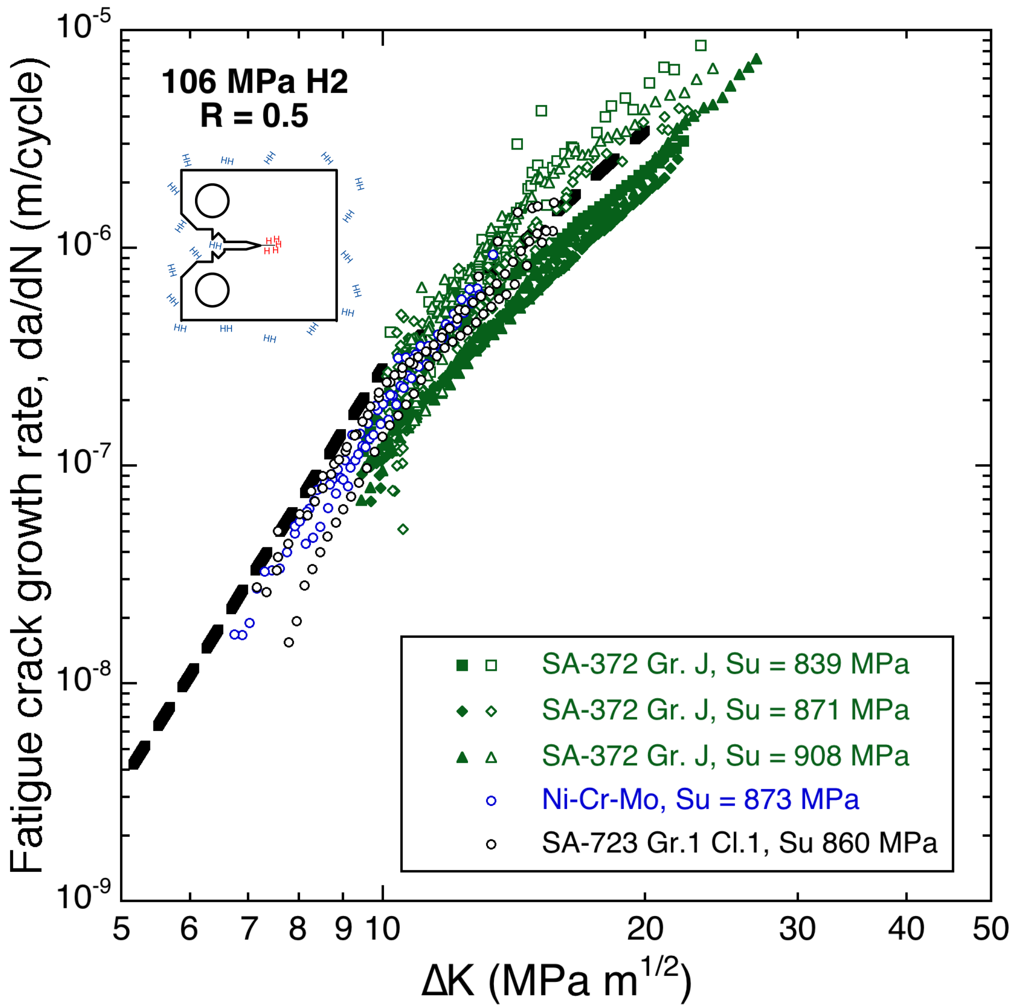
The effects of H2 depend on the microstructure of ferritic steels *more myth than fact*



- Pipeline (carbon) steels show nominally the same fatigue crack growth behavior in gaseous hydrogen
- These steels represent:
  - Wide range of strength
  - Wide range of microstructure

The effects of H2 depend on the microstructure of ferritic steels

more myth than fact

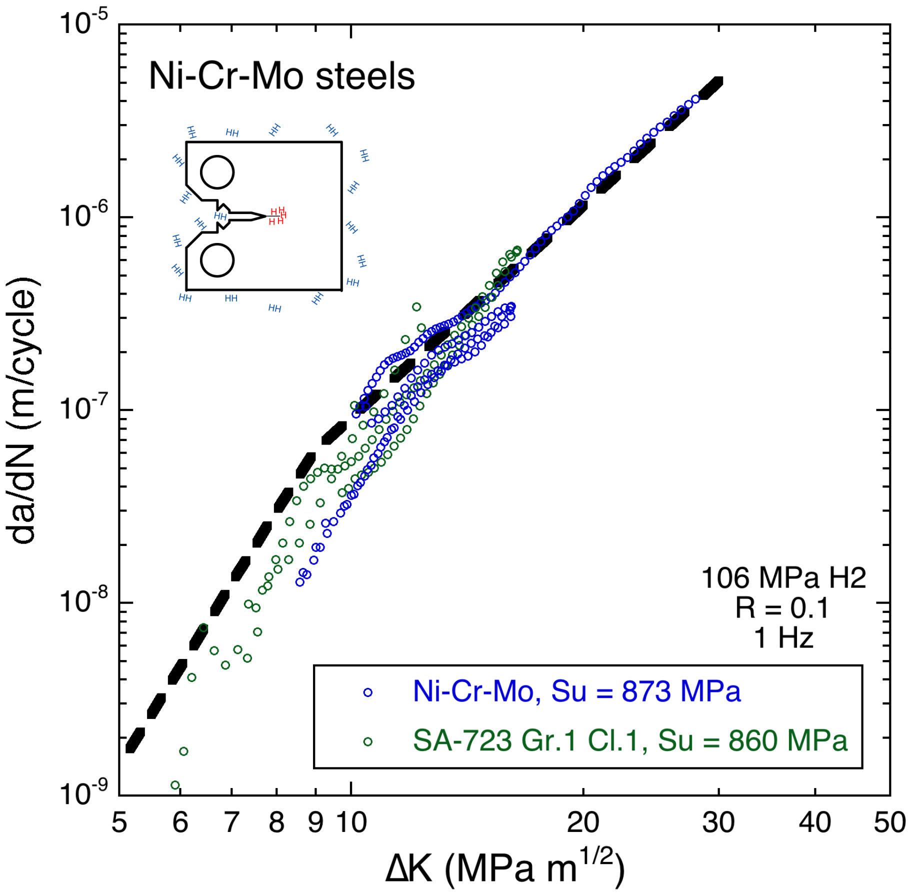


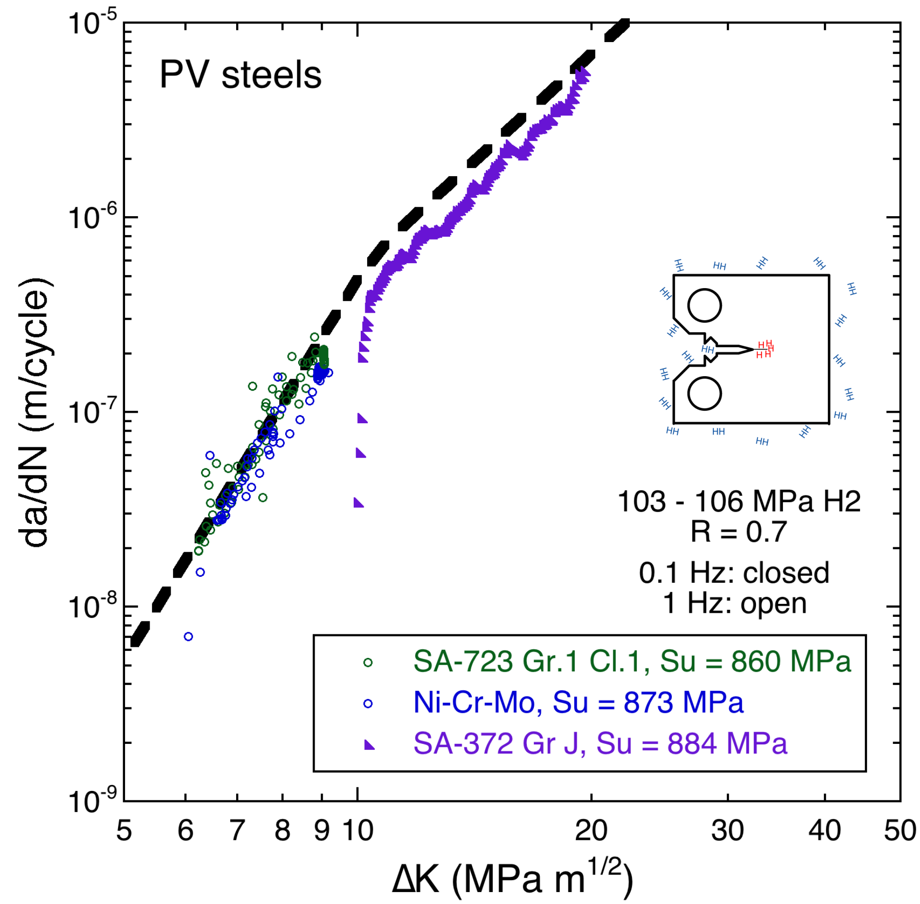
- Pressure vessel steels (low alloy Cr-Mo and Ni-Cr-Mo steels) show same FCGR behavior in gaseous H2 as pipeline steels
- Dashed line represents closed form expression for both pipeline and pressure vessel steels

$$\frac{da}{dN} = C\left[\frac{1 + C_H R}{1 - R}\right]\Delta K^m \left(\frac{f}{f_0}\right)^{1/2}$$

The effects of H2 depend on the microstructure of ferritic steels

more myth than fact

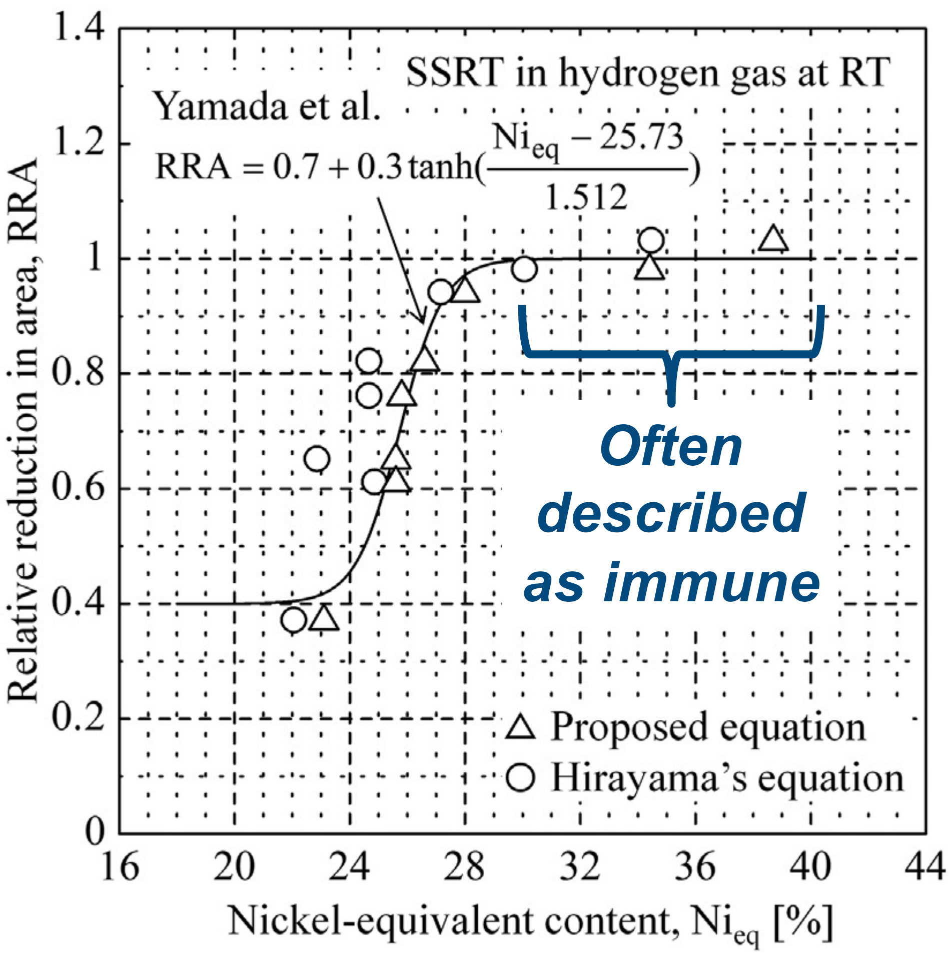




Consistent FCGR behavior for wide range of carbon steels

Austenitic stainless steels can be immune to effects of H2

misleading



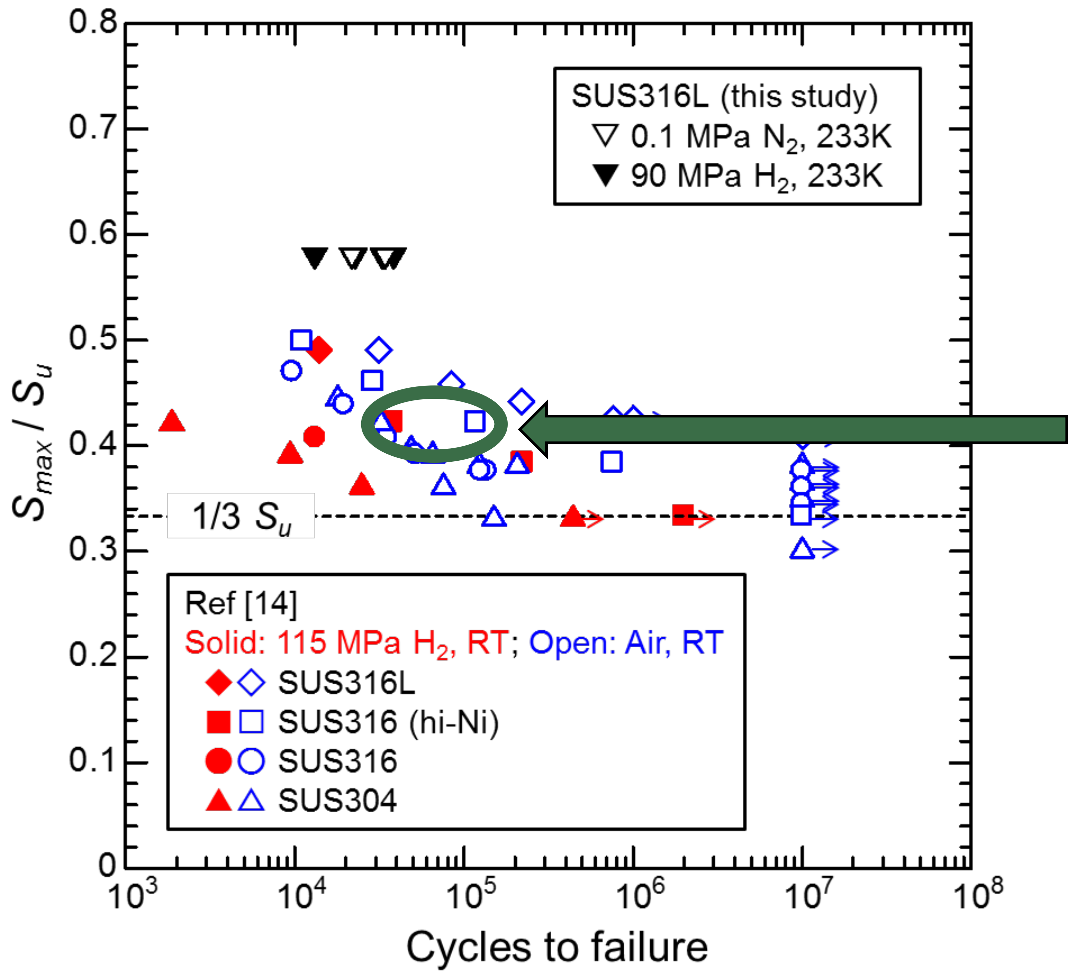
From: Takaki et al *Intern J Hydrogen Energy* **41** (2016) 15095

- Some alloy compositions show little degradation of tensile ductility (RA) in hydrogen
  - Suggesting "immunity"

- Represents narrow compositional space *not* representative of common alloy composition
- Trend does *not* necessarily translate to other properties

Austenitic stainless steels can be immune to effects of H2

misleading



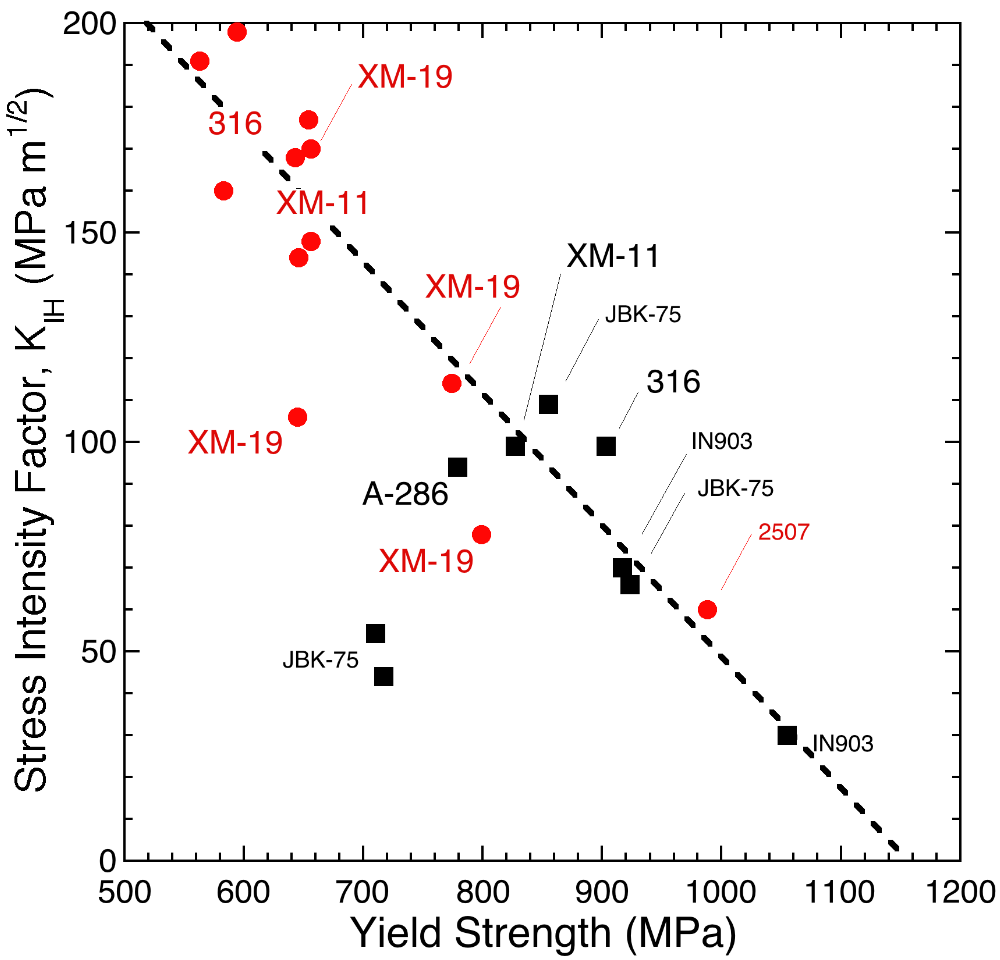
From: San Marchi et al, ASME PVP-2018 conf.
Ref 14: Nakamura et al JSME M&M2017 conf.

- Fatigue life data generally show similar trends with tensile data
- However, fatigue life data of high nickel alloys show ***decrease*** in H2, even with high nickel content

Hydrogen affects low-cycle fatigue even of high-Ni alloys

Austenitic stainless steels can be immune to effects of H2

misleading



- "Immunity" to H2 is often attributed to alloy stability
- However, fracture data show
  - SS alloys are not immune to H2
  - Stable alloys also show strong effect of H2

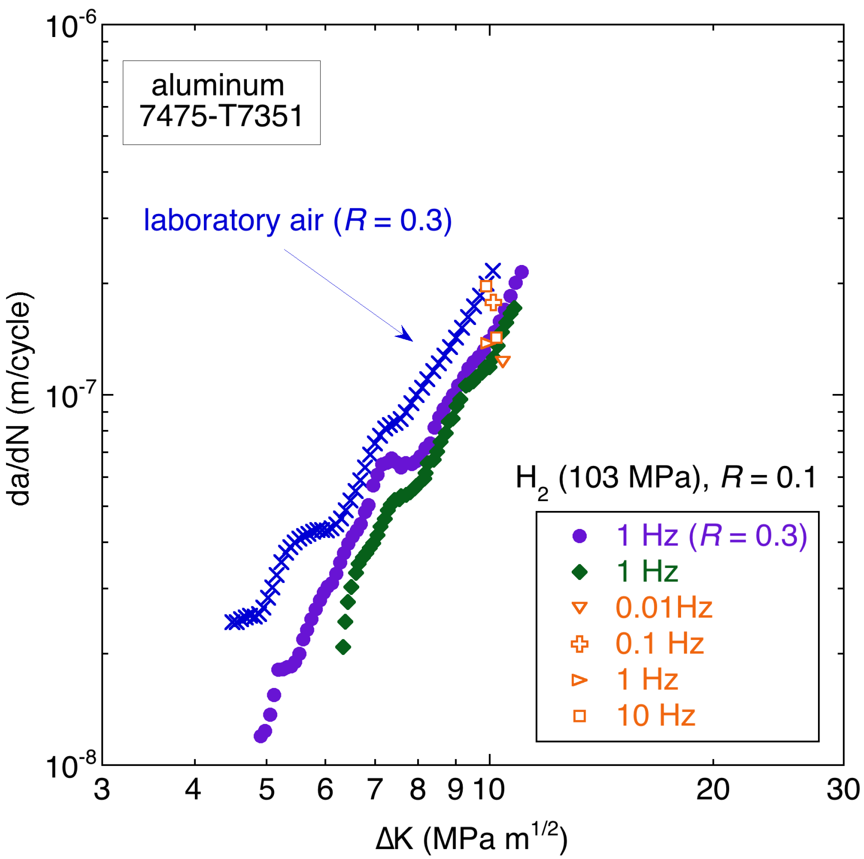
Both high-Ni alloys and stable austenitic stainless steels show significant effects of H2

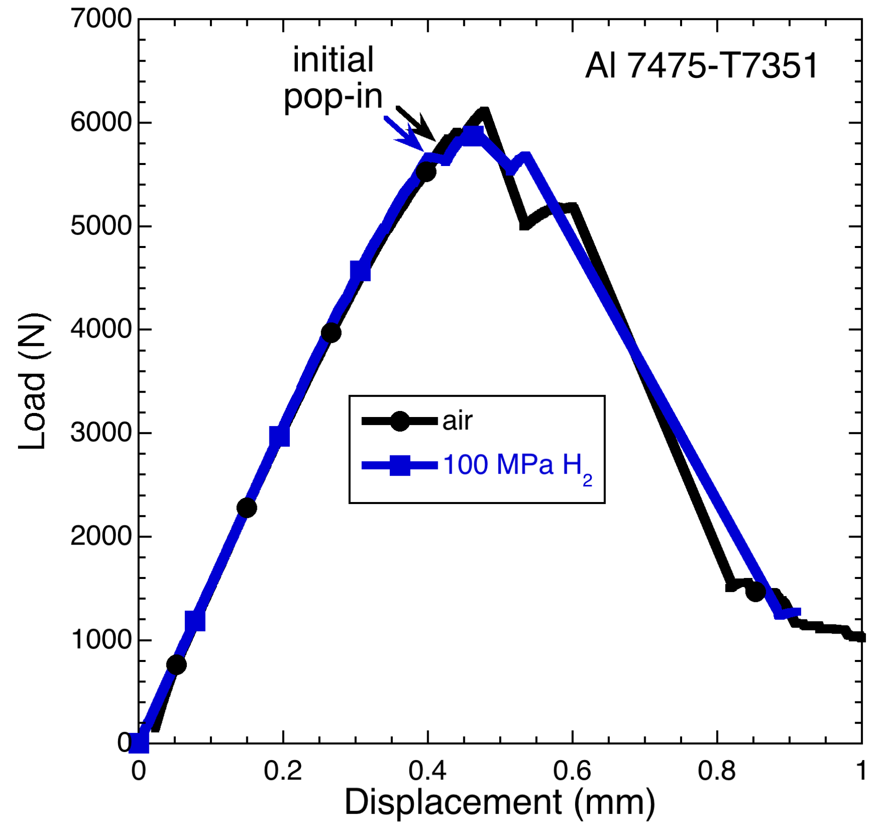
Sandia National Laboratories

H2FC Hydrogen and Fuel Cells Program

Aluminum alloys are immune to effects of H2

seemingly true but misleading





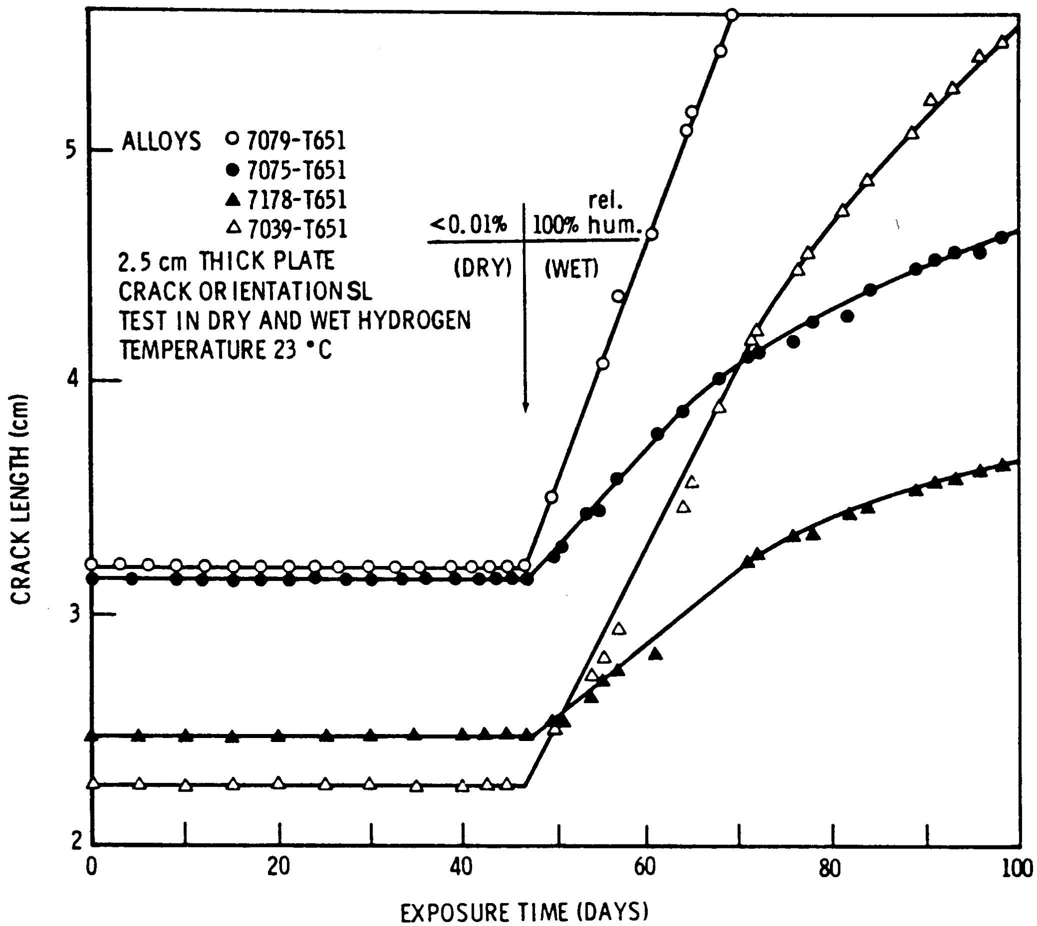
Fatigue crack growth rates in H2 are less then in air

Fracture resistance is nominally the same in H2 and in air

From: San Marchi et al, ASME PVP-2011 conf.

Aluminum alloys are immune to effects of H2

seemingly true but misleading



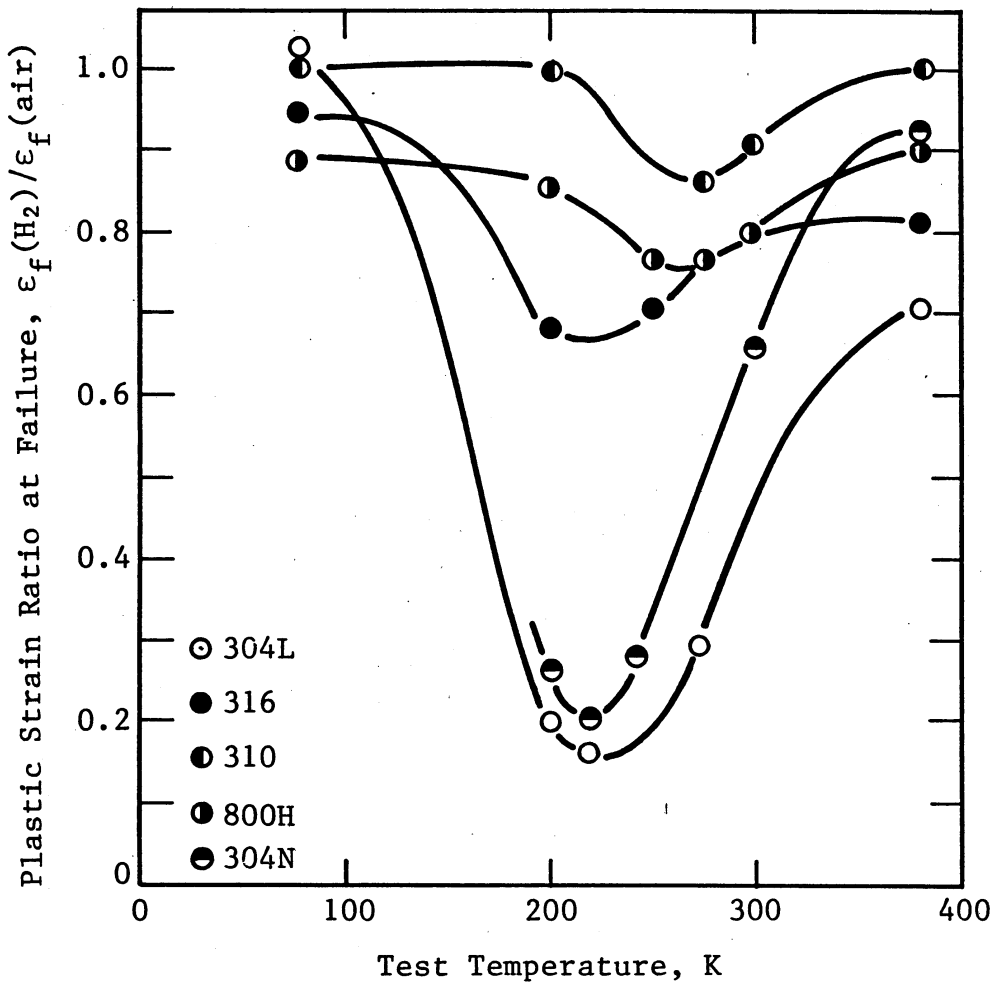
From: Speidel, Hydrogen Embrittlement and Stress Corrosion Cracking, 1984

- **Seminal experiments show clear difference of fracture resistance in dry H2 and wet H2**
- **There are no data that show fracture and fatigue of Al alloys are affected by dry H2**

Moisture in H2 can promote environment-assisted cracking

Austenitic stainless steels are sensitive to H2 at low temperature

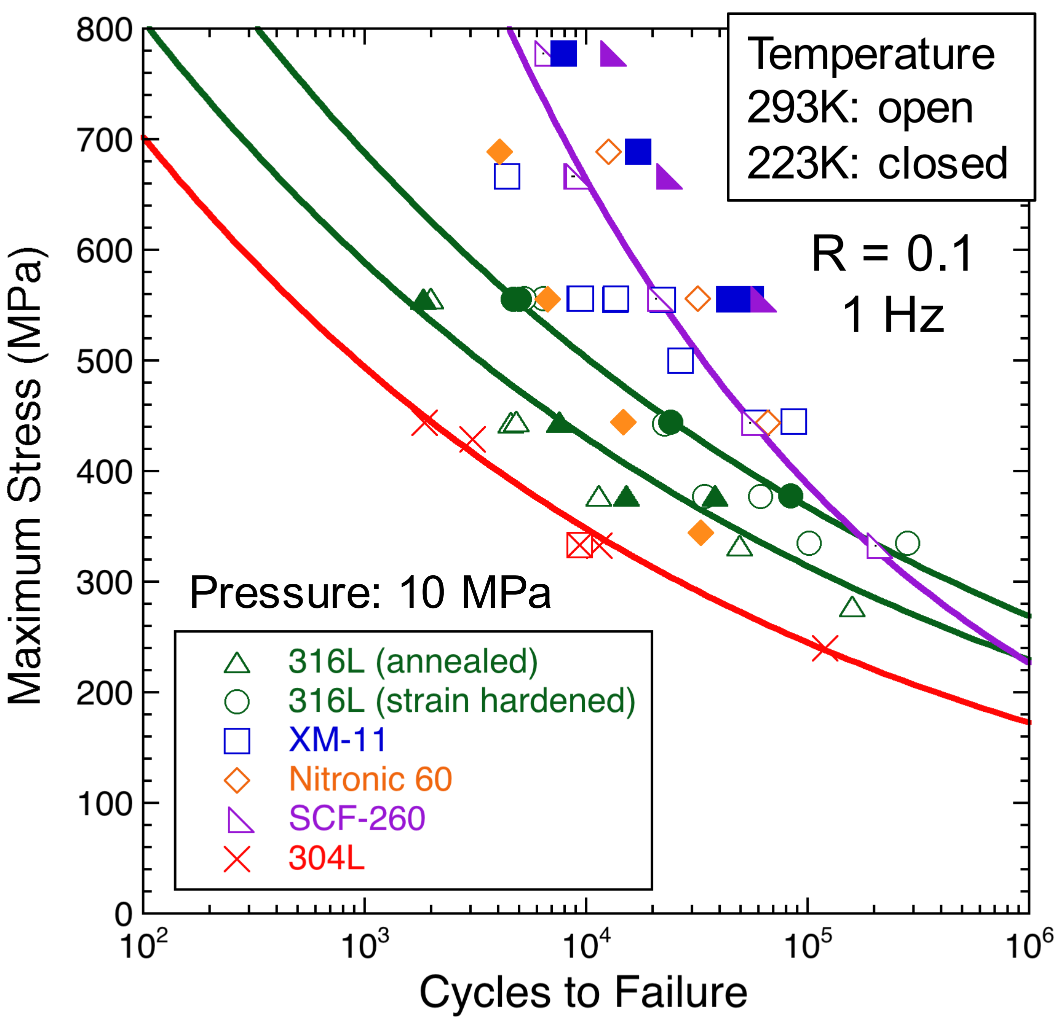
misleading



- Tensile ductility can be significantly degraded in hydrogen at low temperature
- However, tensile ductility does not represent relevant failure modes, such as subcritical cracking and fatigue

From: Caskey, Hydrogen Compatibility Handbook for Stainless Steels, 1983

Austenitic stainless steels are sensitive to H2 at low temperature *misleading*

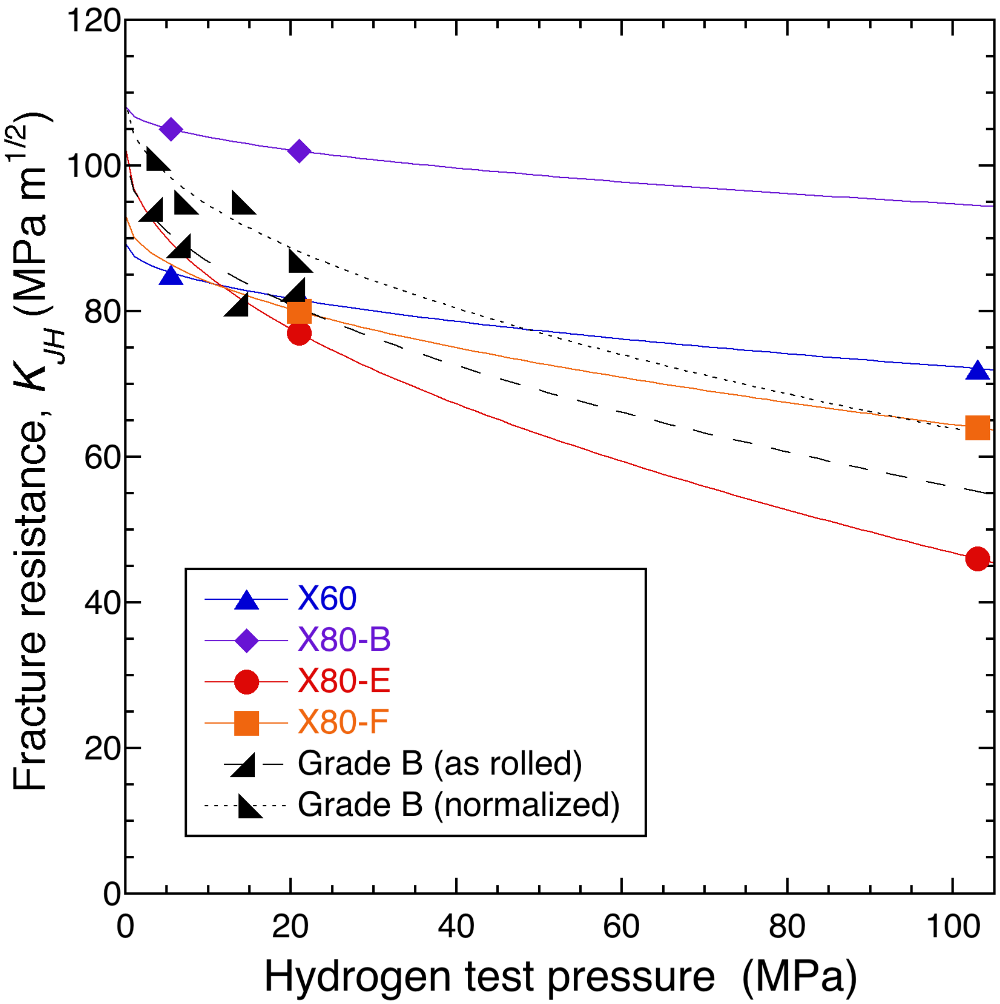


From: San Marchi et al, 43rd MPA Seminar (2017).

- **Fatigue life at low temperature is similar or greater than at RT**
- **Fracture resistance (not shown) is modestly reduced at low temperature but remains large (>100 MPa $m^{1/2}$)**

Fatigue life is not limited by low temperature performance

Low pressure H2 has negligible effect on performance of steels myth



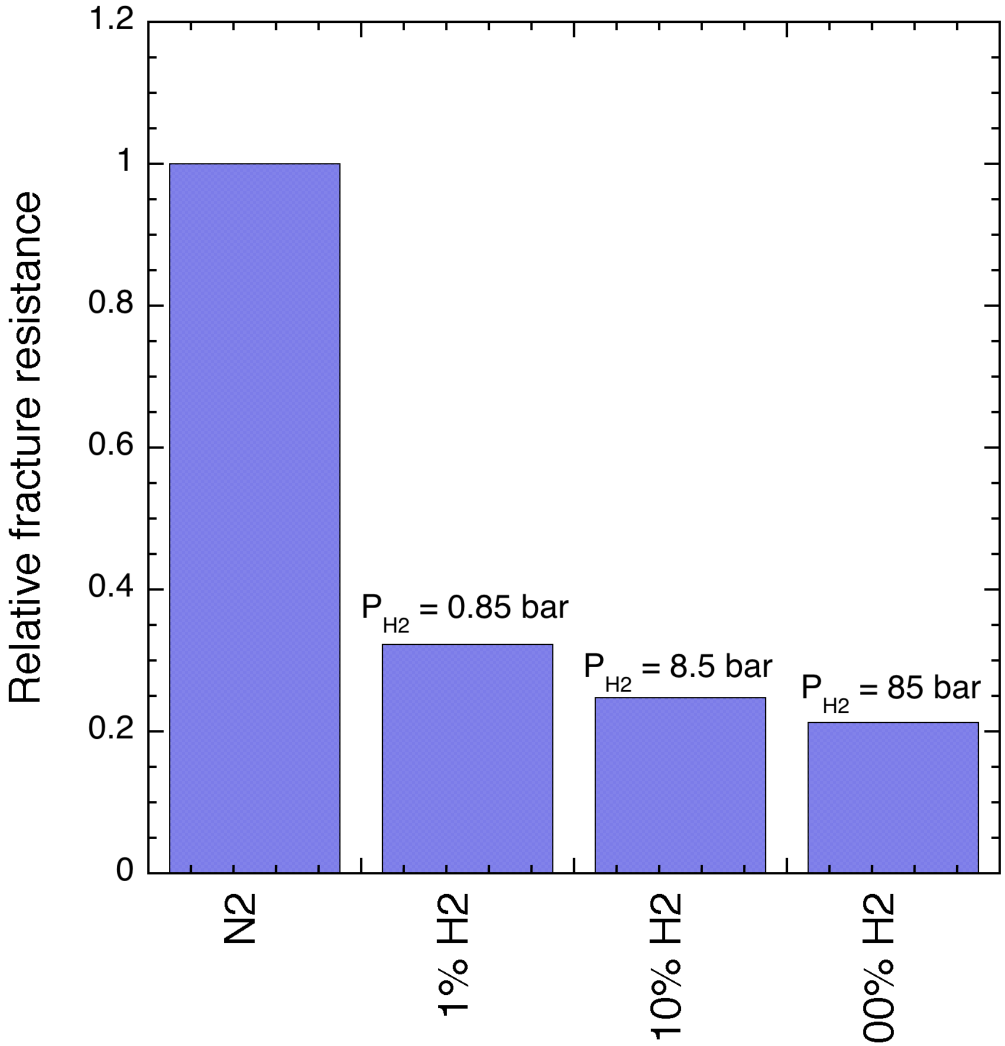
- Data sets that evaluate effect of pressure on fracture are relatively limited
- Available data suggest fracture depends on pressure
- Fracture resistance at low pressure appears to be significantly lower than in air

From: San Marchi et al, ASME PVP-2011 conf.

Sandia National Laboratories

H2FC Hydrogen and Fuel Cells Program

Low pressure H2 has negligible effect on performance of steels *myth*

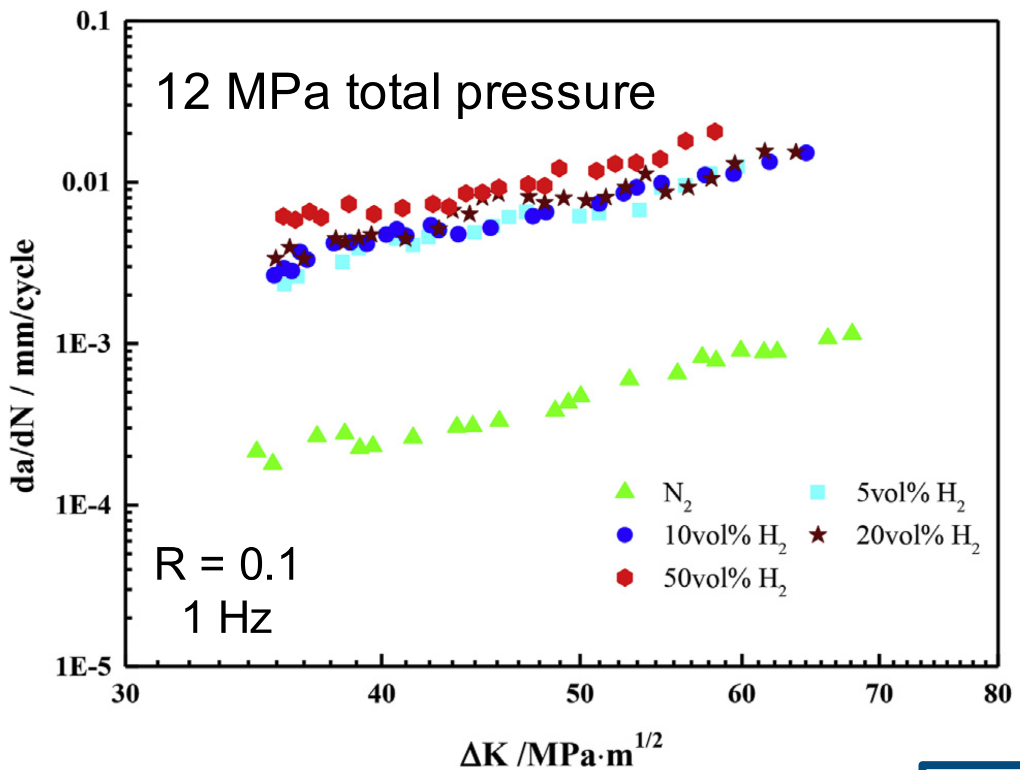


From: Briottet et al, ASME PVP-2018 conf.

- **Measurements in gaseous mixtures of H2 and N2 show substantial reduction of fracture resistance for low H2 partial pressure**
- **Only modest change in fracture resistance for P_{H2} > 1 bar**

<1 bar of H2 reduces fracture resistance

Low pressure H2 has negligible effect on performance of steels myth



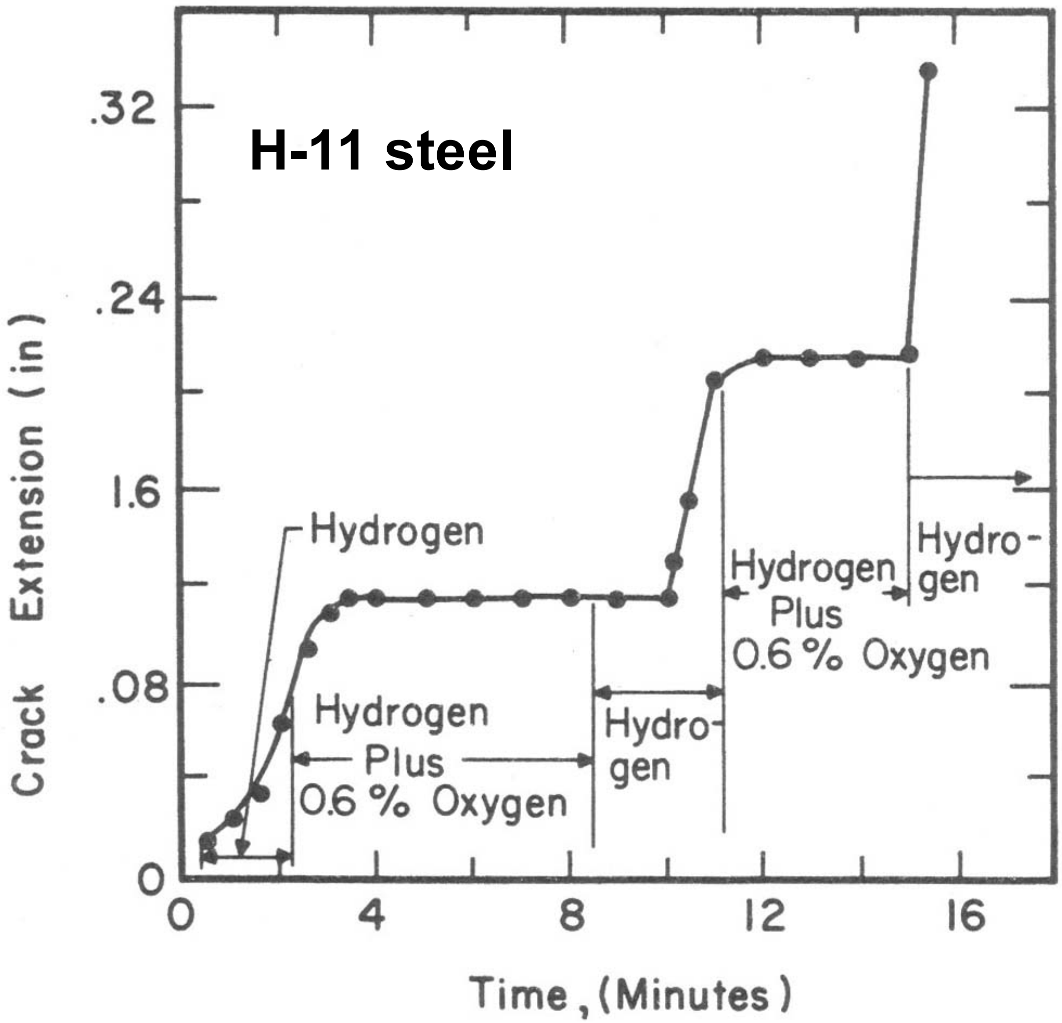
From: Meng et al, *IJ Hydrogen Energy* **42** (2017) 7404.

- **Measurements in gaseous mixtures of H2 and N2 show acceleration of fatigue crack growth rate with 5% H2**
  - **But little additional acceleration with higher H2 content**

Small amounts of hydrogen can have substantial effect on fatigue and fracture

Impurities can mitigate the effects of H2

true for some impurities



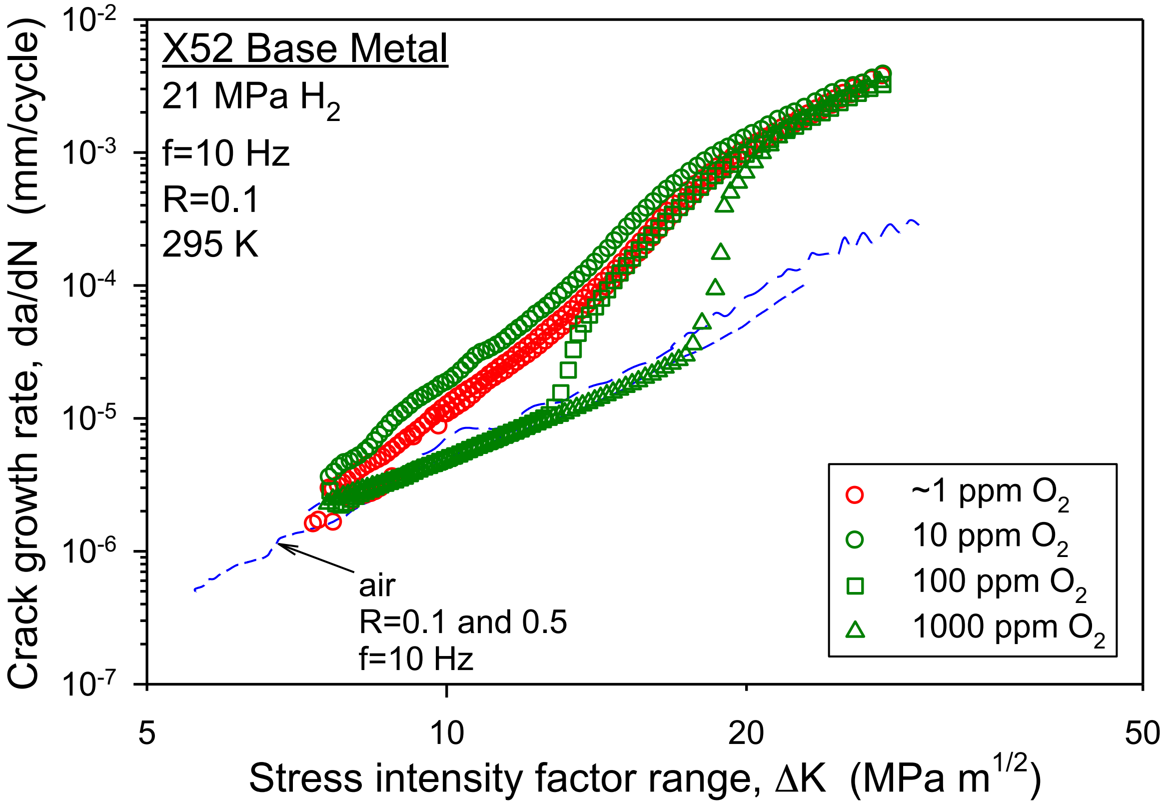
From: H.H. Johnson, Fundamental Aspects of Stress Corrosion Cracking, 1967

- **Seminal experiments show clear effect of O2 on mitigation of H2-assisted crack growth**
- **Early experiments, however, did not quantify effects on meaningful properties and relevant alloys**

Oxygen can have significant effect on crack extension in H2

Impurities can mitigate the effects of H2

true for some impurities



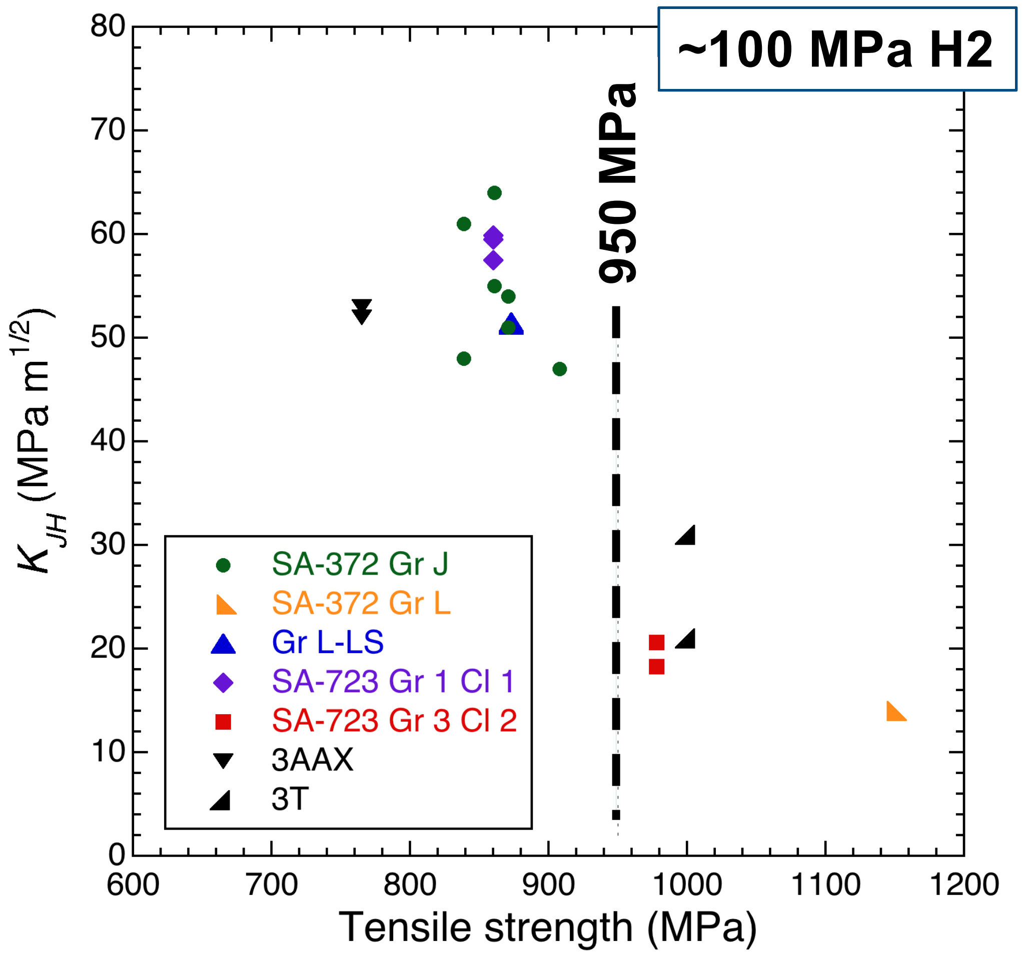
- **Oxygen mitigates H2-accelerated fatigue crack growth rates at low ΔK**
- **Attributed to oxygen diffusion to new crack surfaces**

From: Somerday et al, *Acta Mater* **61** (2013) 6153.

Impurity content in H2 can have substantial effects on both measurements and in-service performance

High-strength steels have low fracture resistance in gaseous H2

generally true

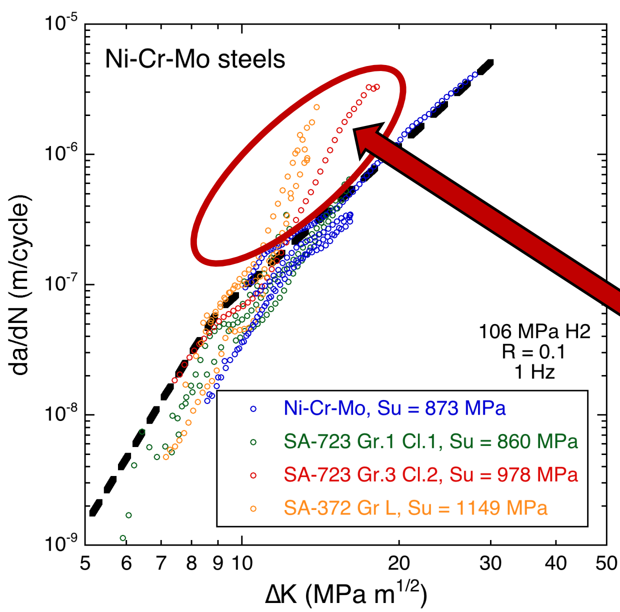


- **Pressure vessel steels display low fracture resistance in H2 when tensile strength >950 MPa**
  - **Cr-Mo and Ni-Cr-Mo quench and tempered low alloy steels**
  - **Low fracture resistance will affect fatigue performance at high ΔK**

Low-alloy steels with >950 MPa tensile strength are not recommended for H2 service

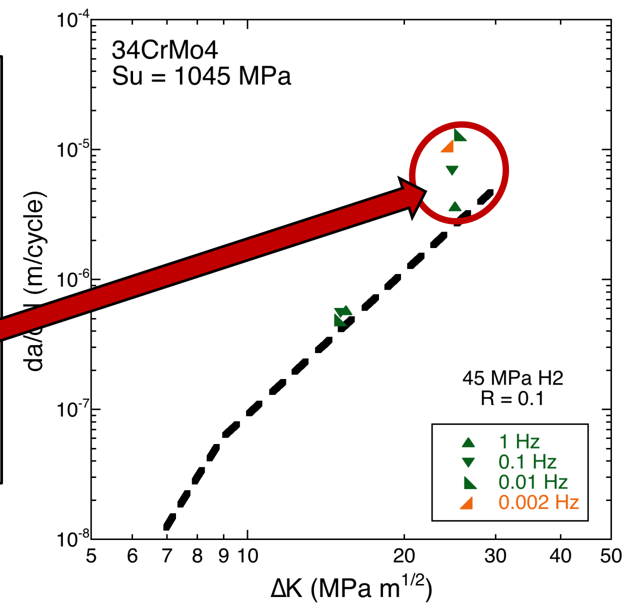
High-strength steels have low fracture resistance in gaseous H2 *generally true* *& impacts fatigue*

- **High-strength steels also show transition to accelerated crack growth (*eg*, stage III) related to baseline H2 behavior**
  - **only observed in tests of high-strength steels: tensile strength > 950 MPa**
  - **Related to K_{max} in fatigue approaching fracture resistance**



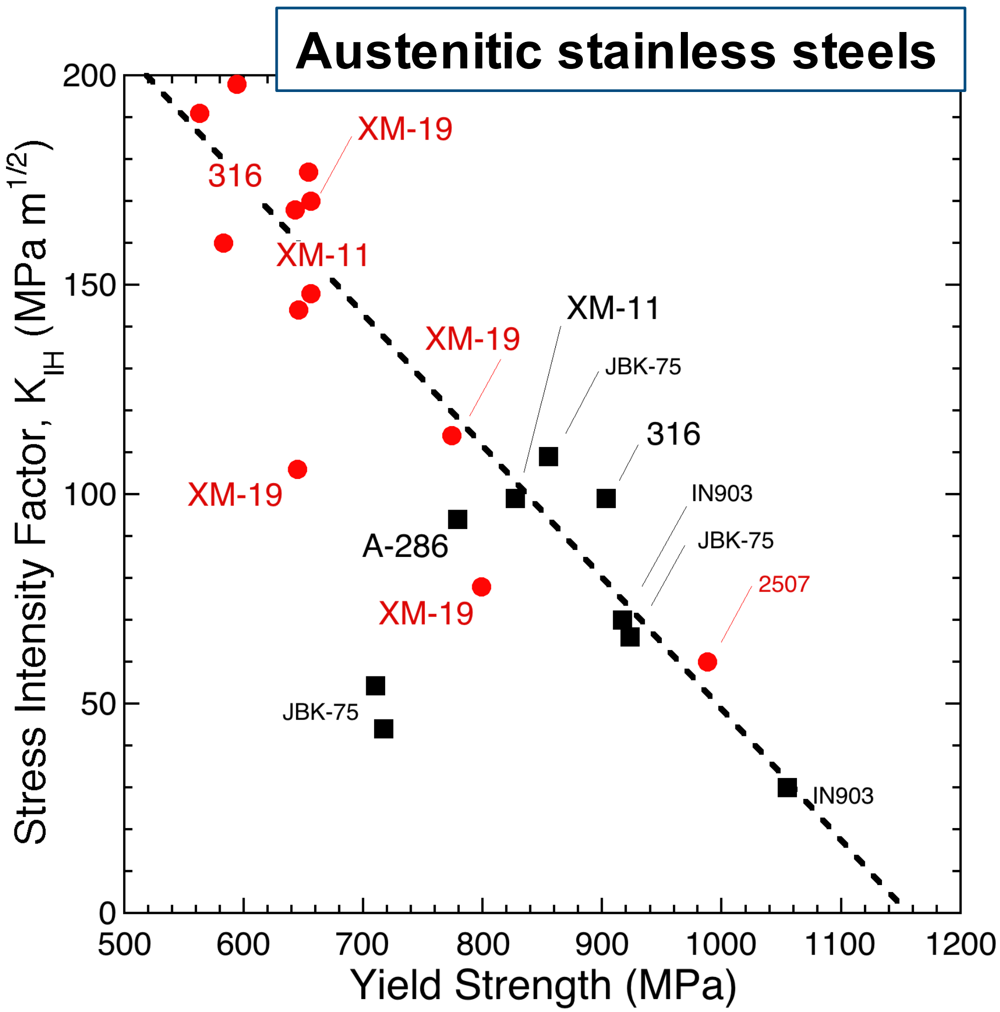
For PV steels with Su > 950 MPa

- Accelerated fatigue crack growth rate is observed
- K_{JH} ~ 20 MPa m$^{1/2}$



High-strength steels have low fracture resistance in gaseous H2

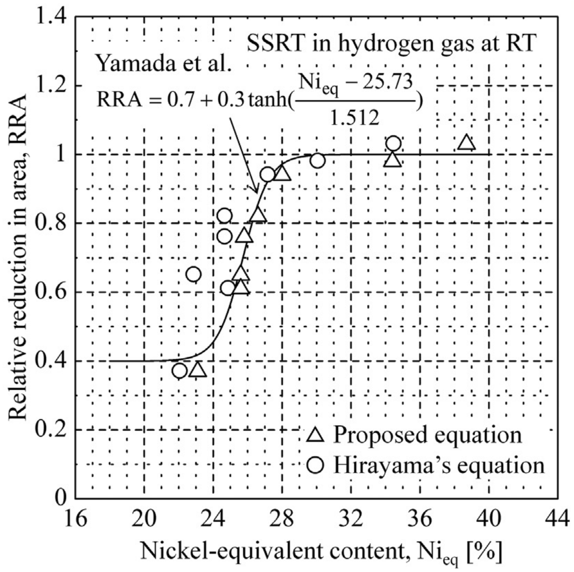
generally true



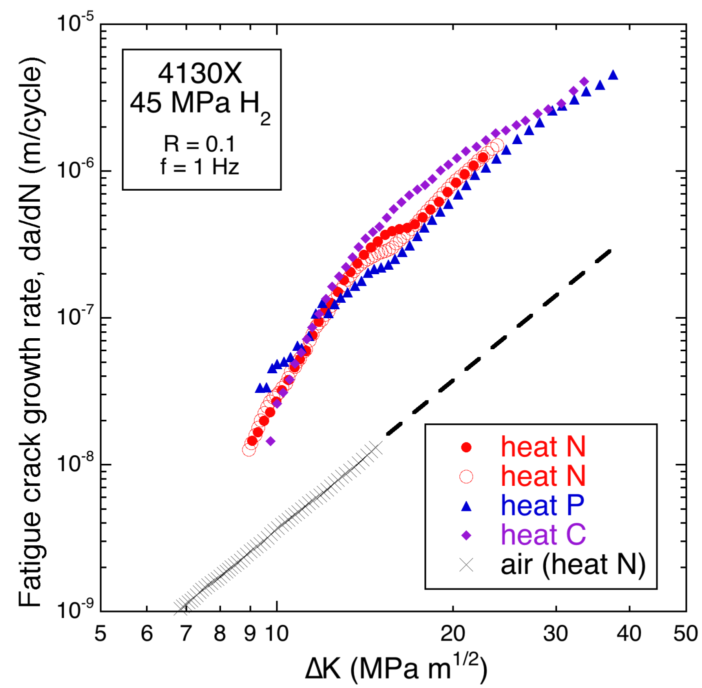
- **For austenitic stainless steels, fracture resistance is a consistent function of yield strength**
  - **However, data is limited in gaseous H2**
- **SS alloys with YS <700 MPa display high fracture resistance in H2 environments**

Austenitic stainless steels appear to maintain high fracture resistance (>50 MPa m$^{1/2}$) in H2

Suitability for H2 service can be assessed with slow strain rate tensile (SSRT) tests in H2 myth



- Strength properties are generally not changed in H2
- Tensile ductility may be reduced H2, although reduction does not equate to lack of fitness for service



- Suitability for H2 service depends on materials that express design properties that are sufficient for the required service environment
  – Usually fatigue and fracture properties

The role of impurities and mixed gas environments should be considered carefully

- Oxygen can mitigate effects of H2 in ferritic steels
  - But sensitive to mechanical and environmental variables
  - Other passivating species can have similar effects
- Water can enhance effects of H2 in aluminum alloys
  - Threshold content is not known
- Nitrogen is inert, natural gas may not be inert
  - NG has many impurities, which aid mitigation of H2 effects
  - Pure methane is inert and does not change effects of H2

Materials performance in hydrogen or mixed hydrogen-containing gas streams will depend sensitively on *materials*, *environmental* and *mechanical* variables

Materials requirements depend on the application and the design

Conclusions

- Materials
  - H2 effects are sensitive to microstructure *more myth than fact*
  - Austenitic stainless steels can be immune *misleading*
  - Aluminum alloys are immune *seemingly true but misleading*
- Environment
  - Stainless steels are sensitive to H2 at low temp *misleading*
  - Low pressure H2 has negligible effect on performance *myth*
  - Impurities can mitigate effects of H2 *true for some impurities*
- Mechanics
  - High-strength alloys have low fracture resistance *generally true*
  - Suitability for H2 service can be assessed with tensile tests *myth*