SAND2017-8212PE

Discussion Topics: Study Group on Materials Testing and Qualification for Hydrogen Service

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Waikoloa Hawaii

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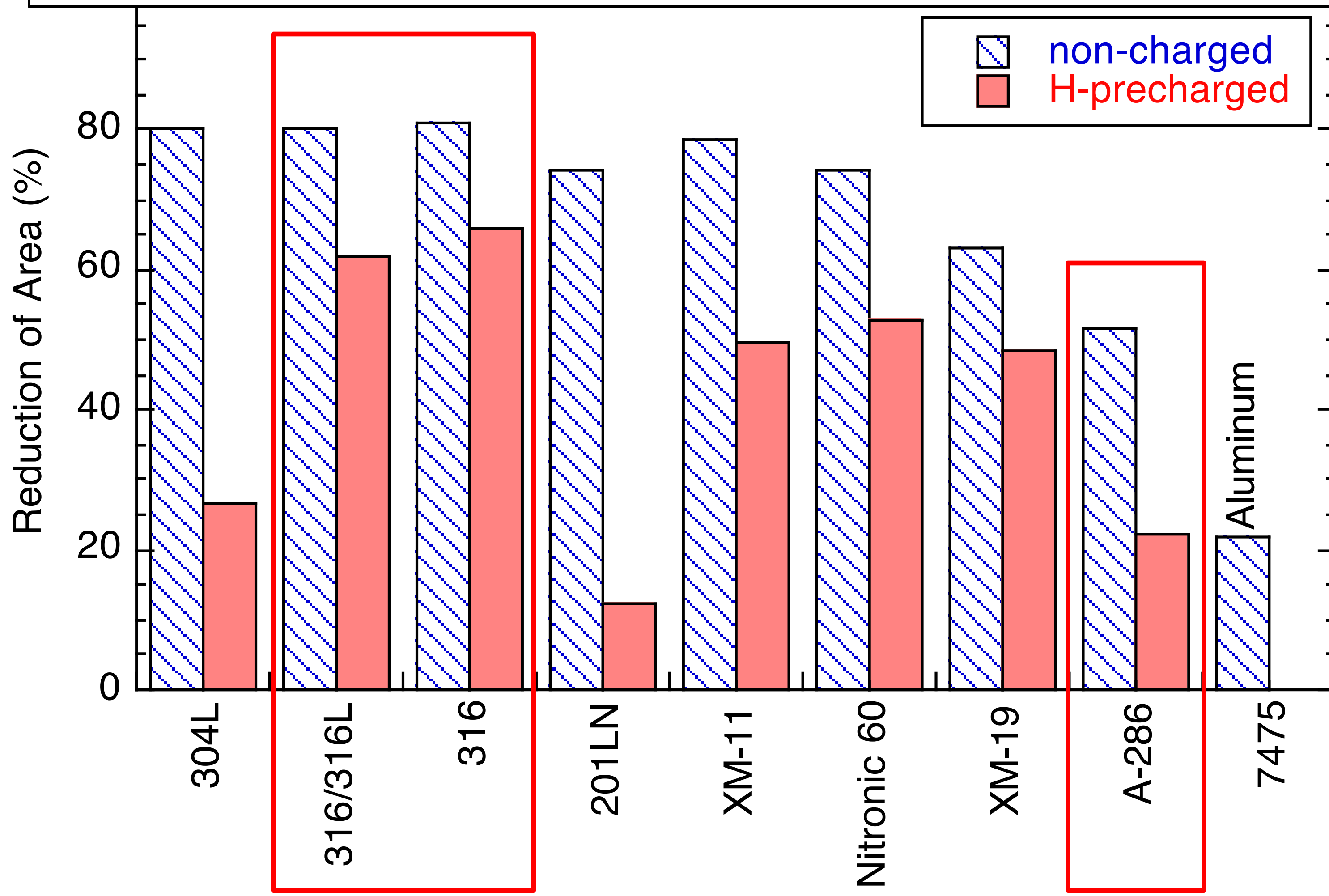
Why are materials such as 304L and XM-11 not considered for hydrogen service?

Tensile ductility for a variety of austenitic stainless steels



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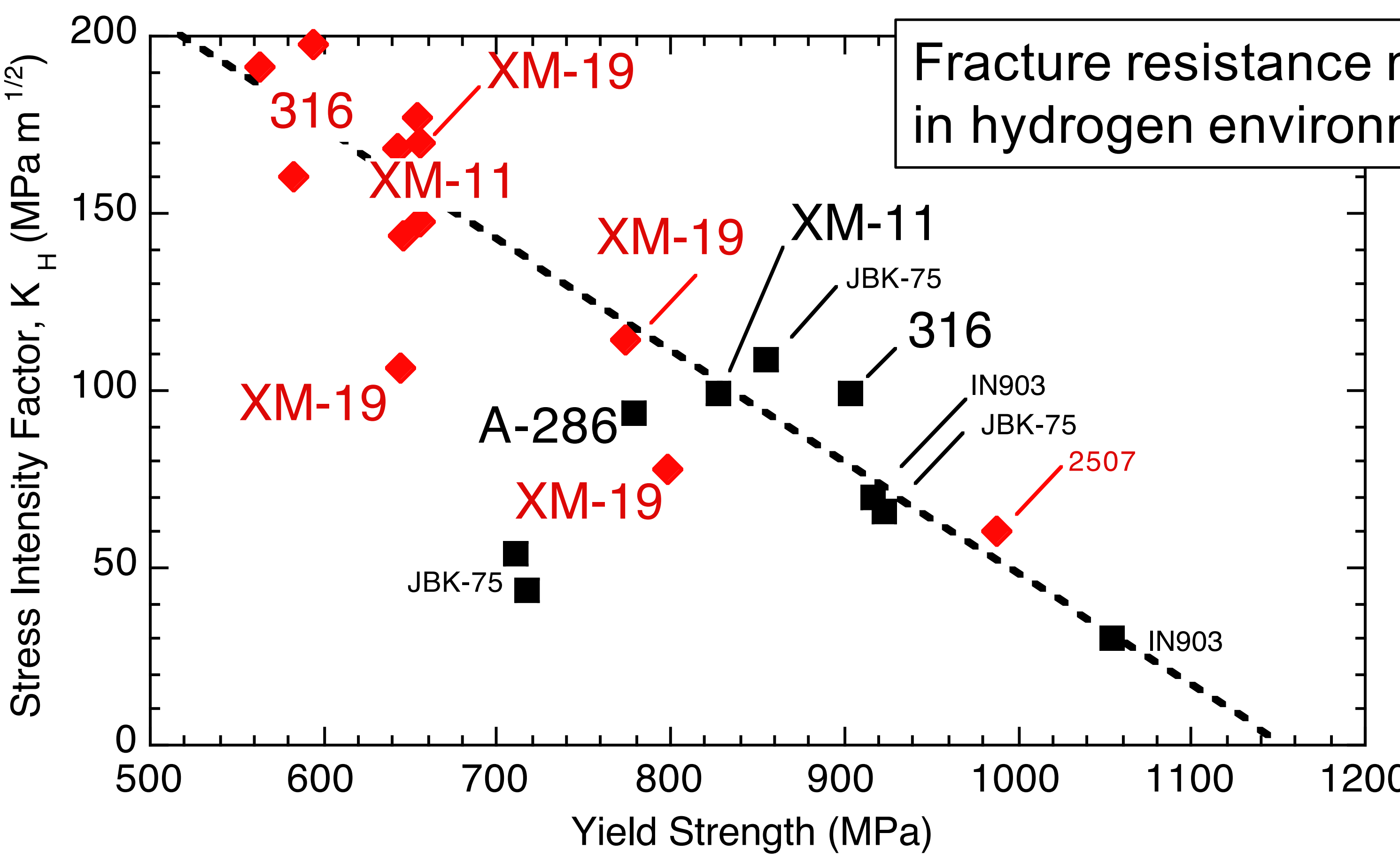
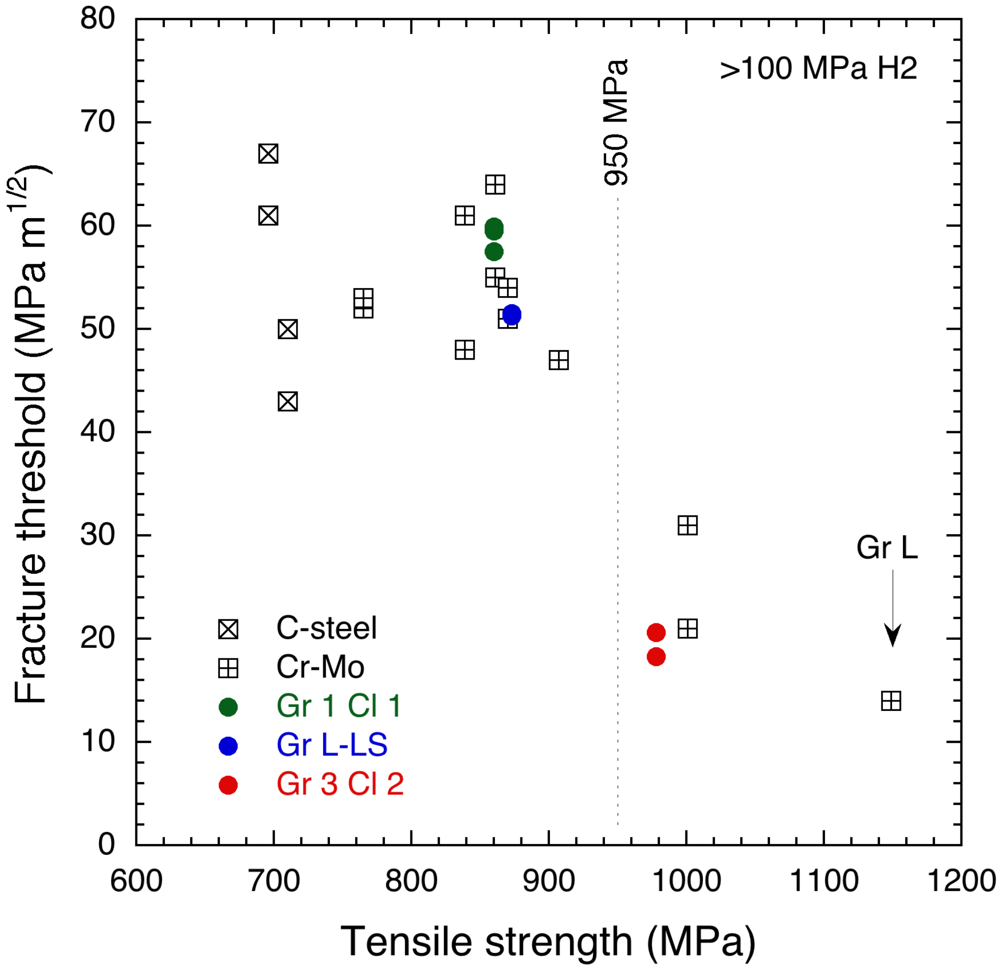
H_2FC Hydrogen and Fuel Cells Program

Fracture resistance of austenitic stainless steel is dependent on strength and microstructure (not necessarily composition)

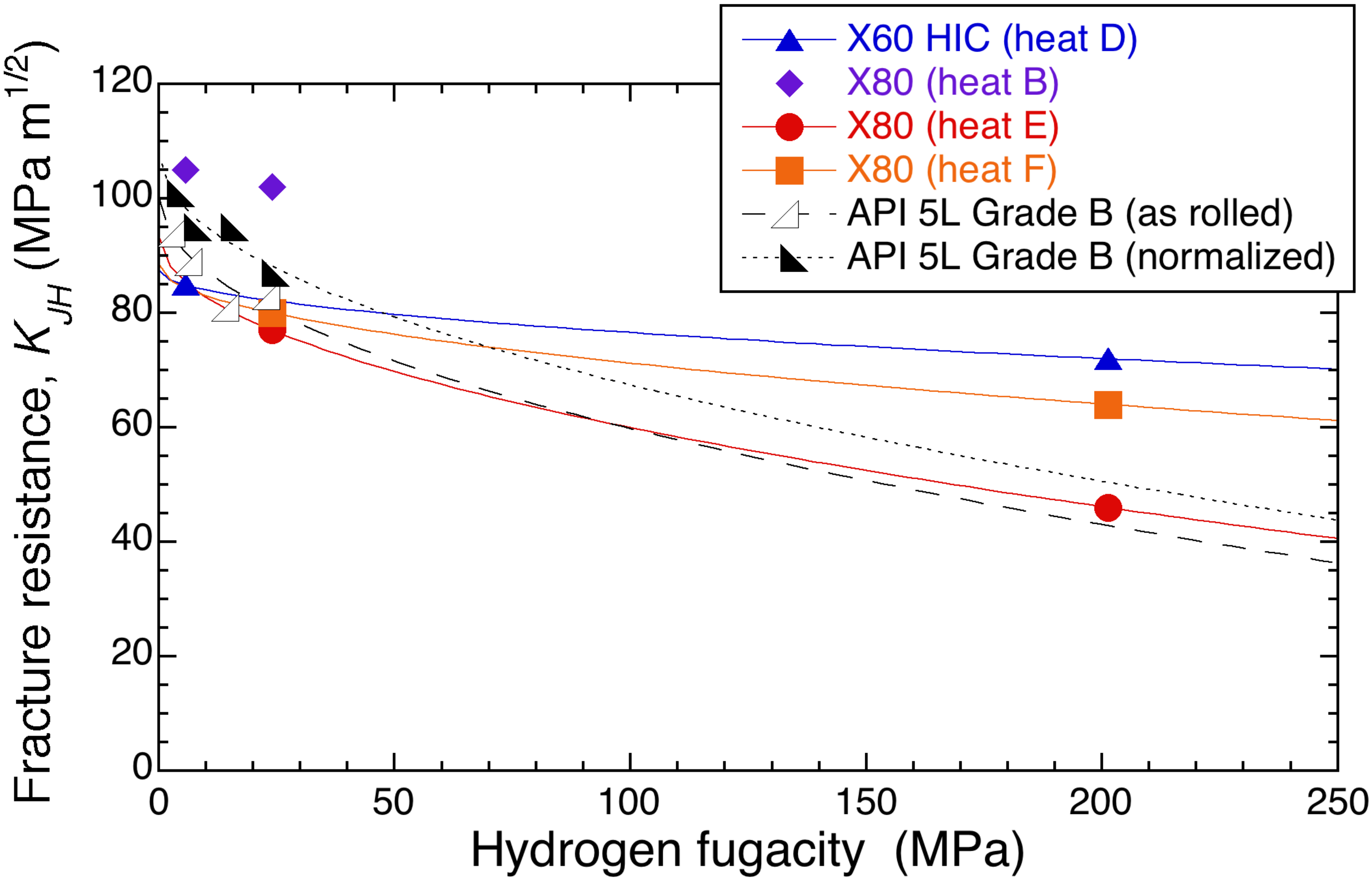
Fracture resistance measured in hydrogen environments



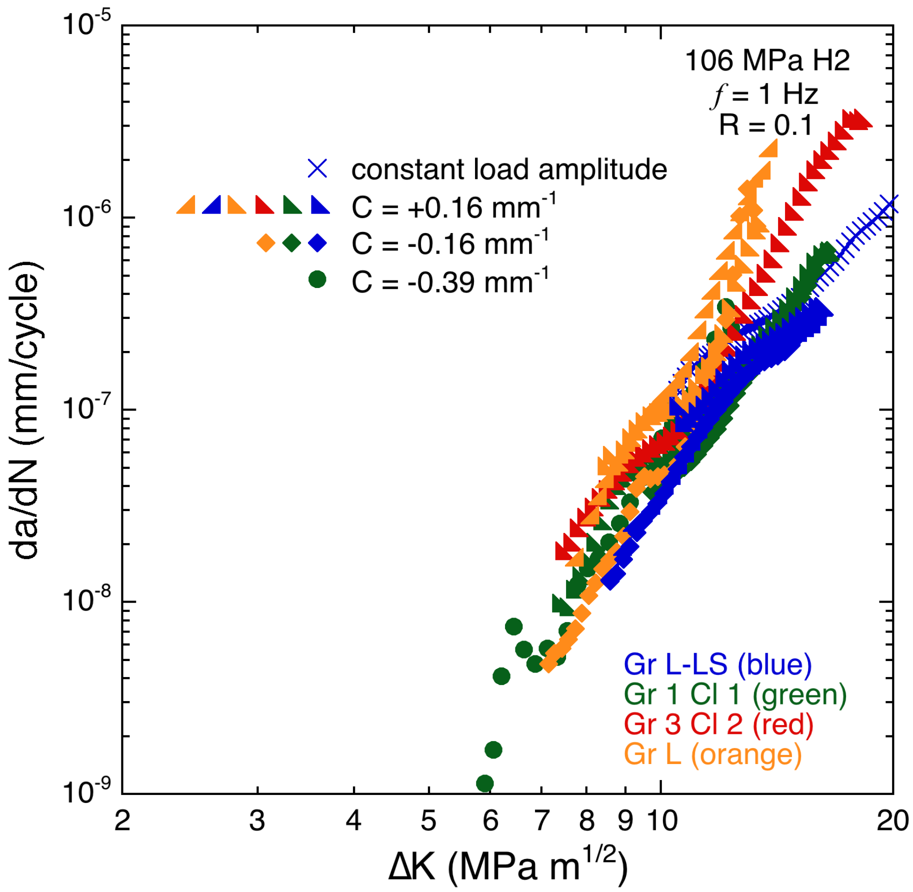
Fracture resistance of steels shows a steep transition in fracture resistance

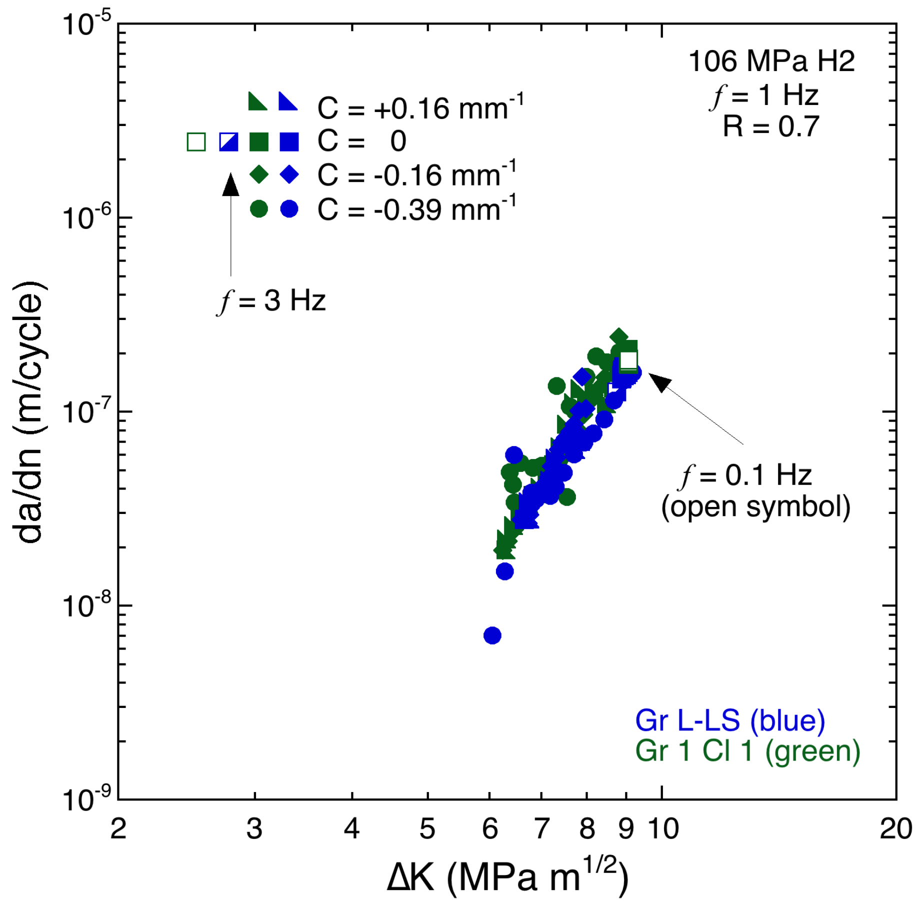


Fracture resistance of steels is dependent on pressure



Low strength steels tend to show very similar fatigue crack growth rates in gaseous hydrogen





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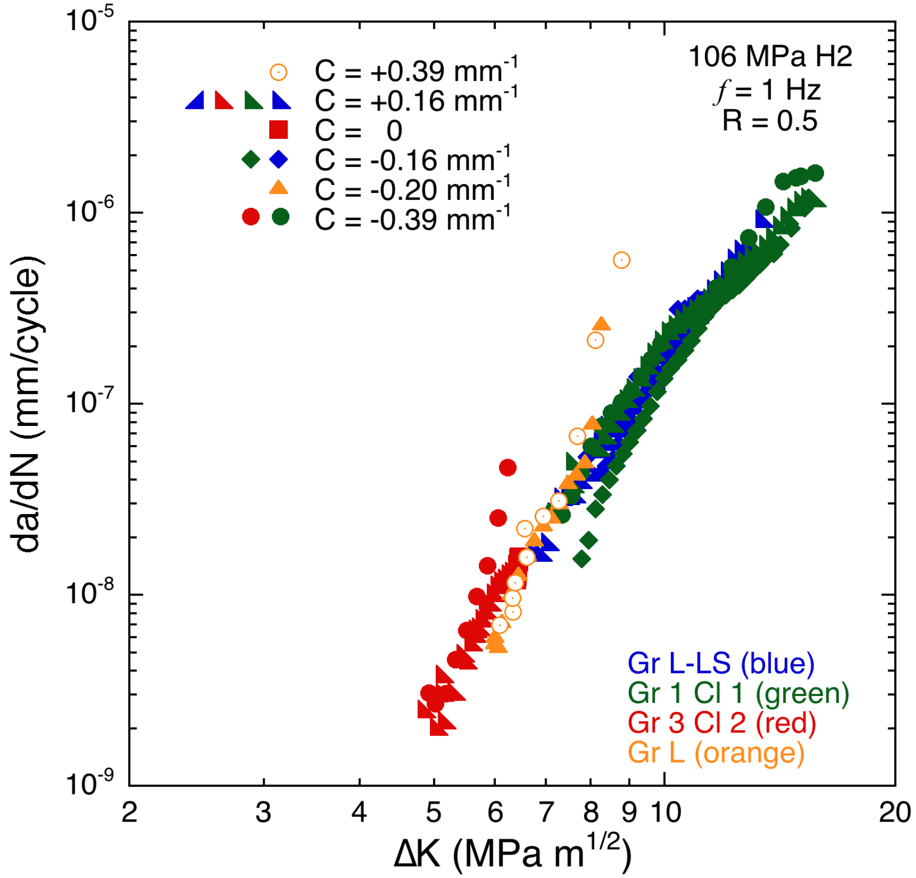
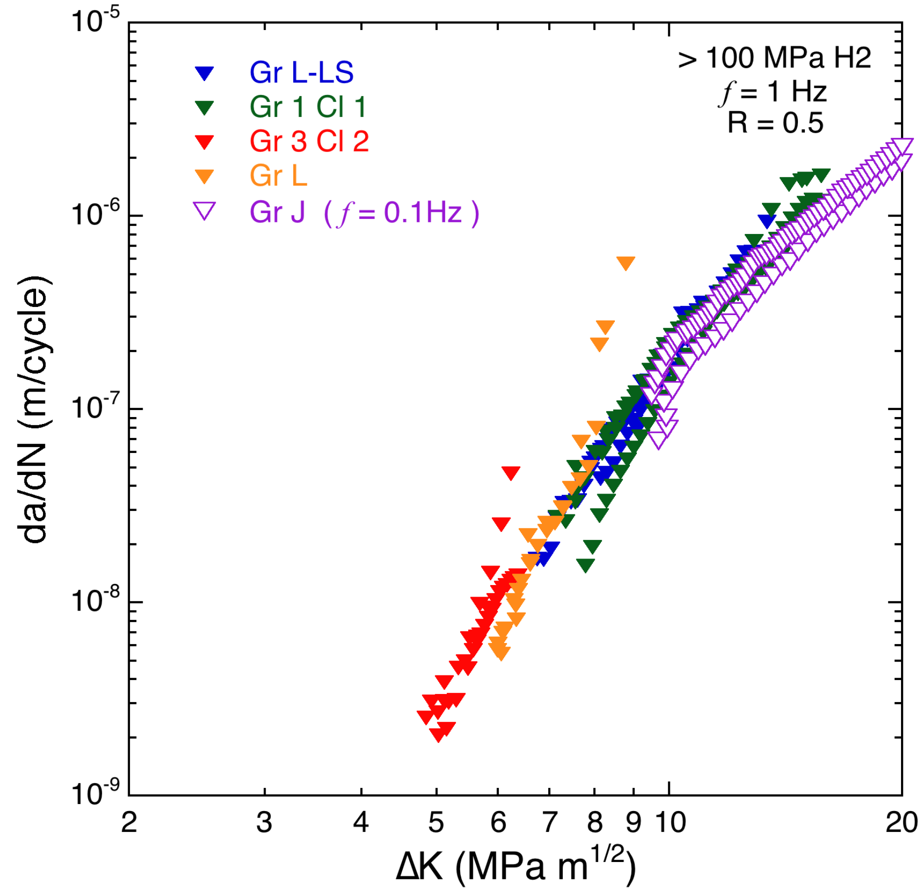
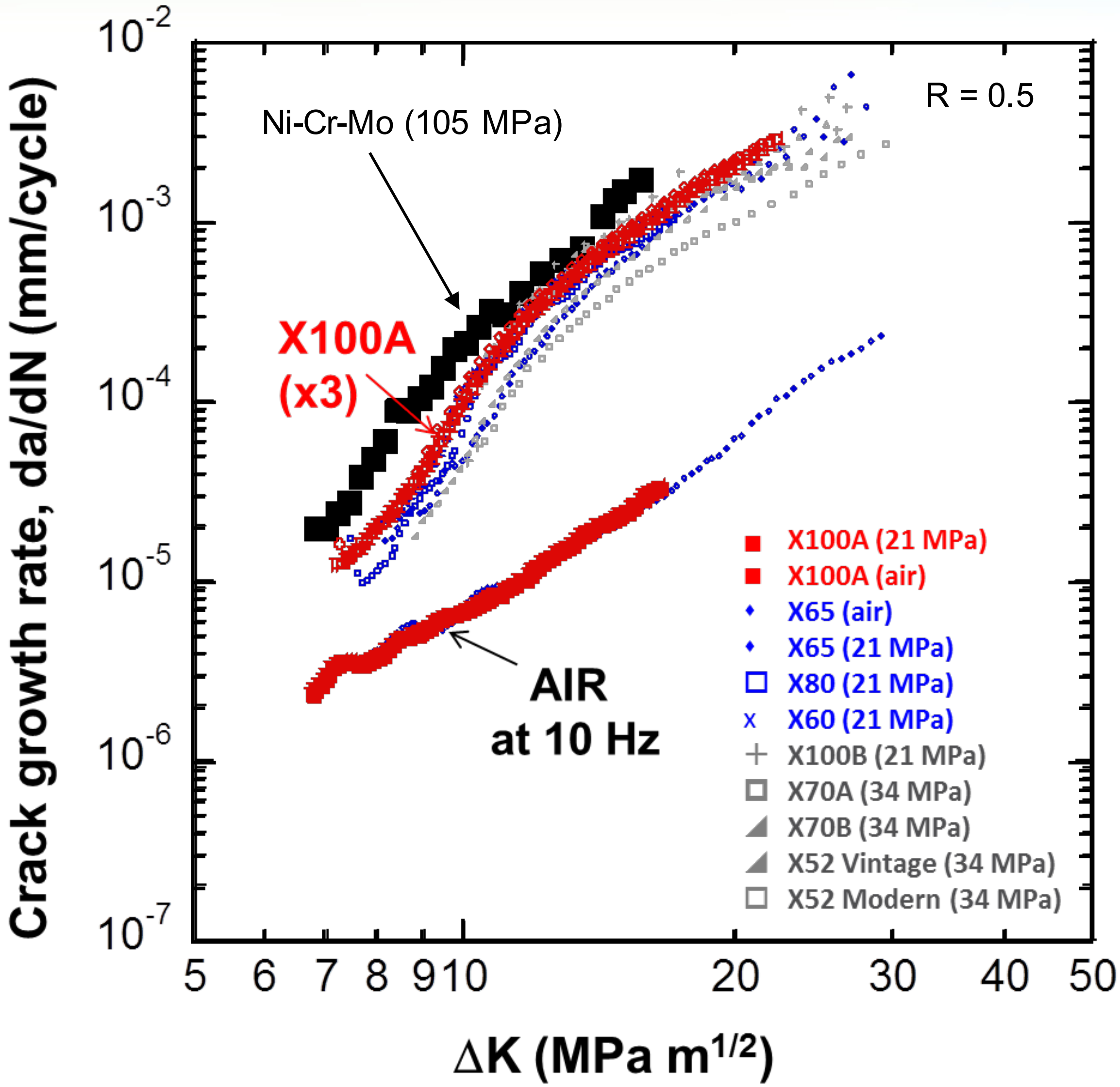




Low strength steels tend to show very similar fatigue crack growth rates in gaseous hydrogen



- A wide variety of pipeline steels display nominally the same fatigue response as HSLA steels
- The effect of pressure on fatigue is generally within the scatter
- Lack of data at low ΔK
  - *the majority of the life of small cracks occurs at low ΔK*

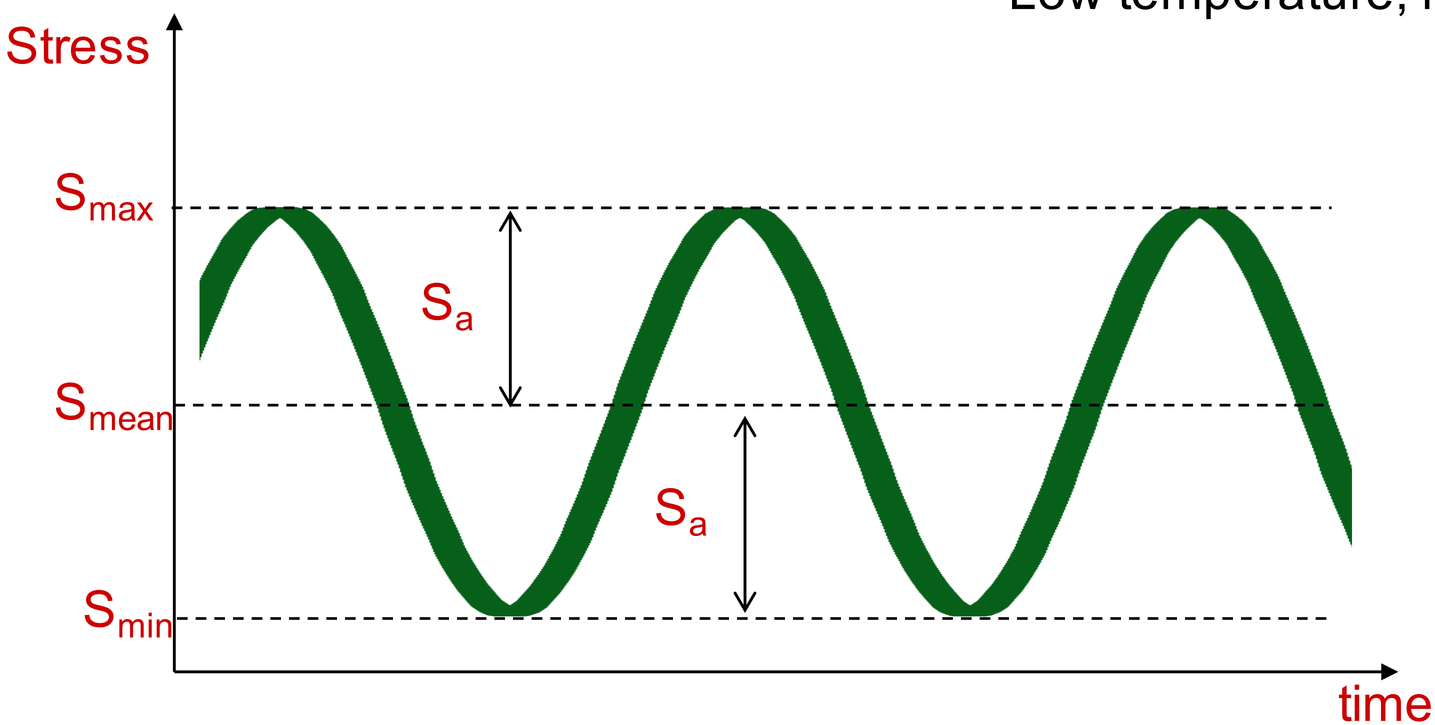
Fatigue life methodology assesses relevant hydrogen-related susceptibilities

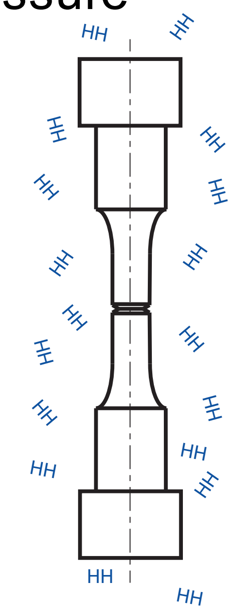
Conventional fatigue life testing

- "smooth" specimens
- Fully reversed loading (R = -1)
- Strain-based for low cycle

Representative fatigue life testing

- "notched" specimens
- Tension-tension loading (R = 0.1)
- Constant stress amplitude (stress-based)
- Low temperature, high pressure





$R = S_{min} / S_{max}$

$S_{max} = 2S_a/(1-R)$

Fatigue loading for pressure applications

Rationale:

- **R > 0** (tension-tension)
  - Simulates loading configuration for most balance-of-plant applications (tubing, valves, etc)
- **Notch**
  - Simulate stress concentration

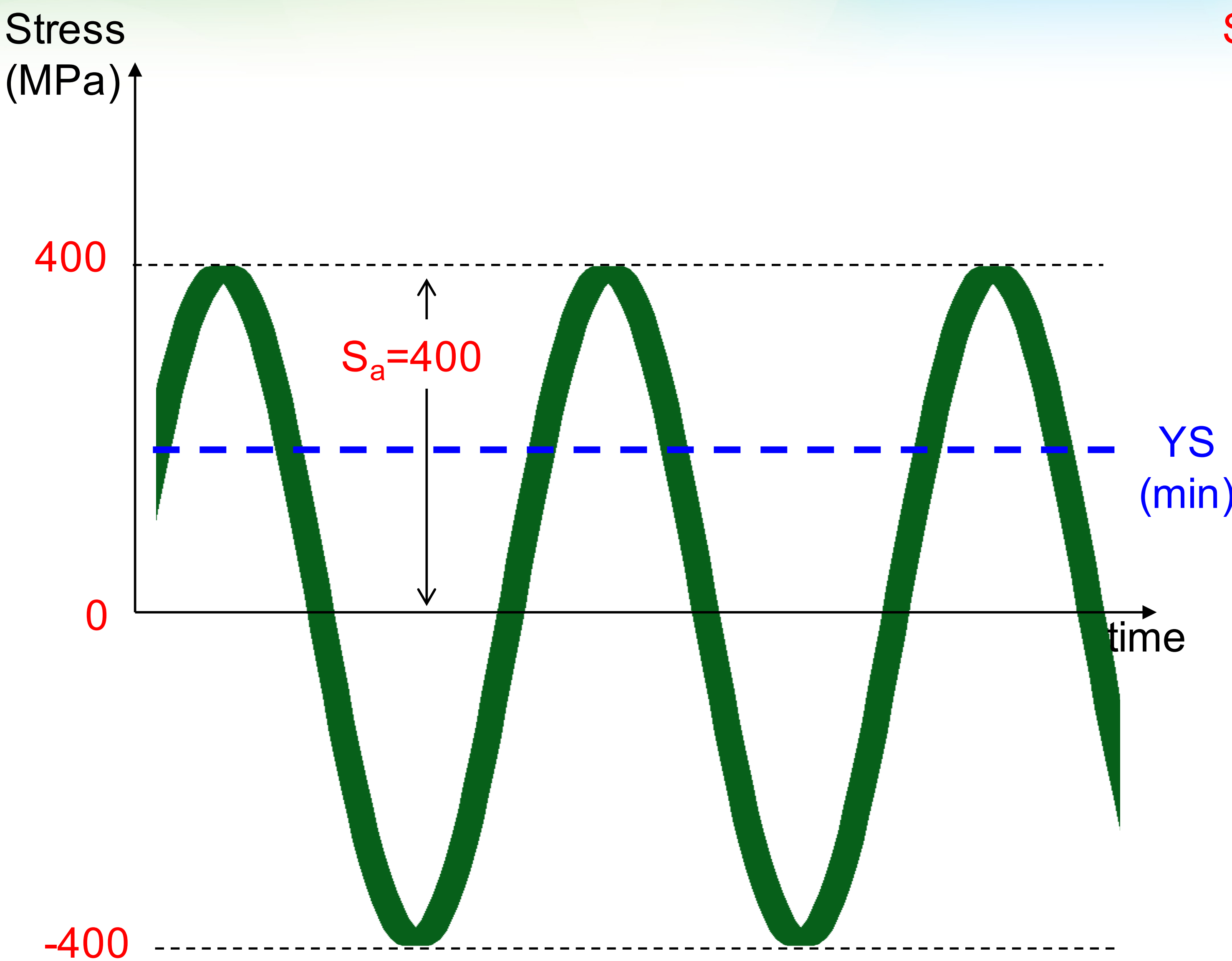
Practical considerations for notched tension-tension fatigue testing:

- Method is standardized in CSA CHMC1
- **R > 0**
  - Facilitates testing in high-pressure environments
  - Enables stress-based testing (alternative is strain-based testing)
- **Notch**
  - Necessary for fatigue failure at low stress amplitude

Load cycle: smooth configuration

$R = S_{min} / S_{max}$

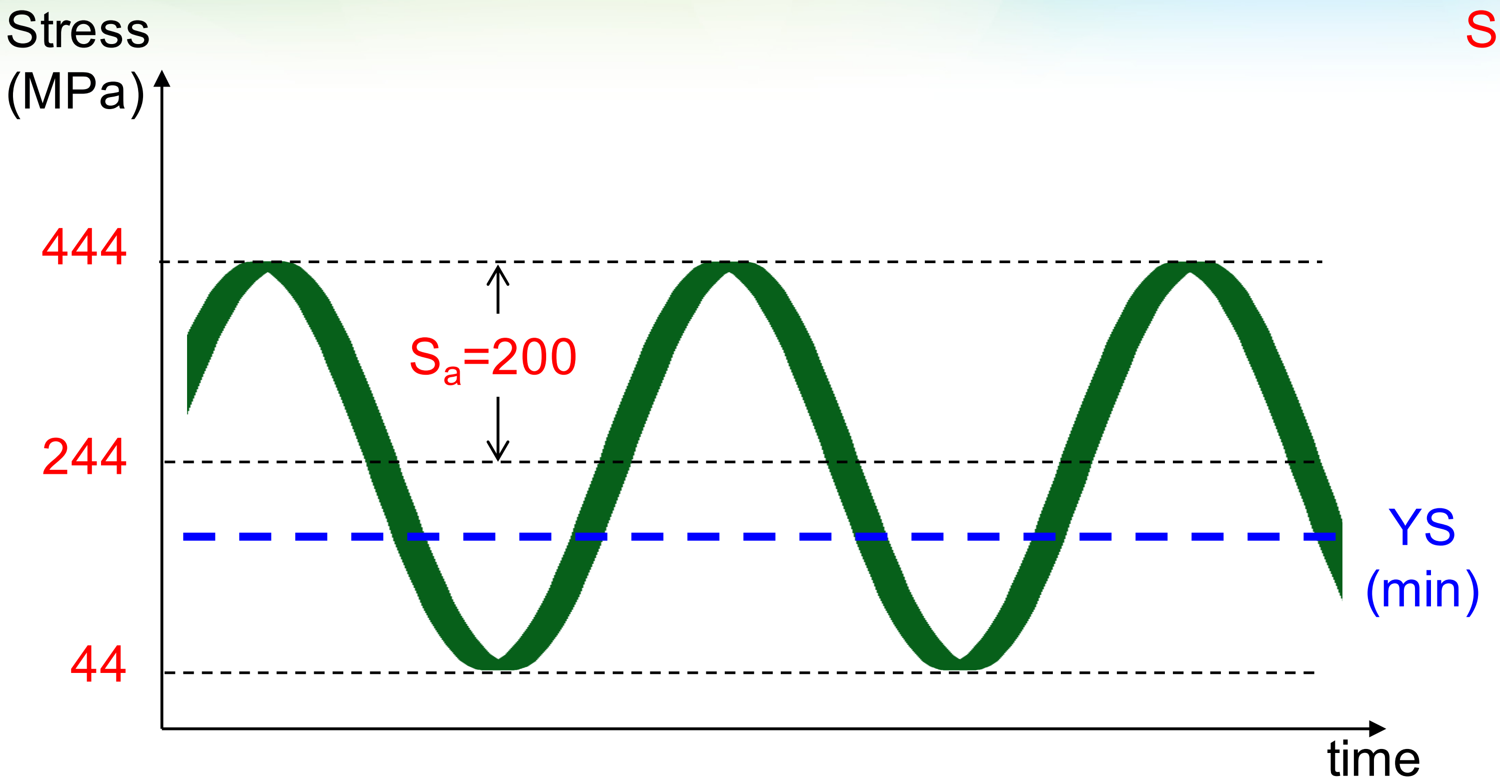
$S_{max} = 2S_a/(1-R)$

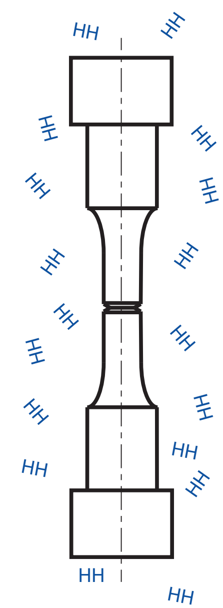


Load cycle: notched configuration

$R = S_{min} / S_{max}$

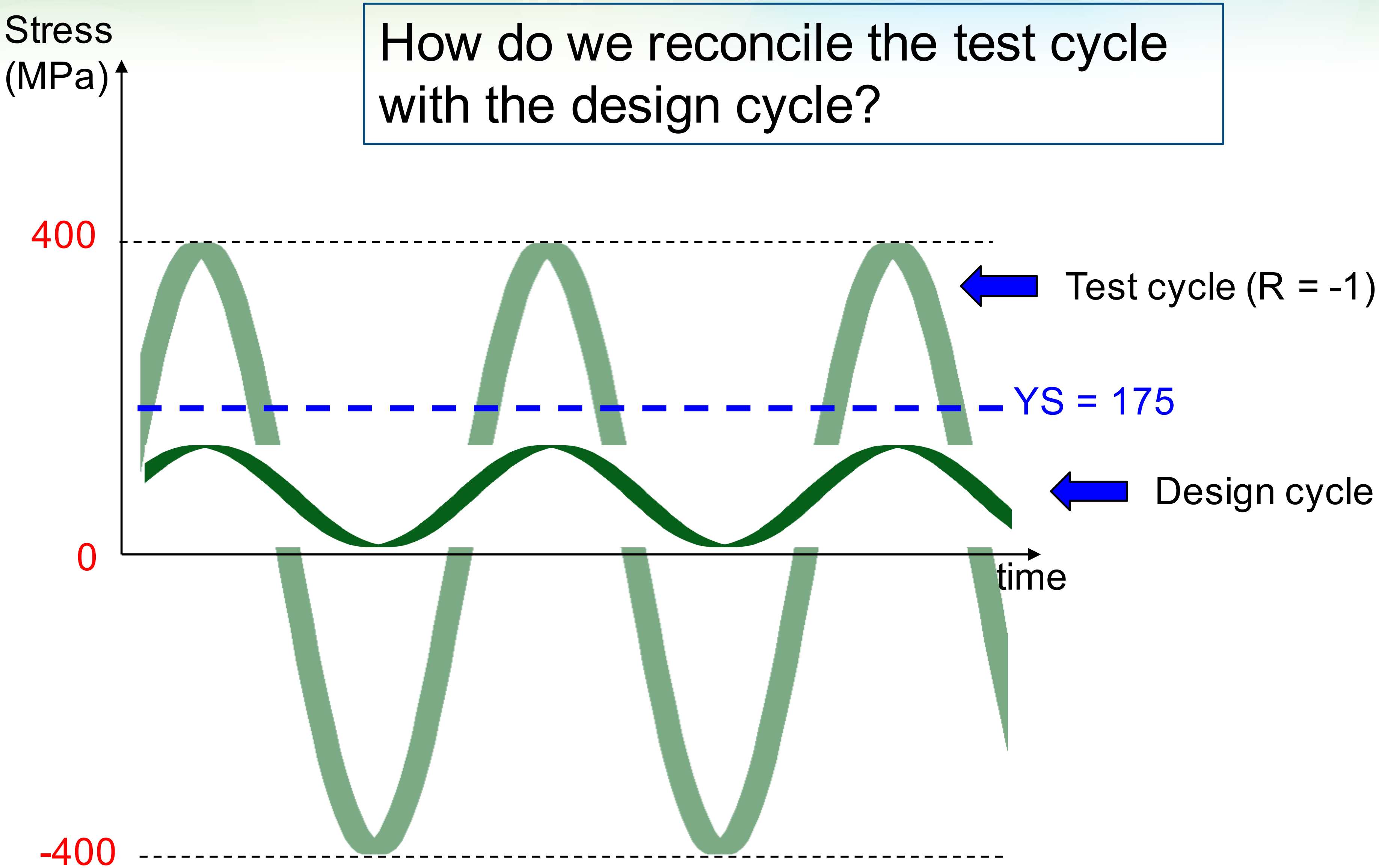
$S_{max} = 2S_a/(1-R)$





Performance vs testing requirements

How do we reconcile the test cycle with the design cycle?

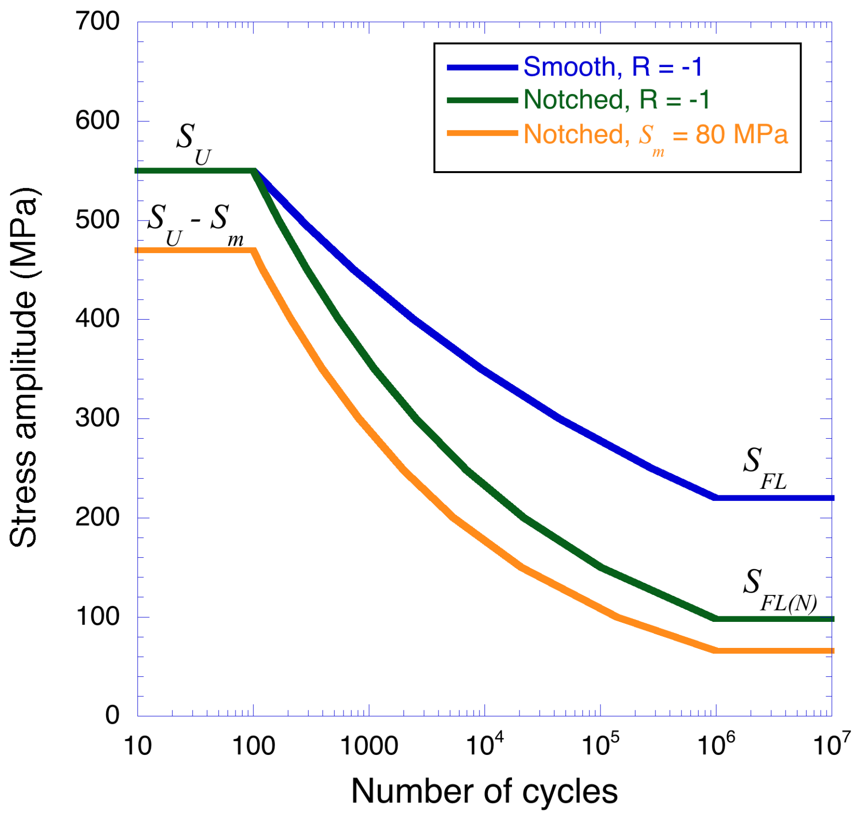


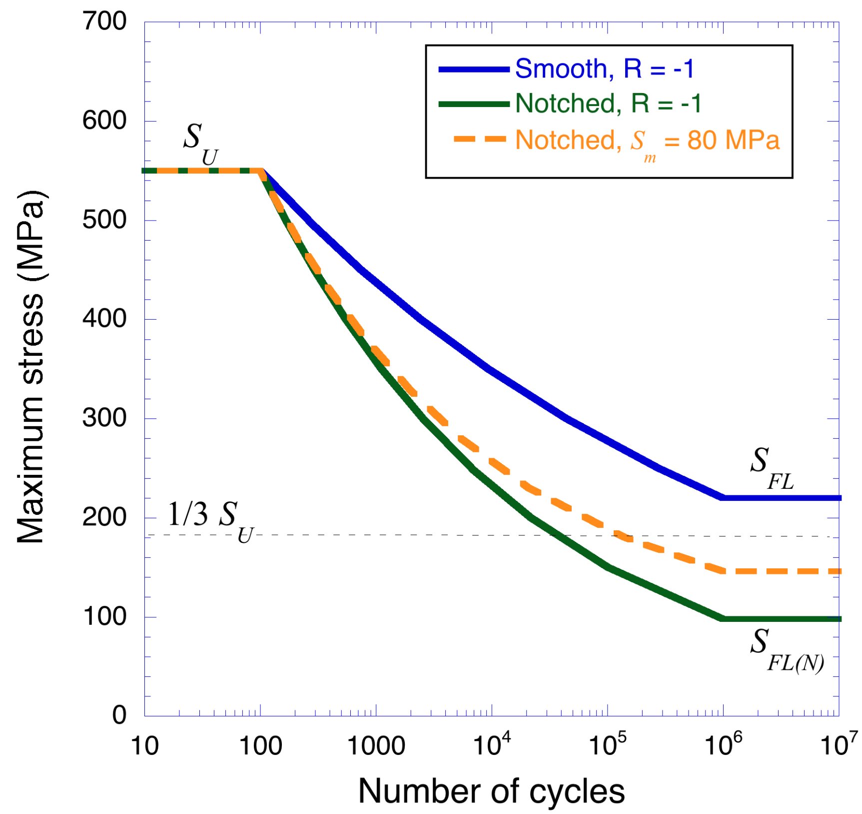
Estimated S-N curves for characteristic stainless steel

- S_U = 550 MPa
- S_{FL} = 220 MPa (40% S_u)
- Notched response derived from smooth curve with K_f = 2.25

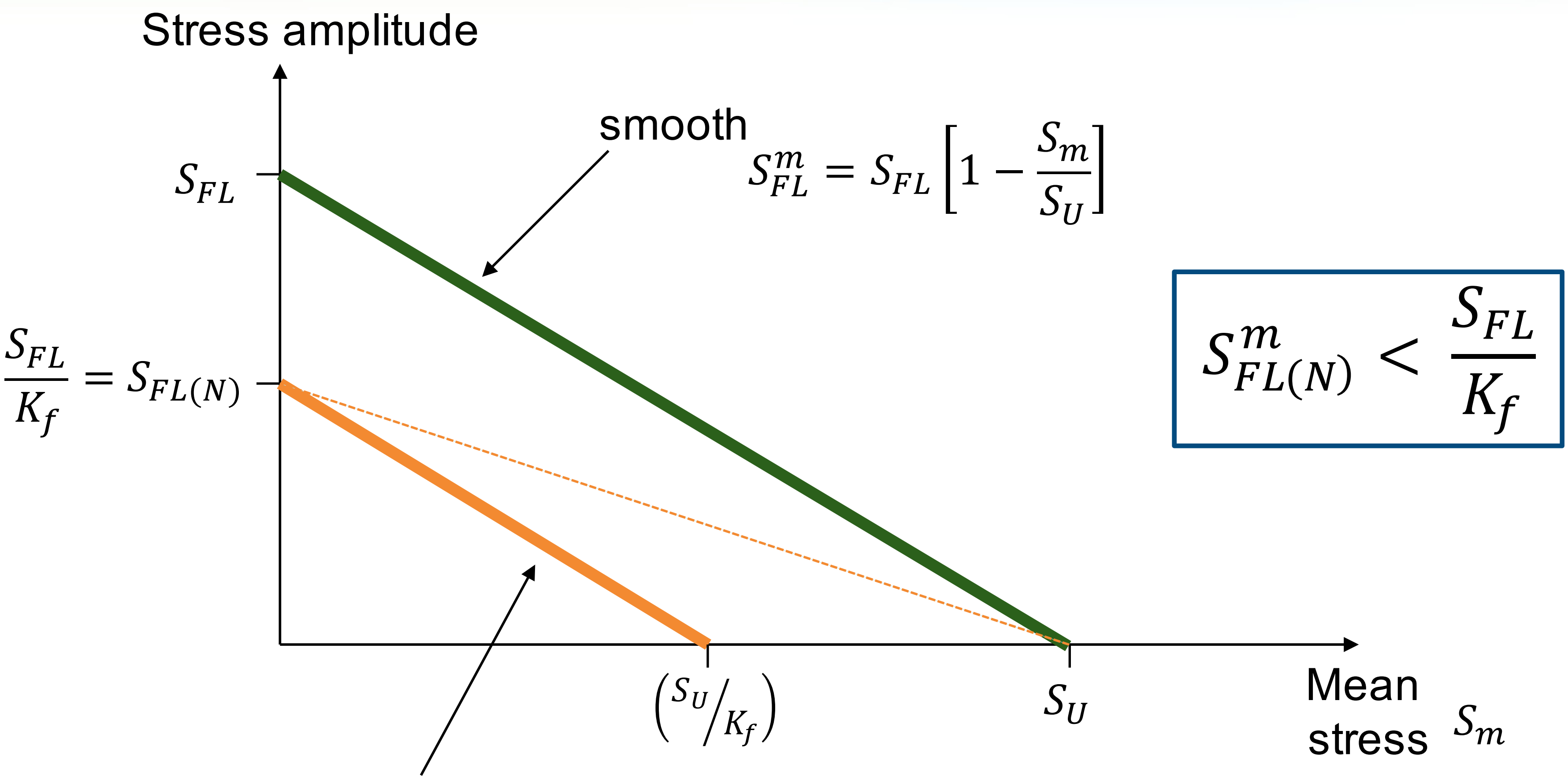
- Constant S_m = 80 MPa
  - R = 0.1 (at N = 10^6 cycles)

$$S_{FL(N)} = \frac{S_{FL}}{K_f} \qquad S_{FL(N)}^m = S_{FL(N)}\left[1 - \frac{S_m}{\left(S_U/K_f\right)}\right]$$





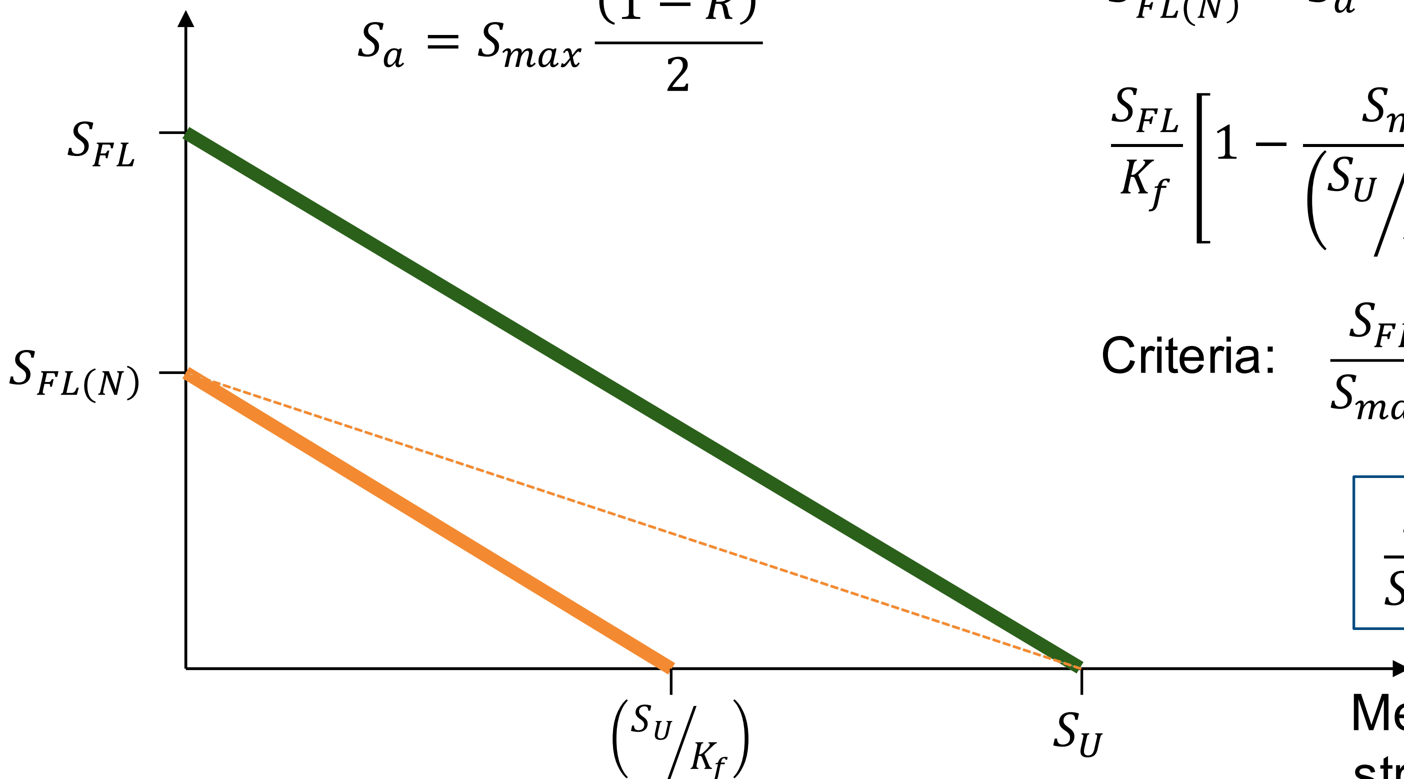
For positive mean stress, notched fatigue limit is always less than fatigue limit normalized by K_f



notched

$$S_{FL(N)}^{m} = S_{FL(N)}\left[1 - \frac{S_m}{\left(S_U/K_f\right)}\right]$$

Establish conditions for which S_{max} of notched configuration represents the fatigue limit (S_{FL})



$$S_a = S_{max}\frac{(1-R)}{2}$$

$$S^m_{FL(N)} = S_a$$

$$\frac{S_{FL}}{K_f}\left[1 - \frac{S_m}{\left(S_U/K_f\right)}\right] = S_{max}\frac{(1-R)}{2}$$

Criteria: $\frac{S_{FL}}{S_{max}} > 1$

$$\frac{S_{FL}}{S_{max}} \sim \frac{(1-R)}{2}K_f > 1$$

Maximum stress will be conservative representation of fatigue limit when:

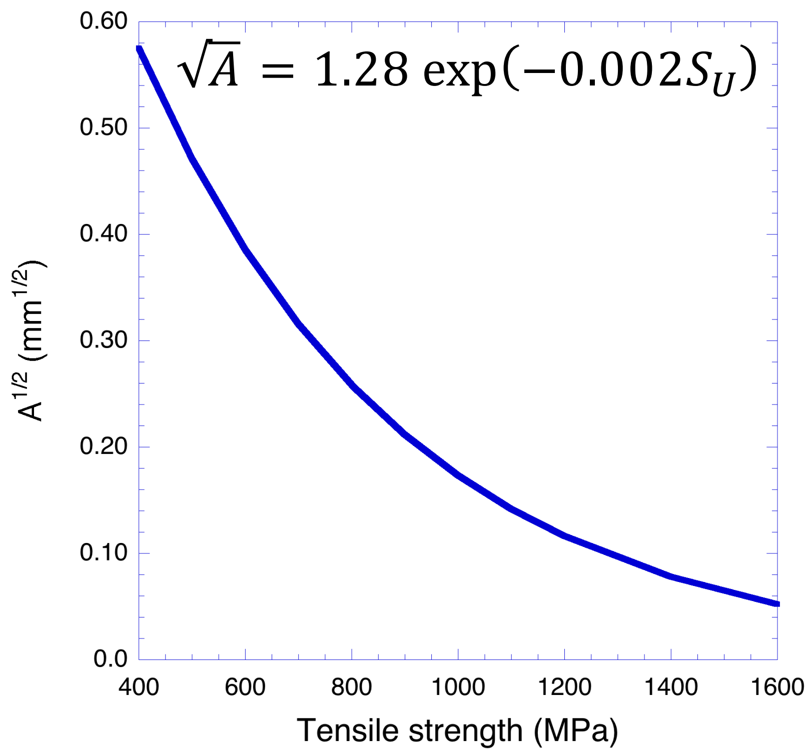
$$K_f > \frac{2}{(1-R)}$$

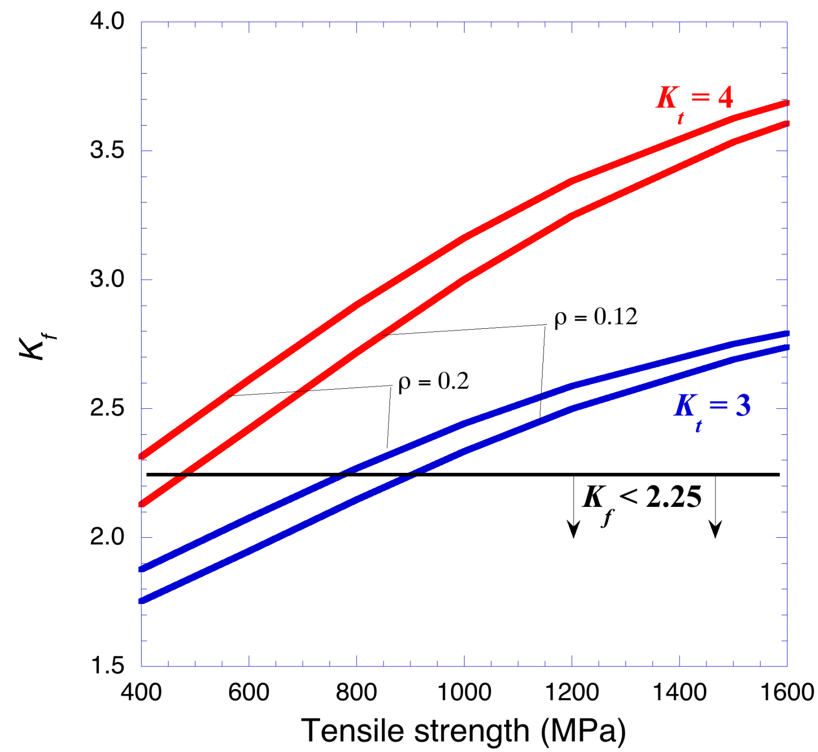
$$K_f(R = 0.1) \sim 2.25$$

Neuber (and others) provide framework for using K_f

Neuber relationship $$K_f = \frac{K_t + \sqrt{A/\rho}}{1 + \sqrt{A/\rho}}$$

ρ is notch root radius
A is materials property





Diverse range of alloys have been considered experimentally

material	Sy (MPa)	UTS (MPa)	Cr	Ni	Mn	N	Typical allowable stress (MPa)
316L	280	562	17.5	12	1.2	0.04	115
CW 316L	573	731	17.5	12	1.2	0.04	218
304L	497	721	18.3	8.2	1.8	0.56	195
XM-11	539	881	20.4	6.2	9.6	0.26	207
Nitronic 60	880	1018	16.6	8.3	8.0	0.16	218
SCF-260	1083	1175	19.1	3.3	17.4	0.64	333

Wide range of strength (i.e., weight)

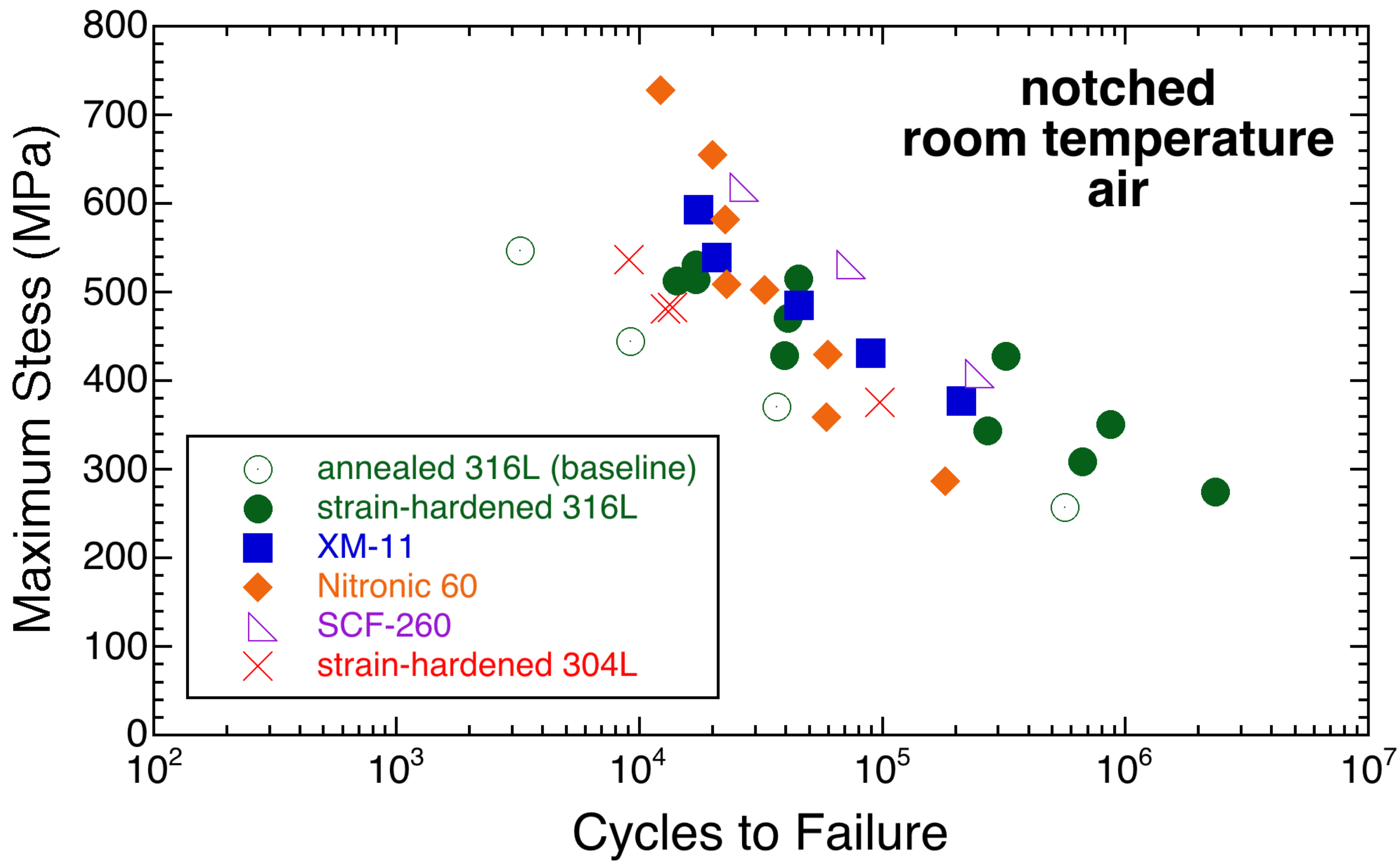
Wide range of Ni & Mn content (i.e., cost)

Assessment of fatigue performance demonstrates that cost and weight reduction targets can be achieved

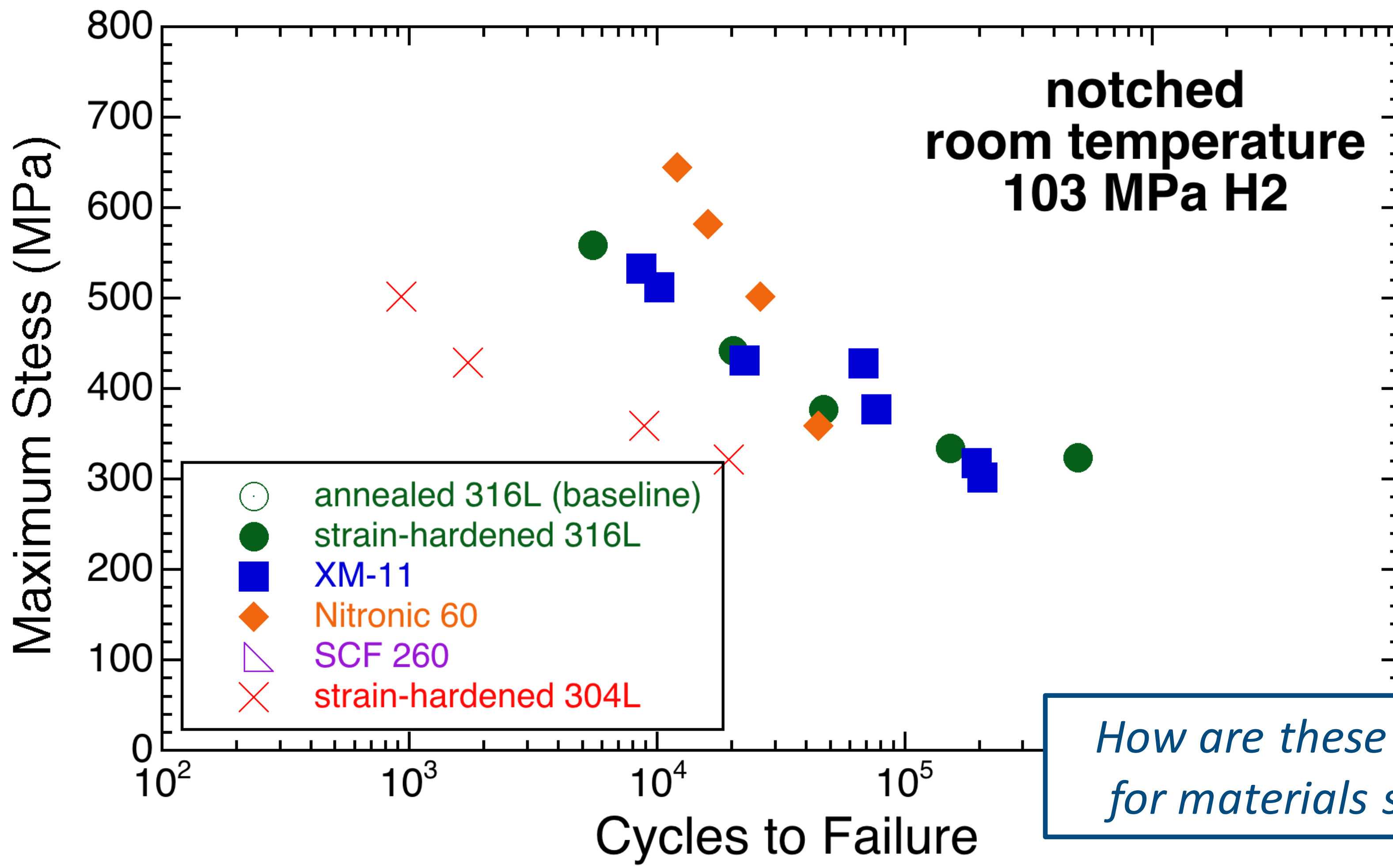
material	Allowable stress (MPa)	Relative weight	Cr	Ni	Mn	N	Relative cost	
316L	115	1.00	17.5	12	1.2	0.04	1.00	
CW 316L	218	0.28	17.5	12	1.2	0.04	0.42	
304L	195	0.34	18.3	8.2	1.8	0.56	0.35	
XM-11	207	**0.31**	20.4	6.2	9.6	0.26	**0.41**	***Low-nickel***
Nitronic 60	218	**0.28**	16.6	8.3	8.0	0.16	**0.40**	***Gall tough***
SCF-260	333	0.15	19.1	3.3	17.4	0.64	0.23	

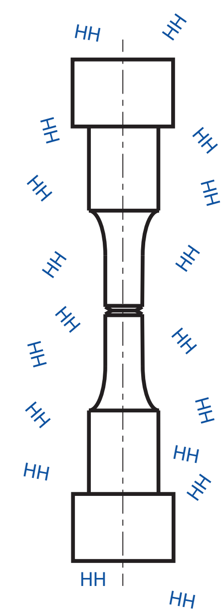
- Verification of fatigue performance in the combination of low-temperature and high-pressure is needed
  - Effects of pressure and H-precharging suggest low-temperature conditions will not be limiting

Fatigue life measurements provide relevant performance metrics for assessing cost/weight reduction



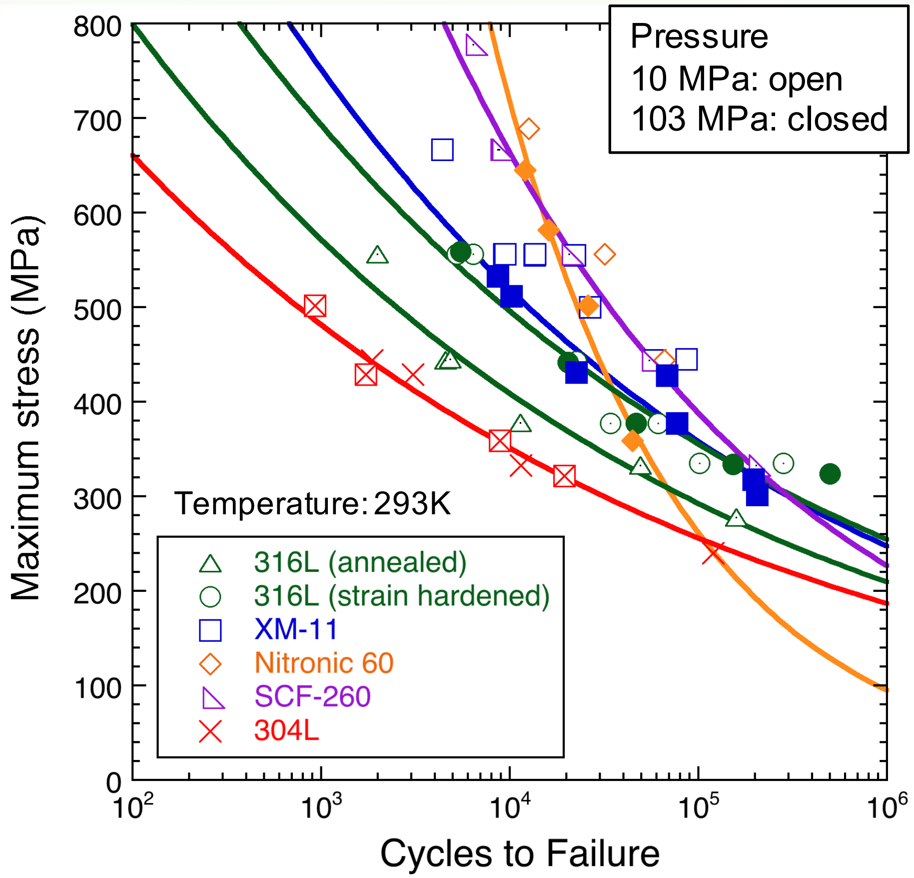
Fatigue life measured in gaseous hydrogen reveals several alloy options comparable to baseline material

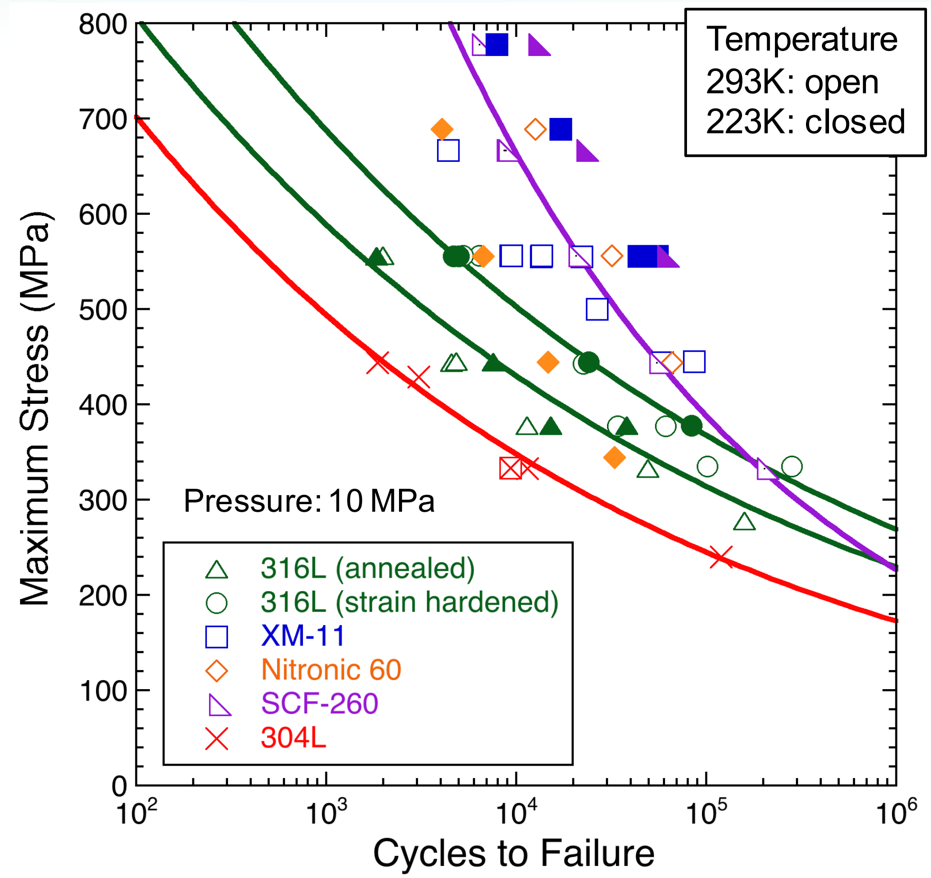




How are these data used for materials selection?

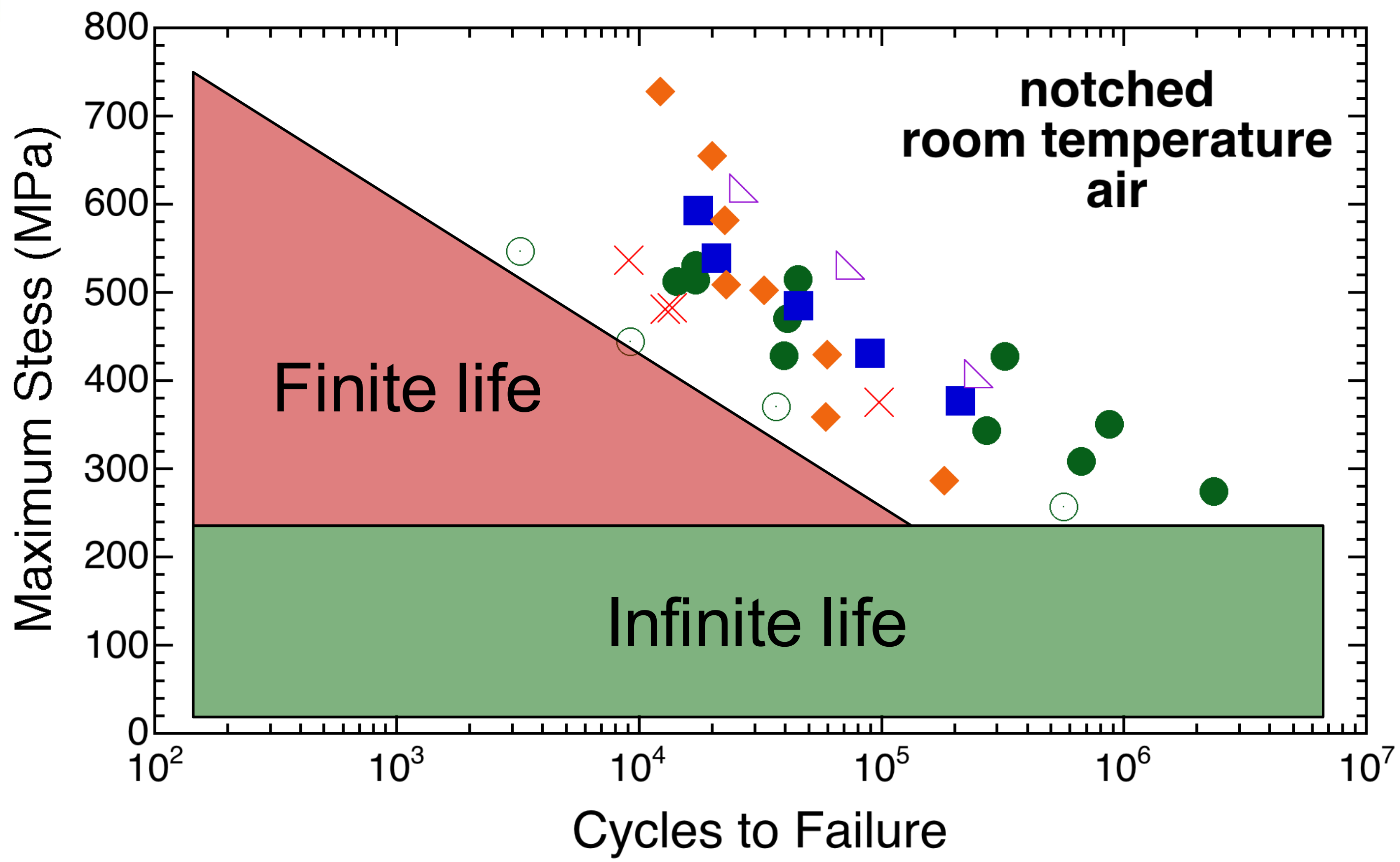
Fatigue life testing at low temperature leads to similar conclusions about performance as at room temperature

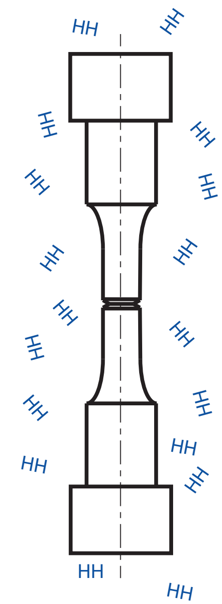




- Pressure has modest effect, if any, on fatigue life
- Temperature has either no effect or increases fatigue life
- Nitronic 60 is an exception for both pressure and temperature

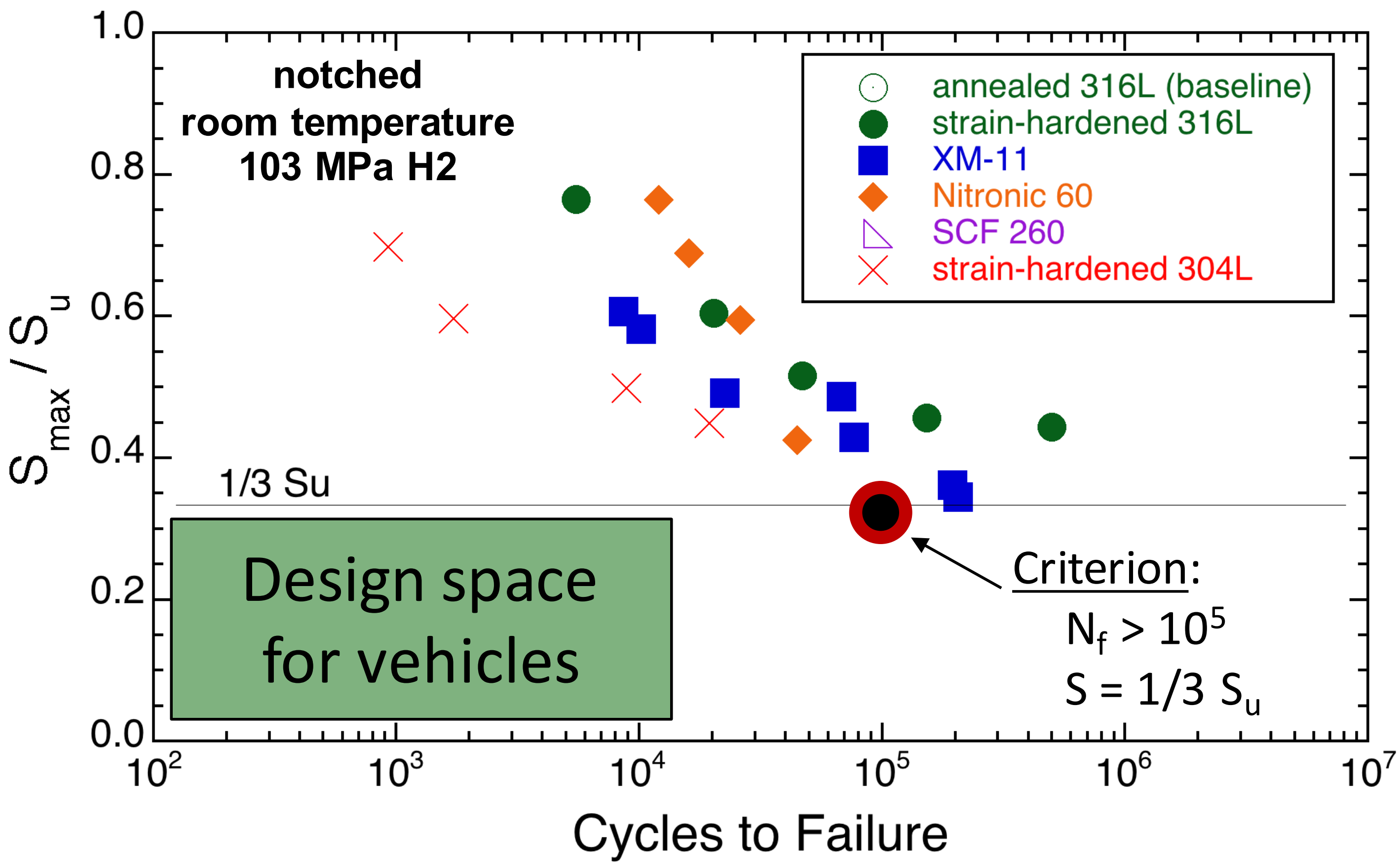
How can fatigue life data be used in a *performance-based* methodology?





- Test data is being generated in storage program (ST113)
- Capability deployment for low-temperature testing in high-pressure gas and application to SCS is part of SCS005

Engineering normalization of hydrogen-assisted fatigue data allows comparison of design performance



Common design criterion:

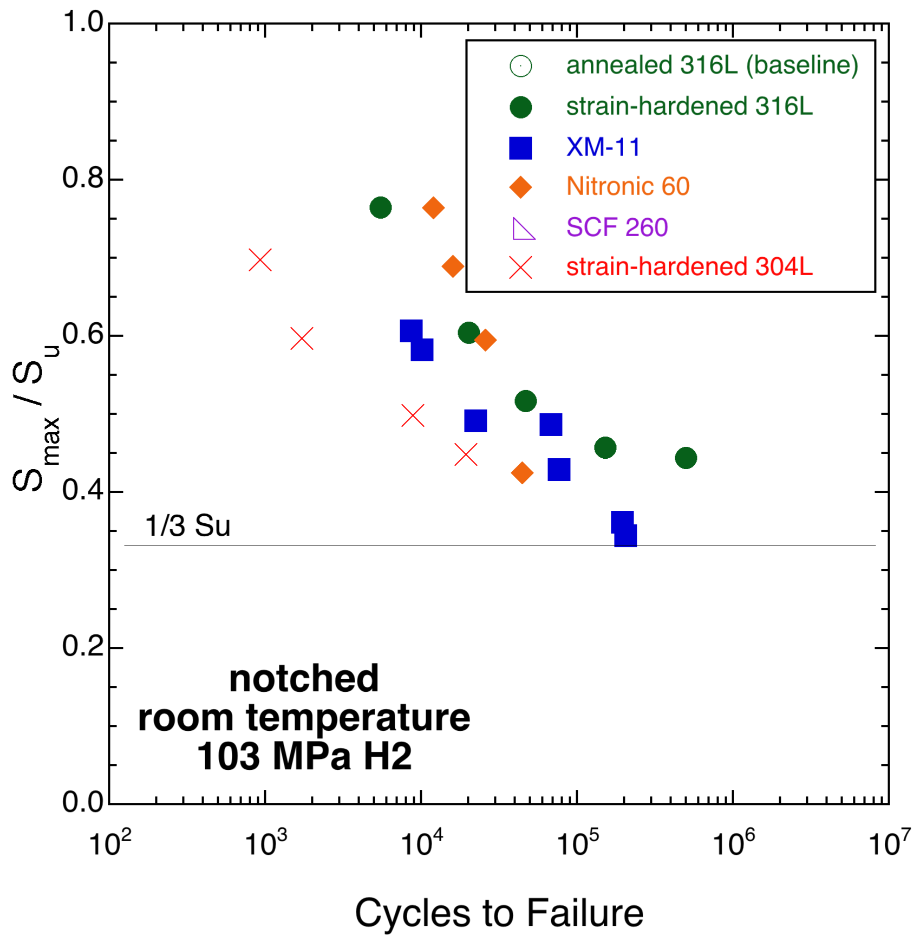
$S \leq 1/3\ S_u$

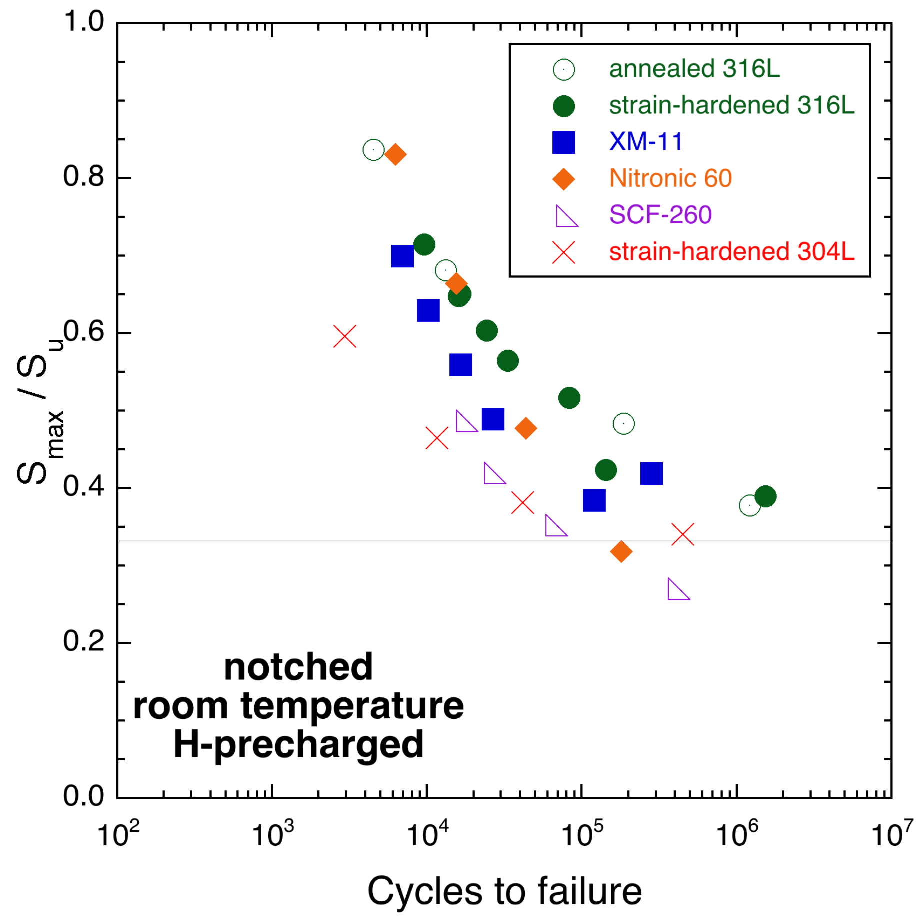
S_u = ultimate tensile strength

S = allowable stress (or design stress)

Conservative materials qualification metric for materials in the vehicle application has been proposed (collaboration with SCS program)

H-precharging produces same results as in gaseous hydrogen





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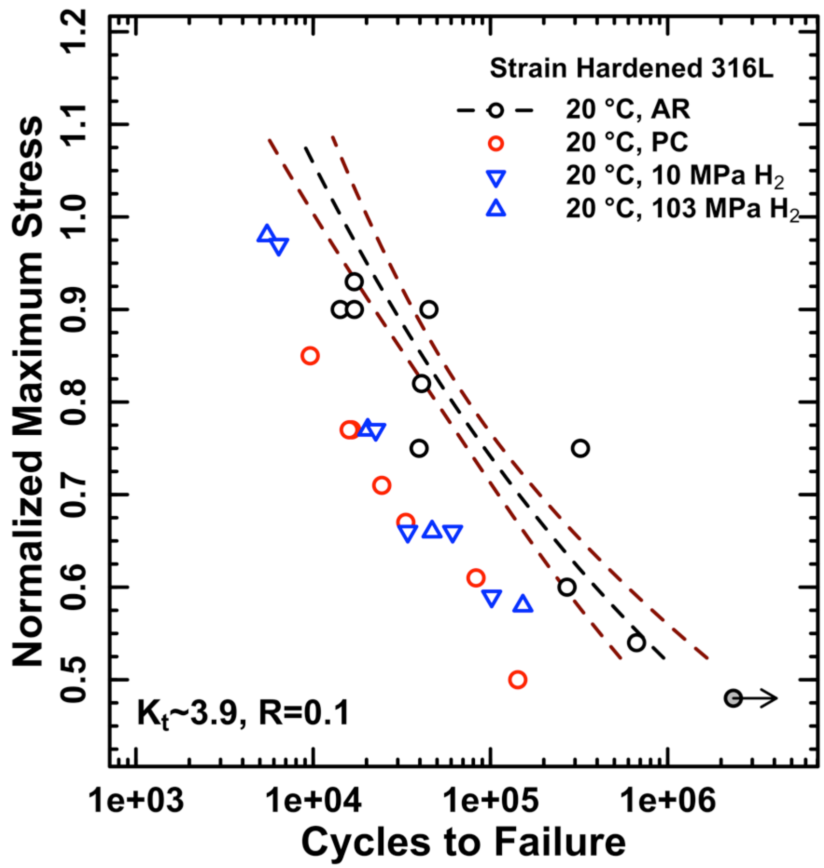
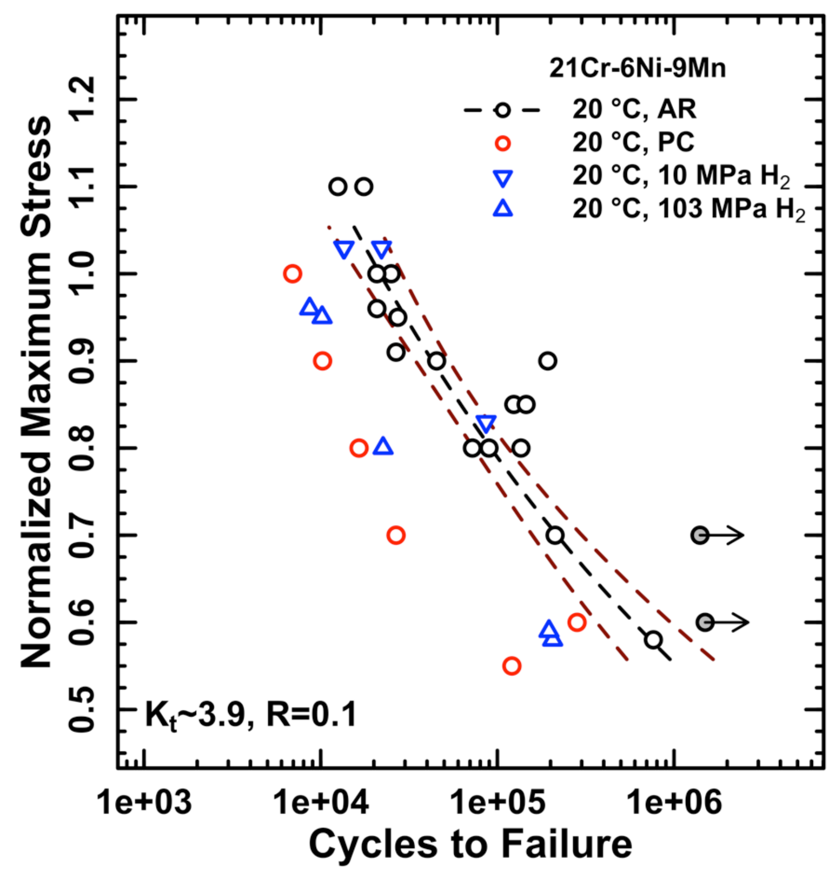
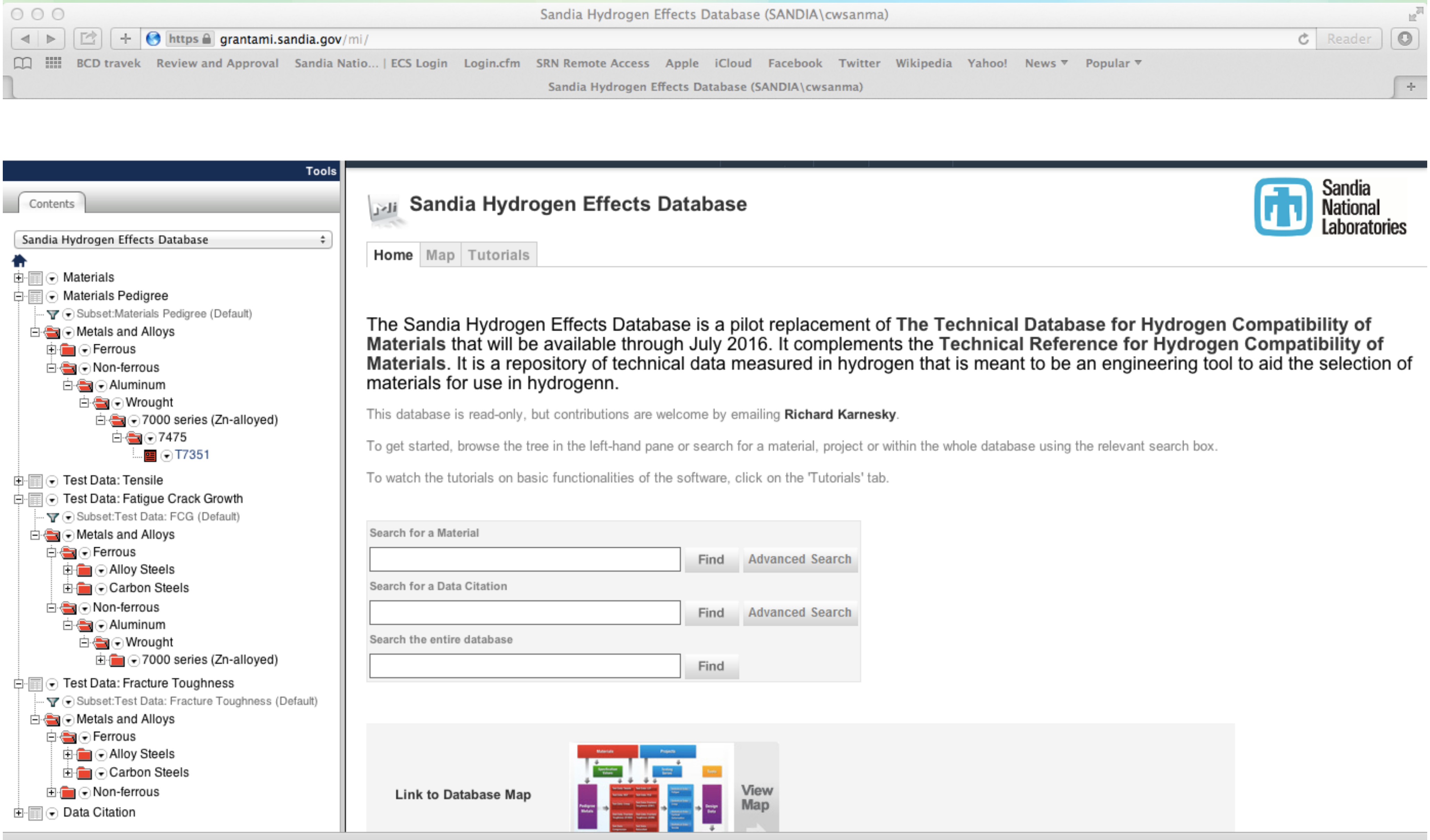




Database slides

Technical Database for Hydrogen Compatibility of Materials



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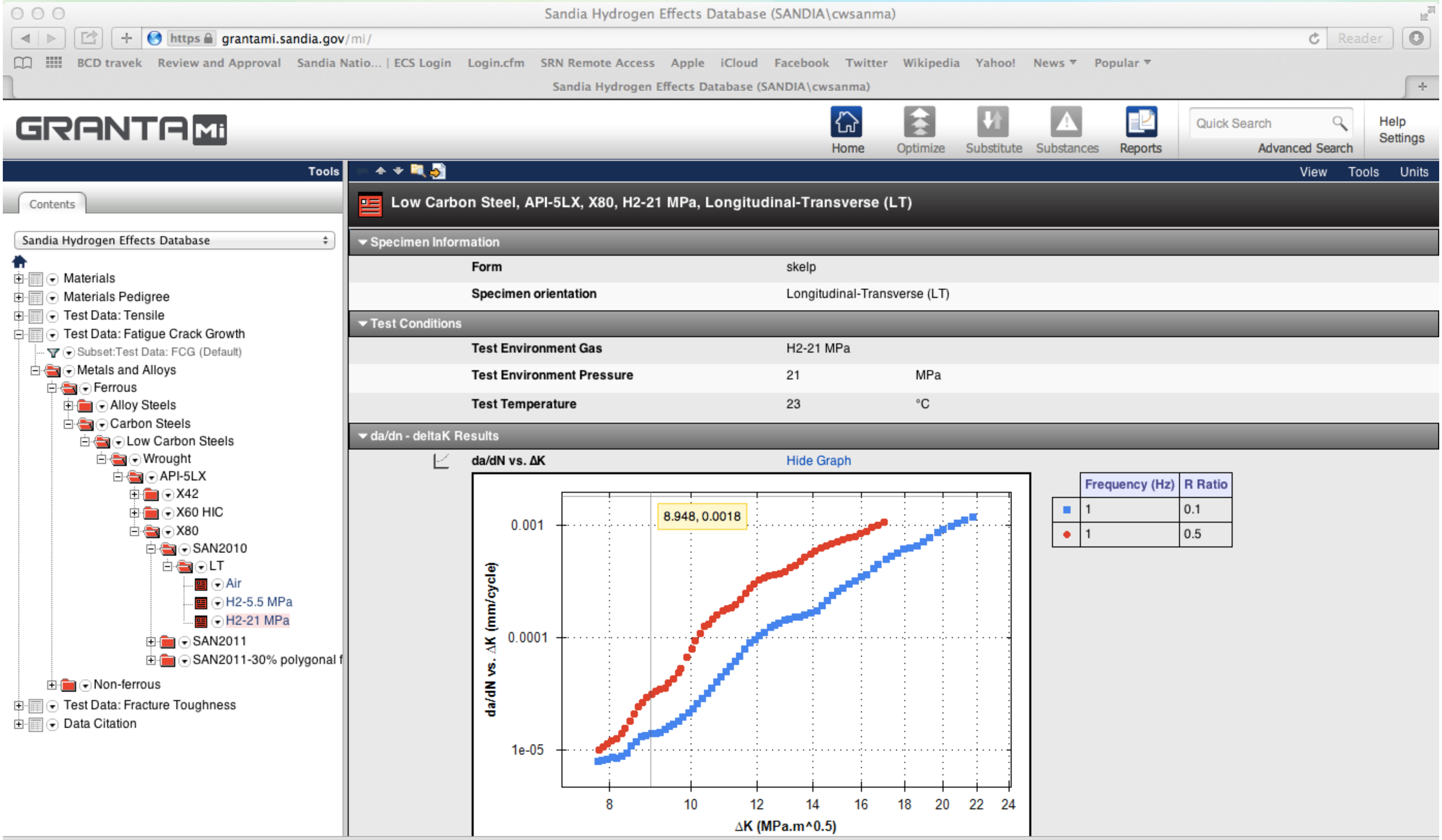

Table Design and Rating System

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

Weighted Value	10	9	8	7	6	5	4	3	2	1	0
Weight Change, %	0-0.25	>0.25-0.5	>0.5-0.75	>0.75-1.0	>1.0-1.5	>1.5-2.0	>2.0-3.0	>3.0-4.0	>4.0-6.0	>6.0	**
Diameter/Length Change, %	0-0.1	>0.1-0.2	>0.2-0.3	>0.3-0.4	>0.4-0.5	>0.5-0.75	>0.75-1.0	>1.0-1.5	>1.5-2.0	>2.0	**
Thickness Change, %	0-0.25	>0.25-0.5	>0.5-0.75	>0.75-1.0	>1.0-1.5	>1.5-2.0	>2.0-3.0	>3.0-4.0	>4.0-6.0	>6.0	**
Volume Change, %	0-2.5	>2.5-5.0	>5.0-10.0	>10.0-20.0	>20.0-30.0	>30.0-40.0	>40.0-50.0	>50.0-70.0	>70.0-90.0	>90.0	**
Mechanical Property Retained, %	≥97	94-<97	90-<94	85-<90	80-<85	75-<80	70-<75	60-<70	50-<60	>0-<50	0
Visually Observed Change	No change	**	**	Slightly discolored	Discolored; slightly flexible	Some stress cracking; flexible	Warping; softening; some swell	Cracking; swelling; brittle	Severe distortion; deteriorate	Decomposed	Solvent dissolved
Break Through Time, min	**	>960	>480-≤960	>240-≤480	>120-≤240	>30-≤120	>10-≤30	>5-≤10	>2-≤5	>1-≤2	≤1
Permeation Rate (*)	≤0.9	**	>0.9-9	**	>9-90	**	>90-900	**	>900-9000	**	>9000
Hardness Change	0-2	>2-4	>4-6	>6-9	>9-12	>12-15	>15-18	>18-21	>21-25	>25	**

Notes:

* in µg/cm2min

** Weighted Value not used in the calculation of PDL Rating

After assigning the Weighted Value to each property for which information is available, the Rating is calculated as an average of Weighted Values. All decimal digits are truncated (not rounded). If the result is equal to 10, a rating of 9 is assigned. Supplier or manufacturer resistance ratings are also figured into the calculation of PDL Rating.

Visually observed changes described in the above table are typical samples of the data available and therefore should not be used as a guideline. Chemical Resistance of Plastics and Elastomers contains a great variety of these data. The rating of changes in appearance is determined on an individual basis by an expert.

Percent Mechanical Property Retained is calculated as an average of the available retention values for mechanical properties. If the percent retention is greater than 100%, a value of 200 minus the percent property retained is used in the calculations.

Additional information on chemical resistance of polymeric material is given in the Resistance Note field. It includes information about changes in color, cracking, warping, decomposition, suitability to different applications, and overall chemical resistance assessment.

Guide to Hydrogen Compatibility of Polymers – H2Tools

Select application	Valve Seals	Weighting: Valve Seals	$C_s=w_1P+w_2F+w_3PCA+…$

Scoring				Test Methodologies					
Polymer	**Description**	**Composite score (1-10)**	**Temperature (° C)**	**Tensile Strength** *% change*	**Permeability** *Φ x 10^9 (mol H_2/m•s•MPa)*	**Friction and Wear** *μ_F/R_w(10^{-5} mm/s)*	**Pressure Cycle Aging**	**Swelling** *10^{-3} %/psi*	**Test 5…**
NBR	poly(butadiene-co-acrylonitrile)	3	25	85%	5.5	1.5/1.6	?	5	
Viton									
PTFE									
…									

Hyperlinked to datasheet details

- Give input selection box at top to change weighting based on application. I.e. compressor may increase friction and wear weighting, while a permeability barrier may increase the permeability weighting. Changing this repopulates the composite score and changes the list order.
- Include links in the data to either separate page or pop-up box describing the methodology for the test and analysis.
- Optional: include temperature and pressure range as an input.
- We should identify future tests including, but not limited to: blistering, in-situ tensile, compression set swelling, absorption (weight increase if any), impact of thermal excursions (high/low), cryogenic, off-gassing of impurities, transition temperature changes, plasticization, fracture/fatigue, other

Backup slides

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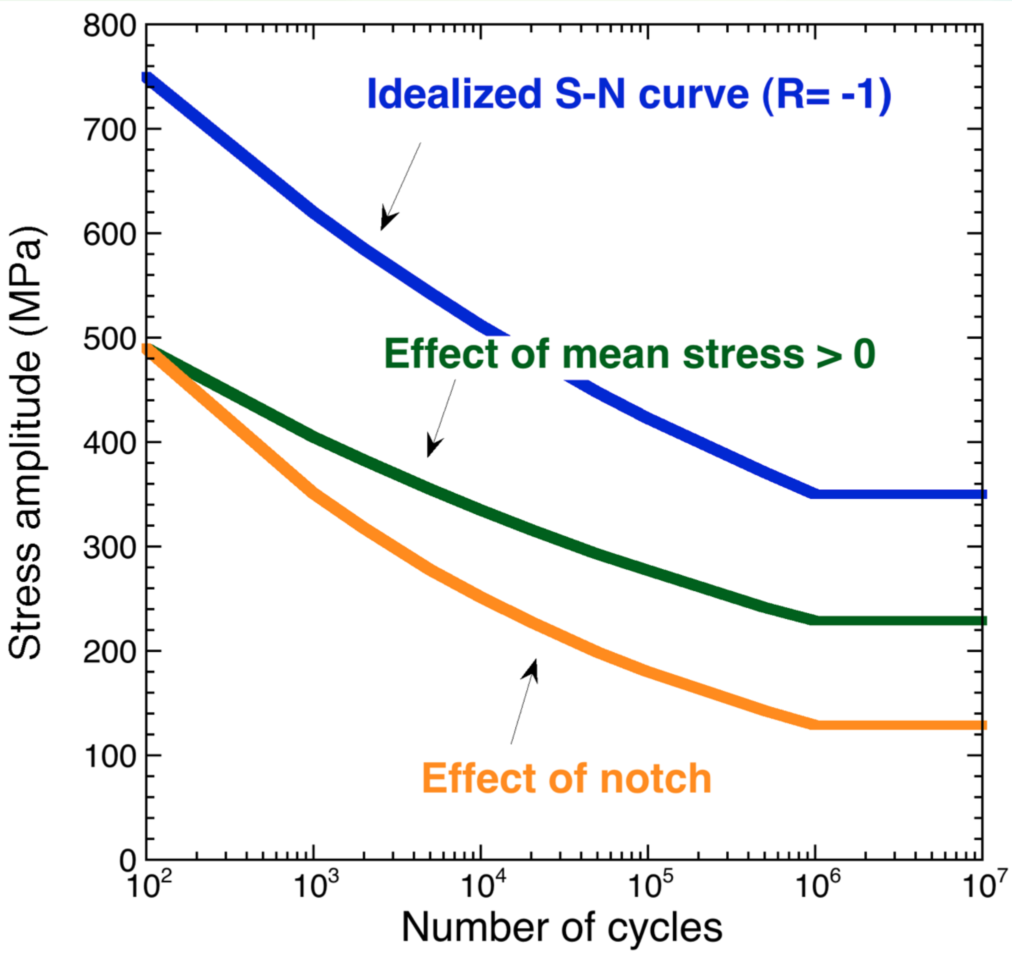
Relationship between loading configurations



- Conventional fatigue testing:
  - R = -1
  - Smooth specimen
- Fatigue applied to hydrogen pressure applications:
  - Tension-tension loading (R>0)
  - Notched specimen

Effect of mean stress:

$$S_f^* = S_f\left[1 - S_m / S_u\right]$$

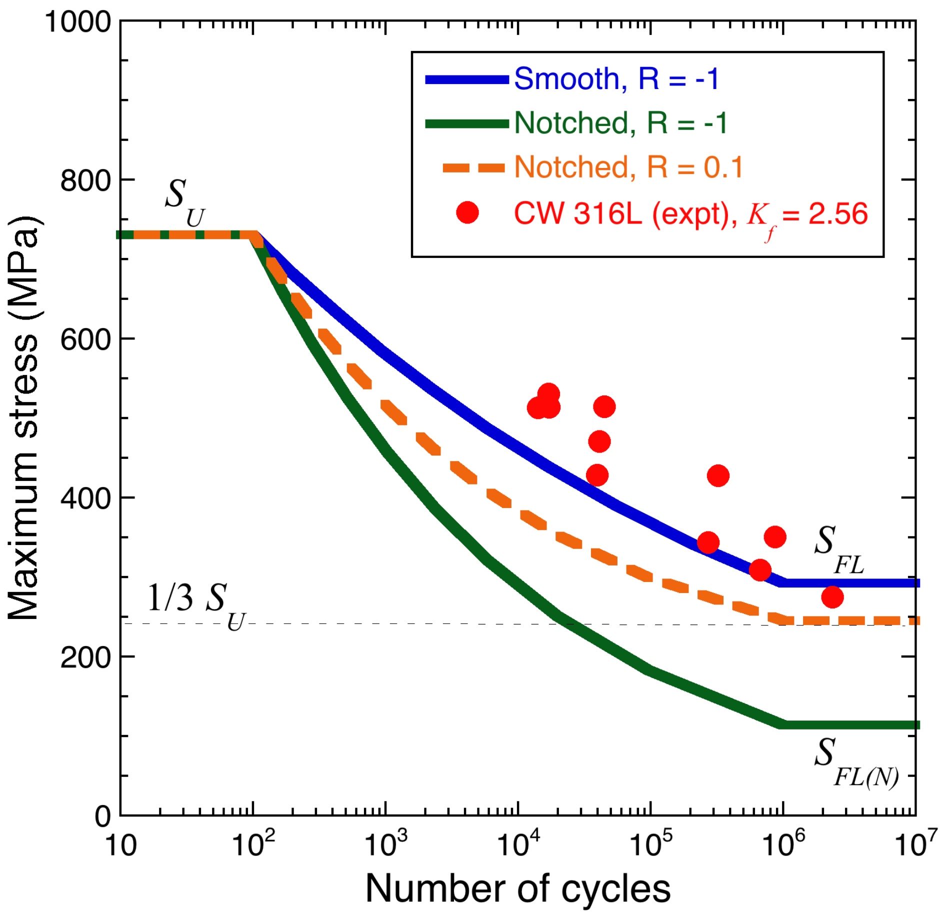
Effect of notch:

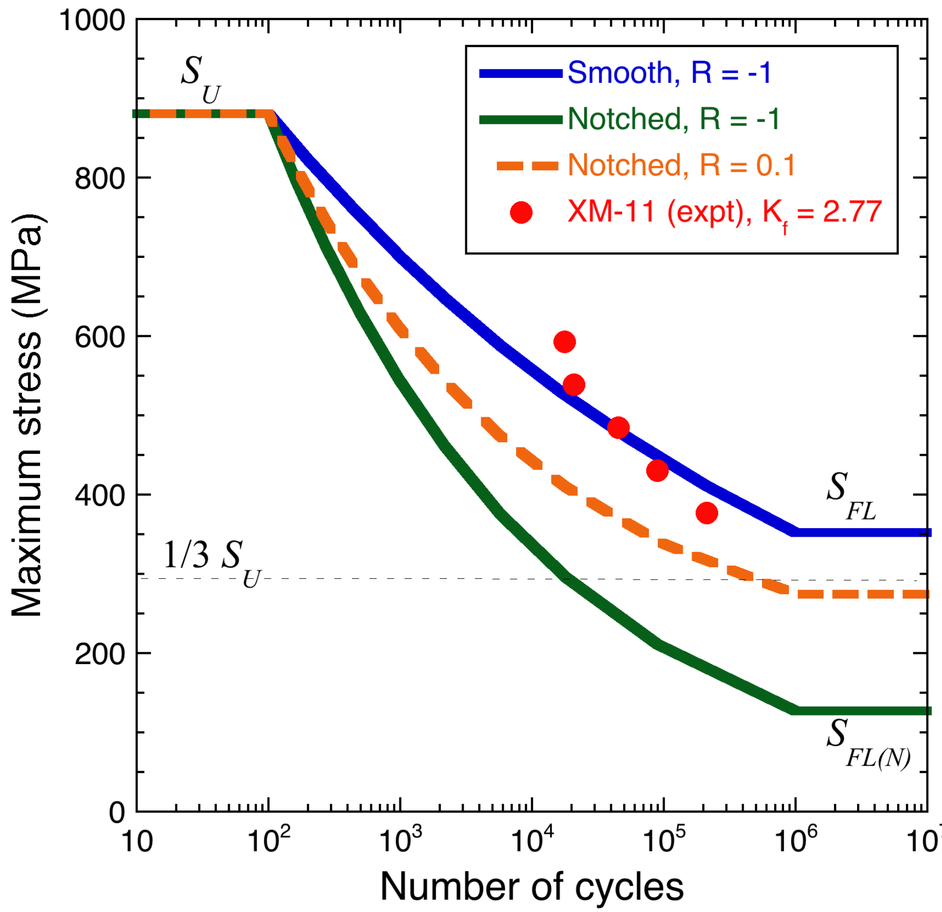
$$S_f^N = S_f / K_f$$

Methods exist to explore similitude between methodologies

Estimated S-N curves for characteristic stainless steel

$$\frac{S_{FL}}{K_f}\left[1 - \frac{S_m}{S_U}\right] = S_{max}\frac{(1-R)}{2}$$

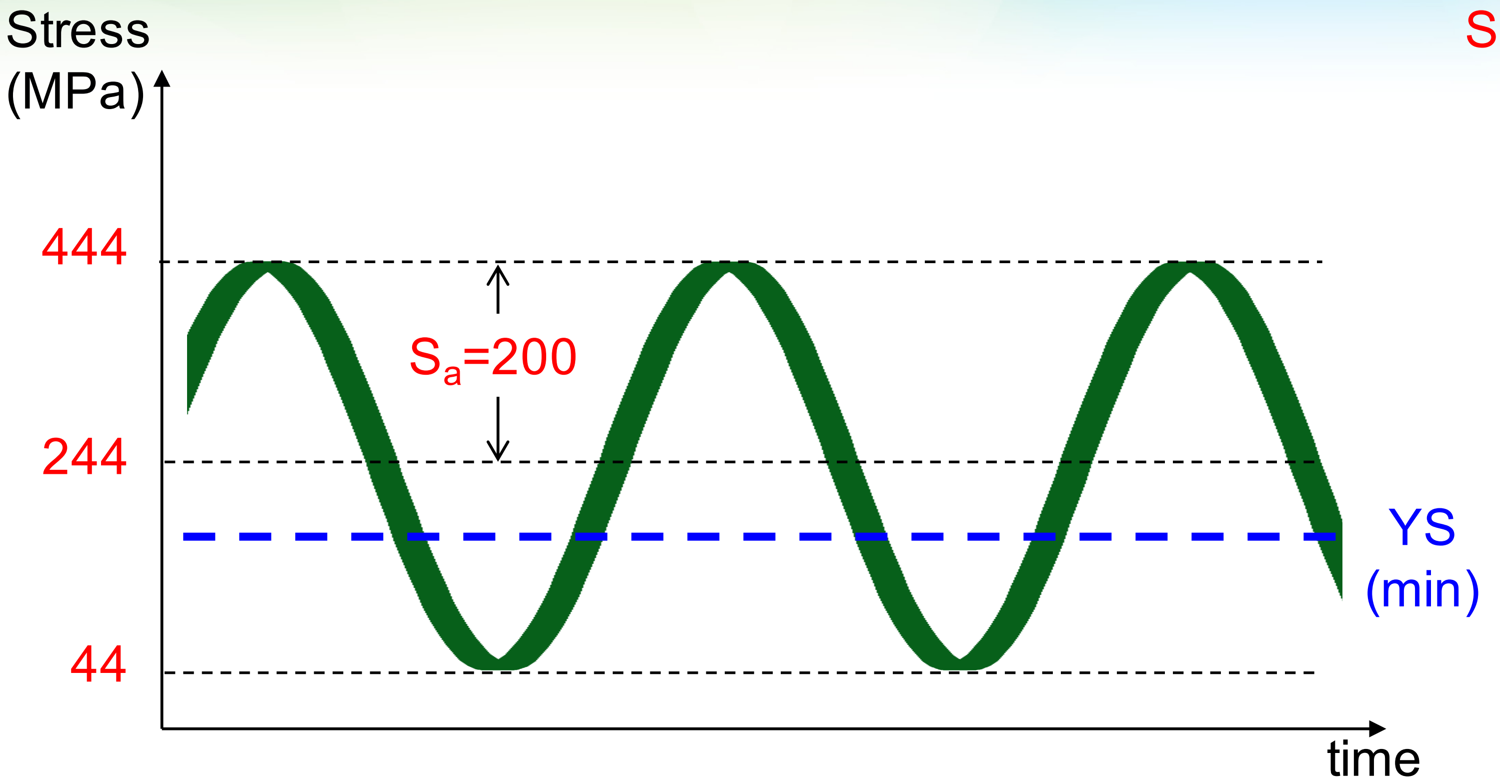


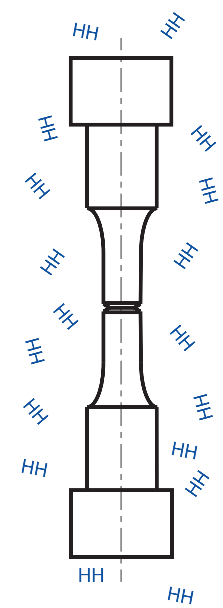


Load cycle: notched configuration

$R = S_{min} / S_{max}$

$S_{max} = 2S_a/(1-R)$

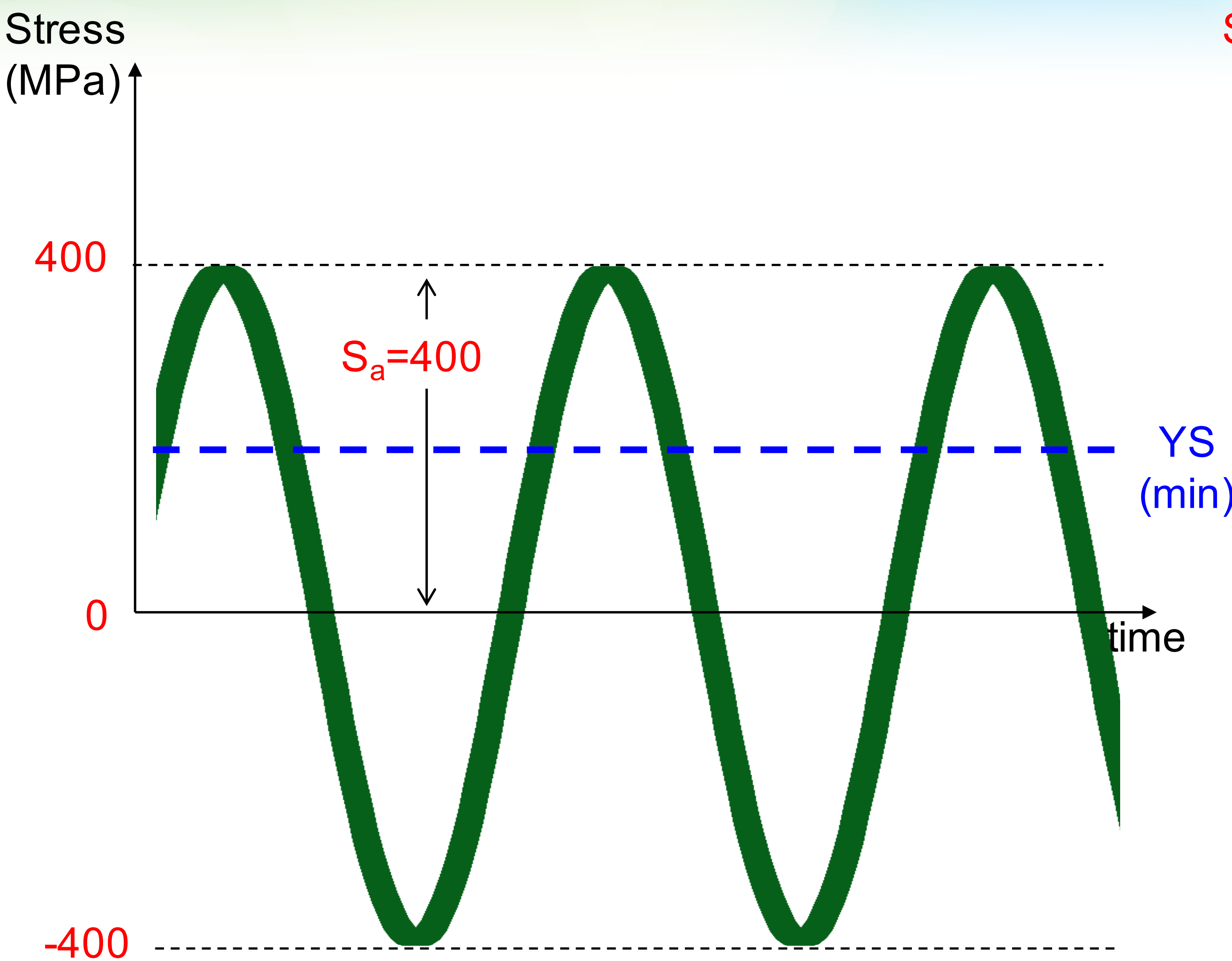




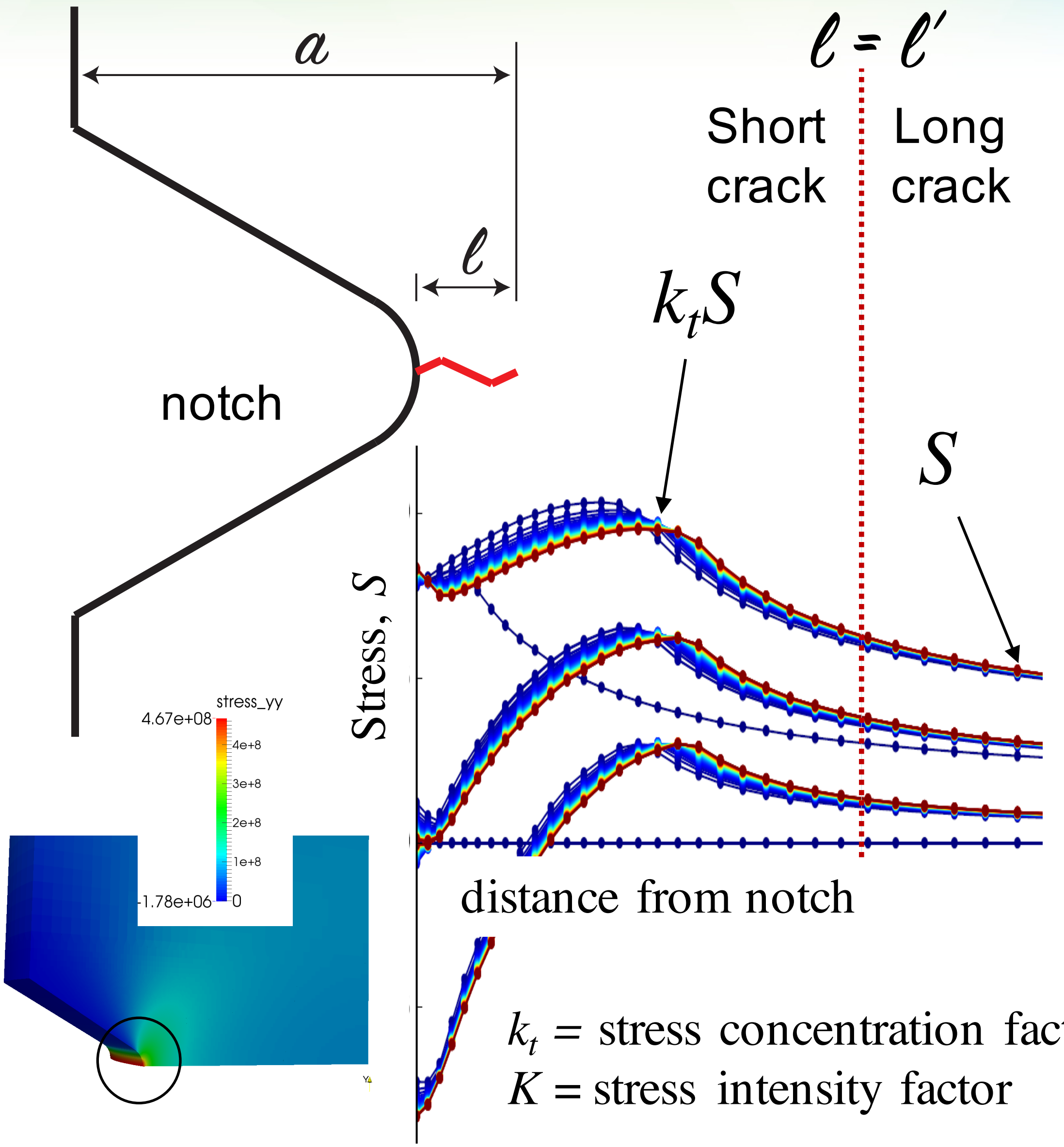
Load cycle: smooth configuration

$R = S_{min} / S_{max}$

$S_{max} = 2S_a/(1-R)$



Solid mechanics: Short crack behavior is difficult to characterize and to generalize



k_t = stress concentration factor
K = stress intensity factor

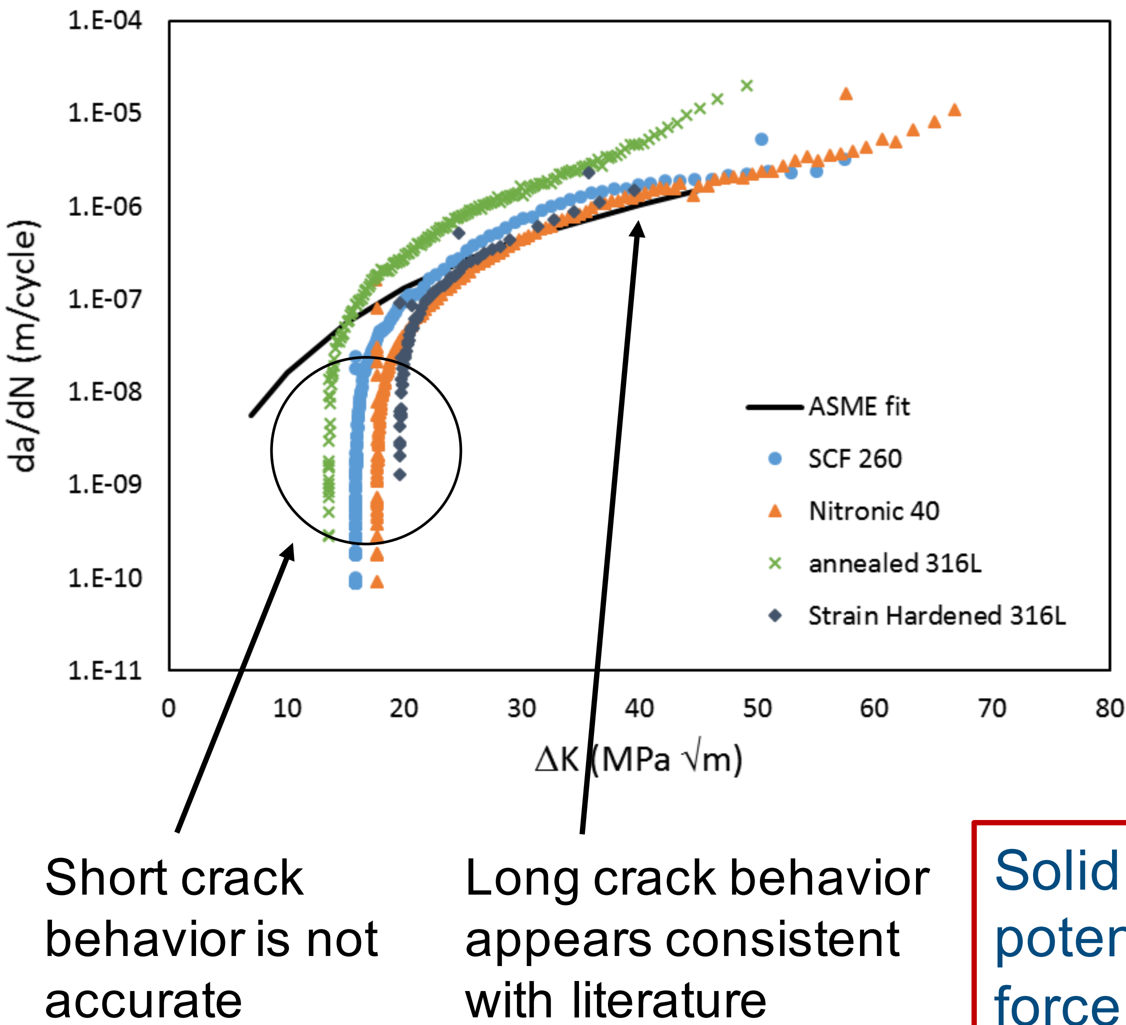
Short crack behavior

- Small ℓ
- $K \propto (k_t S)\,\ell^{1/2}$
- Dominated by stress concentration
- Dominates total life

Long crack behavior

- Large ℓ
- $K \propto S\,a^{1/2}$
- Dominated by crack length

Solid mechanics: Preliminary study appears to show consistency between materials response and literature



- Curves are derived from DCPD data to track crack evolution during fatigue testing
  - Crack evolution relationships to predict crack length are approximations
- Relationships for ΔK are estimates in short crack regime

Solid mechanics modeling has potential to provide insight to driving force and crack evolution equations